EQUILIBRIUM STUDIES WITH PLATINUM COMPLEXES

by

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Author's Note

In general wavelengths are recorded in cm^{-1}. However where exact settings were used on a Unicam SP 500 spectrophotometer, the wavelengths are recorded in mμ. For conversion, 295m is equal to 33,900 cm^{-1}.

The square brackets normally used to enclose Werner complexes have been used in this thesis. However between p.41 and p.52 the use of square brackets denotes concentration.

The abbreviations "all", "but" and "pent" are used to represent the groups $CH_2=CH-CH_2-$, $CH_2=CH-CH_2-CH_2-$ and $CH_2=CH-CH_2-CH_2-CH_2-$ respectively.

ABSTRACT

This thesis describes the measurement of stability constants for olefins with tetrachloroplatinate(II) and silver(I) ions. The two systems studied were

$$ol + PtCl_4^{=} \rightleftharpoons (ol)PtCl_3^{-} + Cl^{-}$$

and

$$ol + Ag(H_2O)_n^{+} \rightleftharpoons (ol)Ag(H_2O)_m^{+}$$

where ol = olefin. The olefins studied were either unsaturated ammonium salts or unsaturated alcohols.

With platinum(II), it is found that olefins give higher stability constants than water, lower than amines and comparable with the heavier halides. With silver(I), olefins give stability constants lower than amines and the heavier halides, but comparable to water and fluoride.

In the case of platinum(II), enthalpy and entropy values were obtained from the temperature dependence of the stability constants. It was found that the overall stability constant was strongly dependent on the entropy change. The variation in the entropy change is ascribed largely to variations in the solvation energies of the ligands and complexes.

Comparison of the enthalpy values for different olefins shows four main trends.

(1) There is an increase in ΔH from allX$^+$ to butX$^+$ (X = NH_3, NEt_3 and $AsEt_3$).

(2) There is an increase in ΔH in the series allX$^+$ where X = NEt_3, NMe_3, $NHEt_2$, NH_2Et and NH_3.

(3) There is an increase in ΔH for allY on replacing $Y=NH_3^+$ by Y=OH.

(4) There is a decrease in ΔH in the series $CH_2=CH-CH_2-NH_3^+$, $CH_2=CH-CH(CH_3)-NH_3^+$ and trans-$CH_3-CH=CH-CH_2-NH_3^+$.

Trends (1) and (2) can be explained in terms of an inductive effect. Both trends indicate that the π-acceptor capacity of the olefin is more important than the σ-donor capacity for the formation of stable platinum-olefin bonds. Trend (3) is shown to be largely the result of solvation energy changes. Trend (4) is shown to result from a combination of steric and inductive effects.

It was found that the stability constants for silver(I)-olefin complexes are much lower than for platinum(II)-olefin complexes. This can be explained in terms of the nature of the metal-olefin bond in the two series of complexes. It was also found that silver(I) showed a much greater preference than platinum(II) for the uncharged alcoholic ligands rather than the positively charged ammonium lignnds. This can be explained in terms of the electrostatic interaction

between the positively charged ammonium group and the central metal group.

From a study of the ultra-violet spectra of the platinum(II)-olefin complexes, it is shown that the relative energies of the d-orbitals in these complexes are $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{yz} > d_{xz}$.

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C H A P T E R 1

Introduction

Although the first olefin complex, Zeise's salt $K^+[(C_2H_4)PtCl_3^-]$, was reported in 1827[1], until fairly recently olefin complexes had only been prepared with Pd^{II}, Pt^{II}, Cu^I, Ag^I, and Hg^{II}. However recent work has shown that olefin complexes can be prepared with the following metals[2].

~~V~~	~~Cr~~	~~Mn~~	~~Fe~~	~~Co~~	~~Ni~~	Cu
~~Mo~~		Ru	Rh	Pd	Ag	
~~W~~	Re	~~Os~~	~~Ir~~	Pt	Au	Hg

The metals which are shaded only form olefin complexes when they are stabilised in a low oxidation state by ligands such as carbon monoxide and the cyclopentadienyl anion. The stabilizing effect of these ligands has been attributed[3] to the greater back-donation of charge (from metal to ligand) by a "true π-bond", that is a π-bond which involves overlap of the π-orbitals of the ligand in the nodal plane, than the

back-donation by a μ-bond, that is a π-bond which involves overlap with the π-orbitals of the ligand at right angles to the nodal plane. Thus a carbonyl group is able to withdraw negative charge from the metal, which results in an increase in the basic strength of the olefin to metal σ-bond.

Since this thesis describes the determination of stability constants for olefin complexes of platinum(II) and silver(I), further discussion will be mainly limited to olefin complexes of these metals.

Platinum(II) forms a variety of complexes with monodentate olefins exemplified by the following: $K^+[(C_2H_4)PtCl_3^-]$[1], $[(C_2H_4)_2Pt_2Cl_4]$[4] which has the halogen-bridged structure shown in figure 1, cis-[5] and trans-[5] $[(C_2H_4)NH_3PtCl_2]$, all three isomers of $[(C_2H_4)NH_3PtClBr]$[6]

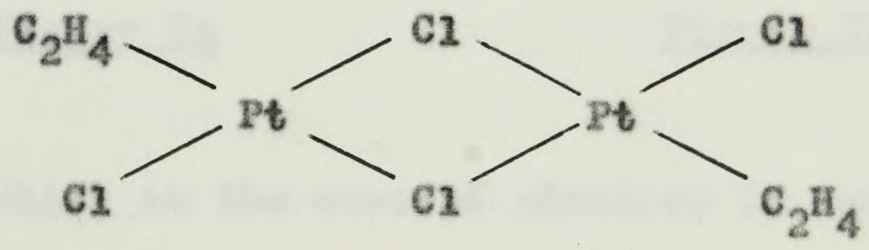


Figure 1

and trans-$[(C_2H_4)_2PtCl_2]$[7,8]. The mono-olefin complexes, $[(ol)PtCl_3^-]$ where ol = olefin, can be isolated as yellow or orange crystalline solids which are stable in air. By contrast, olefin complexes of silver(I) cannot, in general, be isolated from solution[9]. Anhydrous silver complexes

are readily dissociable, low-melting and variable in composition[10]. They have, however, been extensively studied in solution, mainly by distribution techniques.

The molecular orbital treatment which Dewar[11] applied to silver-olefin complexes and which Chatt[12] extended to platinum-olefin complexes gives the currently accepted explanation of the nature of the metal-olefin bond. This essentially involves a σ-bond (olefin to metal) and a π-bond (metal to olefin) - see figures 2a and 2b.

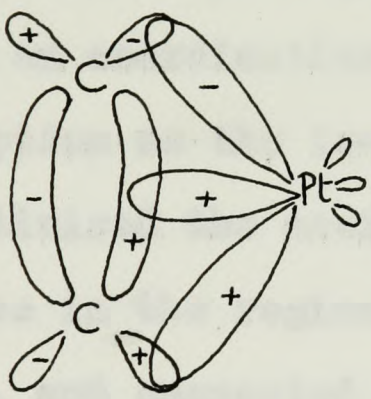


Figure 2a

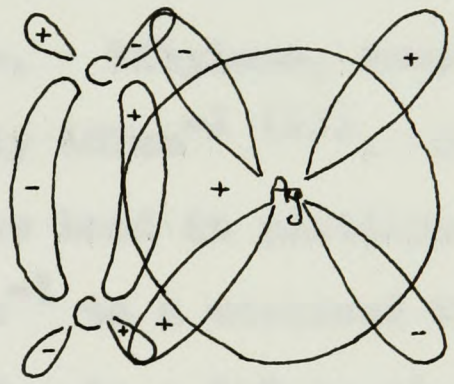


Figure 2b

The σ-bond, which in the case of platinum is formed between the filled olefin π-orbitals and the empty $5d6s6p^2$ hybrid orbital on platinum, causes an unfavourable distribution of negative charge on the metal ion; however the π-back donation, from the filled 5d6p hybrid on platinum to the empty olefin π^*(anti-bonding) orbital relieves this, thus giving a synergic effect. Such a bonding scheme requires the C=C bond of the olefin to be perpendicular to the plane of the

$PtCl_3$ group, and situated symmetrically about it. The bonding in silver-olefin complexes is analogous to that in platinum-olefin complexes. The σ-bond is formed between the olefin π-orbitals and the 5s orbital of silver, and the π-bond is formed between the 4d orbital of silver and the olefin π^*-orbitals.

When first put forward these interpretations of the bonding depended for support very largely on the infra-red data available. Thus it is found (see p.90) that the carbon-carbon stretching frequency of olefins is lowered by about 150cm^{-1} on coordination to platinum. Ethylene, however, is an exception as the lowering is only 107cm^{-1} (13). Gelman(14) has criticised the assignment of the band in platinum-olefin complexes in the region 1490-1510cm^{-1} to a weakened C=C stretch, and suggested that it is due to a deformational vibration of the $=CH_2$ group. However, it has been shown(15) that olefins which do not contain a $=CH_2$ group (e.g. cis- and trans-4-methylpent-2-ene) still give a band in the region 1490-1510cm^{-1} on formation of a complex with platinum. This lowering of the C=C stretching frequency is consistent with a weakened carbon-carbon double-bond such as would result from the bonding described above. It is not consistent with a single bond, such as that in Hel'man's original structure for Zeise's salt(16) (figure 3).

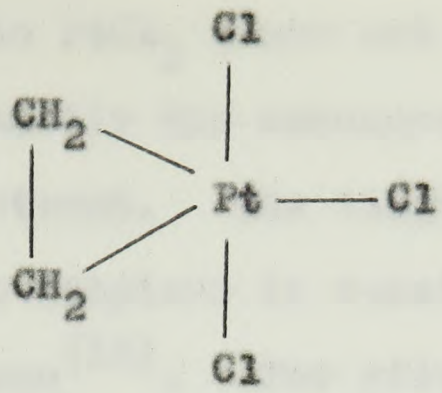


Figure 3

A lowering of about 65cm^{-1} in the C=C stretching frequency of olefins on coordination to silver [9] is found from studies of the infra-red and Raman spectra. This lowering of about 65cm^{-1} for silver, as opposed to about 150cm^{-1} for platinum, is consistent with the weaker σ-bonding which results when the directed 5d6s6p^2 hybrid orbital on platinum is replaced by the non-directed 5s orbital on silver.

The X-ray structure of Zeise's salt[17] provides the best confirmation of the nature of the bonding. The X-ray structure - see figure 4 - shows that the C=C bond of ethylene

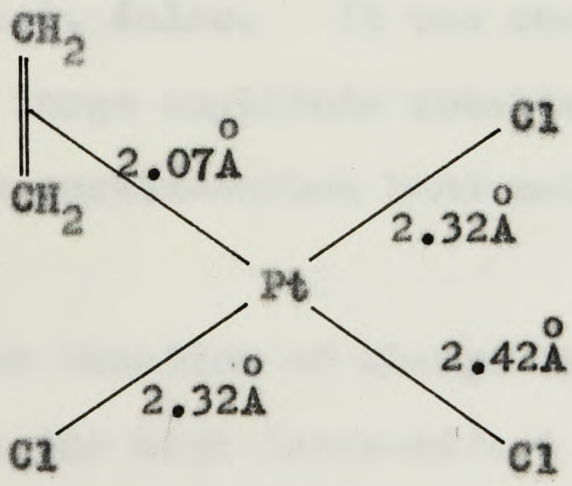
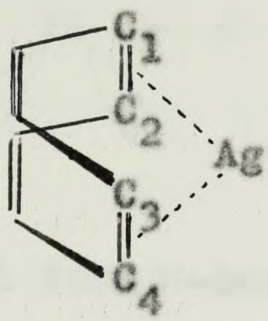


Figure 4

is perpendicular to the $PtCl_3$ plane and situated symmetrically about it. This is exactly the arrangement required by the molecular orbital treatment. The lengthening of the platinum-chlorine bond trans to ethylene is consistent with the high trans-effect of ethylene[18]. For silver, the X-ray structure of the cyclooctatetraene complex, $[Ag(C_8H_8)^+]NO_3^-$ by Mathews and Lipscomb[19] - see figure 5 - is consistent with Dewar's concept of/bonding.
the



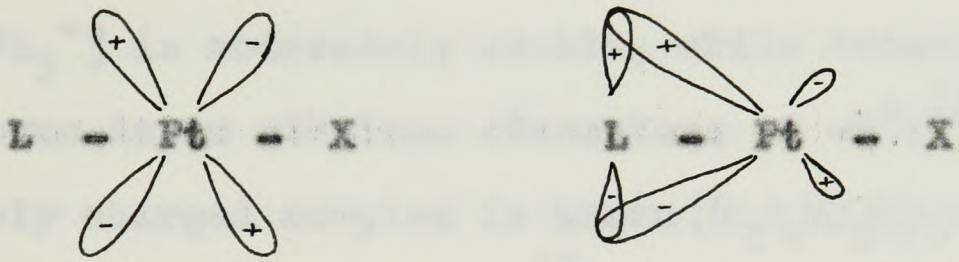
Ag-C_1	2.46Å
Ag-C_2	2.51Å
Ag-C_3	2.78Å
Ag-C_4	2.84Å

Figure 5

Nuclear magnetic resonance studies of Zeise's salt[20] indicate that the rigid structure which might have been envisaged is, in fact, false. It was shown that the ethylene molecule undergoes large amplitude rotational oscillations about two axes, the carbon-carbon bond and the platinum-olefin bond.

The π-back donation of charge from platinum to the olefin accounts for the high trans-effect of olefins attached to platinum. Reviews of the theories put forward to account for the trans-effect[18,21] favour one put forward by Chatt,

Duncanson and Venanzi[22]. These authors suggest that a ligand (L) which can form π-bonds will withdraw some of the electron density of the d_{xz} orbital from the ligand in the trans-positon (X) - see figure 6. This will weaken the Pt-X bond as well as directing an incoming nucleophile towards X, which is the region of lowest electron density.



L does not form π-bonds L forms π-bonds

Figure 6

Dipole moment studies of platinum-olefin complexes by Chatt et al[12,23] led to the conclusion that the total platinum-olefin bond order was 4/3. However this was based on the questionable value of about 6D for the N—Al σ-bond. This value was obtained by considering the complex $C_2H_5NH_2AlCl_3$ which has a dipole moment of about 6.9D[24]. Since Eley[25] reports the moment of the pyramidal $-AlCl_3$ group, such as is found in $C_2H_5NH_2AlCl_3$, as about 4D, a value of 6D for the N—Al σ-bond would seem excessive.

Preparative studies have shown that the stability

of the complex $[(C_2H_4)PtX_3^-]$ falls in the order X = Cl > I > NO_2 > CNS > CN[4,26], which is the order of increasing double-bond character of the Pt-X bond. This double-bonding withdraws electrons from the π-bond formed between the 5d6p hybrid on platinum and the olefin π^* orbital, thus weakening the platinum-olefin bond.

The effect of the overall ionic charge of the olefin complex also indicates the importance of the π-bonding. Thus $K^+[(C_2H_4)PtCl_3^-]$ is moderately stable, while trans-$[(C_2H_4)_2PtCl_2]$ decomposes even in an ethylene atmosphere at -6°c[8]. Only one positively charged complex is known $[(C_2H_4)NH_3(C_5H_5N)PtCl^+]NO_3^-$[27] and this is very unstable. The decreasing stability as the platinum atom becomes more positive is an indication of the importance of the π-bond, since the σ-bond will increase in strength as the platinum atom becomes more positive.

The possibility of cis/trans isomerisation of olefins occurring on coordination to platinum was first suggested by Kharasch and Ashford[28]. However, two studies[29,30] have shown that when a cis- or trans-olefin coordinates to platinum, it is possible to recover the original isomer by displacement with cyanide. A further example is reported by the author (p.75). It is very unlikely that the olefin is isomerised both on coordination to, and displacement from, platinum. Although a trans-isomer might isomerise on coordination to give the cis-isomer, since cis-isomers are known to give

stronger complexes than trans-isomers[31], it is most unlikely that a cis-isomer would also isomerise, on coordination to platinum, to give the corresponding trans-isomer. Either both or neither of the isomers would have to isomerise on coordination to account for the different infra-red spectra obtained for the cis-but-2-ene and trans-but-2-ene complexes with platinum[29].

There have been a number of studies of the complexes formed between unsaturated amines and platinum(II) in acid solution. Liebermann and Paal[32] prepared complexes of the general formula $[(\text{amineH}^+)\text{PtCl}_3^-]$ by prolonged boiling of allylammonium salts with platinum(IV) complexes. They suggested that the complexes were formed by the following mechanism,

$$2C_3H_5NH_3^+ + PtCl_6^{=} \rightarrow (C_3H_5NH_2.HCl)_2PtCl_4 \rightarrow (C_3H_5NH_2.HCl)PtCl_2 + C_3H_5Cl_2NH_2.HCl,$$

in which chlorine has added across the double-bond. They were, however, unable to isolate the chlorinated amine. Rubinstein and Derbisher[33] investigated complexes of diallylamine with $[K_2PtCl_4]$ and $[(NH_4)_2PtCl_4]$ at length. However, their analyses were very unreliable so that most of their conclusions are doubtful. Hel'man[34] isolated a compound formulated as $[(C_3H_5NH_3^+)PtCl_3^-]$ by treating potassium tetrachloroplatinate(II) with allylamine in acid solution. The structure was written as shown in figure 7, in line with Hel'man's structure for Zeise's salt shown in figure 3 (p.5).

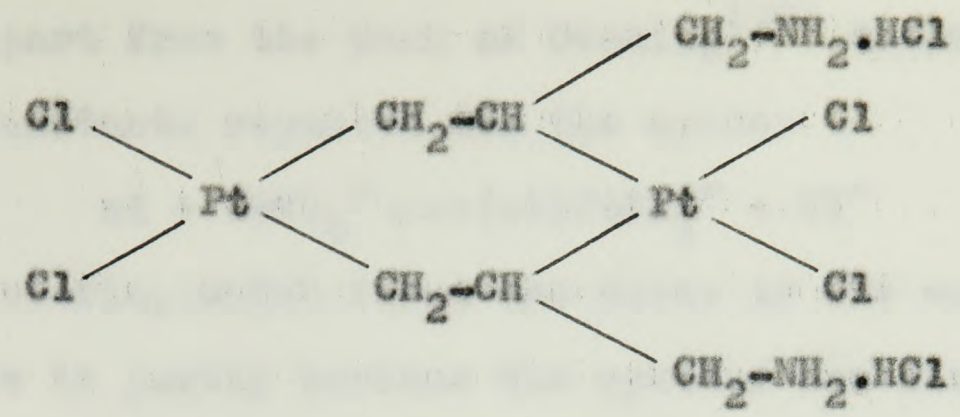


Figure 7

Denning[35] prepared a series of complexes of formula $[(\text{amine}H^+)PtCl_3^-]$ by treating potassium tetrachloroplatinate(II) in acid solution with various allylamines. Using infra-red and ultra-violet spectroscopy these were shown to have the structure shown in figure 8.

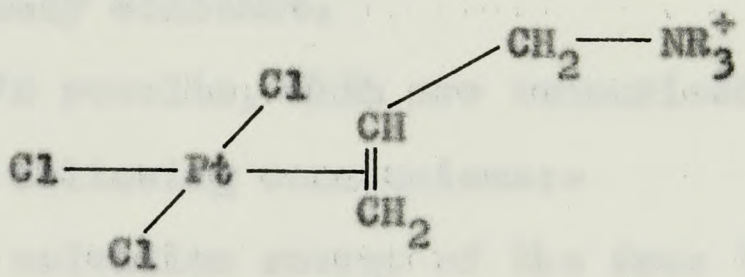


Figure 8

There have been a number of studies of the reaction between unsaturated alcohols and potassium tetrachloroplatinate(II). Biilmann[36] in 1900 first reported the synthesis of $K^+[(CH_2{=}CH{-}CH_2OH)PtCl_3^-]$. Pfeiffer and Hoyer[37] later described the preparation of $[(CH_2{=}CH{-}CH_2OH)PtCl_3^-]Y^+$ and $[(CH_3{-}CH{=}CH{-}CH_2OH)PtCl_3^-]Y^+$ where $Y^+ = [Coen_2Cl_2]^+$ (en = ethylenediamine).

Apart from the work of Denning[38] there are no stability constants reported for the system

$$ol + PtCl_4^{=} \rightleftharpoons (ol)PtCl_3^{-} + Cl^{-}$$

where ol = olefin, which forms the basis of the work reported here. This is partly because the systems are slow to equilibrate, typical equilibration times at 60°c being between one and three days, and partly because of the insolubility of most olefins in water. The presence of the $-NR_3^+$ group (where R = hydrogen or alkyl) in the olefin, once it had been shown not to coordinate to platinum(II)[35] provided an excellent group for making the olefin water-soluble. The use of water as a solvent allowed a background electrolyte to be used, enabling the activity coefficients of the species present to be kept approximately constant.

Denning's results, which are summarised in tables 1 and 2, led to the following conclusions:-

(1) The solvation energy of the free ligand is very important. A large solvation energy was found to decrease the stability constant.

(2) Bulky quarternary ammonium groups as $-NEt_3^+$ give steric interference with the central metal group, which lowers the stability constant.

(3) Groups such as the methyl group, when attached directly to the double-bond, give steric interference, which reduces the stability constant.

TABLE 1

$$K_1^{Cl} = \frac{[(ol^+)PtCl_3^-][Cl^-]}{[PtCl_4^=][ol^+]} \qquad K_1^{Br} = \frac{[(ol^+)PtBr_3^-][Br^-]}{[PtBr_4^=][ol^+]}$$

ol^+	K_1^{Cl} at 59°c	K_1^{Br} at 24.5°c
$allNH_3^+$	1022	306
$allNH_2Et^+$	806	241
$allNHEt_2^+$	386	127
$allNEt_3^+$	112	44.1
$allPEt_3^+$	505	
$allAsEt_3^+$	947	
$CH_3-CH=CH-CH_2NH_3^+$	258	
$C_6H_5CH=CH-CH_2-NH_3^+$	20.8	

TABLE 2

$$PtX_4^= + ol^+ \rightleftharpoons (ol^+)PtX_3^- + X^-$$

X	ol^+	ΔH (Kcals/mole)	ΔS (e.u.)
Cl	$allNH_2Et^+$	-5.9 ± 0.2	-4.4 ± 0.7
Cl	$allNEt_3^+$	-4.9 ± 0.3	-4.6 ± 1.0
Cl	$allAsEt_3^+$	-5.9 ± 0.6	-4.3 ± 2.0
Br	$allNH_2Et^+$	-4.8 ± 0.2	-5.3 ± 0.7

(4) An inductive withdrawal of electrons from the double-bond by a substituent tends to lower the stability constant. This is exemplified by the series allNEt$_3^+$, allPEt$_3^+$ and allAsEt$_3^+$, where the inductive withdrawal is greatest for the -NEt$_3^+$ group and least for the -AsEt$_3^+$ group.

(5) Since the ΔS values - see table 2 - are virtually independent of the number of hydrogen atoms attached to the quarternary nitrogen atom, Denning concluded that no association between this nitrogen atom and the chloride ligands of the type shown in figure 9 occurred.

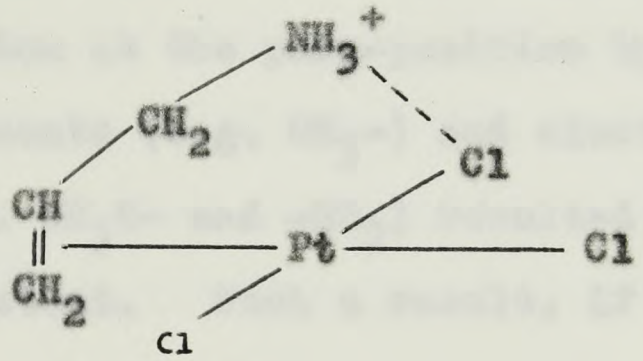


Figure 9

The remainder of the stability constant data involving platinum-olefin complexes falls into two main groups.

(1) Studies of the replacement of the ligand trans to the olefin[39,40]. Such equilibria are rapid and can be readily studied in aqueous solution. Some of the results are given on p. 61.

(2) Studies of the replacement of one olefin by another. Much of this work is qualitative. Anderson[41], from studies of the displacement of one olefin by another and

considerations of the relative volatility of the free olefins, found that the stability of the complexes $K^+[(ol)PtCl_3^-]$ decreased in the order $CH_2=CH_2 > C_6H_5CH=CH_2 >$ indene $>$ cyclohexene $>$ $(C_6H_5)_2C=CH_2$, $(C_6H_5)(CH_3)C=CH_2$. Hel'man[42] found a slightly different order, namely $C_6H_5CH=CH_2 > CH_2=CH-CH=CH_2 \sim CH_2=CH_2 > CH_3-CH=CH_2$. Joy and Orchin[43] measured stability constants for the system

$$[(\text{undecene})PtCl_3^-] + \text{p-subst. styrene} \rightleftharpoons [(\text{p-subst. styrene})PtCl_3^-] + \text{undecene}$$

in anhydrous alcoholic hydrogen chloride (0.01M) using a spectrophotometric method. Their results indicated that replacement of the hydrogen atom at the para-position by both electron-releasing substituents (e.g. CH_3-) and electron-withdrawing substituents (e.g. CH_3O- and $-NO_2$) resulted in an increase in the stability constant. Such a result, if it is an enthalpy as well as a free energy effect, can easily be understood if the σ-bond (olefin to metal) and the π-bond (metal to olefin) are of approximately equal strength.

Silver-olefin stability constants have been measured by a large number of workers. Although a potentiometric method is the most accurate as well as one of the simplest methods for measuring stability constants, it has not been used for silver-olefin complexes, due to the insolubility of most olefins in water. Most of the previous studies have involved distribution of the olefin between carbon tetrachloride and aqueous silver nitrate, the aqueous layer being kept at

constant ionic strength. The results differ widely in magnitude from author to author, probably due largely to the impossibility of maintaining constant activity coefficients in the organic layer. However, the following general conclusions emerge.

(1) Cis-olefins form stronger complexes than trans-olefins[44].

(2) The presence of substituents on the double-bond lowers the stability constant[45].

(3) Conjugation with a phenyl group weakens the silver-olefin bond[45].

(4) In cyclic olefins, as the strain in the double-bond increases, the stability constant increases[46].

(5) Some olefins give complexes such as $[(ol)_2Ag^+]$[45] and $[(ol)Ag_2^{++}]$[47] in addition to $[(ol)Ag^+]$.

The present work describes the measurement of stability constants for platinum-olefin and silver-olefin complexes. The stability constant (K) for the formation of the complex ML by the reaction,

$$M + L \rightleftharpoons ML$$

is defined by the expression

$$K = \frac{a_{ML}}{a_M \cdot a_L}$$

where a_X is the activity of the species X. Since it is very difficult to determine activities accurately, the stability constant is normally written in the approximate form

$$K = \frac{c_{ML}}{c_M \cdot c_L}$$

where c_X is the concentration of the species X. This approximation only becomes valid if a high concentration of an inert electolyte, relative to the metal and ligand concentrations, is used[48]. In comparing stability constants, valid comparisons will be obtained only if the activity coefficients for the two systems are equal. This will be approximately true if the same constant ionic medium is used in each case.

When looking for a suitable method to measure stability constants the following points must be considered.

(1) What is the accuracy?

(2) Can an excess of an inert electrolyte be used to provide a constant ionic strength?

(3) Is the apparatus available or obtainable?

The two methods used in this thesis are potentiometry for the silver-olefin complexes, and spectrophotometry for the platinum-olefin complexes.

Potentiometry is described by Rossotti[49] as "by far the most accurate and widely applicable technique currently available for the study of ionic equilibria". The application

of the method does depend on the availability of a suitable reversible electrode. In the case of silver the silver/silver chloride electrode is simple to prepare and gives excellent results. There is, however, no readily available electrode for platinum.

Ultra-violet spectrophotometry was used to study the formation of platinum-olefin complexes. It is not as accurate as potentiometry; however it is capable of an accuracy of about 2% if a suitable spectrophotometer is used. The use of the method depends on knowing, or being able to obtain, values of the extinction coefficients of all the species present, at the wavelength at which the measurements are made. Interpretation of the results becomes rapidly more difficult, and less accurate, as higher complexes are formed. However, in the systems described here only one complex [(ol)$PtCl_3^-$] is formed, so that the optimum accuracy of about 2% can be achieved.

Object of the present work

(a) Many factors are responsible for the stability constants of platinum(II)-olefin complexes. It was hoped that by continuing the work of Denning[38], using suitable unsaturated ammonium salts, it might be possible, from the entropy and enthalpy values of reation (1) p.19 , to determine the relative contributions of inductive and steric effects to the platinum(II)-olefin bond strength. In particular, it was hoped to determine whether electron-withdrawal from the double-bond increased or decreased the bond strength. An extension of this work to include unsaturated alcohols and acids, would give an opportunity to study groups with very different inductive effects.

(b) There are a very large number of stability constants known for silver(I) with a wide variety of ligands. Since the silver(I)-olefin stability constants reported in the literature vary widely, it was of interest to measure such stability constants for typical olefins to provide comparison with the platinum results.

(c) It was hoped that, from a study of the ultra-violet and visible spectra of the platinum-olefin complexes, it would be possible to determine the relative energies of the d-orbitals in these complexes.

CHAPTER 2

Experimental Details for the Determination of Platinum-Olefin Stability Constants

Introduction

For the determination of platinum-olefin stability constants it was necessary to consider the following equilibria:

$$PtCl_4^{=} + ol^{+} \underset{}{\overset{K_1}{\rightleftharpoons}} (ol^{+})PtCl_3^{-} + Cl^{-} \qquad (1)$$

$$PtCl_4^{=} + H_2O \underset{}{\overset{K_2}{\rightleftharpoons}} PtCl_3(H_2O)^{-} + Cl^{-} \qquad (2)$$

$$PtCl_3(H_2O)^{-} + ol^{+} \underset{}{\overset{K_3}{\rightleftharpoons}} (ol^{+})PtCl_2(H_2O) + Cl^{-} \qquad (3)$$

$$(ol^{+})PtCl_3^{-} + H_2O \underset{}{\overset{K_4}{\rightleftharpoons}} (ol^{+})PtCl_2(H_2O) + Cl^{-} \qquad (4)$$

Reagents

Water

Deionized water, obtained from tap water by a single stage process using a Le Grand, Sutcliff and Gell type C-400 "Stonwata" dual bed deionizer, was used throughout. The specific conductivity was always better than $20 \mu\Omega^{-1}cm^{-3}$. The

water had a very slight absorbance in the ultra-violet at energies greater than 30,000cm^{-1}, which varied slightly from batch to batch. This was compensated for in the spectrophotometric determinations by ensuring that the blank was always prepared with water from the same batch.

Hydrochloric Acid

A stock solution exactly 1N in strength was prepared from BDH AnalaR hydrochloric acid. It was standardised against sodium hydroxide solution using methyl red as an indicator. The sodium hydroxide solution was freshly prepared and standardised against BDH 1N analytical hydrochloric acid. This latter could not be used directly as it contains 0.001% w/v of mercuric chloride, and Hg^{II} is known to form olefin complexes[50].

Sodium Chloride

BDH AnalaR sodium chloride was used. The required quantity was obtained by direct weighing from a sample which had been kept in an oven at 120°c for at least 24 hours and then stored in a dessicator over calcium chloride before use.

Potassium Tetrachloroplatinate(II)

Potassium tetrachloroplatinate(II) obtained from Messrs. Johnson Matthey was twice recrystallised from dilute hydrochloric acid (0.1N). This was necessary to remove potassium hexachloroplatinate(IV) and on occasions platinum metal. The sample was filtered off on a sinter and dried in

a vacuum pistol at room temperature under mercury diffusion pump pressure (10^{-3}mmHg) for about 16 hours. It was stored in sealed specimen tubes in a dessicator over calcium chloride. The sample did not show any tendency to oxidise when it was kept absolutely dry. The required quantity was obtained by direct weighing.

Ligands

The preparation of the ligands is described in chapter 7.

Standardisation of Olefins

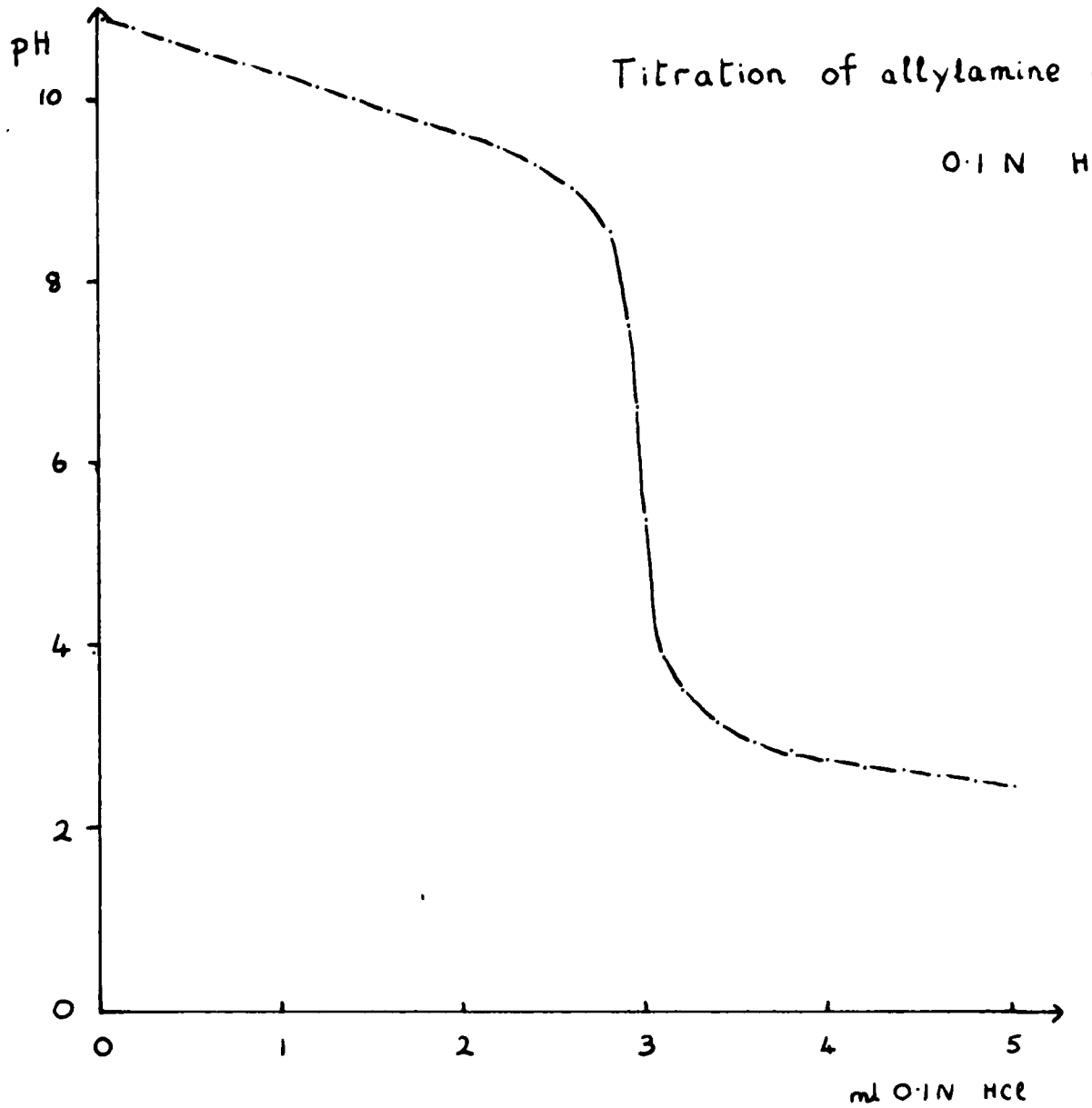
The unsaturated amines were prepared and used either as free amines, alkylammonium perchlorates or alkylammonium chlorides. In each case the particular form used was dictated by convenience of preparation.

Free amines

A stock solution of the amine about 0.1M in strength was made up and standardised by titration against standard 0.1N hydrochloric acid using a pH meter. A typical result is shown in figure 10.

Alkylammonium salts

A stock solution of the alkylammonium perchlorate or chloride was prepared, and standardised by passing a small sample (5ml) through a cation exchange column packed with "Zeo-Karb" 225 (obtained from The Permutit Company) in the H^+


pH
10
8
6
4
2
0
Titration of allylamine against
0·1 N HCl.
0
1
2
3
4
5
ml 0·1N HCl

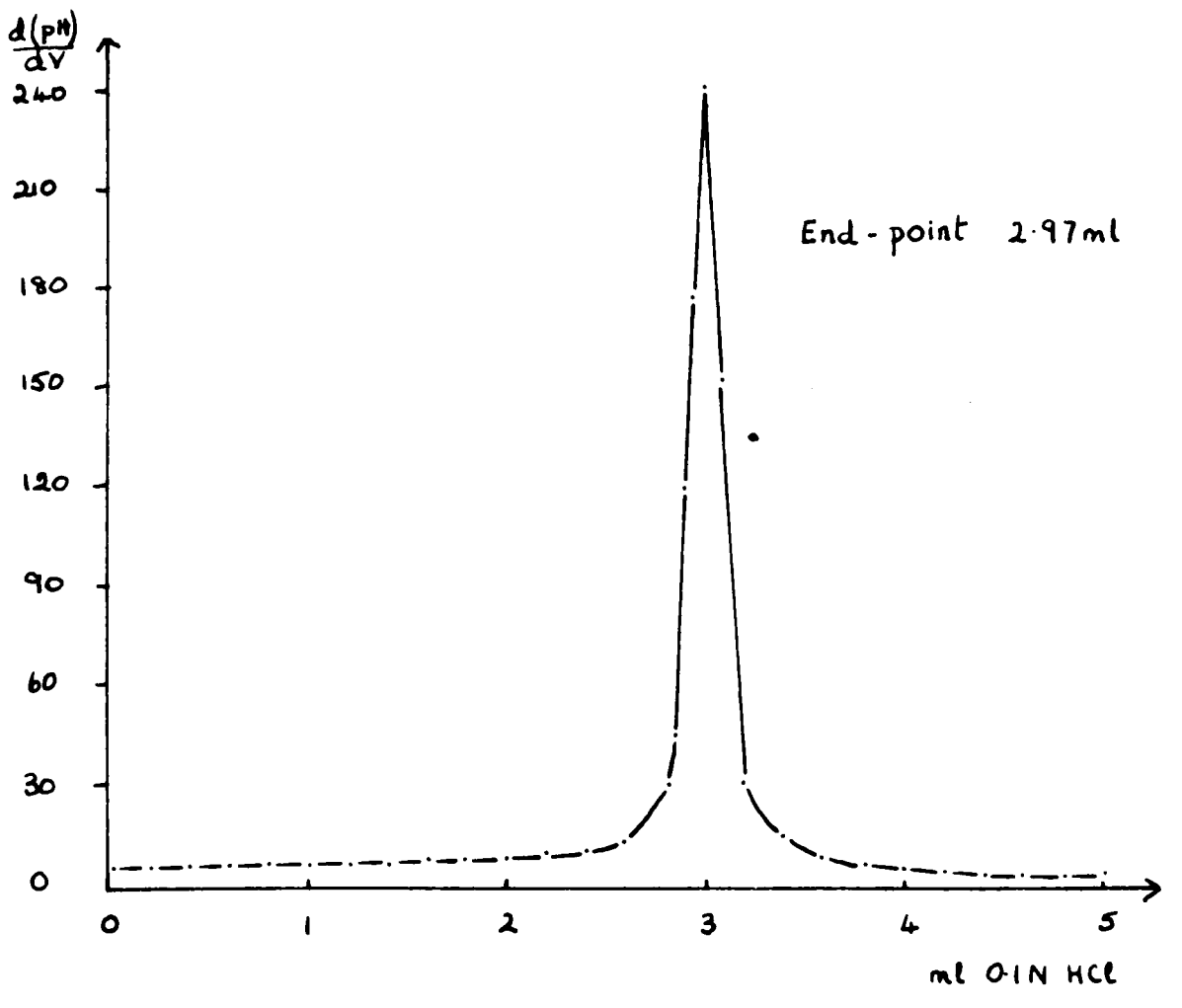

d(pH)/dV
240
210
180
150
120
90
60
30
0
End-point 2·97ml
0
1
2
3
4
5
ml 0·1N HCl

FIGURE 10

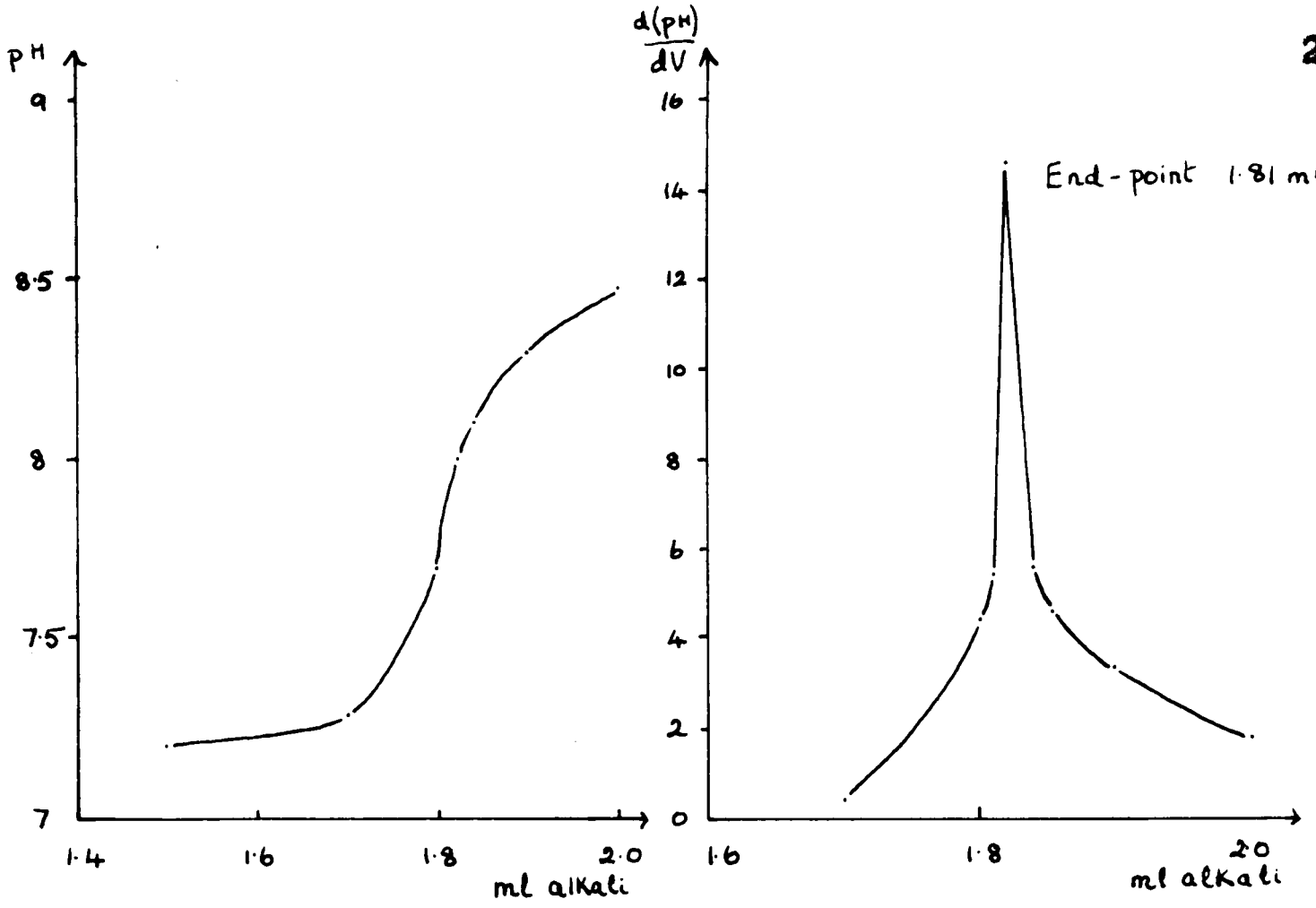
form. The liberated strong acid was eluted with distilled water and titrated against freshly prepared standard sodium hydroxide solution using methyl red as an indicator.

Alcohols

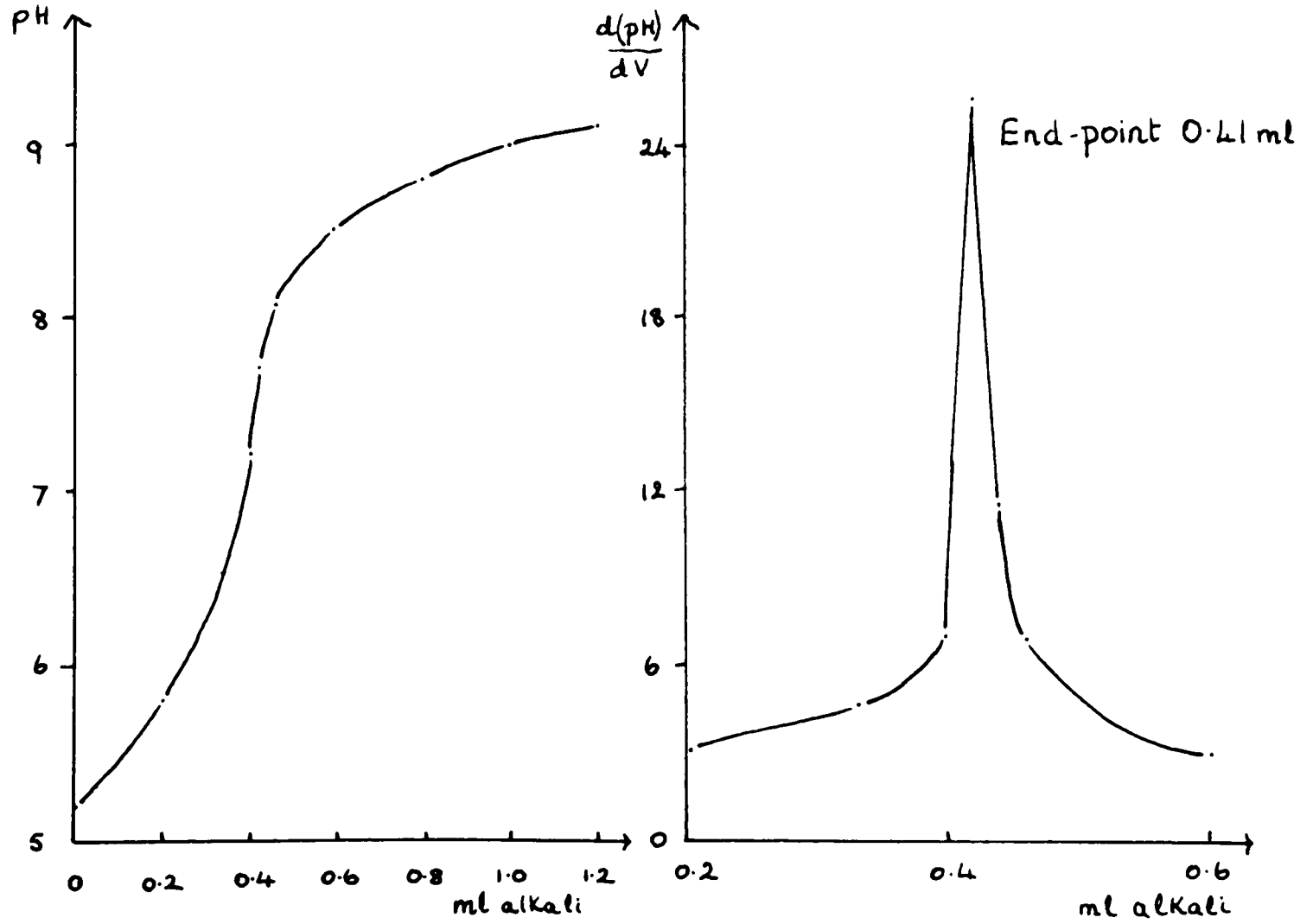
A solution of the unsaturated alcohol in water was shaken for forty minutes with a known excess of an acidic solution of potassium bromide and potassium bromate. After standing for a few minutes the vessel was cautiously opened and an excess of potassium iodide solution added. The iodine liberated was titrated against sodium thiosulphate solution.

Determination of K_2

The value of K_2, the equation constant for $[PtCl_4^{=}]$, was determined by a modification of the method of Grantham et al[51]. A series of solutions (20ml) containing potassium tetrachloroplatinate(II) (0.02M) in sodium chloride (1.98M) were equilibrated at 30°c for 48 hours. To each solution a known volume of sodium hydroxide (1.975×10^{-3}M) was added and the pH measured immediately. This operation took only one and a half minutes, thus minimizing any re-establishment of equilibrium. Since the solution prepared from AnalaR sodium chloride is slightly acidic a blank titration was performed similarly on the sodium chloride solution. The titrations, shown in figure 11, indicate that 1.40ml of 1.975×10^{-3}M sodium hydroxide were required to neutralise the acidic species



(a) Titration of K_2PtCl_4 (0·02M) in NaCl (1·98M) against NaOH ($1·975 \times 10^{-3}$M)



(b) Titration of NaCl (1·98 M) against NaOH ($1·975 \times 10^{-3}$ M)

FIGURE 11

$[PtCl_3(H_2O)^-]$, which corresponds to a value for K_2 at 30°c of 0.0138± 0.0002.

At 60°c the solutions were equilibrated for two hours, and then plunged into an acetone/carbon dioxide bath at -45°c until the solution temperature was 10°c. This procedure effectively froze the equilibrium and allowed the solution to be titrated as before. The end-point corresponded to a value for K_2 at 60°c of 0.0575± 0.001.

The value of K_2 at 45°c (0.029) was obtained from a plot of $\log_{10}K_2$ against the reciprocal of the absolute temperature.

These values are close to those that can be calculated from the data of Grantham et al[51], although their results were obtained from measurements in lithium perchlorate solution (0.318M). The values indicate that under the conditions used about 0.7%, 1.5% and 3% of the tetrachloroplatinate(II) ion is in the form $[PtCl_3(H_2O)^-]$ at 30°c, 45°c and 60°c respectively.

Determination of K_4

The value of K_4, the aquation constant for $[(ol^+)PtCl_3^-]$, was determined in 0.2M perchloric acid by the method of Leden and Chatt[39] for $[(allNH_3^+)PtCl_3^-]$ at 30°c. A reference silver/silver chloride electrode, dipping into a standard sodium chloride solution, was connected via a Wilhelm salt-bridge containing an identical sodium chloride solution to a sample

electrode. (The apparatus is described more fully in chapter 4). A calibration curve of emf developed against concentration of chloride ion present in the sample compartment was prepared. A solution of $[(allNH_3^+)PtCl_3^-]$ (0.3235g; 0.0009moles) in perchloric acid (250ml; 0.2M) was prepared and allowed to equilibrate for ten minutes at 30°c. Leden and Chatt[39] indicate that equilibration should be complete within two minutes. The potential of the electrode remained essentially constant for a period of ten minutes, indicating that the equation was complete.

10mins	114.0 mV
15mins	115.9 mV
20mins	115.0 mV

The potential was taken as 115 ± 1mV which corresponded to a value of K_4 at 30°c in 0.2M perchloric acid of $(2.5 \pm 0.6) \times 10^{-3}$. This value is in good agreement with the value $(3.0 \pm 0.5) \times 10^{-3}$ found by Leden and Chatt[39] for $[(C_2H_4)PtCl_3^-]$ at 25°c in 0.2M perchloric acid and $(2.0 \pm 0.5) \times 10^{-3}$ found by Denning[38] for $[(allNHEt_2^+)PtCl_3^-]$ at 25°c in 0.2M perchloric acid. The rather limited accuracy of these results has been attributed by Leden and Chatt[39] to a slight poisoning of the silver/silver chloride electrode by platinum(II) solutions.

It was found to be impossible to measure K_4 at 45°c or 60°c because the complexes, in the absence of 2M chloride,

decompose to metallic platinum. Although both the higher ionic strength (μ=2) and the higher temperatures (45°c and 60°c) used in the determination of the stability constants described below will increase the value of K_4, it is unlikely that the amount of $[(ol^+)PtCl_2(H_2O)]$ will remain other than negligibly small.

Choice of a Background Medium

A background electrolyte containing 2M chloride was used to maintain a constant ionic strength. Besides acting as a background electrolyte this will also minimize the equation of both $[PtCl_4^=]$ and $[(ol^+)PtCl_3^-]$. The cations chosen were sodium (1.9M) and hydrogen (0.1M). The choice of sodium was dictated by the limited solubility of potassium perchlorate in water[52], since a number of the ligands were used in the form of their perchlorates.

0.1M hydrogen ion was used because many of the olefins used contained primary, secondary or tertiary amino-groups. As amines (am) are known to react with complexes of the type $[(ol)PtCl_3^-]$ to form $[(ol)PtCl_2(am)]$, it was essential to ensure that only the corresponding quaternary ammonium salts were present. The number of pK_a values available in the literature for amines related to this work is very limited. However the values which are available[53] are shown in table 3. The pK_a values of the amines used in this study are likely to be

TABLE 3

Amine	pK_a	Temperature
$CH_2=CH-CH_2-NH_2$	9.5	25°c
$CH_2=CH-CH_2-NMe_2$	8.64	Not Recorded
$CH_2=CH-CH_2-NHMe$	10.11	Not Recorded
$CCl_2=CH-CH_2-NH_2$	9.47	20°c

higher than that of dimethylallylamine so that an acid concentration of 0.1N will result in the maximum amount of free amine present being about 2×10^{-11}M. If one assumes that the K_5 values for the reaction of $[(ol^+)PtCl_3^-]$ with amines are of the same order as that found by Chatt and Gamlen[40] for the reaction

$$(C_2H_4)PtCl_3^- + MeNH_2 \underset{}{\overset{K_5}{\rightleftharpoons}} (C_2H_4)PtCl_2(MeNH_2) + Cl^-$$

($K_5 = 1.3 \times 10^6$) then the amount of amino complex present in solution is always less than 1.5×10^{-2}%. The values of K_5, for the amines reported here, are unlikely to be greater than 1.3×10^6, since amines with pK_a values lower than methylamine ($pK_a = 10.74$) such as ammonia ($pK_a = 9.25$; $K_5 = 2 \times 10^5$) were found[40] to give lower values of K_5. The more sterically hindered amines such as dimethylamine ($pK_a = 10.85$; $K_5 = 3 \times 10^5$) and trimethylamine ($pK_a = 9.89$; $K_5 = 10^3$) also gave lower values of K5.

Concentrations of acid greater than 0.1N were found to be undesirable as they assisted the oxidation of the tetrachloroplatinate(II) ion (see p.40).

The Presence of Only One Olefin Complex in Solution

The presence of only one olefin complex [$(ol^+)PtCl_3^-$] in solution was confirmed by the existence of an isosbestic point[54] at about 380mμ for each of the systems studied. An isosbestic point will only arise if there are just two species containing platinum present in appreciable amounts. For this purpose [$PtCl_4^=$] and [$PtCl_3(H_2O)^-$] count as one species since they are always present in a fixed ratio to one another, independent of olefin concentration. If any other platinum species is present (e.g. [$(ol^+)_2PtCl_2$] or [$(ol^+)PtCl_2(am)$], where am = unsaturated amine) no isosbestic point will be observed unless the extinction coefficient of these species is identical, at the isosbestic wavelength, to the extinction coefficient of either [$PtCl_4^=$] or [$(ol^+)PtCl_3^-$]. The presence of more than one isosbestic point is obviously an advantage; however in the 1cm cells dictated by the availability of a thermostatted cell-housing only one such point could be detected.

The isosbestic points were very sharp, being within the experimental error of the spectrophotometer. A typical example is that for 4-pentenylamine shown in figures 12a and 12b.

Further confirmation of the presence of only one species

Isosbestic point for the system pent NH_3^+ + $PtCl_4^-$

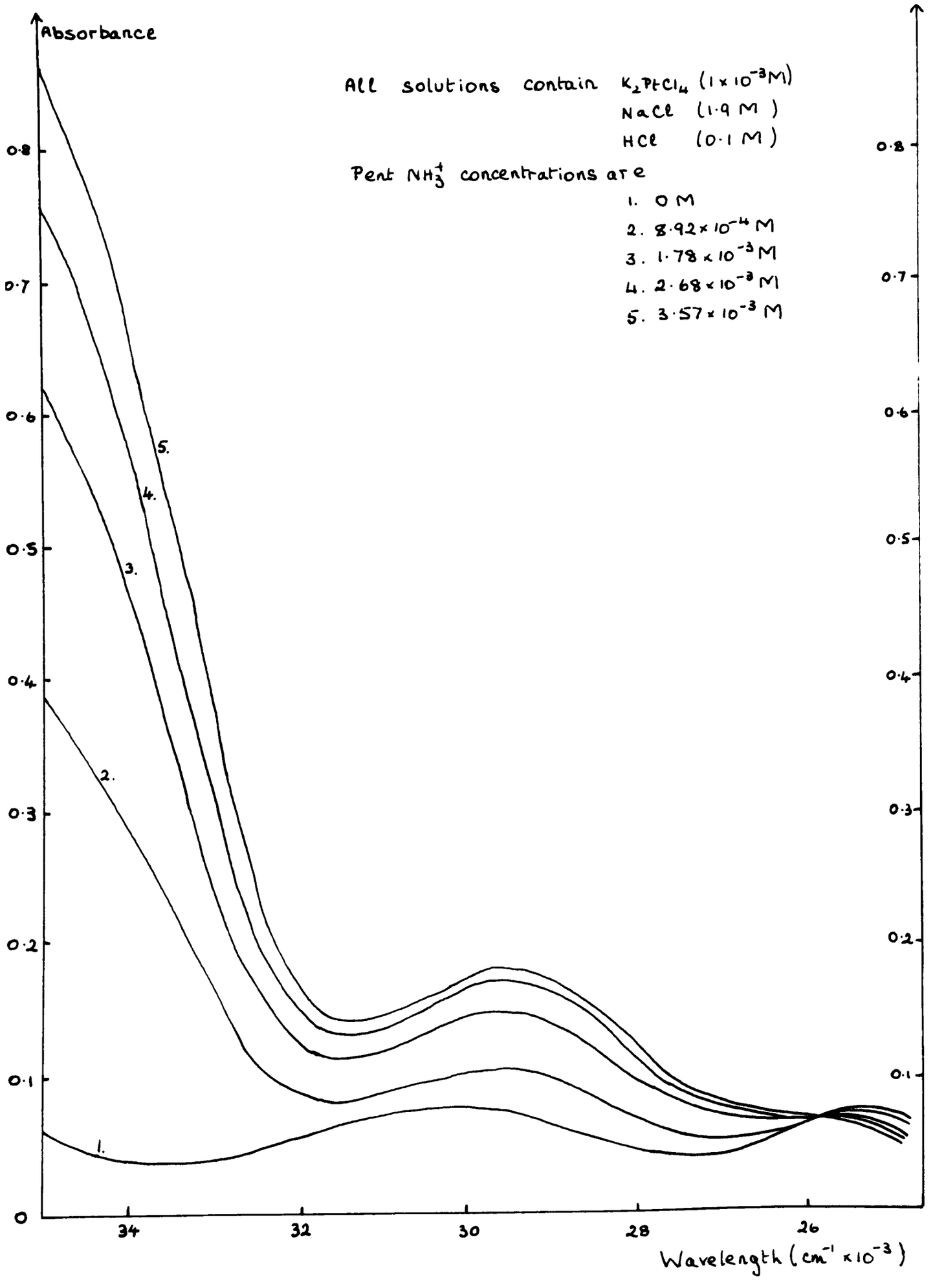


FIGURE 12a.

Isosbestic point for the system pent NH_3^+ + $PtCl_4^=$

(detail from figure 12a)

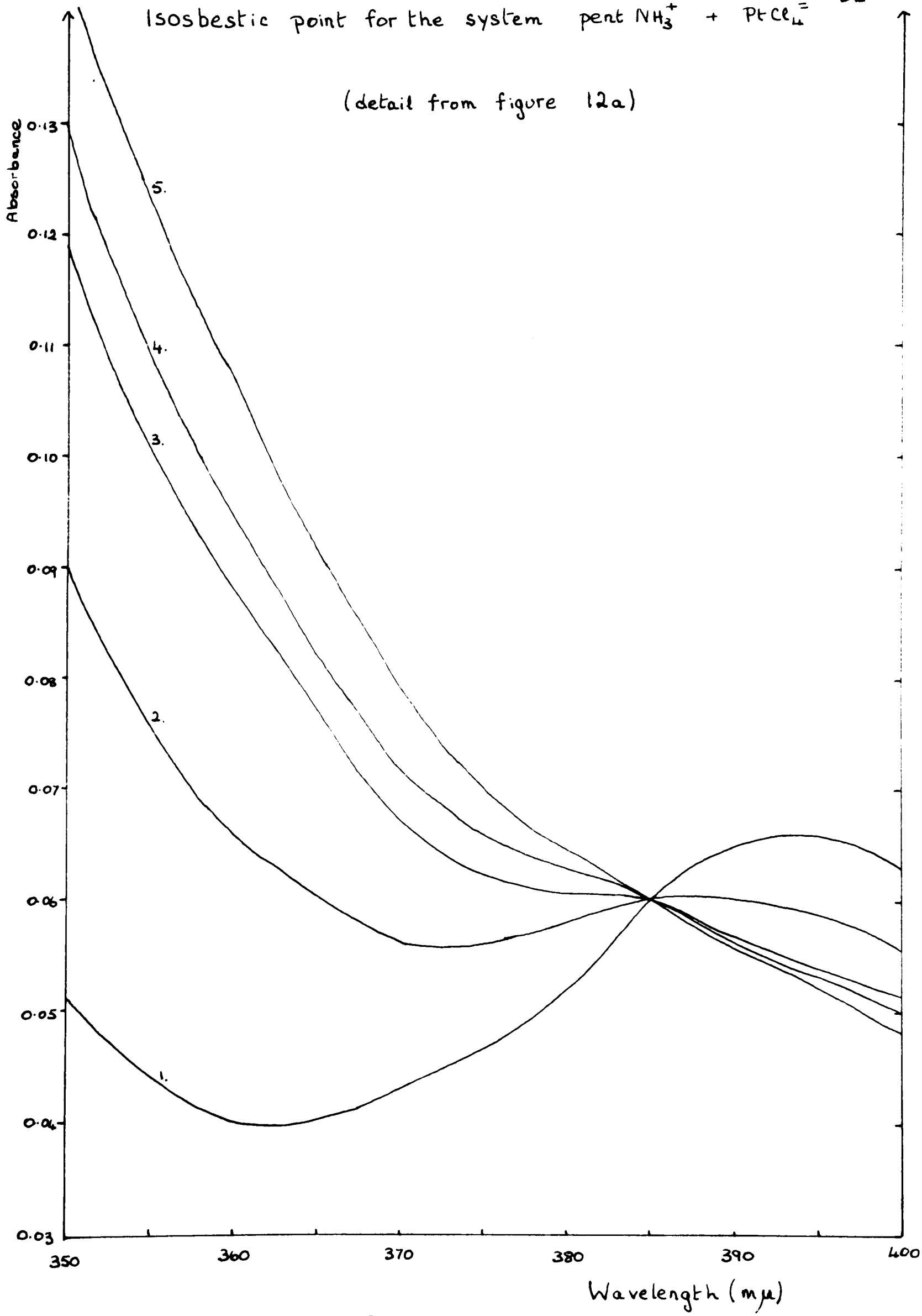
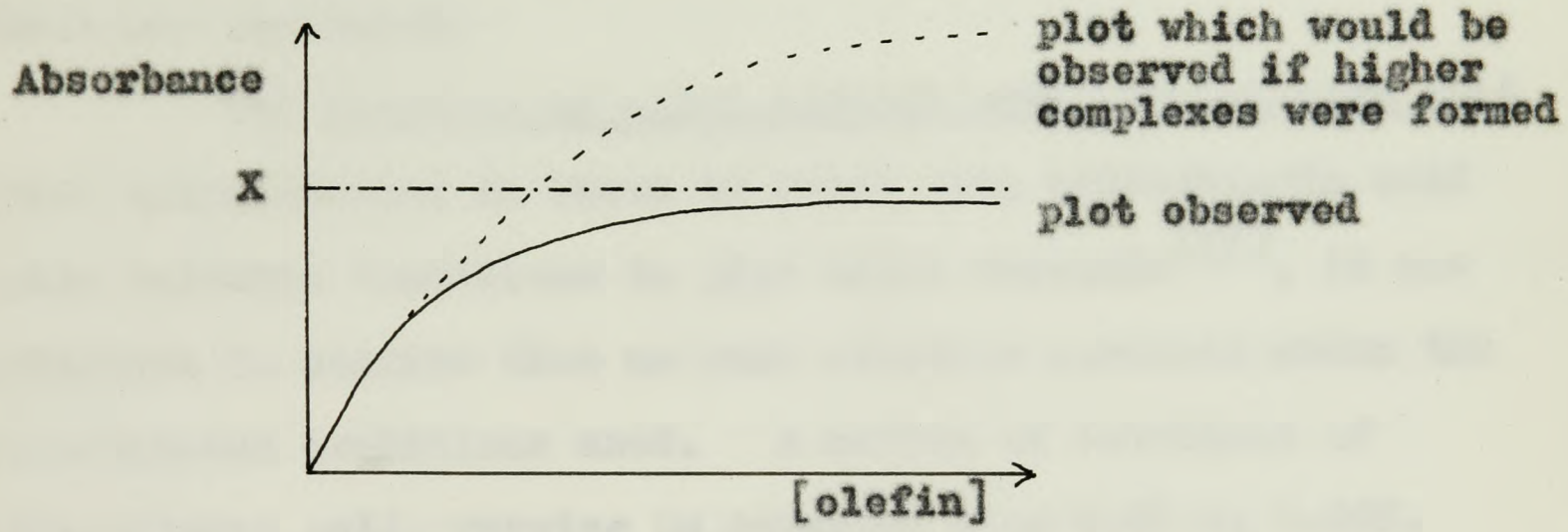


FIGURE 12b

is obtained from a plot of the absorbance at equilibrium against the concentration of olefin, at constant platinum concentration. This plot approaches asymptotically the absorbance value (X) predicted from the extinction coefficient of the species $[(ol^+)PtCl_3^-]$. An approximate value for this extinction coefficient can be obtained by dissolving an analysed sample of the species $[(ol^+)PtCl_3^-]$ in the background electrolyte and measuring the absorbance as rapidly as possible.



Stability Constants of Unsaturated Alcohols

Before determining the stability constants for unsaturated alcohols by the method used for unsaturated ammonium salts it was first necessary to establish that (a) no alcohol was lost by evaporation or decomposition, (b) the alcohol did not react with the hydrochloric acid present, (c) only one complex, $[(ol)PtCl_3^-]$, was formed and (d) no complexes were formed in which the alcohol was bound to platinum through the oxygen atom.

(a) Loss of allyl alcohol by evaporation or decomposition. To ensure that at 60°c no allyl alcohol was lost by evaporation, a solution of allyl alcohol was standardised, maintained at 60°c for one week and restandardised. No change in strength was found, indicating that in the loosely stoppered flasks used no loss by evaporation occurred. That no loss occurred by decomposition was confirmed both by this result and by the ultra-violet spectrum of the solution, which was unaltered.

(b) Reaction of allyl alcohol with hydrochloric acid Since allyl alcohol is known to react with hydrochloric acid under suitable conditions to give allyl chloride[55], it was important to confirm that no such reaction occurred under the experimental conditions used. A series of solutions of hydrochloric acid, varying in strength from 0.5N to 0.05N, were prepared. Two 25ml samples of each strength of acid were pipetted out. Allyl alcohol (1.0ml) was added to one of the samples, and the solutions maintained at 60°c for one week before being titrated against standard alkali. In each case the flask with allyl alcohol and the flask without gave identical titres. To ensure that this was not due to a rapid reversal of an equilibrium, a solution of allyl chloride (0.1M) in a mixture of water and ethanol was titrated against standard alkali. One drop of sodium hydroxide (0.1N) immediately made the solution alkaline to litmus.

(c) <u>The presence of only one complex</u> The presence of only one olefin complex ($[(ol)PtCl_3^-]$) in solution was demonstrated by the methods described above for the unsaturated ammonium ligands. In addition the existence of a maximum at equimolar concentrations of olefin and tetrachloroplatinate(II) in the spectrophotometric Job plots[56] at 275, 285, 295, 305 and 315mμ for each of the unsaturated alcohols provided further evidence. This should, however, only be regarded as confirmatory evidence as the sensitivity of such plots to higher complexes is low. A typical plot is shown in figure 13. It was obtained by equilibrating solutions, at 60°c for 48 hours, which were prepared from stock potassium tetrachloroplatinate(II) solution (K_2PtCl_4, 10^{-3}M; NaCl, 1.9M; HCl, 0.1M) and stock allyl alcohol solution (allyl alcohol, 10^{-3}M; NaCl, 1.9M; HCl, 0.1M). Seven flasks were made up as follows:

Flask	Stock K_2PtCl_4(ml)	Stock allyl alcohol (ml)
1	0	50
2	15	35
3	20	30
4	25	25
5	30	20
6	35	15
7	50	0

Job Plot for the system allyl alcohol + K_2PtCl_4

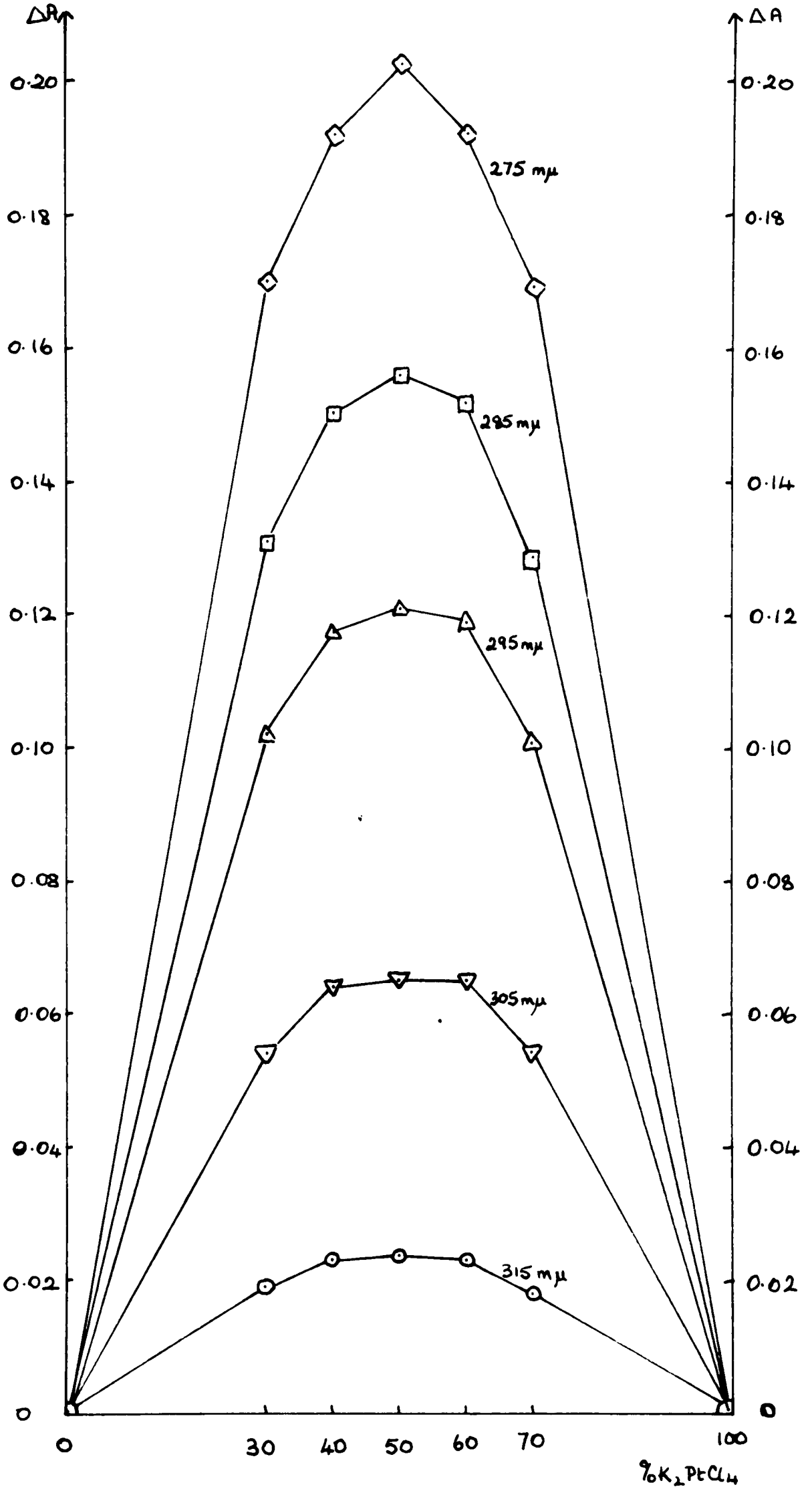


FIGURE 13

(d) <u>Absence of complexes in which the alcohol is bound to platinum through the oxygen atom</u>. There are no stability constants available for reactions of the type

$$PtCl_4^{=} + ROH \underset{}{\overset{K_6}{\rightleftharpoons}} (ROH)PtCl_3^{-} + Cl^{-}$$

where ROH is an alcohol bound to platinum via oxygen. The only available results are for water. The values of K_6 when R = H are given on p.25 as 1.38×10^{-2} (at 30°c) and 5.75×10^{-2} (at 60°c). The stability constant for an alcohol is likely to be lower rather than higher than this value, due to steric interference by the carbon chain. Using this value, the maximum amount of tetrachloroplatinate(II) ion present in the form $[(ROH)PtCl_3^{-}]$ is 2×10^{-3}% at 60°c. The value of K_4, the equation constant for $[(ol^{+})PtCl_3^{-}]$ (see p.26), indicates that the maximum amount of $[(ROH)PtCl_2(ol)]$ present is even less (2×10^{-4}%).

The absence, within experimental error, of any complexes in which the alcohol is bound to platinum through the oxygen atom is of course confirmed by the presence of an isosbestic point in the region 380-385mμ.

<u>Choice of a wavelength for the determination of K_1</u>

The absorbances were measured at 295mμ (33,900cm^{-1}) since at this wavelength the spectra of $[PtCl_4^{=}]$ and $[(ol^{+})PtCl_3^{-}]$ were appreciably different - see figure 14. At

Spectra of $[(all\,NH_3^+)PtCl_3^-]$ (1.) and $[K_2PtCl_4]$ (2.) in 1·9M NaCl + 0·1 M HCl.

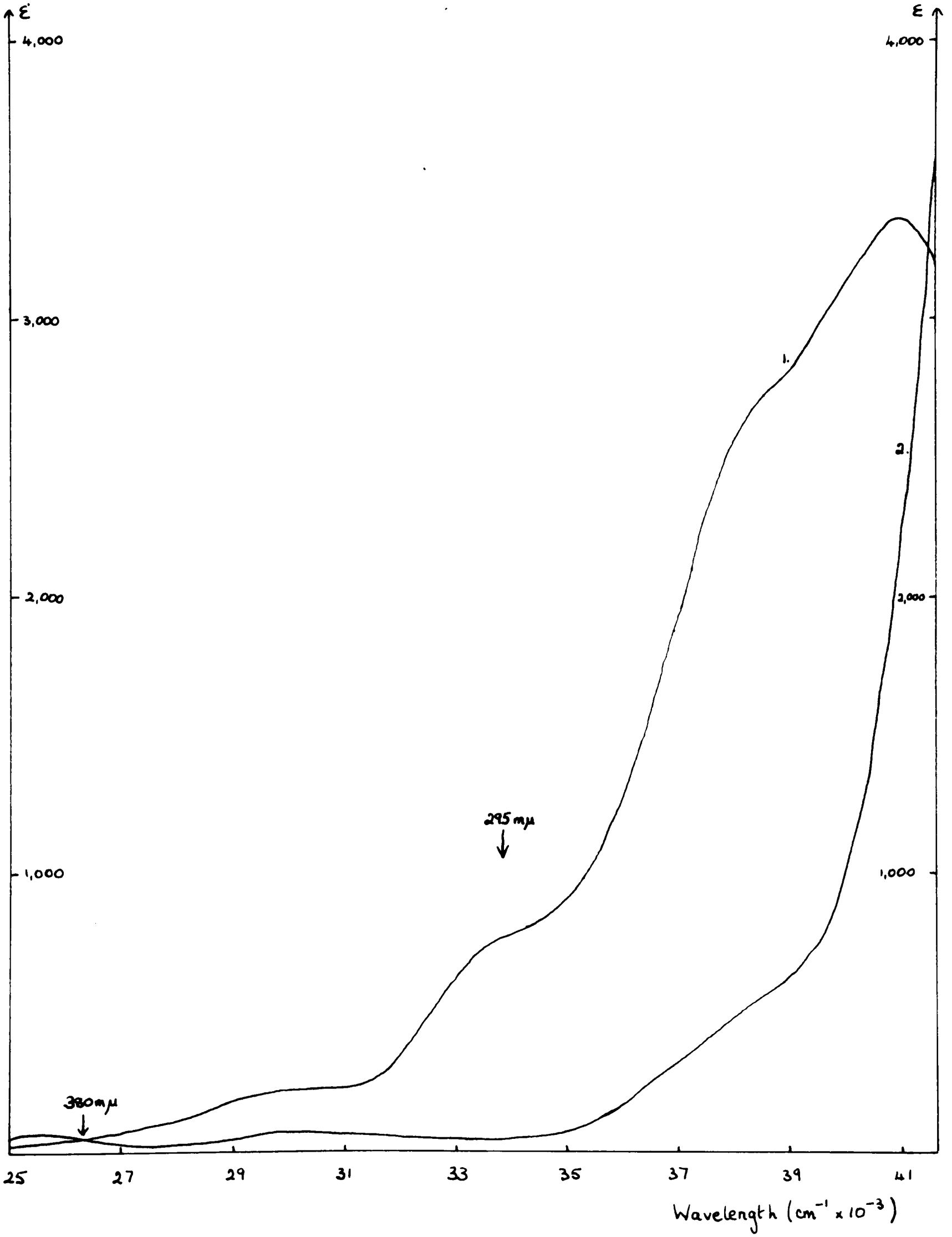


FIGURE 14

this wavelength also the change of extinction coefficient with wavelength was not too great, thus reducing any error which might arise as a result of a slight shift in the wavelength calibration of the spectrophotometer. In addition, the ligands did not absorb at this wavelength.

Determination of K_1

A series of fourteen solutions (50ml) were prepared, each containing, at 20°c, potassium tetrachloroplatinate(II) (10^{-3}M), sodium chloride (1.9M), hydrochloric acid (0.1M) and varying concentrations (ca 10^{-2}M) of the ligand in the cationic form. The concentration of ligand was varied over as wide a range as possible consistent with obtaining absorbance readings in the region 0.15 to 0.5, wherever this was possible. The ligand was introduced as the alkylammonium perchlorate, alkylammonium chloride, free amine or alcohol. Use of the free amine caused a negligible change in the hydrogen ion concentration. When the ammonium salts were used, a compensating solution of sodium perchlorate or sodium chloride was used to keep the ionic strength constant over all the flasks.

The concentrations at 60°c, 45°c and 30°c were calculated by allowing for the expansion of water with increase in temperature. The validity of this was checked for potassium tetrachloroplatinate(II) and sodium chloride by preparing solutions at 20°c, analysing them and then heating

them to 60°c and analysing again. For potassium tetrachloroplatinate(II), analysis was carried out by the colorimetric method described in chapter 7. For sodium chloride, analysis was carried out using silver nitrate and dichlorofluorescein[57]. The results, shown in table 4, are in good agreement with one another.

TABLE 4

Method	q
From "Kaye and Laby"[58]	0.9849
K_2PtCl_4	0.9814
NaCl	0.986

q = Constant by which a solution made up at 20°c must be multiplied to obtain the concentration at 60°c.

The values of q used at 45°c and 30°c were taken directly from Kaye and Laby[58]; they were 0.9920 and 0.9974 respectively.

The absorbances were measured at 295mμ after equilibration. The time taken to equilibrate varied according to the ligand, the limits are shown in table 5. The equilibrium readings were checked after a further period to ensure complete equilibration. Equilibration was performed in a tank thermostatted to $\pm$ 0.1°c. The absorbances

TABLE 5

Temperature	Time
60°c	1-3 days
45°c	3-12 days
30°c	14-50 days

were measured on a Unicam SP500 spectrophotometer fitted with an Adkins thermostatted cell-housing with a stability of ±0.2°c.

The first flask of the series contained no olefin. It was found that the absorbance of this flask tended to rise slowly with time due to the slow formation of potassium hexachloroplatinate(IV), which has an extinction coefficient of 6300 at 295mμ. For a total platinum concentration of 10^{-3}M, 0.1% of Pt^{IV} (i.e. 10^{-6}M) would increase the absorbance from 0.025 to 0.0313. No drift was observed in flasks which contained olefin, due to the reducing nature of the olefin. Accordingly, the absorbance of the flask which did not contain olefin was always measured after 24 hours at 60°c. The value of this absorbance still varied slightly, due to the time which elapsed between preparing the stock solution (K_2PtCl_4, 2×10^{-3}M; NaCl, 3.8M; HCl, 0.2M) and making up the individual flasks. In 0.2M acid, Pt^{II} is slowly oxidised to Pt^{IV}. The presence of a trace of potassium hexachloroplatinate(IV)

was shown by Milburn[59] not to affect the results, since it did not take part in the reaction, nor did it oxidise the olefin. This latter result indicates that although olefins will prevent the oxidation of Pt^{II} to Pt^{IV} they are not sufficiently strong reducing agents to reduce Pt^{IV} to Pt^{II}.

The experimental readings for all the platinum-olefin systems studied are recorded in Appendix II. A typical result, showing the time stability of the absorbance readings at equilibrium is illustrated in table 6.

Calculation of K_1

Two possible methods for calculating the results were considered. The method adopted, which involved the use of a computer, is described first (method 1). In this section only, the use of square brackets denotes concentration. The square brackets normally used to enclose Werner complexes have been omitted for the sake of clarity.

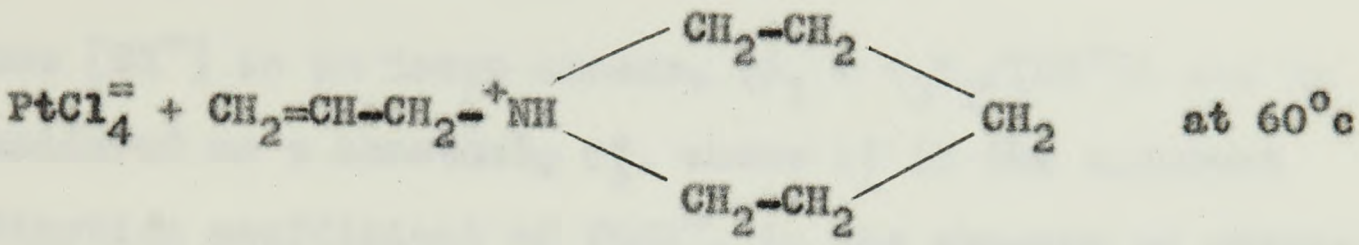
Method 1

The total absorbance of the solution, in 1cm cells is given by

$$A = \varepsilon_1[PtCl_4^{=}] + \varepsilon_2[PtCl_3(H_2O)^{-}] + \varepsilon_3[(ol^{+})PtCl_3^{-}]$$

where ε_1, ε_2 and ε_3 are the extinction coefficients of the three species respectively. From the equilibrium relationship for K_2, it follows that

TABLE 6



Solution	[ol$^+$] added	Abs. 23 hrs.	Abs. 30 hrs.
Blank	-	0.026	0.027
1	0.413×10^{-3} M	0.094	0.095
2	0.826	0.1535	0.154
3	1.032	0.180	0.179
4	1.445	0.224	0.222
5	1.858	0.272	0.274
6	2.271	0.302	0.303
7	2.864	0.332	0.332
8	3.096	0.359	0.359
9	3.509	0.385	0.387
10	3.922	0.409	0.409
11	4.335	0.430	0.428
12	4.748	0.445	0.446
13	5.161	0.4605	0.460

$$A = \varepsilon_1[PtCl_4^{=}] + \varepsilon_2K_2[PtCl_4^{=}]/[Cl^-] + \varepsilon_3[(ol^+)PtCl_3^-]$$

whence $$A = [PtCl_4^{=}]\left\{\varepsilon_1 + \frac{\varepsilon_2K_2}{[Cl^-]}\right\} + \varepsilon_3[(ol^+)PtCl_3^-] \qquad (1)$$

Since $[Cl^-]$ is in large excess, $(\varepsilon_1 + \varepsilon_2K_2/[Cl^-])$ can be considered as a constant, ε_1', where ε_1' is the apparent extinction coefficient of $PtCl_4^{=}$, in the absence of olefin after aquation is complete. The total platinum concentration $[Pt]_T$ is given by

$$[Pt]_T = \frac{K_2[PtCl_4^{=}]}{[Cl^-]} + [PtCl_4^{=}] + [(ol^+)PtCl_3^-]$$

$$\text{or } [Pt]_T = [PtCl_4^{=}]\{K_2/[Cl^-] + 1\} + [(ol^+)PtCl_3^-]$$

Substituting for $[PtCl_4^{=}]$ in (1) and rearranging,

$$[(ol^+)PtCl_3^-] = \frac{A - \varepsilon_1'[Pt]_T/\{K_2/[Cl^-] + 1\}}{\varepsilon_3 - \varepsilon_1'/\{K_2/[Cl^-] + 1\}} \qquad (2)$$

$$\text{and } [PtCl_4^{=}] = \frac{[Pt]_T - [(ol^+)PtCl_3^-]}{\{K_2/[Cl^-] + 1\}} \qquad (3)$$

The value of K_1 can now be calculated since,

$$K_1 = \frac{[(ol^+)PtCl_3^-][Cl^-]/[PtCl_4^=]}{\{[ol^+]_T - [(ol^+)PtCl_3^-]\}}$$

where $[ol^+]_T$ = total olefin concentration.

The value of ε_1' was obtained from the "blank" solution used in each determination. An approximate value of ε_3 can be obtained by dissolving a known amount of the complex in the background medium and measuring the absorbance as rapidly as possible, before the equilibria have had time to alter the concentration of the complex appreciably. Using this value of ε_3 it is possible to calculate the value of K_1 for each of the thirteen solutions containing olefin. When these stability constants are plotted against ligand concentration one of three graphs will be obtained - see figure 15. The "true value" of ε_3 is that which gives a straight line parallel to the abscissa. The values of K_1 for the points on this line also exhibit the lowest standard deviation. Thus, by calculating the standard deviation for each value of ε_3, a plot such as is shown in figure 16 is obtained. The "true stability constant" is then obtained using the "true value" of ε_3.

Before calculating the standard deviation it was important to take account of the experimental significance of the values of K_1 obtained from the thirteen flasks. Thus the

Plot of K_1 v. total ligand concentration for the system all $NH(CH_2)_5^+ + PtCl_4^=$

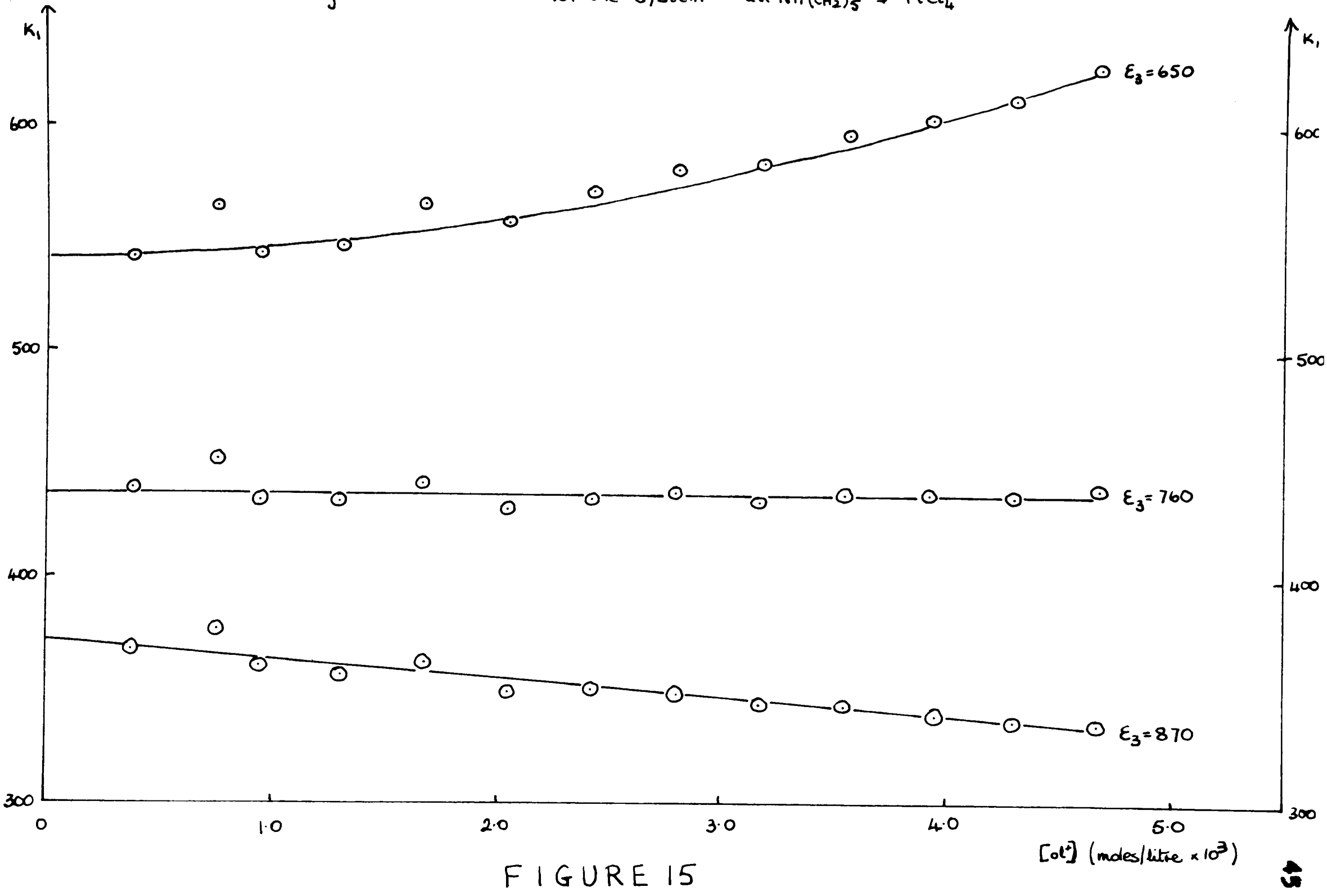


FIGURE 15

Plot of the standard deviation (σ) against ε_3 for the system $all\,NH(CH_2)_5^+ + PtCl_4^=$

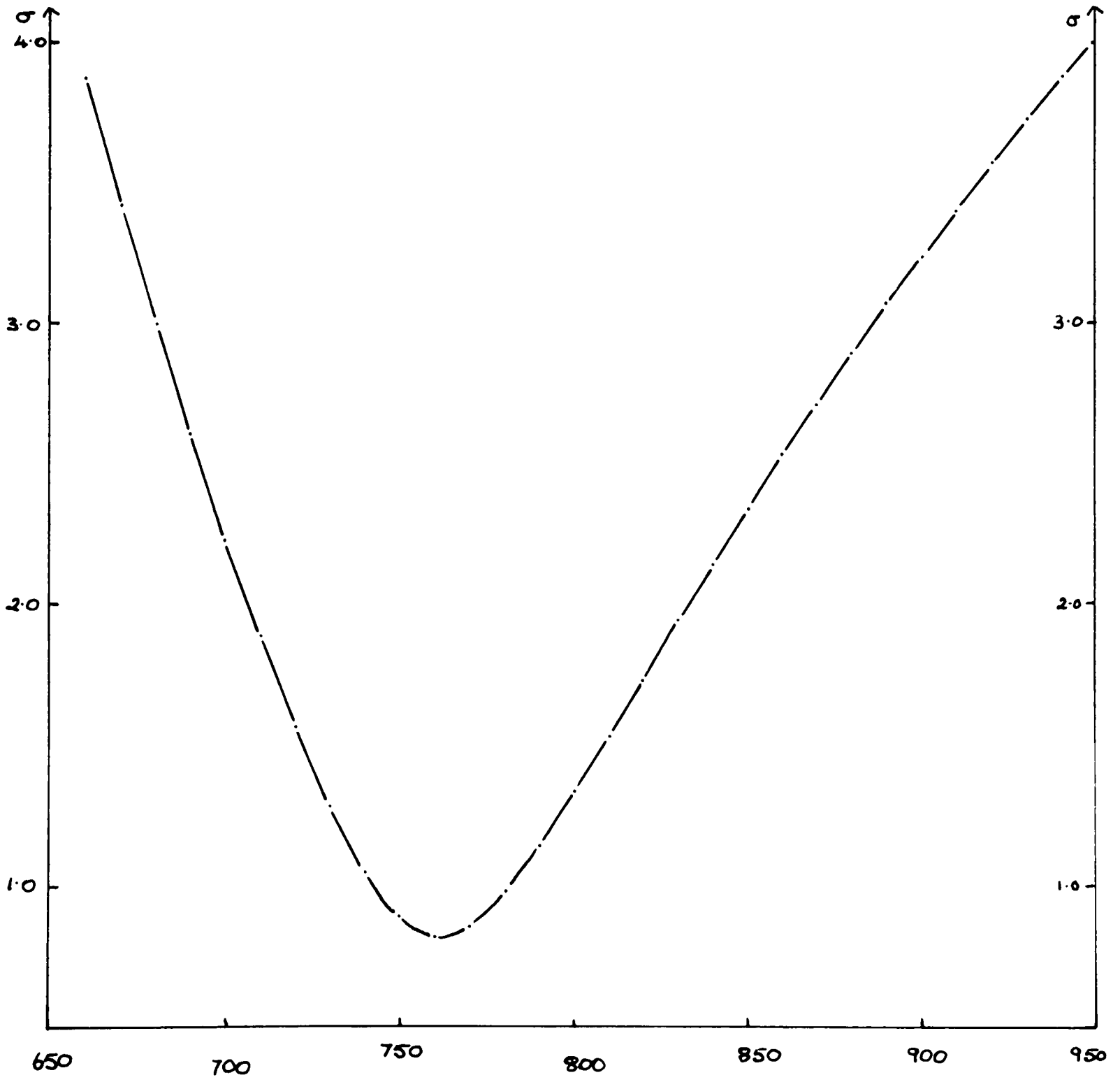


FIGURE 16

values where the concentration of the complex is large have greater experimental significance than where it is small. This is because it is possible to measure the larger absorbance values more accurately than the smaller ones. A system of weighting was used to take this into account. The thirteen equilibrium constants were recalculated using absorbance values 0.001 units less. Such a difference could arise from dust on the cell faces. The difference in the two equilibrium constants (ΔK) so obtained was calculated. A weighting factor 'r' was then taken as $\Delta K_{minimum}/\Delta K_{observed}$. The factors 'r' were then normalised so that

$$\sum_{i=0}^{i=13} \frac{K_{minimum}}{K_{observed}} = 13 = \text{total number of observations}$$

The normalised weighting factors R_i were then multiplied by the observed equilibrium constants (K_i). The product (K_iR_i) then had a value proportional to the experimental significance as judged by its response to an artificially induced error. The weighted mean equilibrium constant ($\overline{K_1}$) was given by

$$\overline{K_1} = \frac{\Sigma K_i R_i}{13}$$

and the weighted standard deviation (σ) by

$$\sigma = \sqrt{\frac{\{|\overline{K_1} - K_i| R_i\}^2}{13}}$$

An example of this process is shown in table 7.

TABLE 7

Calculation of K_1 and σ for $PtCl_4^{=}$ + allNH$(CH_2)_5^{+}$ assuming $\varepsilon_3^{=}760$

K_1	K_1'	ΔK	r_i	R_i	K_iR_i	$\lvert\bar{K}-K_1\rvert$	$R_i\lvert\bar{K}-K_i\rvert$	$(R_i\lvert\bar{K}-K_i\rvert)^2$
439.6	427.5	22.1	0.113	0.157	69.2	2.9	0.46	0.21
453.1	446.3	6.8	0.368	0.512	225.1	16.4	8.40	70.51
434.4	428.8	5.6	0.446	0.622	270.1	2.3	1.43	2.04
433.0	428.6	4.4	0.568	0.791	342.6	3.7	2.93	8.57
442.6	438.8	3.8	0.658	0.916	405.5	5.9	5.41	29.22
431.4	428.0	3.4	0.735	1.024	441.7	5.3	5.43	29.45
436.1	433.0	3.1	0.806	1.123	489.8	0.6	0.67	0.45
438.2	435.3	2.9	0.862	1.201	526.1	1.5	1.80	3.24
434.5	431.7	2.8	0.893	1.243	540.3	2.2	2.74	7.49
437.2	434.6	2.6	0.962	1.339	585.4	0.5	0.67	0.45
437.4	434.8	2.6	0.962	1.339	585.7	0.7	0.94	0.88
436.2	433.6	2.6	0.962	1.339	584.1	0.5	0.67	0.45
439.4	436.9	2.5	1.000	1.393	611.9	2.7	3.76	14.14

$\Sigma K_iR_i = 5677.5$ $\quad \Sigma(R_i\lvert\bar{K}-K_i\rvert)^2 = 167.11$

$\bar{K} = 436.7$ $\quad \sigma = 0.82\%$

The actual computation of the results was carried out using the Oxford University KDF 9 computer. The programme is described in Appendix I p.178.

Method 2

An alternative method of calculation was also attempted. This was based on the graphical method described by Rossotti[60].

The concentration of olefin complex is related to the absorbance by

$$[(ol^+)PtCl_3^-] = \Delta A/l\Delta\varepsilon \qquad (1)$$

where $\Delta A = A - l\varepsilon_1'[Pt]_T$, l = cell length in cm., A = observed absorbance and $\Delta\varepsilon = \varepsilon_3 - \varepsilon_1'$.

From the equilibrium relationship,

$$[(ol^+)PtCl_3^-] = \frac{K_1[ol^+]_f[PtCl_4^=]}{[Cl^-]}$$

where $[ol^+]_f$ = concentration of free olefin.

but $[PtCl_4^=] = [Pt]_T - [(ol^+)PtCl_3^-]$

and $[ol^+]_f = [ol^+]_T - [(ol^+)PtCl_3^-]$

whence $[(ol^+)PtCl_3^-] = \dfrac{[ol^+]_T[Pt]_T}{[Cl^-]/K_1 - [(ol^+)PtCl_3^-] + [Pt]_T + [ol^+]_T}$

If $[(ol^+)PtCl_3^-] \ll [Cl^-]/K_1 + [Pt]_T + [ol^+]_T$ (2)

$$\text{then } [(ol^+)PtCl_3^-] = \frac{[ol^+]_T[Pt]_T}{[Cl^-]/K_1 + [Pt]_T + [ol^+]_T} \qquad (3)$$

Combining (1) and (3)

$$\frac{1[Pt]_T[ol^+]_T}{\Delta A} = \frac{[Pt]_T + [ol^+]_T}{\Delta\varepsilon} + \frac{[Cl^-]}{K_1\Delta\varepsilon}$$

Thus a plot of $1[Pt]_T[ol^+]_T/\Delta A$ against $[Pt]_T + [ol^+]_T$ should give a straight line of slope $1/\Delta\varepsilon$ and intercept $[Cl^-]/K_1\Delta\varepsilon$. Because of condition (2) the method will work best when K_1 is small.

Figures 17 and 18 show the application of this method to $CH_2{=}CH{-}CH_2NMe_3^+$ and $CH_2{=}CH{-}CH_2OH$. The results are summarised in table 8.

TABLE 8

Ligand at 60°c	Computer calculation (method 1)		Graphical calculation (method 2)	
	K_1	ε_3	K_1	ε_3
$CH_2{=}CH{-}CH_2NMe_3^+$	117.0	760	116.8	760
$CH_2{=}CH{-}CH_2OH$	3890	770	1154	855

Since this method was only applicable where the values of K_1 were low, and since even then it involved an

Graphical Plot (Method 2) for the system

allyl alcohol + $PtCl_4^=$

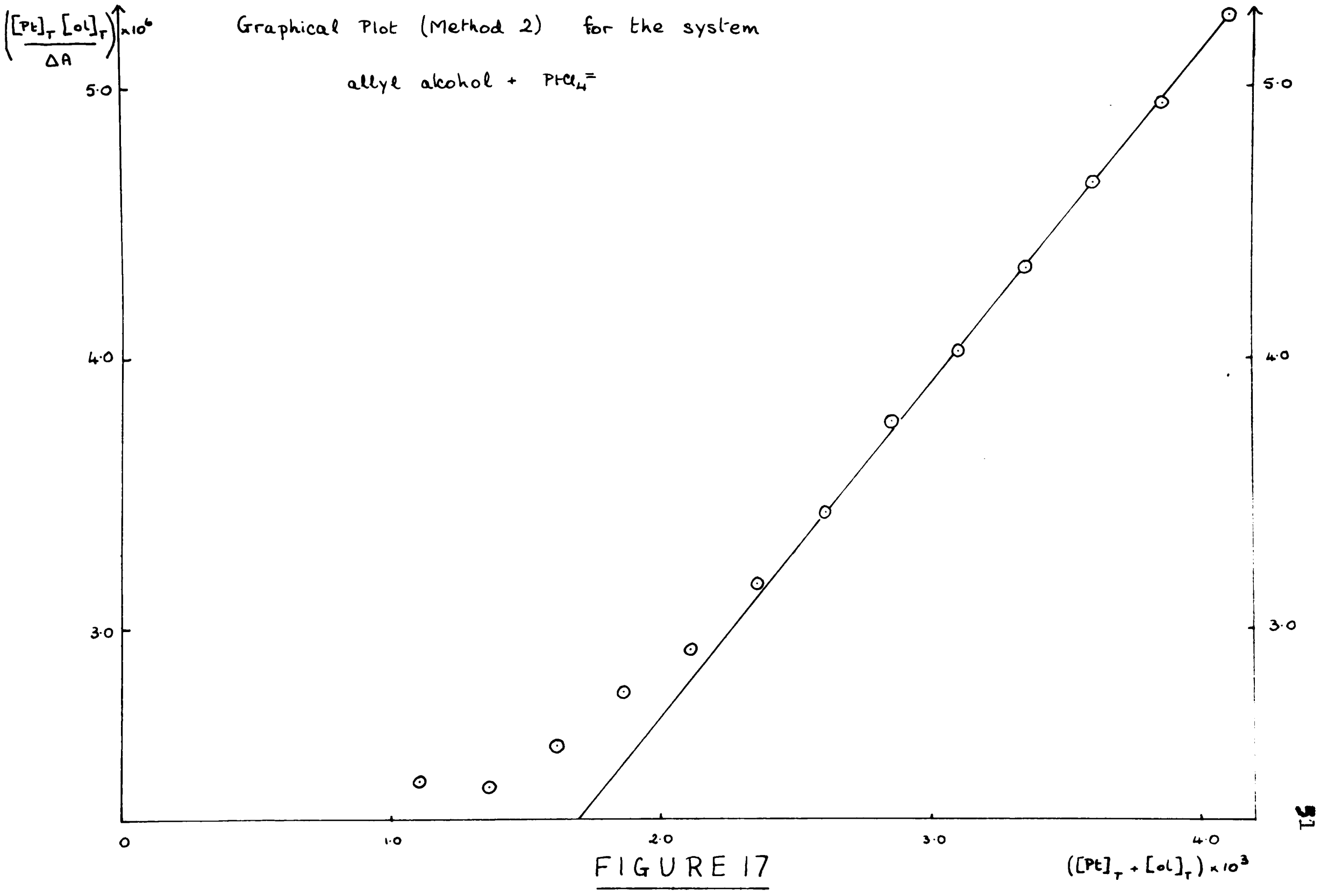


FIGURE 17

Graphical plot (Method 2) for the system $allNMe_3^+ + PtCl_4^=$

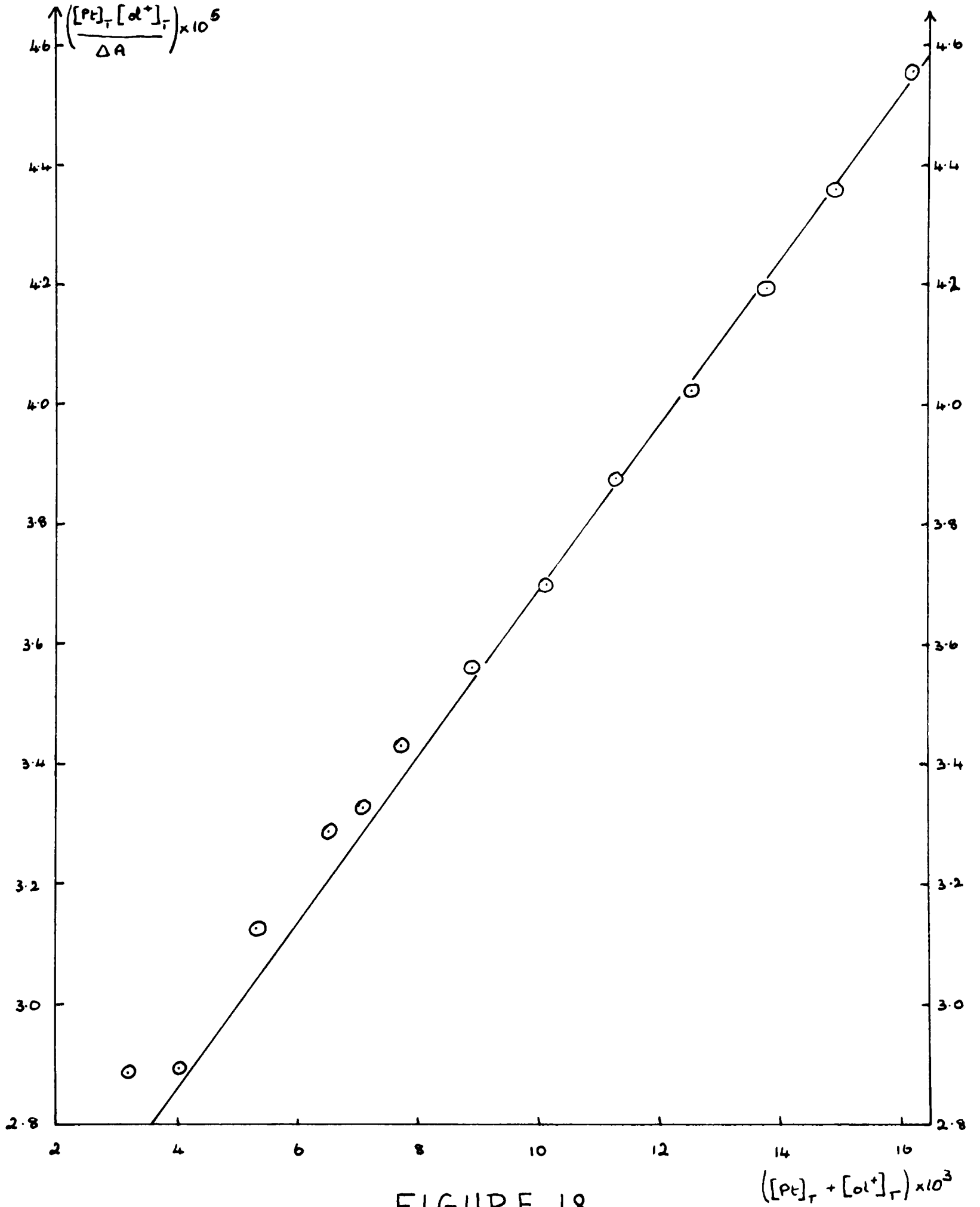


FIGURE 18

approximation, it was rejected in favour of the computer calculation which did not involve any approximation and which was applicable to all the systems studied.

Calculation of the errors in K_1

The actual value of K_1 recorded in table 9 is the value of K_1 which corresponds to the value of ε_3 which gives the lowest standard deviation. Assuming ε_3 to be correct, the standard deviation can be read off from the computer output. However there will also be an error in the value of ε_3. The probable error in ε_3 was estimated from the steepness of the minimum in the plot of ε_3 against σ. The error in K_1 corresponding to this error in ε_3 was then calculated, and the total error taken as the sum of the two individual errors.

The high error of 16%, which corresponds to $\pm$0.4 in the value of K_1, observed for the 3-methylbut-2-enylammonium cation arises from the fact that the ligand absorbs slightly at the wavelength used and also gives a very low stability constant. This resulted in low absorbance values which were below the range of maximum accuracy (0.15 - 0.50) on the spectrophotometer. As only 0.22% of the total ligand was present in the form of a complex, the absorbance due to the ligand was calculated by assuming that all the ligand was present in the form of the free ligand.

TABLE 9

Stability constants of platinum(II)-olefin complexes [(ol)$PtCl_3^-$]

Olefin	Temp. (°c)	K_1	Error (%)
$allNH_3^+$	44.0	1737	2.5
	30.2	2829	1.5
$allNHEt_3^+$	45.3	551	2.5
	30.0	865	1.2
$allNMe_3^+$	60.0	117	1.0
	44.5	173	1.2
	30.0	259	1.2
$allN^nPr_3^+$	60.0	131	2.0
$allN^nBu_3^+$	60.0	308	2.0
$allNH(CH_2)_4^+$	60.0	689	2.0
$allNH(CH_2)_5^+$	60.0	437	1.2
$butNH_3^+$	60.0	2038	2.0
	44.5	3017	2.0
	30.0	4396	4.0
$butNEt_3^+$	60.0	4449	2.0
	44.8	5911	3.0
	30.0	7778	3.0
$butAsEt_3^+$	60.0	5459	2.5
	44.8	7014	3.0
	30.0	8962	3.0
$pentNH_3^+$	60.0	1124	3.0

TABLE 9 continued

Olefin	Temp. (°c)	K_1	Error (%)
trans-CH_3-CH=CH-CH_2-NH_3^+	60.2	209	1.0
	44.5	304	1.2
	30.0	450	2.5
CH_2=CH-CH(CH_3)-NH_3^+	60.0	804	1.5
	45.3	1282	1.5
	30.0	2194	3.0
CH_2=C(CH_3)-CH_2-NH_3^+	60.0	3.2	5.5
$(CH_3)_2$C=CH-CH_2-NH_3^+	60.0	2.6	16
allOH	60.0	3890	3.5
	44.5	7250	2.5
	30.0	13011	3.5
trans-CH_3-CH=CH-CH_2OH	60.0	3008	2.0
pentOH	60.0	2525	3.5

Calculation of the component ΔH and ΔS values for K_1

The component ΔH and ΔS values, given in table 10, were obtained by plotting $\log_{10} K_1$ against the reciprocal of the absolute temperature (figure 19). The slope of the plot is then $-\Delta H/2.303R$ and the intercept is $+\Delta S/2.303R$, where ΔH is in Kcals/mole and ΔS is in entropy units. Since only three points (30°c, 45°c and 60°c) were available for each plot a precise estimate of the error was not possible. However an estimate was obtained in each case by taking the maximum possible value of $\log_{10} K_1$ at 60°c, as indicated by the error in K_1, and the minimum possible at 30°c, and recalculating the values of ΔH and ΔS. For $allNH_3^+$ and $allNHEt_2^+$ the values of K_1 at 59.0°c were taken from the work of Denning[38] reported on p.12.

TABLE 10

Enthalpies and entropies of formation of complexes $[(ol)PtCl_3^-]$

Olefin	ΔH (Kcals/mole)	ΔS (e.u.)
$allNH_3^+$	-7.1 ± 0.2	-7.6 ± 0.7
$allNHEt_2^+$	-5.6 ± 0.2	-5.0 ± 0.6
$allNMe_3^+$	-5.3(5) ± 0.2	-6.6 ± 0.6
$butNH_3^+$	-5.1 ± 0.4	-0.2 ± 1.2
$butNEt_3^+$	-3.8 ± 0.4	+5.4 ± 1.2
$butAsEt_3^+$	-3.3 ± 0.35	+7.2 ± 1.1
$CH_3CH{=}CH{-}CH_2NH_3^+$	-5.1 ± 0.25	-4.6(5) ± 0.7
$CH_2{=}CH{-}CH(CH_3){-}NH_3^+$	-6.7 ± 0.3	-6.9 ± 1.0
allOH	-8.1 ± 0.5	-7.8 ± 1.5

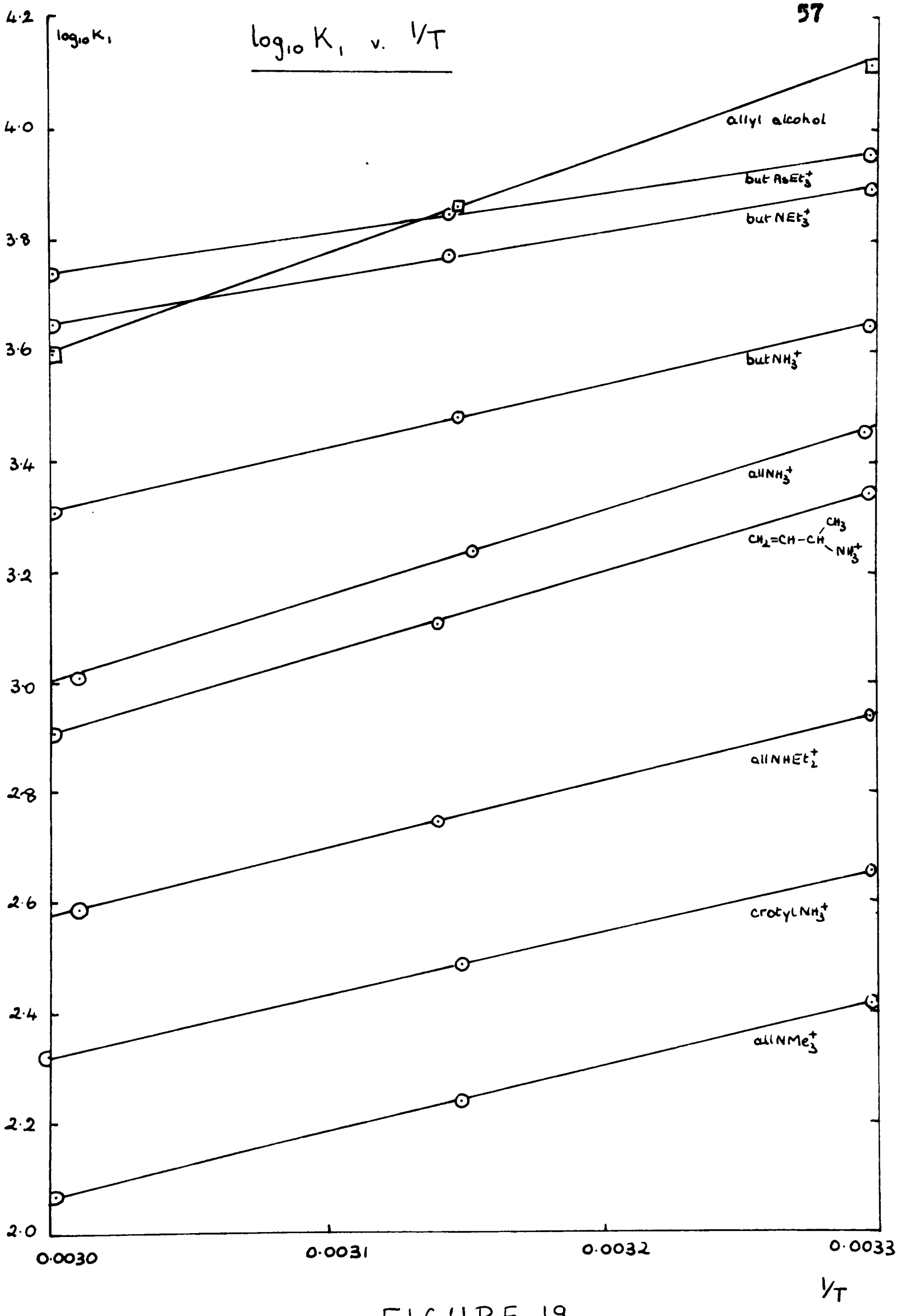

log10 K1 v. 1/T
log10 K1
4·2
4·0
3·8
3·6
3·4
3·2
3·0
2·8
2·6
2·4
2·2
2·0
0·0030
0·0031
0·0032
0·0033
1/T
allyl alcohol
but AsEt3+
but NEt3+
but NH3+
all NH3+
CH2=CH-CH(CH3)NH3+
all NHEt2+
crotyl NH3+
all NMe3+

FIGURE 19

CHAPTER 3

Discussion of Platinum-olefin Stability Constants

(1) Enthalpy and Entropy Terms

In order to discuss the physical origins of a given stability constant, it is important to consider the enthalpy and entropy terms which make up the resultant free energy, according to the equation,

$$\Delta G = \Delta H - T\Delta S = -RT\ln K$$

The enthalpy and entropy data reported on p.56 apply to the complete reaction,

$$PtCl_4^{=} + ol \rightleftharpoons (ol)PtCl_3^{-} + Cl^{-} \qquad (1)$$

in aqueous solution.

Hepler[61] has shown that the enthalpy and entropy terms can be usefully subdivided into internal and external components. The internal component arises from the nature of the bonding in the solute; whereas the external component results from the interaction of the solute and the solvent.

(a) Entropy

The change in the internal entropy, ΔS_{int}, will be governed by the number of degrees of freedom present in the initial species, and the number of degrees of freedom present in the products.

The change in the external entropy, ΔS_{ext}, will depend on the number of molecules of water associated with each of the species in equation (1). When comparing two olefins, the ΔS_{ext} values associated with the tetrachloroplatinate(II) and chloride ions should remain constant.

(b) Enthalpy

The change in the internal enthalpy, H_{int}, will depend on

(1) The bond energies of (a) the platinum-chloride bond that is broken, (b) the platinum-olefin bond that is formed, and (c) any change in the bond energies of the platinum-chloride bonds that are not broken.

(2) The steric effect of the quarternary ammonium group.

(3) The electrostatic interaction, or hydrogen bonding, between the hydrophilic group and the central metal group ($-PtCl_3^-$).

The change in the external enthalpy, ΔH_{ext}, will depend on the heats of solvation of each of the species present

in equation (1). Both the Powell-Latimer[62] and Born[63] models for the ion-solvent interaction lead to the reasonable conclusion that ΔH_{ext} is proportional to ΔS_{ext}, i.e. $H_{ext}=\beta\Delta S_{ext}$ Hepler[61] in his studies of the acidities of organic acids in water found that $270^{o}A<\beta<320^{o}A$. Brown[64], after a detailed study of a wide variety of organic reactions, found that $\beta=300\pm20^{o}A$. Thus to a first approximation the value of ΔH_{ext} will be equal to the value of ΔS_{ext}. As a result, whenever a favourable ΔS_{ext} change is observed, there will be an unfavourable ΔH_{ext} change of approximately the same magnitude, so that the ΔH_{int} value will be correspondingly larger than the observed value of ΔH.

When comparing two olefins, the ΔH_{ext} values associated with the tetrachloroplatinate(II) and chloride ions should remain constant.

(2) Comparison of Olefins with other Ligands

A number of stability constants for platinum(II) complexes are given in table 11. Since at 25°c a change of substrate from $[PtCl_4^{=}]$ to $[(C_2H_4)PtCl_3^{-}]$ causes a decrease in stability constant for a given ligand by a factor of about 5, a comparison of the platinum-olefin stability constants reported here with the literature data shows that olefins give higher stability constants with the tetrachloroplatinate(II) ion than water, lower than amines and comparable with the heavier halides.

TABLE 11

Stability constants (K) for reactions of platinum(II) complexes[a]

$$PtXY_3 + Z \underset{}{\overset{K}{\rightleftharpoons}} PtXY_2Z + Y$$

$PtXY_3$	Z	K
$PtCl_4^=$	H_2O	1.8×10^{-2} (b)
		1.38×10^{-2} (c)
		5.75×10^{-2} (d)
	Br^-	14.5 (c)
$(C_2H_4)PtCl_3^-$	H_2O	3×10^{-3} (f)
	Cl^-	1 (f)
	Br^-	3.4 (f)
	I^-	120 (f)
	SCN^-	>120 (f)
	NH_3	2×10^5 (g)
	$MeNH_2$	1.25×10^6 (g)
	Me_2NH	3.16×10^5 (g)
	Me_3N	ca. 10^3 (g)

(a) All at 25°c unless otherwise stated
(b) In 0.318M lithium perchlorate, ref. 51
(c) At 30°c in 2M sodium chloride, p. 25
(d) At 60°c in 2M sodium chloride, p. 25
(e) In 0.318M sodium perchlorate, ref. 65
(f) In 0.2M perchloric acid, ref. 39
(g) In 0.2M perchloric acid, ref. 40

(3) Correlation of Free Energy and Enthalpy data with the Inductive Effect

An attempt was made to correlate both the free energy and the enthalpy of reaction with the inductive effect for a series of olefins containing the allyl group. The Taft σ^* value[66,67] was used to obtain a quantitative measure of the inductive effect. The plot of free energy against the value of σ^* for the substituent X in allX$^+$ (figure 20), shows that there is very little correlation between the two. This indicates the importance of the entropy term, since a plot of the enthalpy against σ^* (figure 21) does give a straight line. Allyl alcohol ($\Delta H = -8.1 \pm 0.5$; $\sigma^* = +0.55$[66]) lies well away from any possible straight line. This is to be expected since the heats of solvation of both the free ligand and the complex will be very different to those of a quaternary ammonium salt and its complex.

The slope of the plot of H against σ^* (figure 21) is positive, indicating that withdrawal of charge from the double-bond increases the stability constant[68]. This implies that in the platinum-olefin bonding it is the π-bond (platinum to olefin) rather than the σ-bond (olefin to platinum) which is the more important.

So far the heats of solvation, which might have been expected to vary appreciably over the series, have been neglected. The heats of solvation of the complexes

Plot of ΔG at 60°c v. σ^* for the system

all X^+ + $PtCl_4^=$

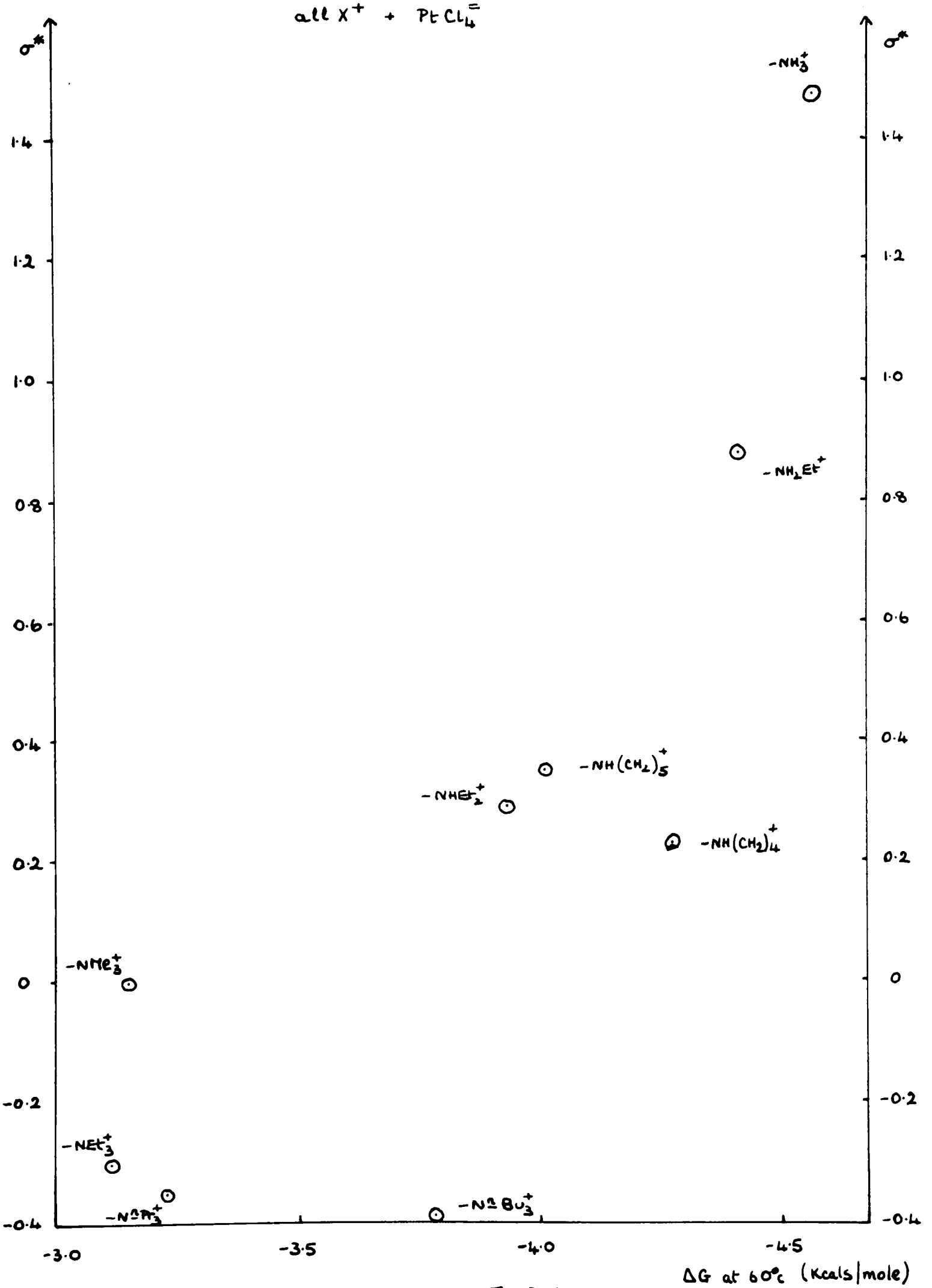


FIGURE 20

Plot of ΔH v. σ^* for the system $all X^+ + PtCl_4^=$

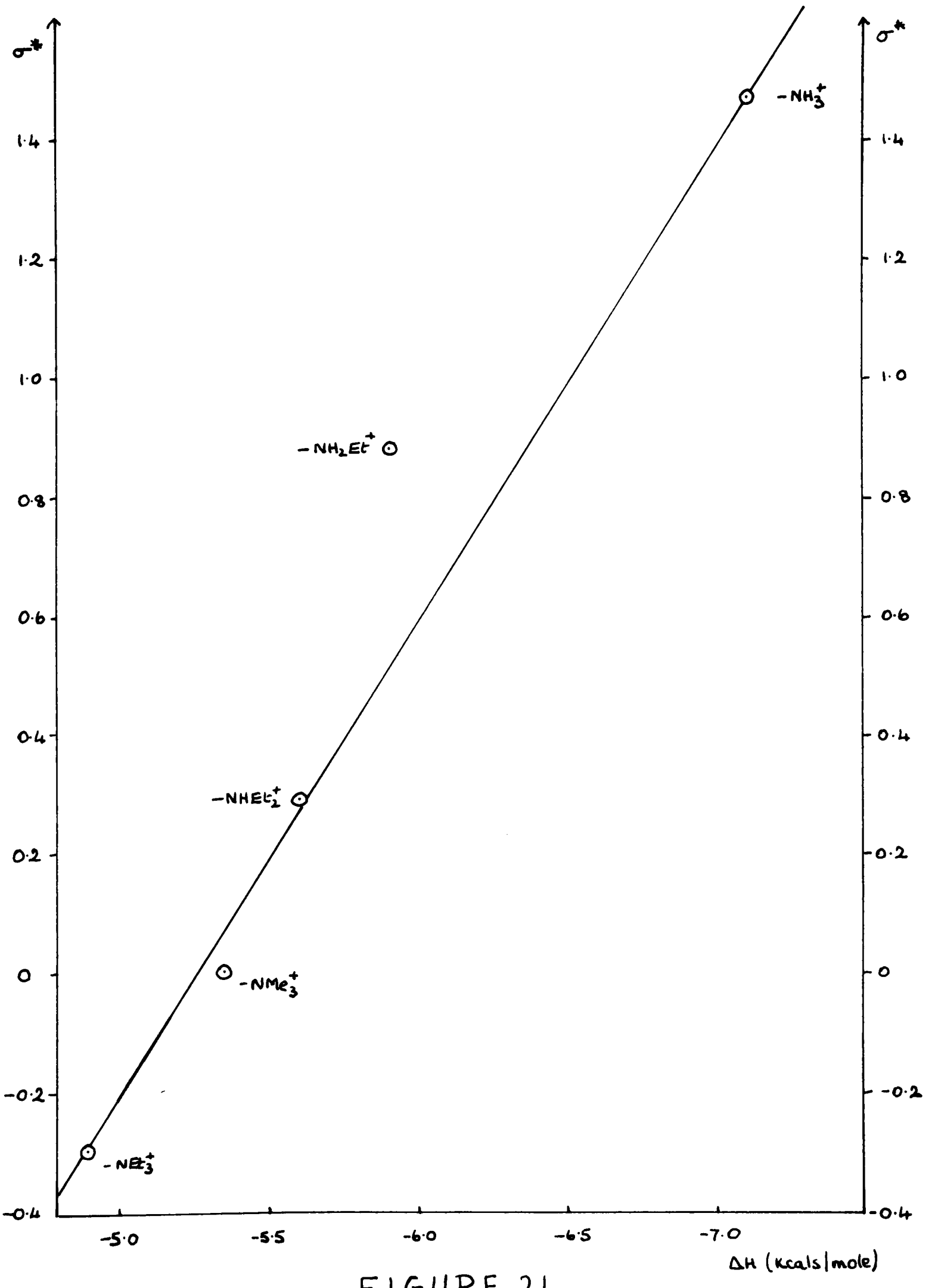


FIGURE 21

$[(ol^+)PtCl_3^-]$ should not differ as markedly for a series of allylammonium salts as the heats of solvation of the free ligands. The greater the heat of solvation of the free ligand relative to that of the complex, the lower the observed value of ΔH should be. Thus to obtain the relative order of the values of ΔH_{int} it will be necessary to add the heat of solvation of the free ligand to the observed value of ΔH. Since the solvation of amines occurs primarily through the hydrogen atoms attached to the nitrogen, the heats of solvation should increase in the order $allNEt_3^+$, $allNMe_3^+ < allNHEt_2^+ < allNH_2Et^+ < allNH_3^+$. Thus a consideration of the heats of solvation reinforces the conclusion that the π-acceptor capacity of the olefin is more important than the σ-donor capacity.

Steric interference between the quaternary group and the cis-chloride ligands could account for the observed result. However, it is shown below (p.69) to be either absent, or at any rate of only minor importance, when comparing the ligands $allX^+$ and $butX^+$ where X = NH_3, NEt_3 and $AsEt_3$. It is therefore unlikely to be of dominant importance in the present series.

Molecular models indicate that, in the case of allyl ligands, the possibility of association between the quarternary group and the cis-chloride ligands is very hindered. This is further supported by the almost constant value of ΔS in the series $allX^+$ where X = NH_2Et, $NHEt_2$ and NEt_3. If association

occurred it would be expected to vary with the number of hydrogen atoms bound to nitrogen, leading to a change in the value of ΔS across the series.

Thus the increase in ΔH in the series $allX^+$, where $X = NEt_3$, NMe_3, $NHEt_2$, NH_2Et, NH_3 can be rationalised in terms of an increase in the metal-olefin bond strength resulting from an increase in the electron-withdrawing capacity of the quarternary ammonium group. Such a result suggests that the π-bond from platinum to olefin is of greater importance than the σ-bond from olefin to platinum.

(4) Thermodynamic Data for Corresponding Allyl and Butenyl Systems

It is well known that the inductive effect falls off rapidly along a saturated carbon chain. Transmission factors ranging from 0.33 to 0.53 for each carbon atom have been suggested[69]. If the thermodynamic data for a series of pairs of ligands, one containing an allyl (CH_2=CH-CH_2-) and the other a butenyl (CH_2=CH-CH_2-CH_2-) group, are compared, it should be possible to determine the effect of an inductive withdrawal of charge from the double-bond. The results obtained are summarised in table 12.

(A) Enthalpy

The net difference, $\Delta(\Delta H)$, in the ΔH values for the allyl and butenyl systems can be divided into a number of energy terms.

TABLE 12

Ligand		ΔH(Kcals/mole)		ΔS(Kcals/mole at 30°c)
allNH$_3^+$		-7.1		-2.3
butNH$_3^+$		-5.1		-0.06
	Δ(ΔH)[a]	-2.0	Δ(ΔS)	-2.24
allNEt$_3^+$		-4.9		-1.4
butNEt$_3^+$		-3.8		+1.6
	Δ(ΔH)	-1.1	Δ(ΔS)	-3.0
allAsEt$_3^+$		-5.9		-1.4
butAsEt$_3^+$		-3.3		+2.2
	Δ(ΔH)	-2.6	Δ(ΔS)	-3.6

[a] Δ(ΔX) = ΔX for the allyl ligand - ΔX for the butenyl ligand

(a) Heats of Solvation It is reasonable to assume the the heats of solvation of the complexes with allyl and butenyl ligands will differ less than the heats of solvation of the free ligands, unless there is considerable association between the quarternary group and the cis-chloride ligands in the butenyl complex, but not in the allyl complex - see (d) below. The heat of solvation of the butenyl ligand is probably less than that of the allyl ligand. Thus consideration of the heats of solvation leads to the prediction that the enthalpy change for the butenyl ligand will be greater

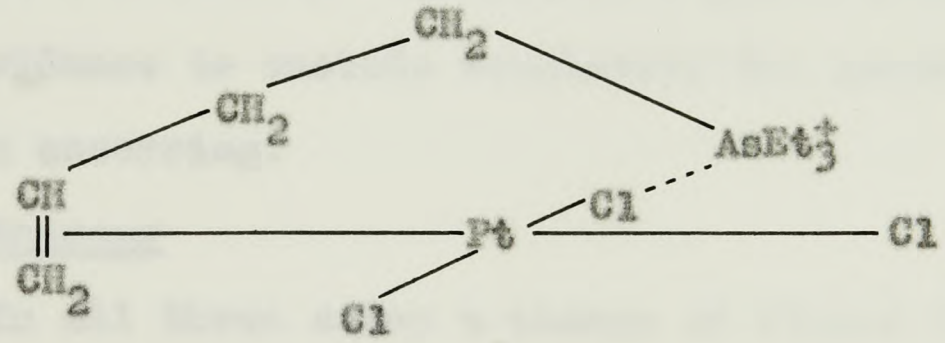
than for the allyl ligand. Since the reverse is observed, the heats of solvation cannot account for the observed trend in the $\Delta(\Delta H)$ values.

(b) Platinum-olefin bond energy As can be seen from table 12, in all three cases the value of ΔH for the allyl ligand is greater than for the butenyl ligand. The inductive effect, which arises from the positive charge, will cause a greater withdrawal of electron density from the double-bond in the allyl than in the butenyl ligands. Thus the ΔH values, if due to bonding, can be explained in terms of the inductive effect, if the π-back donation (platinum to olefin) is more important than the σ-bonding (olefin to platinum).

The maximum difference between the $\Delta(\Delta H)$ values is only 1.5 Kcals/mole. To argue that such a difference is due to inductive effects requires a fairly accurate measure of the inductive effect of the substituents. Such a measure could best be obtained from the Taft inductive constant. However, whilst values for $-NEt_3^+$ and $-NH_3^+$ are available, no value is available for $-AsEt_3^+$. The σ^* values for $-NEt_3^+$(-0.30[66]) and $-NH_3^+$ ($+1.47$[66]) indicate that $-NH_3^+$ is a stronger electron-withdrawing group than $-NEt_3^+$. Thus if the $\Delta(\Delta H)$ values are due to bonding, they can be explained in terms of the inductive effect, if the π-acceptor capacity of the olefin is more important in determining the platinum-olefin bond strength than the σ-donor capacity.

(c) Steric interference Any steric interference of the $-LEt_3^+$ group with the $-PtCl_3^-$ group will be greater for allyl than butenyl ligands. Steric interference not only decreases ΔH_{int} but also ΔH_{ext}, due to disturbance of the solvent sheath. Any steric interference therefore leads to an increase of ΔH on replacing allyl by butenyl, which is exactly the reverse of the observed result.

(d) Association Molecular models indicate that any association of the quarternary group with the cis-chloride ligand is very hindered for the L-substituted allyl ligands, $allLEt_3^+$. Association is also very difficult for $butNEt_3^+$, but possible for $butAsEt_3^+$.



Such an association should increase the value of ΔH_{int} for $butAsEt_3^+$. This increase would almost certainly make the resultant value of $\Delta(\Delta H)$ for $-AsEt_3^+$ less than for $-NEt_3^+$, although the increase will be to some extent compensated by a decrease in ΔH_{ext}. The change in ΔH_{ext} cannot be estimated since any calculation of the magnitude of ΔH_{ext} requires a quantitative model of the solvation of the $-LEt_3^+$ group.

At present the apparently conflicting evidence from Stokes's law[70], which predicts no primary solvation layer, and ultrasonic studies[71], which predict a large primary solvation layer, is interpreted by assuming an increase in the structure of the water in the immediate vicinity of the quarternary salt[72]. Such a model is obviously not amenable to quantitative calculations.

The entropy changes resulting from association are also impossible to predict. ΔS_{int} will be lower and ΔS_{ext} will be higher than if no association occurred, but the total observable value cannot be predicted.

In conclusion, it may be said that it is unlikely that any association occurs. However, at present there is insufficient evidence to exclude completely the possibility of any association occurring.

(B) Entropy

In all three cases a change of ligand from allyl to butenyl causes a net gain in entropy. This can tentatively be explained by considering the breakdown of the water structure which immediately surrounds the organic group[72]. Molecular models indicate that when both allyl and butenyl ligands are coordinated to $-PtCl_3^-$, the whole of the organic molecule between the double-bond and the group V atom is so close to the $-PtCl_3^-$ group that no water can be present on the platinum side of the carbon chain. Since the butenyl group

is larger than the allyl group, more of the water structure will be broken up when the former coordinates, giving a net gain in the entropy term $\Delta(\Delta S)$.

Summary

The relative values of the stability constants are largely determined by the entropy changes. These entropy changes can be accounted for by considering the solvation of the free ligands and the complexes.

The observed ΔH values can be understood in terms of an inductive effect. It is found that bringing a positive charge closer to the reaction site increases ΔH, which suggests π-bonding in the platinum-olefin bond is more important than σ-bonding. This interpretation of the ΔH value should not be taken to exclude all others. Other factors such as have been discussed above will contribute, but it is not possible at present to evaluate these contributions.

(5) C-substituted Allylammonium salts

From the stability constants observed (table 9 p.54) it can be seen that replacement of a hydrogen atom in the allyl group by a methyl group, causes a decrease in the stability constant. This effect is greatest for substitution at the C_2-carbon atom and least for substitution at the C_1 carbon atom.

$$\overset{3}{C}H_2=\overset{2}{C}H-\overset{1}{C}H_2-NH_3^+$$

Disubstitution leads to a further reduction in the stability constant. These effects have been observed previously in the formation of silver(I)-olefin complexes[45] and have been attributed to steric effects. Since a complete discussion of stability constants requires enthalpy and entropy values, these were determined for typical olefins. The results are shown in table 13.

TABLE 13

Olefin	ΔH(Kcals/mole)	ΔS(Kcals/mole at 30°c)
$CH_2=CH-CH_2-NH_3^+$	-7.1	-2.3
trans-$CH_3-CH=CH-CH_2-NH_3^+$	-5.1	-1.4
$CH_2=CH-CH(CH_3)(NH_3^+)$	-6.7	-2.1

A comparison of the ΔH values of the C-substituted allylammonium ions with the allylammonium ion is likely to be complicated by the heats of solvation of the olefins and of the complexes. However, a comparison of the ΔH values for the trans-crotylammonium and for the 1-methylprop-2-onylammonium cations should not be complicated in this way, as both the free ligands and the complexes are likely to have very similar heats of solvation due to their having the same number of carbon atoms. Thus, the lower stability constant

and ΔH value found for the formation of the complex with the trans-crotylammonium cation may be due to a weaker platinum-olefin bond. It is expected that the inductive effect of a methyl group should increase the σ-donor capacity[73] and decrease the π-acceptor capacity[74] of the substituted olefin. This leads to the conclusion that either the π-acceptor capacity of the olefin is of primary importance in determining the platinum-olefin bond strength, or that steric hindrance by substituents on the double-bond is responsible for bond-weakening.

Although only three values were available, a plot of the ionization potential of the olefin $olCH_3$[73] against the observed ΔH value for the corresponding olefin $olNH_3^+$ was made (figure 22). The effect on the ionization potential, resulting from the replacement of $-CH_3$ by $-NH_3^+$ should be constant throughout, since in each case there is one methylene group separating the $-NH_3^+$ group from the double-bond. The plot shows that the value of ΔH increases as the ionization potential increases. Since a high ionization potential indicates a weak σ-donor capacity of the double-bond, the result suggests that the inductive effect of a substituent on the double-bond is almost certainly significant. Previously it has been assumed that the effect of a substituent on the double-bond was purely steric in nature.[41,45]

A further way in which the steric and inductive effects could be separated would be to determine the stability

Plot of $-\Delta H$ for $o\ell NH_3^+$ against Ionization Potential of $o\ell CH_3$.

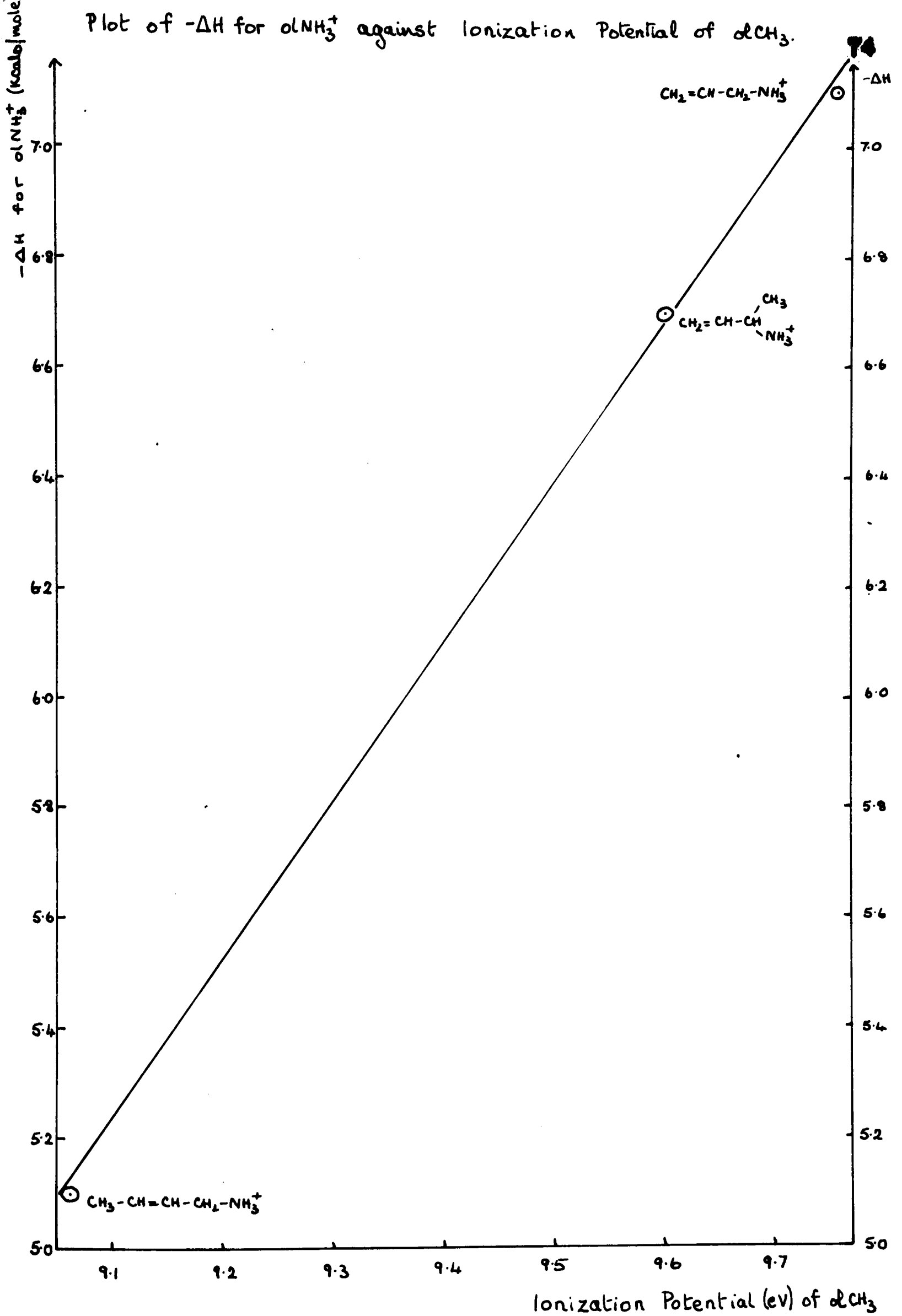


FIGURE 22

constant for the olefin $Cl-CH=CH-CH_2-NH_3^+$. Gould[75] suggests that the van der Waal's radii of a methyl group (2.0Å) and of a chlorine atom (1.8Å) are very similar. This would result in an almost constant steric effect, enabling the inductive effect to be observed. However, it was found impossible to obtain stability constants with this ligand. A fuller discussion is given later (p.78).

The stability constant for the crotylammonium cation obtained in this work differs from that given previously by Denning[38]. The higher value reported by Denning probably arises from the use of the cis-crotylammonium cation, either pure or as a mixture of cis- and trans-isomers.

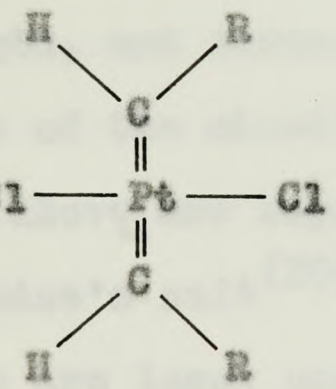
The possibility of cis/trans isomerisation occurring on coordination to platinum suggested below for the 3-chloroprop-2-enylammonium cation was checked with reference to the crotylammonium cation. No isomerisation was detected. The complex formed between the trans-crotylammonium ion and the tetrachloroplatinate(II) ion was isolated, and the crotylammonium ion displaced with potassium cyanide. The infra-red spectrum of the displaced crotylammonium chloride indicated that it was the trans-isomer. For the reasons outlined in chapter 1 (p.8) it is very unlikely that the isomerisation of the olefin occurs both on coordination to and displacement from platinum(II).

The observation that cis-olefins form stronger complexes with both platinum(II)[31] and silver(I)[44] can be

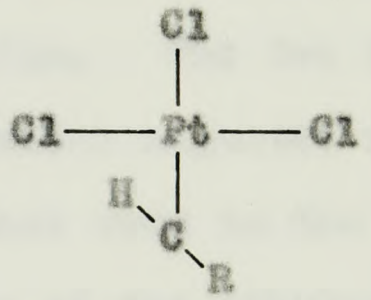
rationalised in two separate ways. (1) Cis-olefins are more strained than trans-olefins and this strain is reduced on complex formation. (2) Complexes formed by cis-olefins are more stable than those formed by trans-olefins.

The first alternative is advocated by Gardner et al[76], who compared complex formation between olefins and silver with hydrogenation of the olefins. It is found that cis-olefins have higher heats of hydrogenation than trans-olefins, which is attributed to the relief of strain arising from bond oppositions present in the cis-olefins[77]. By analogy the authors suggest that on complex-formation the p-orbitals are twisted sufficiently to relieve the bond oppositions present in a planar cis-olefin by permitting a slight rotation about the double-bond. The relatively large 5s orbital of silver should still be capable of giving overlap with these p-orbitals to give the 3-centre molecular orbital required for complex formation. Since this twisting is not observed in the free olefin it must lead to considerable bond weakening. In support of this theory it can be argued that the lowering of the C=C stretching frequency in the infra-red indicated a reduction in the bond-order. Approximate calculations have suggested a bond-order of about 5/3[78]. A similar bond order is obtained using the carbon-carbon bond length of 1.47Å observed by Alderman et al[79] for ethylene in trans-$[(C_2H_4)PtCl_2(NH(CH_3)_2)]$.

The second alternative, suggested by the present author, can be explained in terms of electronic and steric factors. The structure of the platinum-olefin complexes described by Chatt[12] is now well established. In Zeise's salt the plane of the ethylene molecule is perpendicular to the platinum-olefin ethylene bond (see p. 5). In the case of a cis-disubstituted olefin this plane would twist about the C=C axis in such a way as to remove any steric interference between the substituents and the cis-chloride ligands. This would leave the C=C axis still vertical.

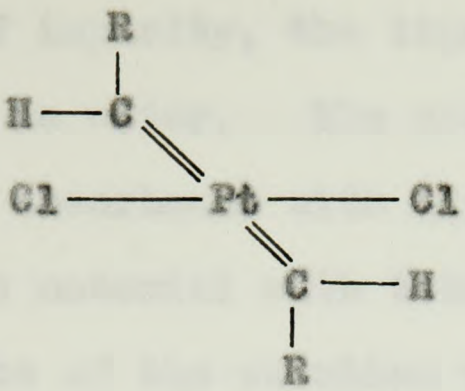


View along the ol-Pt-Cl axis

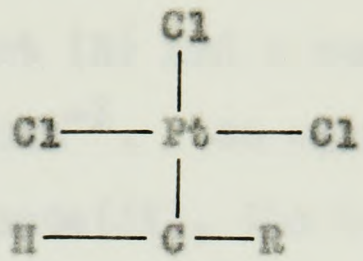


View from vertically above the $PtCl_3$ plane

This would reduce the orbital overlap by a small amount and so lower ΔH, the heat of formation of the complex. To remove any steric interaction in the trans-disubstituted olefin it would be necessary to twist the olefin about the platinum-olefin axis.



View along the ol-Pt-Cl axis



View from vertically above the $PtCl_3$ plane

Whilst not affecting the σ-bond, this will markedly reduce the overlap between the filled d-orbitals of the platinum and the empty π^* orbitals of the olefin, thus reducing the overall bond strength, and lowering the observed value of ΔH more than in the case of the cis-disubstituted olefin. The two rotations postulated above are supported by the nuclear magnetic resonance study of Zeise's salt[20], which showed that even in the solid state there are large amplitude rotations of the ethylene molecule about the platinum-olefin bond and about the C=C axis.

It is, of course, likely that is is a combination of the two effects discussed, which leads to the observed result that cis-olefins form stronger complexes than trans-olefins.

$Cl\text{-}CH{=}CH\text{-}CH_2\text{-}NH_3^+$

An attempt was made to determine the stability constant of this ligand with tetrachloroplatinate(II). The ligand (A) had a slight absorbance in the ultra-violet, with a peak at $33{,}000cm^{-1}$. Since this absorbance might have been due to

traces of impurity, the ligand was boiled up with animal charcoal in water. The resulting product (B) had a much stronger absorbance with a peak at 34,200cm^{-1}. On equilibrating this material with tetrachloroplatinate(II), the total absorbance of the solution was much less than that of the free ligand, even assuming that one equivalent of the ligand had complexed with tetrachloroplatinate(II) and that the extinction coefficient of the species formed was zero. The ligand which had been equilibrated with potassium tetrachloroplatinate(II) (C) was isolated and found to have a weak absorbance in the ultra-violet with a peak at 33,000cm^{-1}. The infra-red spectra of all three products in the region 5,000-625cm^{-1} were identical, except at about 1,260cm^{-1} - see table 14. The origin of this band is obscure, so that no assignments can be made from it.

TABLE 14

Product	Infra-red(cm^{-1})	Ultra-violet(cm^{-1})
A	1259,1265 (both weak)	33,000
B	1260 (strong)	34,200
C	1260 (strong)	33,000

All three products exhibited a band at 1,320cm^{-1} in the infra-red, which is close to the band at 1,333cm^{-1} found by Wolfe[20]

to be diagnostic of the cis-Cl-CH=CH-C- group. The possibility of cis/trans-isomerisation occuring was considered, but since there was no significant difference in the infra-red spectra of the three products in the region 900-625cm^{-1}, it was unlikely to have occurred to any appreciable extent. Attempts to prepare a complex by the standard method, with product A , gave a complex which was not identified, and which contained only 40.7%Pt as opposed to the 49.5% required by $[(Cl\text{-}CH{=}CH\text{-}CH_2\text{-}NH_3^+)PtCl_3^-]$.

(6) Stability constants for unsaturated ammonium salts containing the $CH_2{=}CH\text{-}(CH_2)_n$- group

In addition to the enthalpy data discussed above, there are a number of systems for which stability constants have been measured at only one temperature (60°c). Any interpretation based on stability constants alone is of a speculative nature. For example, the stability constants for allNH_3^+ (1022 at 59°c) and butNH_3^+ (2038 at 60°c) might suggest that the platinum-olefin bond is weaker in the former than the latter complex. However, the enthalpies suggested the reverse.

A comparison of the stability constants shows the following trends:

(1) There is an increase in the stability constant in the series allX^+ where X = $NHEt_2$ < $NH(CH_2)_5$ < $NH(CH_2)_4$. The σ^* values[67] for these groups, together with the observed free energies are given in table 15.

TABLE 15

X	ΔG(for allX$^+$ at 60°c)	σ*
$NHEt_2$	-3.93	0.29
$NH(CH_2)_5$	-4.01	0.35
$NH(CH_2)_4$	-4.27	0.23

No obvious correlation is possible. However the ΔG values only differ by 0.35 Kcals/mole. Very slight differences in enthalpy or entropy values due to either solvation differences or the slightly different steric requirements of the quarternary group would readily account for this difference.

(2) The stability constants for the straight chain unsaturated ammonium salts are in the order allNH_3^+ < butNH_3^+ > pentNH_3^+. As mentioned above enthalpy and entropy values are needed to rationalise the series. Unfortunately, none are available for pentNH_3^+.

(3) The stabilities constants for the olefins allNR_3^+, where R is a straight chain alkyl group, vary in the order Me > Et < ^{n}Pr < ^{n}Bu. Enthalpy and entropy values are available only for the first two - see table 16. Enthalpy and entropy values for allN^{n}Pr$_3^+$ and allN^{n}Bu$_3^+$ could not be obtained because of the low solubility in water of both the ligands and the complexes.

The sharp drop in enthalpy on replacing -NMe_3^+ by NEt_3^+ is consistent with the decrease in the inductive withdrawal

TABLE 16

	ΔH(Kcals/mole)	ΔS(Kcals/mole at 30°c)	σ* for $-NR_3^+$
allNMe_3^+	-5.3(5)	-2.0	0.00
allNEt_3^+	-4.9	-1.4	-0.30

of charge from the double-bond as indicated by the Taft σ* value for the $-NR_3^+$ group[67]. This inductive withdrawal is not expected to be very different for $-N^nPr_3^+$ (σ* = -0.35) and $-N^nBu_3^+$ (σ* = -0.39). However, the increase in entropy on replacing $-NMe_3^+$ by $-NEt_3^+$ is expected to continue and so account for the observed stability constants. The bulkier ligands tend to organise the water structure around themselves more than the less bulky ligands. This is exemplified by the apparent hydration numbers for Me_4^+N (5.0) and Et_4^+N (8.7) obtained from ultra-sonic studies in solution[71]. On co-ordination much of this organised water structure will be destroyed. As a result the bulkier the ligand is, the more favourable the expected entropy change on complex formation will be.

(7) Equilibrium studies for Platinum(II) with unsaturated alcohols

Some stability constants for unsaturated alcohols with platinum(II) were determined. It was hoped that the very different inductive effect of -OH as opposed to $-NH_3^+$ would

provide further information on the relative importance of the σ-donor and π-acceptor capacities of the olefin.

The results indicated that the replacement of $-NH_3^+$ by -OH did in fact cause a significant increase in the stability constant. Only allyl alcohol was studied over a range of temperature to determine the enthalpy and entropy of the reaction. It was found that the enthalpy increased on replacing $-NH_3^+$ by -OH and that the entropy was virtually unaltered. This can be accounted for by considering the heats of solvation involved.

When comparing allyl alcohol and $allNH_3^+$ it is necessary to consider the heats of solvation of both the free ligands and the complexes. The heats of solvation of the free ligands are 11 Kcals/mole - see chapter 7 - and about 86 Kcals/mole[81] for allyl alcohol and the allylammonium ion respectively. The heats of solvation of the complexes are also expected to be very different. Thus $[(C_3H_5NH_3^+)PtCl_3^-]$ which is a zwitterion with a net charge of zero would be expected to have a lower heat of solvation than $[(C_3H_5OH)PtCl_3^-]$ which carries a charge of -1. Some support for this is provided by the fact that the allylammonium complex is sparingly soluble in water, whereas the allyl alcohol complex is freely soluble in water, although it must be remembered that solubility in water depends on many other factors, particularly lattice energies. Thus the heats of solvation of the ligands and complexes would suggest that

the alcohol would have the higher ΔH value. It is not suggested that other effects, such as the inductive effect, are not present, but rather that they do not determine the observed result.

The stability constant for crotyl alcohol was less than for allyl alcohol, as found for the unsaturated ammonium salts. A combination of inductive and steric effects - see p. 73 - is probably responsible.

4-Penten-1-ol gave a lower stability constant than allyl alcohol. This drop is probably analogous to the drop in stability constant from but-3-enylammonium to pent-4-enylammonium.

When an attempt was made to determine the stability constant of 3-buten-1-ol with potassium tetrachloroplatinate(II) at 60°c, it was found that the absorbance increased with time over a period of 144 hours. Since the other alcohols reported took between 48 and 60 hours to equilibrate, a Job plot[56] was prepared. The plot at 295mμ (figure 23) indicates that, within experimental error, only one complex is present after 24 hours at 60°c, a trace of polynuclear complex is present after 48 hours at 60°c and that the presence of polynuclear species is pronounced after 144 hours at 60°c.

Since both Jonassen[82] and Chatt[83] have shown that a polynuclear species is formed between butadiene and potassium tetrachloroplatinate(II), an attempt was made to

Job Plot at 295 mμ for the system 3-buten-1-ol + K_2PtCl_4

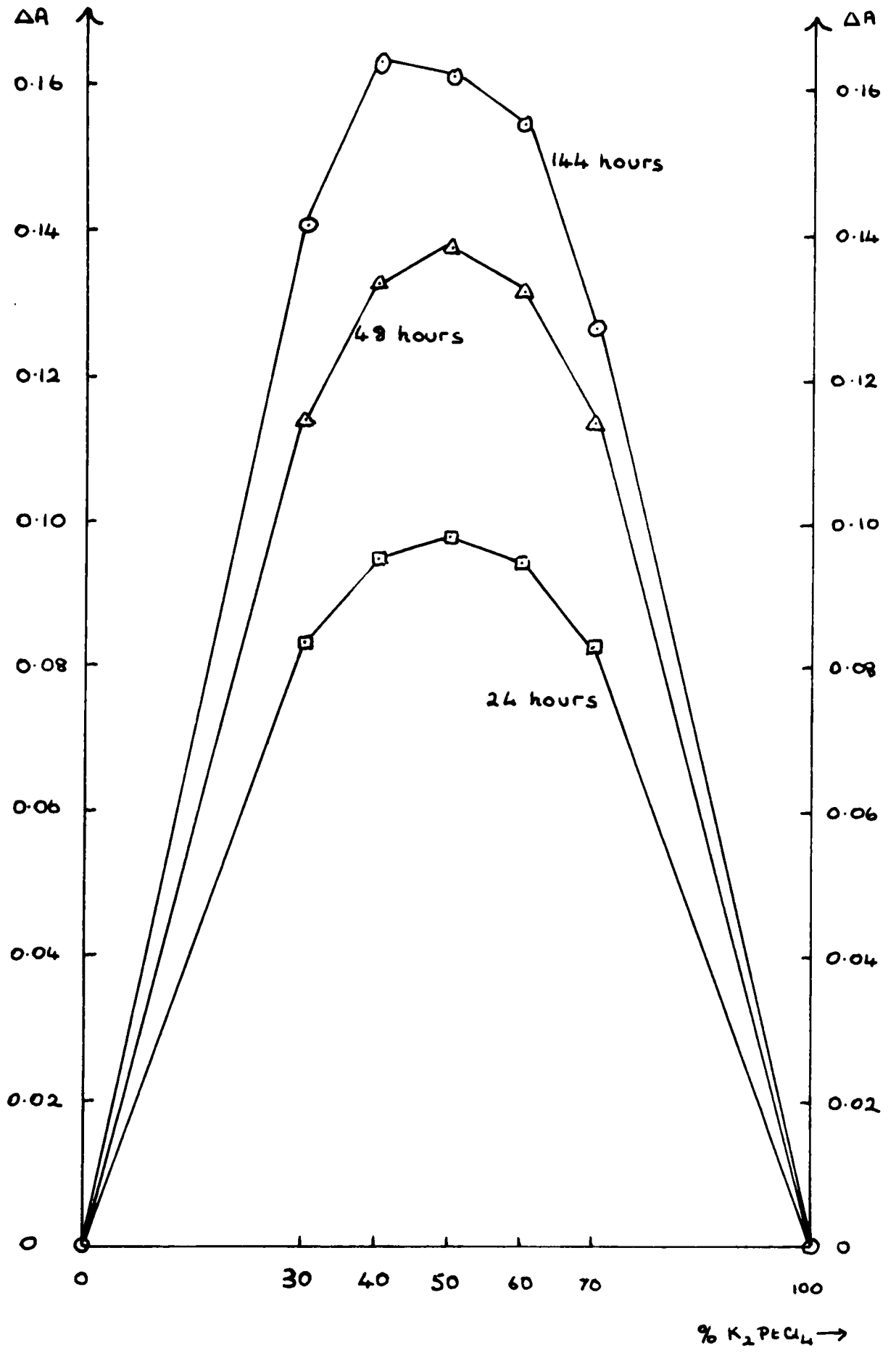
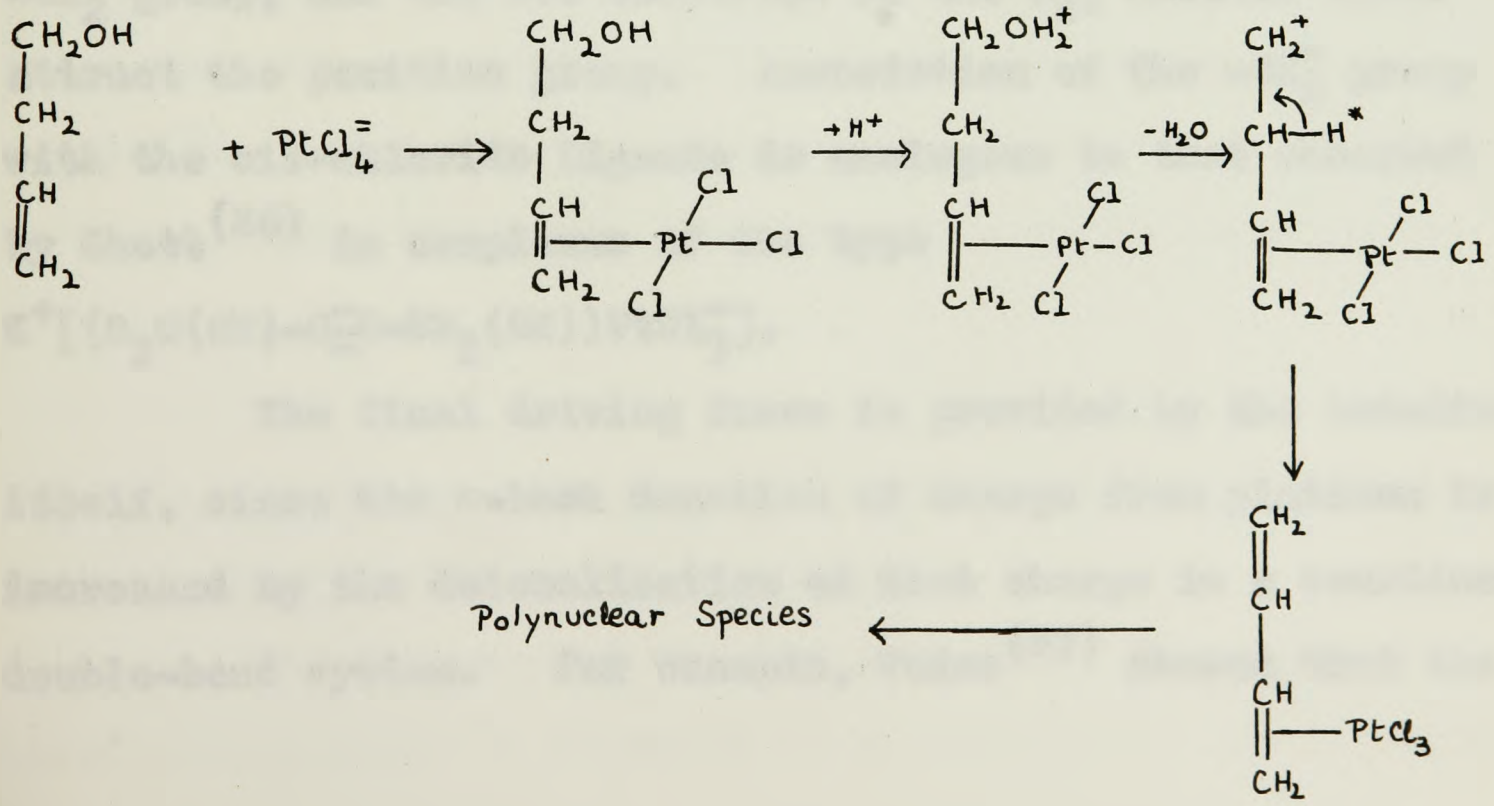


FIGURE 23

detect the presence of butadiene by gas chromatography. After heating 3-buten-1-ol with potassium tetrachloroplatinate(II) in dilute hydrochloric acid at 78°c for ninety minutes, a sample was withdrawn, treated with potassium cyanide and the solution extracted with benzene. The benzene layer exhibited a peak which exactly corresponded to butadiene. When a solution of 3-buten-1-ol was treated in exactly the same manner in the absence of potassium tetrachloroplatinate(II), butadiene could not be detected.

Thus, under these conditions, the tetrachloroplatinate(II) ion is essential for the formation of butadiene from 3-buten-1-ol. Since the Job plot at 24 hours does not, within experimental error, indicate any appreciable concentration of polynuclear species, it is likely that the reaction proceeds via the olefin complex. A mechanism such as the following is envisaged.



Such a mechanism is analogous to that put forward by Milgrom and Urry[84] for the acid catalyzed etherification of allyl alcohol. The role of the platinum(II) is probably twofold.

(1) By withdrawing electrons to itself it tends to increase the acidity of H*. There is probably also some association of H* with the chlorine atoms. Both platinum and palladium are good catalysts for reactions which involve loss or intramolecular movement of groups from this carbon atom. Obvious examples are the formation of π-allyl complexes on treating allyl alcohol with palladous chloride[10] or allylmagnesium chloride with $[(PEt_3)_2Pt_2Cl_4]$[85].

(2) A 5- or 6-membered ring can be formed by association of the $-OH_2^+$ group with either the platinum d_{z^2} orbital or the chloride ligands. The latter is perhaps more likely since the former depends on a balance of two opposing effects - the residual positive charge on platinum which repels the positive $-OH_2^+$ group, and the two electrons in the d_{z^2} orbital which attract the positive group. Association of the $-OH_2^+$ group with the cis-chloride ligands is analogous to that observed by Chatt[86] in complexes of the type $K^+[(R_2C(OH)-C\equiv C-CR_2(OH))PtCl_3^-]$.

The final driving force is provided by the butadiene itself, since the π-back donation of charge from platinum is increased by the delocalisation of that charge in a coordinated double-bond system. For example, Weiss[87] showed that the

complexes formed between butadiene or maleic acid and iron enneacarbonyl are more stable than the complexes formed by the corresponding unconjugated olefins.

(8) Equilibrium studies for platinum(II) with unsaturated acids

An attempt to determine the stability constant for crotonic acid, by the same method as was used for unsaturated alcohols and ammonium salts, failed. After eleven days at 60°c the absorbances of the solutions were still increasing. Since the alcohols and ammonium salts required about two days at 60°c to reach equilibrium, it was thought that side reactions were probably occurring. No decomposition to platinum metal was observed. It was subsequently discovered that Biilmann and Hoff[38] had reported that acids such as crotonic acid react more slowly than allyl alcohol with platinum(II).

In addition to the difficulties mentioned above there was the problem of ionization of the acid. Under the conditions used the percentage of CH_3-CH=CH-COO^- present was 2×10^{-2}%. However, it was uncertain whether coordination to platinum(II) would raise or lower the acid dissociation constant.

(9) Relation between the enthalpy of formation of the complex and the C=C stretching frequency

The lowering of the C=C stretching frequency on coordination might be expected to be related to the strength

of the metal-olefin bond. For example, this work has shown that olefins give lower stability constants with silver than with platinum, and it is well known that the lowering of the C=C stretching frequency of olefins is less on coordination to silver (about 65cm^{-1} (9)) than to platinum (about 150cm^{-1}). The observed value of ΔH contains both ΔH_{int} and ΔH_{ext}. Since ΔH_{int} should be related to the lowering of the C=C stretching frequency on coordination ($\Delta\nu_{C=C}$), a plot of ΔH against $\Delta\nu_{C=C}$ might be expected to throw some light on the value of ΔH_{ext}. The C=C stretching frequencies observed are shown in table 17, and a plot of ΔH against $\Delta\nu_{C=C}$ is shown in figure 24. It is obvious from the plot obtained that no correlation exists. This is because although the lowering of the C=C stretching frequency will be more for greater metal-olefin bond strengths, several other factors also affect the C=C stretching frequency.

The C=C bond in the complexes under consideration is orientated perpendicularly to the metal-olefin bond. Hence the motions of the carbon atoms in the C=C vibration will be perpendicular to the rest of the molecule. There will therefore be very little interaction between them and the central metal group. Hence, comparison of the lowering of the C=C stretching frequencies for the same olefin with different metals should give useful indications of the metal-olefin bond strength.

TABLE 17

Infra-red C=C stretching frequencies

Ligand	$\nu_{C=C}$ (cm^{-1}) Free ligand	[(ol)$PtCl_3^-$]	$\Delta\nu$(cm^{-1})
allNH_3^+	1650	1504	146
allOH	1645	1498	147
allNMe_3^+	1641	1482	159
allNEt_3^+ (a)	1640	1495	145
allN^{n}Pr_3^+	1641	1480	161
allN^{n}Bu_3^+	1645	1480	165
allPEt_3^+ (b)	1641	1493	148
allAsEt_3^+ (b)	1641	1490	151
allNH_2^+Et (a)	1648	1503	145
allNHEt_2^+ (a)	1643	1495	148
allNH$(CH_2)_5^+$	1648	1500	148
allNH$(CH_2)_4^+$	1644	1500	144
butNH_3^+ (c)	1640	1488	152
butNEt_3^+	1646	1489	157
butAsEt_3^+	1645	1493	152
pentNH_3^+ (c)	1640	1500	140
CH_2=CH-CH(CH_3)-NH_3^+	1651	1500	151
CH_3-CH=CH-CH_2-NH_3^+	1673	1510	163
CH_2=C(CH_3)-CH_2-NH_3^+	1667	1494	173

(a) Ref 35
(b) Ligands and complexes prepared by M.H. Pritchard
(c) Ref 89

Plot of ΔH v. $\Delta\nu_{(C=C)}$

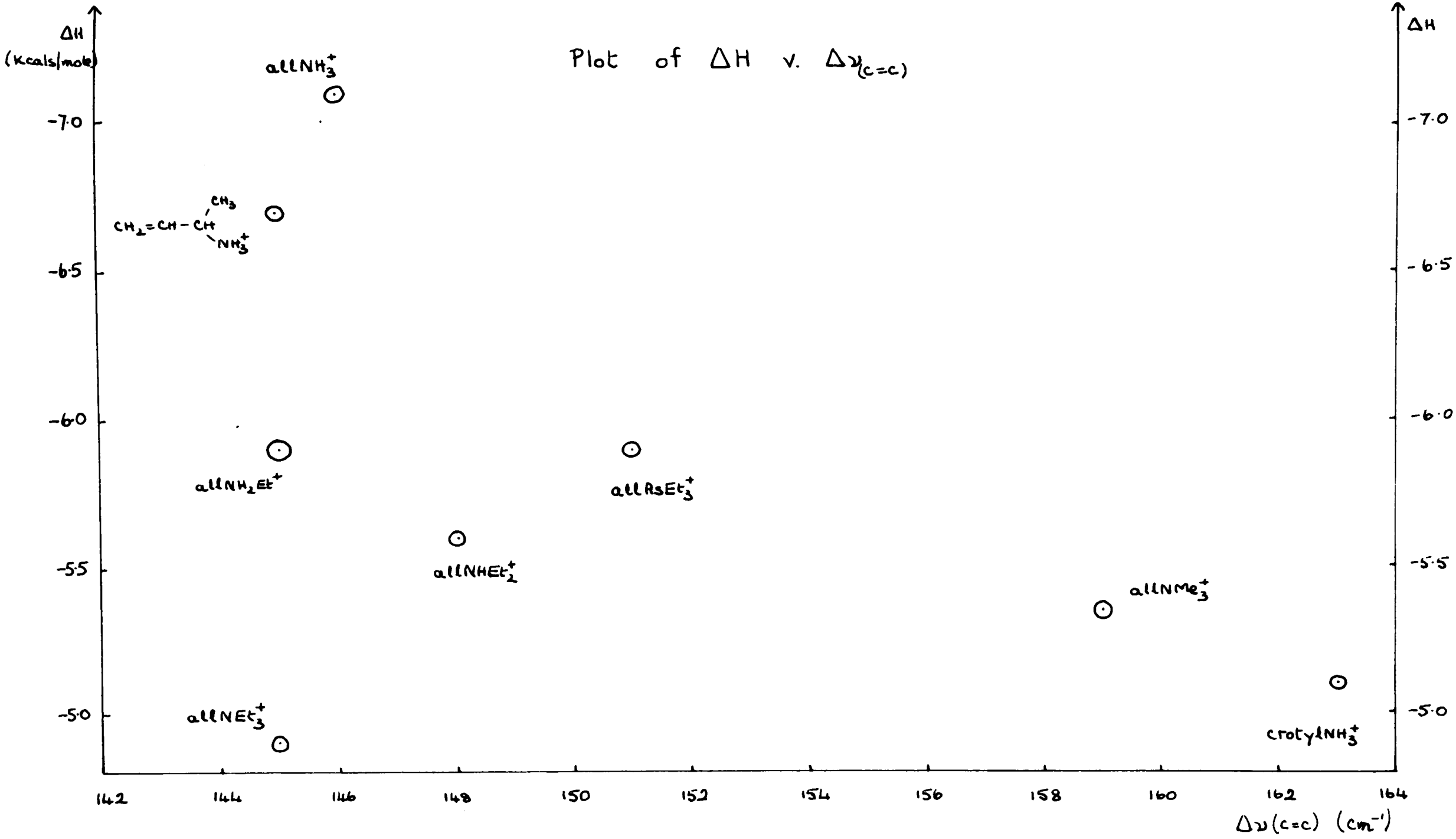


FIGURE 24

A comparison of different olefins coordinated to the same metal is more complicated since the frequencies of the uncoordinated double-bonds vary widely - see table 17. There are three possible reasons for this.

(1) Coupling to other vibrations The motion of the carbon atoms will couple with other motions of the same symmetry representation. The nature and frequency of the other vibrations of the molecule will be different for each olefin, and will give rise to differences in the C=C vibration frequencies. These interactions will alter on coordination, particularly when a change of symmetry occurs. Hence the molecular structure will affect not only the frequency of the uncoordinated double-bond, but also the frequency shift caused by coordination.

(2) Effect of strain When an olefin is in a strained form, the C=C bond is weakened and lengthened[90] so that the strain is to some extent released. The resulting shift from the uncoordinated strained olefin frequency will thus be low relative to the metal-olefin bond strength, while the shift from the frequency of an unstrained double-bond vibration will be high relative to the metal-olefin bond strength.

(3) Electronic effects Different groups such as -OH and $-NH_3^+$ near to the double-bond will affect the double-bond to different extents. Some examples are given below.

allyl-OH	1645cm^{-1}	crotyl-OH	1690cm^{-1}	3-buten-1-ol	1645cm^{-1}
$-NH_3^+$	1650	$-NH_3^+$	1673	$-NH_3^+$	1640
$-NH_2$	1642	$-NH_2$	1670	$-NH_2$	1640

This interaction, which is not readily predictable in terms of an inductive effect, will be different in the metal-olefin complex to the free olefin.

In conclusion, it can be seen that correlations of the C=C stretching frequency with the metal-olefin bond strength for the same olefins with different metals are useful, but for different olefins with the same metal are virtually non-existent.

(10) Conclusions

The stability constants of olefins with platinum(II) have been found to be comparable to the stability constants of the heavier halides with platinum(II). It has been found that both solvation and inductive effects are important in determining the stability constant.

It was impossible to determine the steric effect of bulky hydrophilic groups, or whether any association of the hydrophilic group with the cis-chloride ligands did occur in the cases where such association was possible. The failure to confirm the presence of these effects should not necessarily be taken to imply their absence, but rather that in the olefins

studied they are not the effects which determined the observed result.

The enthalpy of formation of the complexes was found to increase as the inductive withdrawal of charge from the double-bond increased. Studies with C-substituted allylammonium salts indicated that electron-donating groups decreased the observed enthalpy values. Both results indicated that the π-bond (platinum to olefin) was more important than the σ-bond (olefin to platinum). This is consistent with the observation that the complex C_2H_4-BMe_3 does not exist[91], since such a complex can only contain a σ-bond.

C H A P T E R 4

Experimental Details for the Determination of Silver-Olefin Stability Constants

(1) Reagents

Those reagents, such as deionized water, which have already been described in chapter 2 will not be described again.

Nitrogen

British Oxygen "white spot" nitrogen was used. It was saturated with water to the correct vapour pressure by bubbling it through a wash-bottle, fitted with a sintered glass disc to produce a stream of fine bubbles, containing 2M sodium perchlorate solution. A long flexible vinyl tube, which prevented any of the saturating solution being carried over mechanically, was used to connect the wash-bottle to the bubbler, which was also made of sintered glass.

Sodium Perchlorate

Commercial sodium perchlorate always contained chloride ions which could not be removed by recrystallisation.

Chloride free sodium perchlorate was prepared from AnalaR sodium carbonate and AnalaR perchloric acid by the method of Rossotti et al[92]. AnalaR anhydrous sodium carbonate (610g) was partially dissolved in distilled water (1 litre) in a 5-litre flat-bottomed flask. AnalaR perchloric acid (1250ml; 60%) was added in small portions until all the sodium carbonate had been decomposed (pH~2). This solution was boiled in a 5-litre beaker to remove carbon dioxide and to reduce the volume to about 1.5 litres. A watch-glass covered the beaker during the boiling to prevent the formation of a crust of sodium perchlorate on the wall, and its subsequent decomposition to sodium chloride by local heating. A solution of AnalaR sodium hydroxide (~1M) was then added until the solution gave a grey colour to a methyl red - bromocresol green external indicator (pH~5). After standing for three days a slight precipitate of silica was filtered off on a Whatman 42 filter paper. Tests for Fe^{III}, Cl^- and ClO_3^- were all negative. The solution was analysed by heating three samples (~0.8g) to constant weight which took about three and a half days at 120°c. The three analyses agreed to within 0.02%.

Perchloric Acid

A stock 2M solution was made up from AnalaR perchloric acid (60%). It was standardised against 1M sodium hydroxide solution, which in turn was standardised against BDH 1M analytical hydrochloric acid.

Silver Perchlorate

A stock solution (~0.1M) was prepared as follows. An approximately 0.1M solution of AnalaR sodium hydroxide (7g) in distilled water (175ml) was added slowly to a hot solution of silver nitrate (30g in 250ml water). The precipitated silver oxide was filtered off and washed twenty times with distilled water in a glass sinter funnel.

An approximately 0.1M solution of perchloric acid (7.6ml of 72% acid) in distilled water (1l.) was boiled up with an excess of the silver oxide. The cooled solution was filtered through an AGx4 sinter and the volume of the solution made up to 1 litre. The solution was standardised using a potentiometric titration[93] against a standard solution prepared from AnalaR sodium chloride. A silver electrode and a saturated calomel reference electrode were used. Three titrations agreed exactly - see figure 25.

Stock Silver Perchlorate Solutions

The following stock silver perchlorate solutions were prepared.

(1) ~0.02M $AgClO_4$ (500ml)

100ml 0.0987M $AgClO_4$	i.e. 0.0197M
25ml 2M $HClO_4$	i.e. 0.1M
126.55ml 7.429M $NaClO_4$	i.e. 1.8803M

Potentiometric Titration of silver perchlorate solution (10ml)

against sodium chloride solution

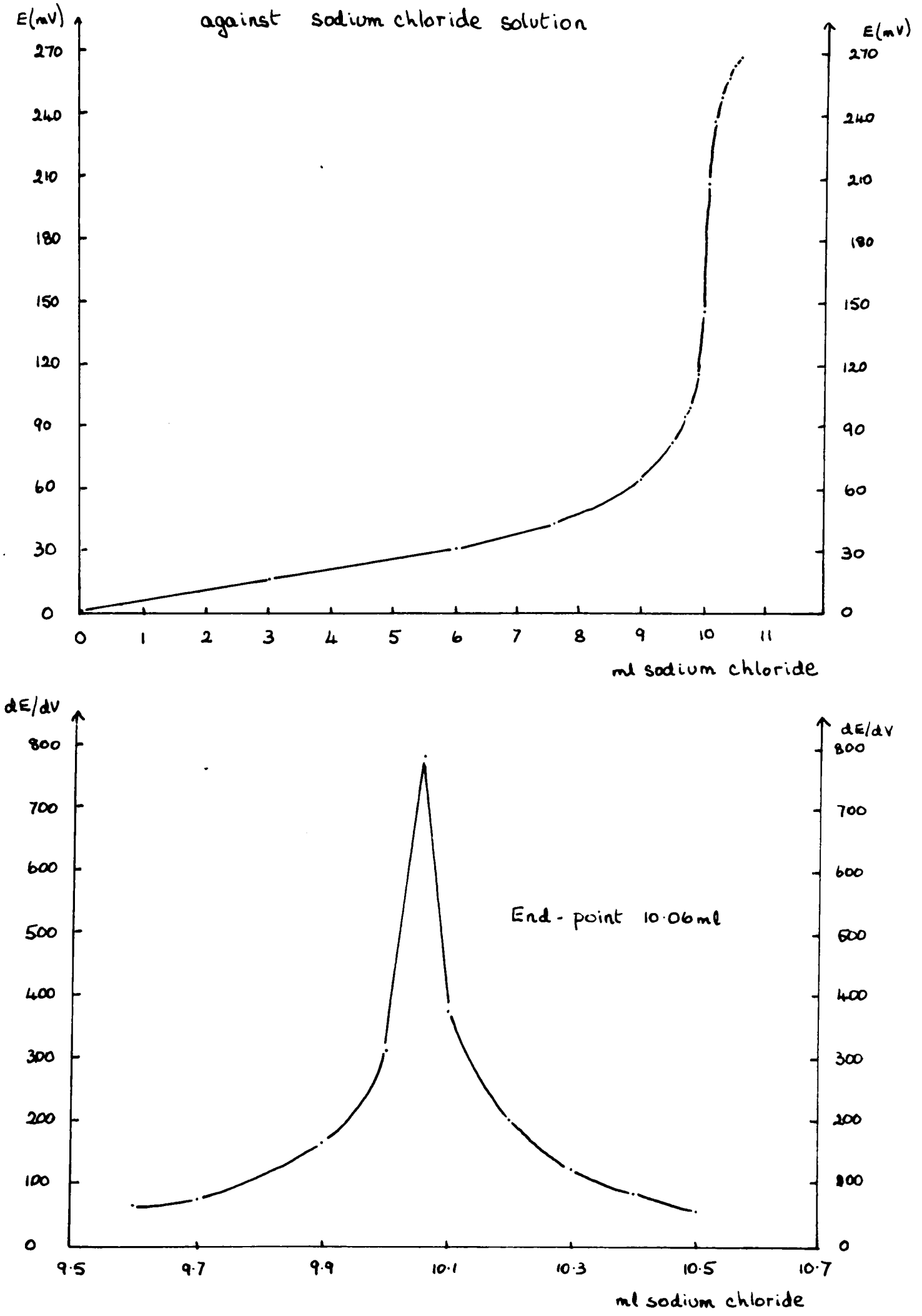


FIGURE 25

(2) ~0.01M $AgClO_4$ (500ml)

50ml 0.0987M $AgClO_4$	i.e. 0.00987M
25ml 2M $HClO_4$	i.e. 0.1M
127.16ml 7.429M $NaClO_4$	i.e. 1.8901M

(3) ~0.005M $AgClO_4$ (500ml)

25ml 0.0987M $AgClO_4$	i.e. 0.00493(5)M
25ml 2M $HClO_4$	i.e. 0.1M
127.54ml 7.429M $NaClO_4$	i.e. 1.8951M

Ligands

The preparation of the ligands is described in chapter 7.

Preparation of the Silver/Silver Chloride Electrodes

The silver/silver chloride electrodes were prepared by the method of Brown[94]. The electrodes were prepared in batches of six by sealing platinum wire (0.02cm diameter) into soft glass, leaving 2cm projecting at the end. The electrodes were immersed in boiling nitric acid to remove any grease, well washed with water and then mounted as cathodes in a bath of potassium silver cyanide. The potassium silver cyanide solution was treated with sufficient silver nitrate to cause a faint precipitation, and filtered immediately before use, to remove any excess cyanide ions. The anode consisted of a platinum wire (0.05cm diameter) mounted inside a glass tube fitted with a sintered glass disc at the bottom. A current of 1.5 milliamps was passed for five hours.

When the electrolysis was complete the electrodes were washed by immersing them in ammonium hydroxide solution

(3M) and then left standing in distilled water overnight.

The silver electrodes prepared above were chloridised by electrolysis for half-an-hour in 0.1N hydrochloric acid at a total current of 2 milliamps, using a platinum cathode separated from the main bulk of the solution by a glass tube fitted with a sintered glass disc. The electrodes were washed with distilled water and stored in dilute potassium chloride solution.

The electrodes were stored in the dark, although Brown has reported that they are not light sensitive. The initial plum colour became white for the 2mm nearest the glass support after storing for forty-eight hours. No further colour change was observed. The electrodes were aged[95] until the emf developed no longer changed with time, which generally took about one week.

The emf difference between the electrodes when dipped in the same silver solution was observed. Those electrodes which differed by more than 0.2mV were rejected. The reversibility of the remainder to silver ion concentration was checked - see figure 26. The average life-time of the electrodes (before breakage) was three to four weeks. No loss of reversibility was observed during this time. One electrode, however, survived for eleven weeks, after which the uniform plum colour became flecked with white spots and a loss of reversibility was observed.

Reversibility of silver/silver chloride electrode to silver ion concentration.

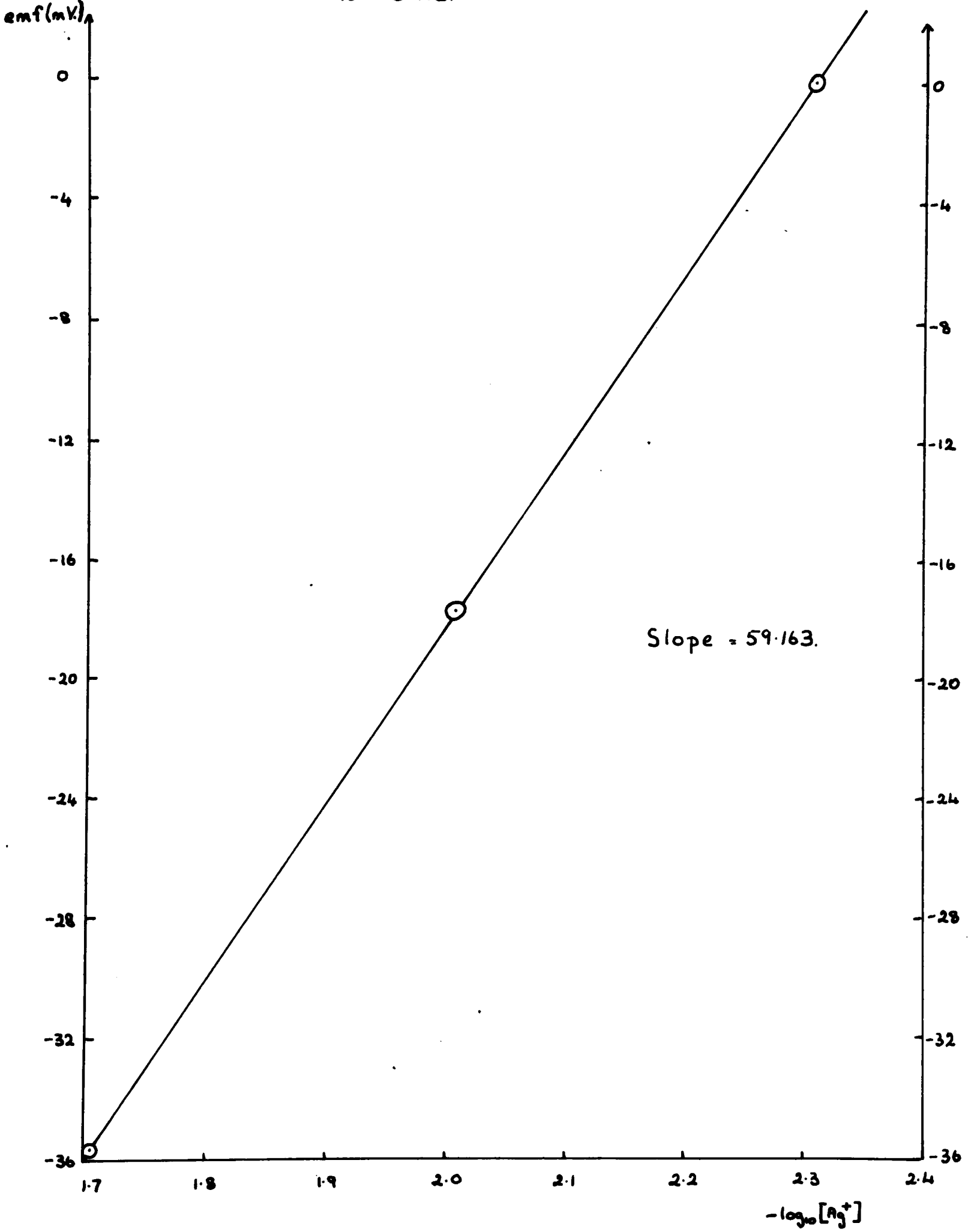


FIGURE 26

(2) Discussion of the Experimental Method

In contrast to the platinum-olefin complexes, the silver-olefin complexes come to equilibrium very rapidly, allowing a titrimetric procedure to be used. The free silver ion concentration was determined potentiometrically using a silver/silver chloride electrode. Silver/silver chloride electrodes were used as Leden[96] found silver electrodes to be unsatisfactory. Because it is possible to measure a small emf difference more accurately than a large one, a reference electrode, which consisted of a silver/silver chloride electrode dipping into a silver solution of the same concentration as initially present in the titration cell, was used.

Since the emf measured was directly related to the silver concentration and as the complexes formed were weak it was found best to keep the total silver concentration constant. This eliminated the emf change due to dilution which would have been considerably greater than the emf change due to complex formation in the case of the weaker complexes. This was achieved by running in equal volumes of the ligand solution and a silver perchlorate solution exactly double the strength of the silver perchlorate being titrated.

The solutions used were made up with air-free distilled water, and the reference electrode "sealed in" to eliminate the presence of any oxygen in solution. "White spot"

nitrogen, presaturated with water vapour was bubbled round the sample electrode. This performed the dual function of eliminating oxygen and stirring the solution. Oxygen must be eliminated since it has been shown[95] that in chloride solutions a potential drift occurs due to the reaction,

$$2Ag + 2HCl + \tfrac{1}{2}O_2 \rightleftharpoons 2AgCl + H_2O$$

It is possible that an analogous reaction takes place in perchlorate solutions.

In order to obtain valid comparisons between the platinum-olefin and silver-olefin stability constants it was necessary to use a very similar background electrolyte. Since a background electrolyte containing chloride ions was obviously inapplicable for the study of silver-olefin systems, a background electrolyte containing 1.9M sodium perchlorate and 0.1M perchloric acid was used.

A concentration of 0.1M hydrogen ion effectively ensures that no complexes are formed between silver and the free amine. A value of 7.17 for $\log_{10}\beta_2$ for allylamine with silver(I) at 16°c and an ionic strength of 0.01M has been reported[97]. The values for methylamine and silver(I) at 25°c in 0.5M solution were reported as $\log_{10}K_1 = 3.15$ and $\log_{10}K_2 = 3.53$[98].

If one assumes a value of 3.5 for $\log_{10}K_1$ for allylamine and a pK_a for allylamine of 9.5[53], then under our

experimental conditions $3x10^{-4}$% of the silver ion is present as $[Ag(C_3H_5NH_2)aq]^+$ and $1.4x10^{-9}$% as $[Ag(C_3H_5NH_2)_2aq]^+$. These species can therefore be neglected.

(3) Apparatus

The apparatus used consisted of two silver/silver chloride electrodes connected to each other by a Wilhelm salt-bridge with a "J-shaped" liquid junction of the type described and illustrated by Rossotti[99]. The potential developed was measured using a Pye precision potentiometer fitted with three ranges: (a) 0-1.75v. in steps of 0.1mv., (b) 0-0.175v. in steps of 0.01mv., (c) 0-0.0175v. in steps of 0.001mv. The balance point was detected using a Pye Scalamp galvanometer (Cat. No. 7901/S) connected to the potentiometer bridge by a Pye Galvanometer Pre-amplifier (Cat. No. 11330). Using this it was possible to detect changes as small as 0.004mV, which gave a deflection of 0.5mm. A standard cell (Weston normal cell No. L-335739, manufactured by the Cambridge Instrument Co. Ltd.)was employed for calibration purposes.

Because of the extreme sensitivity of this equipment to very small changes in voltage, a very reliable accumulator was needed. A heavy duty "Trojan" 2v. accumulator supplied by "The Super Accumulator Co. Ltd." was used. Before starting, the accumulator was well-shaken to dislodge any gas bubbles present on the plates. It was then left connected to the

potentiometer for one-and-a-half hours, when it was again shaken without disconnecting. It was then left undisturbed for the rest of the experiment. Even using this procedure it was necessary to make small adjustments to the compensating resistance on the potentiometer from time to time. The zero was checked carefully before and after each reading.

The titration cell, salt-bridge and reference electrode were immersed in a constant temperature tank maintained at 25.0$\pm$ 0.1°c. The experiments were performed in a room thermostatted to 25 $\pm$ 0.5°c.

(4) Experimental details

25 ml of the silver salt solution were pipetted with an 'A' grade pipette into the titration flask which was fitted with a silver/silver chloride electrode, gas bubbler, salt-bridge and two burettes - see figure 27. The apparatus was placed in a constant temperature bath and the two electrodes connected to the potentiometer. The accumulator, standard cell and galvanometer were then connected and the apparatus left for one-and-a-half hours. The emf was then measured on the 0-0.0175v. range of the potentiometer.

Exactly 1ml of the ligand solution (0.3M) and 1ml of a silver perchlorate solution exactly double the strength of that in the flask were then added from 10ml 'A' grade burettes. The flask was then gently swirled and left to stand for six minutes, after which the emf was measured. 10ml

Titration flask for the determination of Silver-olefin stability constants.

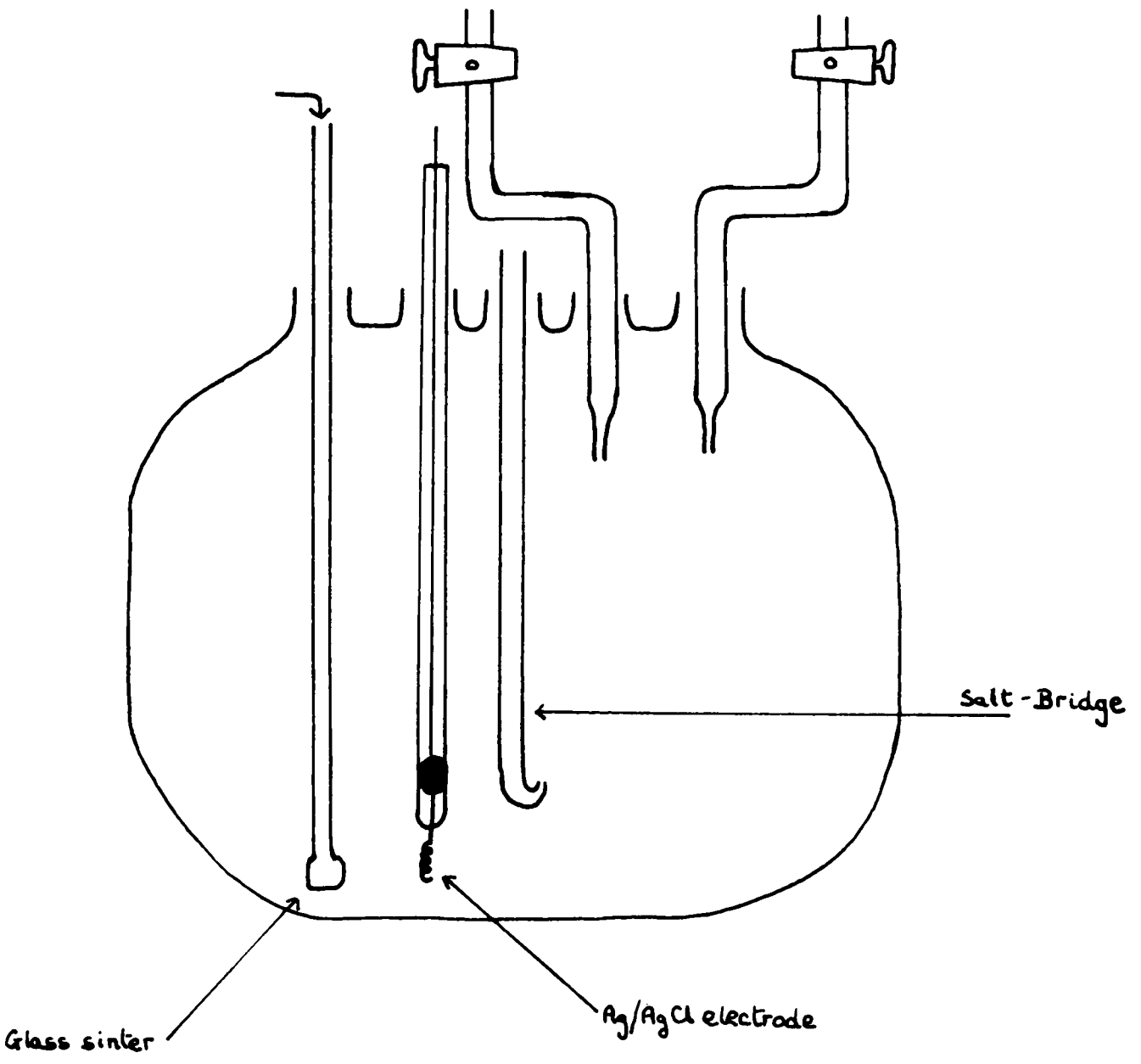


FIGURE 27

was added in 1ml aliquots using the same procedure. The time of six minutes was adopted as it was found that the emf did not alter after about three minutes for at least three-quarters of an hour.

Each ligand was titrated against two different silver concentrations (see p.110) and each titration at a given silver concentration was repeated twice with different silver/silver chloride electrodes.

(5) Calculation of results

The method of calculation was based on Leden's method[96] described in English by Rossotti[100].

A function $\bar{\nu}$ is defined as the average number of ligands per complex.

$$\text{Then } \bar{\nu} = \frac{A - a}{B - b} \qquad (1)$$

where A = total ligand concentration, a = free ligand concentration, B = total metal concentration, and b = free metal concentration.

A function α_c is defined as the degree of formation of the complex BA_c. Then α_o is the degree of formation of BA_o. i.e. $\alpha_o = b/B$. If only mononuclear complexes are present then

$$B = b(1 + \beta_1 a + \beta_2 a^2 + - - - - \beta_N a^N)$$

where β_n = overall stability constant for the formation of BA_n.

If only two complexes are formed,

$$\frac{b}{B} = \frac{1}{1 + \beta_1 a + \beta_2 a^2} = \alpha_o$$

If a function F(B) is defined such that

$$F(B) = \frac{1 - \alpha_o}{a\alpha_o}$$

then $F(B) = \beta_1 + \beta_2 a$.

A plot of F(B) against 'a' will give a straight line of slope β_2 and intercept β_1. If higher complexes are formed, the line will start to curve upwards at higher values of 'a'.

Since $\bar{\bar{\nu}} = \frac{A - a}{B - b}$, $a = A - \bar{\bar{\nu}}(B - b)$.

If only the first complex is formed, $\bar{\bar{\nu}}$ is unity. If two complexes are present, $\bar{\bar{\nu}}$ increases from 1 to 2 as 'a' increases. For crotyl alcohol the error due to taking $\bar{\bar{\nu}}$ as 1 was insignificant. For allyl alcohol it amounted to 0.3%. Consequently a first improved value of $\bar{\bar{\nu}}$ was calculated for each reading as follows:

from equation (1), $\bar{\bar{\nu}} = \frac{A - a}{B - b}$

since $B = b(1 + K_1 a + K_1 K_2 a^2)$ $\quad (K_1 \equiv \beta_1 \; ; \; K_1 K_2 \equiv \beta_2)$

and $A = a(1 + K_1 b + 2K_1 K_2 ab)$

it follows that $\bar{\bar{\nu}} = \frac{A - a}{B - b} = \frac{K_1 + 2K_1 K_2 a}{K_1 + K_1 K_2 a}$

The value of 'a', the free ligand concentration, was obtained using the approximate value of $\bar{\nu} = 1$. The new value of $\bar{\nu}$ was then used to recalculate 'a' and F(B). Further refinement gave insignificant differences in the values of K_1 and K_2.

In the presence of ligand, the cell potential (E_A) is given by

$$E_A = E_0' + E_j - \frac{RT}{z\mathfrak{F}} \ln b$$

where E_0' = constant for a particular cell, E_j = liquid junction potential and z = charge on free metal. In the absence of ligand, the cell potential ($E_{A=0}$) is given by

$$E_{A=0} = E_0' + E_j - \frac{RT}{z\mathfrak{F}} \ln B$$

$$\text{whence } \Delta E = (E_A - E_{A=0}) = -\frac{RT}{z} \ln \alpha_0$$

$$\therefore \log_{10} 1/\alpha_0 = \frac{\Delta E}{(RT/z\mathfrak{F})\ln 10}$$

The value of $RT\ln 10/z\mathfrak{F}$ was taken as 59.157mV[101].

Thus from a series of measurements of potential against ligand concentration it is possible to obtain the first and second stability constants. The assumptions implicit in the above calculation are discussed more fully below.

(1) <u>The Presence of Polynuclear Species</u>

The calculation above has assumed that polynuclear species are not formed. The validity of this was checked

experimentally by measuring the stability constants at more than one silver concentration. If polynuclear species are formed the stability constants will not be equal.

(2) Liquid Junction Potential

In the above calculation the liquid junction potential has been assumed to be constant throughout the titration. This in fact will not be so. Henderson[102], by making certain assumptions about the composition of the boundary between two solutions (I and II), showed that if only monovalent ions are present,

$$E_j = \frac{RT}{zF} \ln\left\{\frac{\Sigma(c_i l_i)_{II}}{\Sigma(c_i l_i)_I}\right\}$$

where c = concentration and l = equivalent conductivity at that concentration. This expression is however of limited accuracy. With the ligands used in this work it was possible to allow for the liquid junction potential by performing two titrations. In the first the olefin solution (0.3N) was used, whilst in the second a solution of the corresponding saturated compound (0.3N) was used. The saturated compound did not form a complex so that the potential change was principally due to the liquid junction potential.

With crotylammonium perchlorate, where no second stability constant was found, a plot of F(B) against free ligand concentration had a negative slope - see figure 28a. However,

when the sum of ΔE obtained from $CH_3-CH=CH-CH_2-NH_3^+$ and ΔE from $CH_3-CH_2-CH_2-CH_2-NH_3^+$ was used the plot had a slope of zero - see figure 28b.

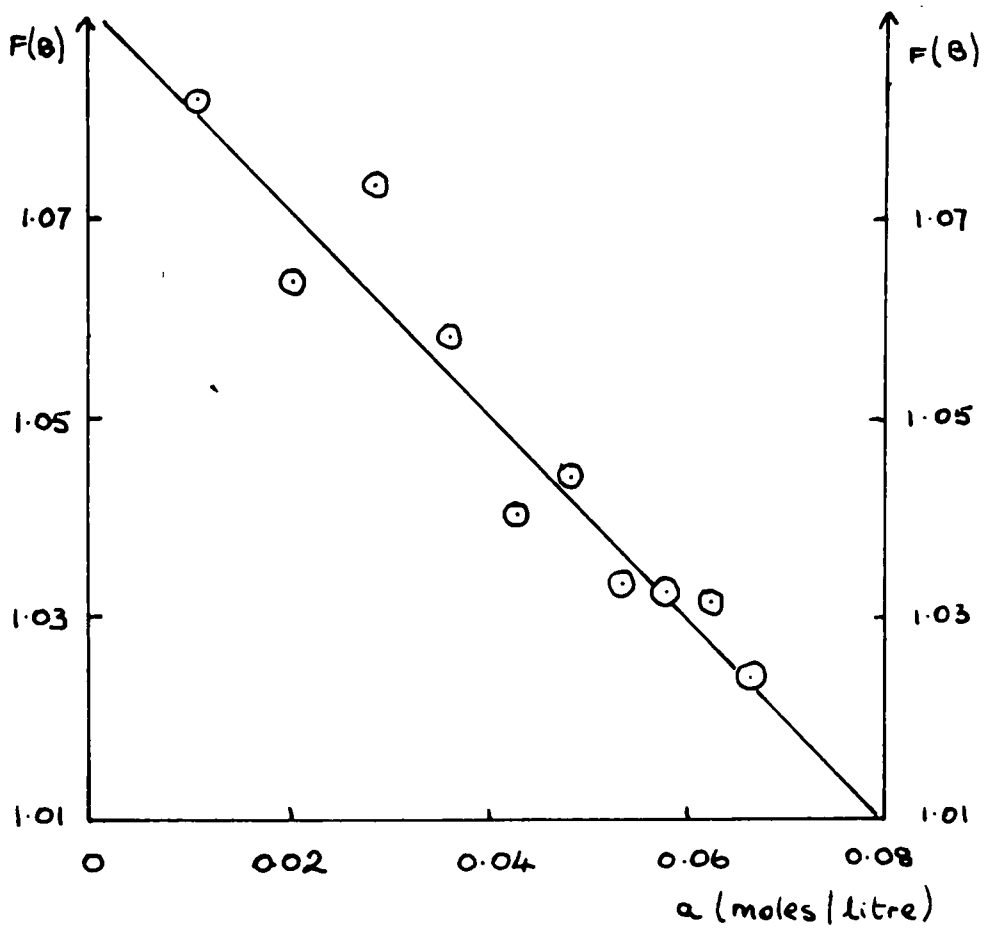
(3) Constant Ionic Strength

In the calculation above concentrations rather than activities have been used. This is only valid if the ionic strength has been kept constant. In this work the ionic strength was maintained at 2M - see p.103. Lewis and Randall[48] pointed out that activity coefficients are independent of the medium only at very low concentrations. Although the ligand solutions used here were 0.3M in ligand, the concentration of the ligand in the titration vessel only varied between zero and 0.065M, so that the activity coefficients should remain effectively constant.

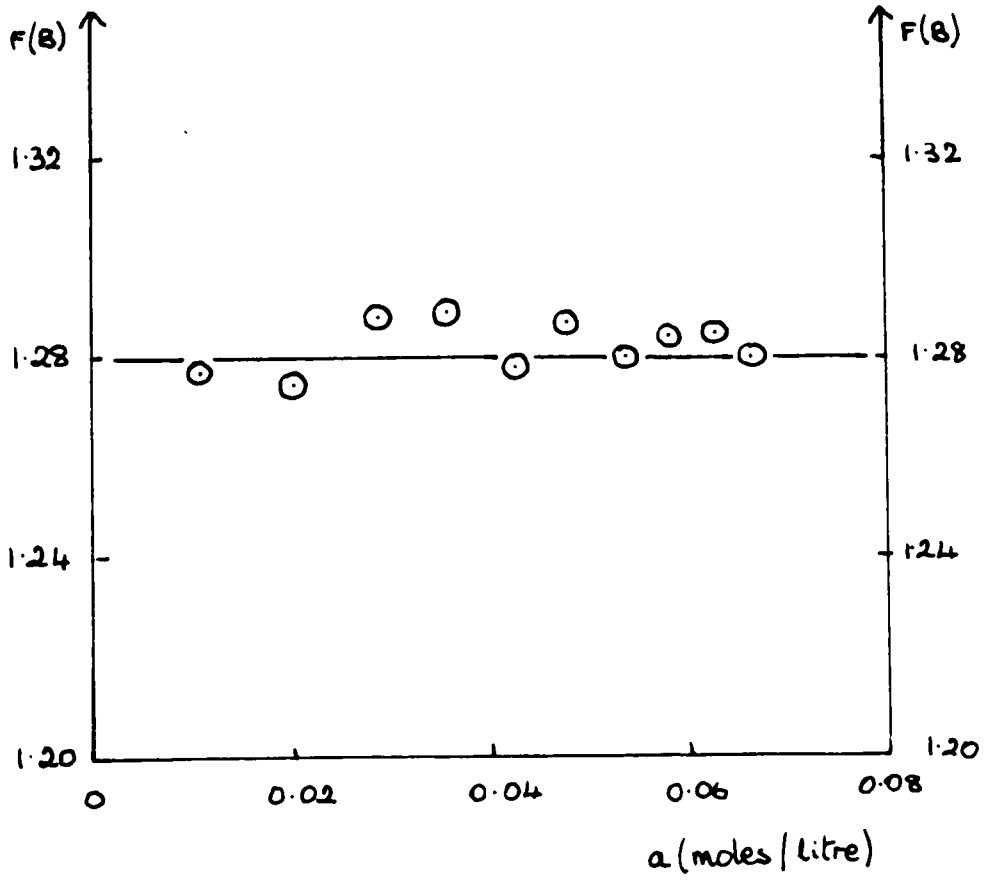
Results

The experimental readings are recorded in Appendix III.

For the allylammonium and crotylammonium cations the stability constants were calculated with the aid of the Oxford KDF9 computer. The programme used is given in Appendix I. The plots of F(B) against free ligand concentration had zero slopes - see figure 28b - and the programme gave the stability constnnt directly. The second half of the programme, which is exactly analogous to that described for the calculation of platinum-olefin stability constants, calculates the standard deviation by a "least-squares" treatment.



(a) F(B) v. a for $CH_3-CH=CH-CH_2-NH_3^+$



(b) F(B) v. a for $CH_3-CH=CH-CH_2-NH_3^+$ + $CH_3-(CH_2)_3-NH_3^+$

FIGURE 28

For allyl alcohol and crotyl alcohol the slope of the plot of F(B) against free ligand concentration was positive. The results at both silver concentrations were plotted and the "best line" was drawn with the aid of a "least-squares" calculation - see figures 29 and 30. For allyl alcohol the plots at different silver concentrations do not coincide. This is almost certainly due to experimental error as the standard deviation of K_1, obtained from the mean of all the points is 0.38%, which is only slightly greater than that for crotyl alcohol (0.24%). It is, however, possible that a complex containing two atoms of silver, $[Ag_2(ol)^{++}]$, is formed. If it is assumed that such a complex is not present at the lower silver concentration, then the difference between the two lines leads to a value of K' of 0.75 ± 0.05, where $K' = [Ag_2(ol)^{++}]/[Ag^+][Ag(ol)^+]$.

The value of K' was calculated using the expression for the total silver concentration (B),

$$B = b + \beta_1 ab + \beta_2 a^2 b + 2\beta_1 K' ab^2$$

$$\text{whence } K' = \frac{B - b - \beta_1 ab - \beta_2 a^2 b}{2\beta_1 ab^2}$$

Values of B and b corresponding to given values of 'a' were obtained from the plot of F(B) against 'a' using the relation

$$F(B) = \frac{B - b}{ab} .$$

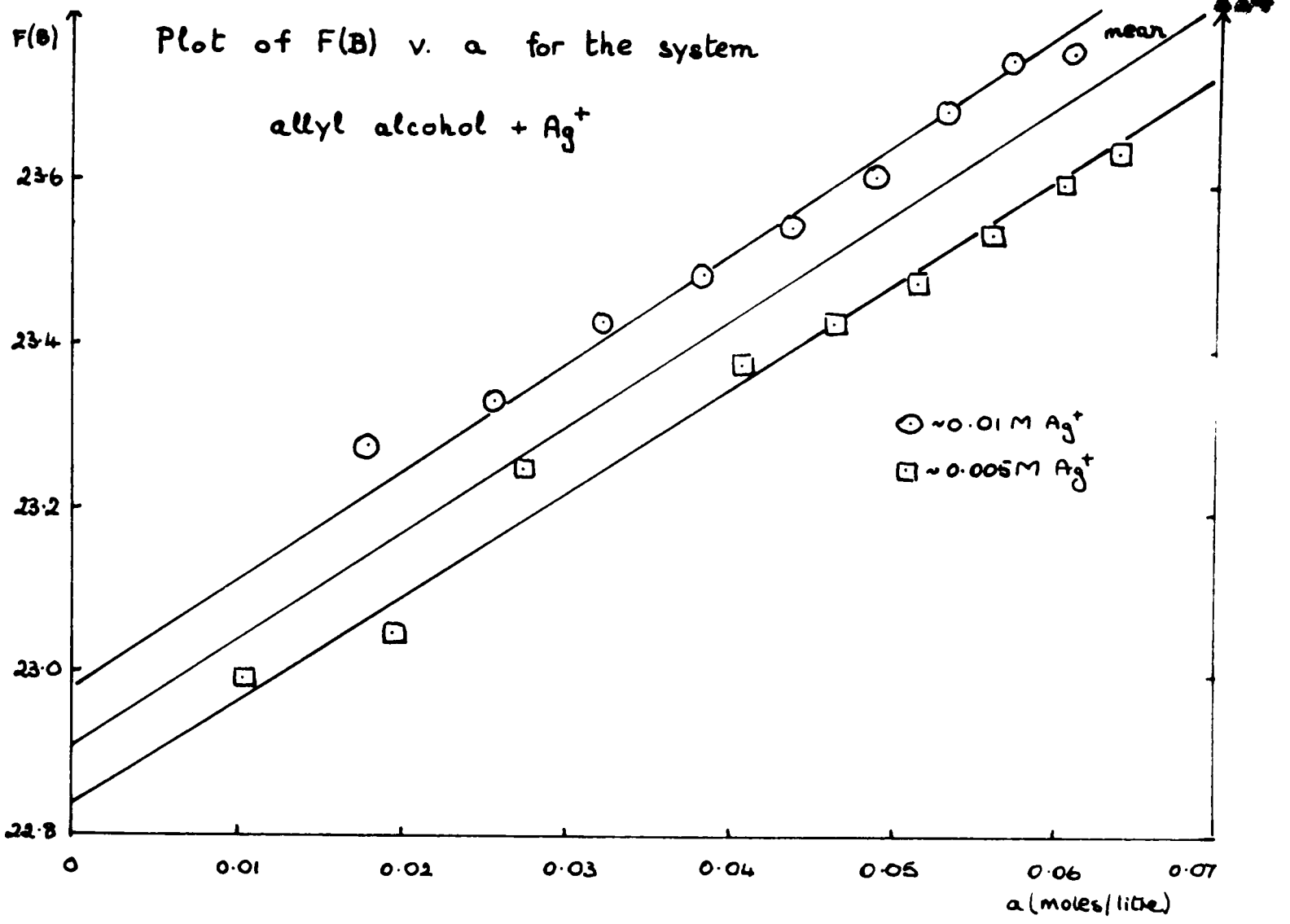


FIGURE 29

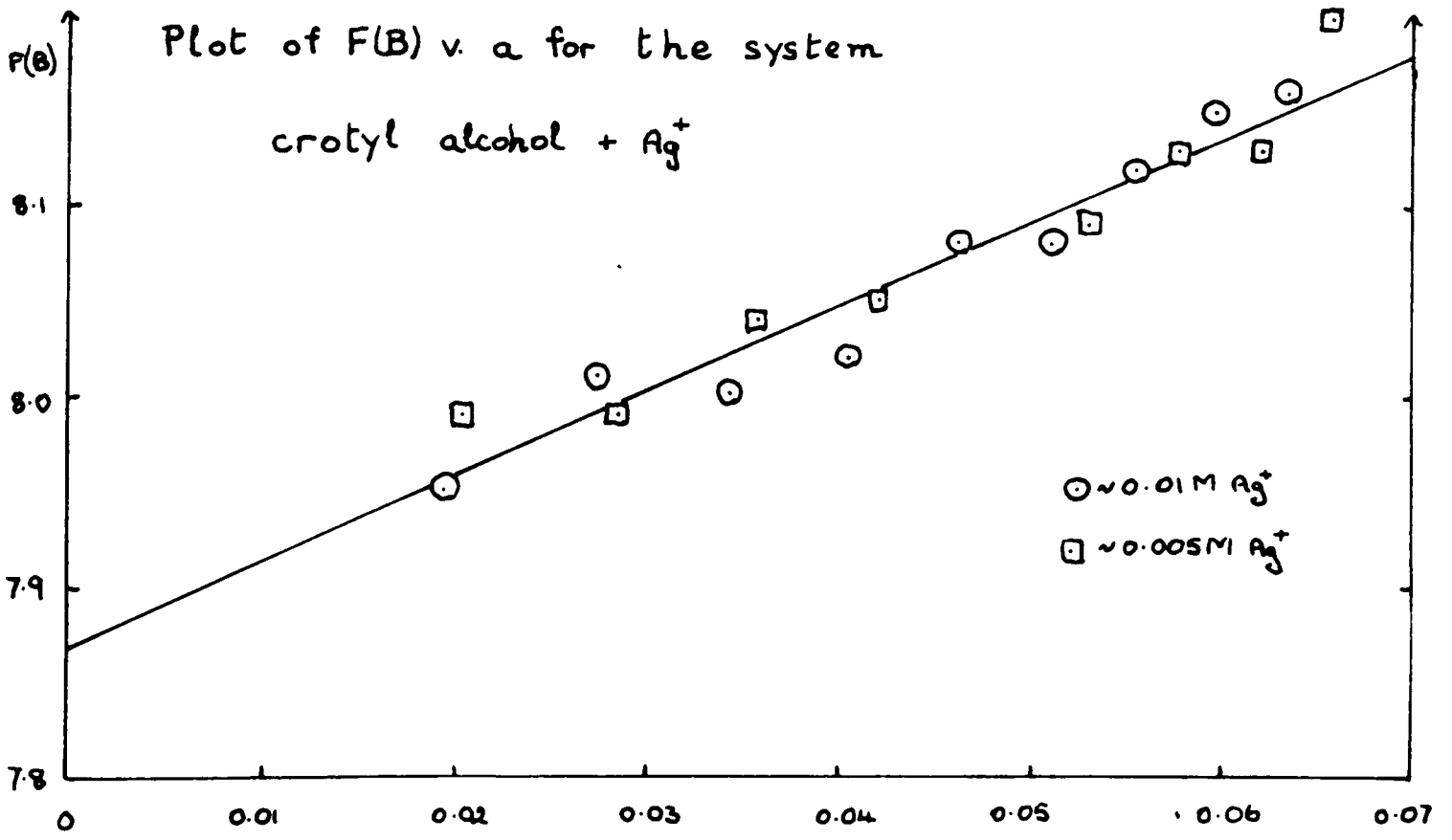


FIGURE 30

The "least-squares" calculation of the "best line" followed that given by Modo[103]. If the straight line under consideration is written as $y = mx + c$ and if N is the number of points on the graph, then the "least-squares" values of m and c are given by

$$m' = \frac{N\Sigma x_i y_i - (\Sigma x_i)(\Sigma y_i)}{N\Sigma(x_i)^2 - (\Sigma x_i)^2}$$

$$c' = \frac{\Sigma(x_i)^2(\Sigma y_i) - \Sigma(x_i)(\Sigma x_i y_i)}{N\Sigma(x_i)^2 - (\Sigma x_i)^2}$$

Using the "least-squares" value of c (i.e. c') and values of x and y for each point, the calculated value of m for each point was obtained (m"). The standard deviation (σ) was then given by

$$\sigma = \sqrt{\frac{\Sigma|m' - m''|^2}{N}}$$

The same was done for c.

The results are given in table 18.

TABLE 18

Silver-olefin stability constants

$$K_1 = \frac{[Ag(ol)^+]}{[Ag^+][ol]} \qquad K_2 = \frac{[Ag(ol)_2^+]}{[Ag(ol)^+][ol]}$$

Ligand	Silver conc.	K_1 at 25°c	K_2 at 25°c
$CH_2{=}CH{-}CH_2{-}NH_3^+$	0.00987M	1.292 ± 0.016	
	0.00493_5M	1.304 ± 0.009	
	Mean[a]	1.30 ± 0.01	
trans-$CH_3{-}CH{=}CH{-}CH_2{-}NH_3^+$	0.00987M	1.279 ± 0.007	
	0.00493_5M	1.283 ± 0.004	
	Mean[a]	1.28 ± 0.005	
$CH_2{=}CH{-}CH_2{-}OH$[b]	0.00987M	22.98 ± 0.025	0.58 ± 0.05
	0.00493_5M	22.84 ± 0.027	0.56 ± 0.05
	Mean[c]	22.91 ± 0.087	0.57 ± 0.16
trans-$CH_3{-}CH{=}CH{-}CH_2{-}OH$	0.00987M 0.00493_5M	7.87 ± 0.02[c]	0.57 ± 0.07

(a) Weighted mean of results for each silver concentration

(b) $K' = [Ag_2(ol)^{++}]/[Ag^+][Ag(ol)^+] = 0.75 \pm 0.05$ - see p.113

(c) Obtained by plotting the "least-squares" line through the points obtained for both silver concentrations.

C H A P T E R 5

Discussion of Silver-Olefin Stability Constants

A very large number of stability constants have been determined for silver(I) with a wide variety of ligands. However, the number of stability constants which have been determined for platinum(II) is very limited. It was of interest therefore to determine the stability constants for four typical olefins, two unsaturated alcohols and two unsaturated ammonium salts, with silver(I), to provide data directly comparable to that obtained for platinum(II)-olefin complexes.

Discussion of the silver-olefin stability constants, which were reported on p.116, will be limited to the first stability constant (K_1) since no second stability constants were observed for platinum(II).

The results obtained for allyl and crotyl alcohols are in reasonable agreement with those obtained previously at different ionic strengths - see table 19.

TABLE 19

	0.1M KNO_3 (a)	1.0M KNO_3 (b)
Allyl alcohol	14	12
Crotyl alcohol	3.9	5.17

(a) Ref. 104

(b) Ref. 45

Comparison of Olefins with other ligands

A number of stability constants for silver(I) taken from the literature are given in table 20. A comparison of the silver-olefin stability constants reported here with the literature data, shows that the olefins give comparable stability constants to water, acetate and fluoride, and much lower stability constants than the heavier halides or amines.

TABLE 20

Ligand	K_1	Reference
F^-	2,3	105
Cl^-	1.1×10^3	105
Br^-	2.4×10^4	105
I^-	$1.3(5) \times 10^8$	105
H_2O	1.0	106
CH_3COO^-	2.3(5)	96
CH_3NH_2	1.4×10^3	106
NH_3	2.0×10^3	106
CN^-	2×10^5	107

Comparison of stability constants for olefins with silver(I) and platinum(II)

The stability constants observed for platinum(II)-olefin complexes are much larger than for silver(I)-olefin complexes. This difference, which is paralleled by the difference in the lowering of the C=C stretching frequency, can be understood by considering the nature of the metal-olefin bonding. In the case of silver, the σ-bond is formed between the olefin π-orbitals and the non-directed 5s orbital on silver - see p. 3. The overlap integral for this molecular orbital will be less than for that formed between the directed $5d6s6p^2$ hybrid orbital on platinum and the olefin π-orbitals. The same is found for the π-bond, which in the case of silver is formed by overlap of the 4d silver orbitals with the olefin π^*-orbitals, whereas in platinum the hybrid 5d6p orbital is used. Thus in both the σ- and π-bonds the overlap is greater for platinum(II) than silver(I), leading to higher bond strengths and also higher stability constants for platinum(II) than silver(I) olefin complexes.

On p.89 it was stated that comparison of the lowering of the C=C stretching frequencies on coordination ($\Delta\nu_{C=C}$) for the same olefin with different metals should give useful indications of the metal-olefin bond strength. Since none of the silver-olefin complexes studied in this work were isolated, a value of $65cm^{-1}$ (9) will be taken for the lowering of the

C=C stretching frequency on coordination to silver. For platinum - see table 17, p.90 - the average lowering is about 150cm^{-1}. The ratio of $\Delta\nu_{C=C}$ for platinum to $\Delta\nu_{C=C}$ for silver is therefore 2.3. Ideally this value would be compared to the enthalpy of formation of the complexes. Unfortunately, the method used to determine the silver-olefin stability constants could not readily be adapted to use over a range of temperature, so that no enthalpy values were determined for silver-olefin complex formation. However the ratio can be compared with the ratio of the free energies shown in table 21.

TABLE 21

Ligand	$\Delta G_{Pt}/\Delta G_{Ag}$ at 25°c
$CH_2=CH-CH_2-OH$	3.1
$CH_2=CH-CH_2-NH_3^+$	31.1
$CH_3-CH=CH-CH_2-NH_3^+$	25.4

It can be seen that the unsaturated ammonium salts show a very much greater preference for platinum(II) relative to silver(I), than the lowering of the C=C stretching frequency in the infra-red would predict. For allyl alcohol the preference for platinum(II) is of the same order as that predicted from the lowering of the C=C stretching frequency on coordination.

If it is assumed that the preference for platinum(II) relative to silver(I) shown by the unsaturated ammonium salts

is due to an enthalpy effect, it could arise from changes in the heats of solvation and/or metal-olefin bond energies. Since the 'radii' of the ions $[Ag^+(CH_2=CH-CH_2-NH_3^+)]$ and $[Ag^+(CH_2=CH-CH_2-OH)]$ will not be very different, it is expected that their heats of solvation will be in the approximate ratio 4:1[63]. A minimum value of the heat of solvation of $[Ag^+(CH_2=CH-CH_2-OH)]$ can be obtained by calculating the approximate 'radius' for this ion, e.g. by assuming that it is equal to half the sum of the bond lengths of the C=C, C-C, C-O and O-H bonds (~2.6Å) and calculating the heat of solvation of a hypothetical ion of this radius by extrapolation of the heats of solvation of the alkali metal ions[70]. This gives a value of about 30 Kcals/mole. The maximum value of the heat of solvation of this ion can be taken as the heat of solvation of the allylammonium ion (86 Kcals/mole[81]). Thus the heat of solvation of $[Ag^+(CH_2=CH-CH_2-OH)]$ should be in the range 30-86 Kcals/mole, and, therefore, that of $[Ag^+(CH_2=CH-CH_2-NH_3^+)]$ in the range 120 - 344 Kcals/mole. The difference in the heats of solvation of the two complexes (90 - 258 Kcals/mole) is therefore larger than that between the free ligands, which is about 75 Kcals/mole (p. 83), so that a consideration of the heats of solvation would suggest that silver(I) would prefer the charged to the uncharged ligand. Similar considerations for the corresponding platinum(II) complexes lead to the conclusion that differences in the heats of solvation should

favour the formation of the allyl alcohol complex relative to that with the allylammonium ion (see p. 83). Thus a consideration of the heats of solvation cannot account for the preference for platinum(II) relative to silver(I) shown by the unsaturated ammonium salts. This preference can however be accounted for by considering the direct electrostatic interaction between the positive charge on the nitrogen atom and the central metal group. In the platinum complex, the central metal group ($-PtCl_3^-$) carries an overall negative charge, so that the electrostatic interaction is one of attraction. In the case of silver, the central metal group ($Ag(H_2O)_n^+$) carries a positive charge, so that the force is one of repulsion.

There is a very small difference between the stability constants for $allNH_3^+$ and $crotylNH_3^+$ with silver(I), whereas there is a much larger difference between the corresponding alcohols. If this is an enthalpy effect, it probably arises from the electrostatic repulsion, in the case of the unsaturated ammonium salts, dominating the steric and inductive effects of the methyl group attached to the double-bond. In the case of the alcohols, this electrostatic repulsion is absent, so that the steric and inductive effects of the methyl group are observed.

In the case of the platinum(II), it has been shown that the π-bond (platinum to olefin) is more important than the σ-bond (olefin to platinum). Since no enthalpy data were obtained for silver with a suitable series of olefins, it is

impossible to decide whether the σ- or the π-component of the bond is the more important.

In conclusion, it can be seen that the lower stability constants for silver(I)-olefin complexes relative to platinum(II)-olefin complexes can be attributed to the nature of the metal-olefin bonding. The lower stability constants observed for olefins which carry a positive charge with silver(I), relative to those for uncharged olefins can be attributed to the electrostatic interaction between the positive charge and the central metal group.

C H A P T E R 6

The Ultra-violet Spectra of the Platinum-Olefin Complexes

(1) Discussion

Since the spectrophotometric determination of the stability constants of the platinum-olefin complexes utilizes the ultra-violet absorption spectra of these complexes, it was of interest to study the origin of these spectra.

Before considering the olefin complexes themselves it is necessary to consider the splitting of the d-orbitals in the square-planar field of $[PtCl_4^{=}]$. This ion has been the subject of a number of investigations.

With the exception of one paper by Martin[108], which was later superceded[109], in which potassium tetrachloroplatinate(II) was studied both as a solid and in solution and in which the order of the d-orbitals, in terms of decreasing energy, was given as $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz}$, d_{yz}, the investigations fall into two main groups. Those [109,110] which give the order of the d-orbitals as $d_{x^2-y^2} > d_{xy} > d_{xz}$, $d_{yz} > d_{z^2}$ and those[111,112] which give the order as

$d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xz}, d_{yz}$. The former order was arrived at using solution studies, solid studies with the aid of plane polarised light and magnetic circular dichroism studies in solution[113]. The latter order was arrived at from solution studies alone.

These three descriptions of the relative energies of the d-orbitals only differ in their positioning of the d_{z^2} orbital. It is this orbital which polarisation studies on the solid compound give most help in assigning. It has been pointed out that in the solid state it is this orbital which is most susceptible to the change in environment. In accordance with this Williams et al[114] have examined the polarised crystal spectra of $K_2[PtCl_4]$ and $[Pt(NH_3)_4][PtCl_4]$, since the Pt-Pt axial bond length is 4.13Å in $K_2[PtCl_4]$ and only 3.25Å in $[Pt(NH_3)_4][PtCl_4]$. Their results are consistent with either of the two main assignments (i.e. $d_{x^2-y^2} > d_{xy} >$ "the rest").

When considering orbitals in complexes of the type $[(ol)PtCl_3^-]$ it will be assumed that the order of the d-orbitals is $d_{x^2-y^2} > d_{xy} >$ "the rest", with the relative positions of "the rest" uncertain.

If the olefin complexes are taken as

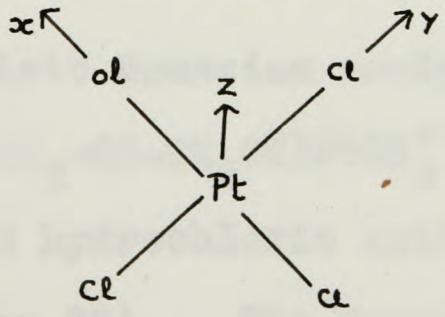


Figure 31

then the introduction of π-bonding from the metal to the empty π* orbitals of the olefin suggested by Chatt[12] will remove the degeneracy of the d_{xz} and d_{yz} orbitals, leading to the following energy level diagram.

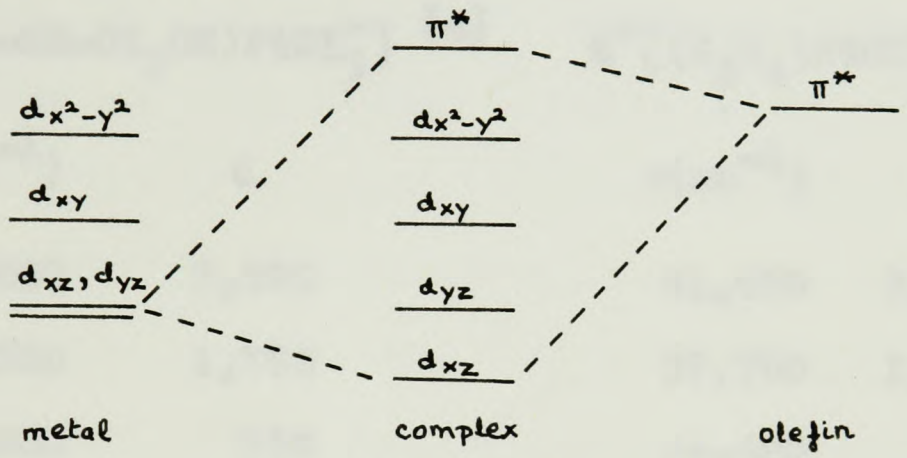


Figure 32

The position of the d_{z^2} orbital is uncertain, except that it lies below the d_{xy} orbital. The overlap of the metal d_{xz} orbital and ligand π* orbital will give two new molecular orbitals. Taking the metal d_{xz} and ligand π* orbitals to have widely differing energies (see p.130), there will be one bonding molecular orbital of slightly lower energy than the original metal orbital mainly concentrated on the metal, and one anti-bonding molecular orbital of slightly higher energy than the ligand π* orbital and mainly concentrated on the ligand.

A complete Gaussian analysis was undertaken for the spectrum of $K^+[(CH_2{=}CH{-}CH_2OH)PtCl_3^-]$ in a medium of 1.9M sodium chloride and 0.1M hydrochloric acid in the region 27,000-45,000cm^{-1} (figure 35). The spectrum[a] is very similar to

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(a) All the figures for this chapter are between p.145 and p.151

that of Zeise's salt obtained by Martin[115] (figure 40) The peaks are shown in table 22.

TABLE 22

$K^+[(CH_2=CH-CH_2OH)PtCl_3^-]$ (a)		$K^+[(C_2H_4)PtCl_3^-]$ (b)	
$\nu(cm^{-1})$	ε	$\nu(cm^{-1})$	ε
41,000	3,325	41,600	3,220
38,000	1,780	37,700	1,360
34,800	850	34,400	750
29,800	180.5	30,000	250

(a) Solution in 1.9M sodium chloride and 0.1M hydrochloric acid.

(b) Solution in dilute hydrochloric acid and excess aqueous potassium chloride[115].

Thus both olefin complexes exhibit three main peaks in the region 30,000cm^{-1} to 45,000cm^{-1} with extinction coefficients in the region 750-3,325. Further spectra of platinum(II)-olefin complexes are shown in figures 37-39.

Denning[38] has argued that these three peaks are due to charge transfer bands from the metal to the ligand. Thus the three peaks could be due to

(a) d → d transitions

(b) transitions within the ligand

(c) charge transfer from metal to ligand

(d) charge transfer from ligand to metal.

Case (b) can be immediately eliminated since free ethylene does not absorb below 58,000cm^{-1} (116). Any $\pi \rightarrow \pi^*$ transition in the free ligand will be raised in energy by coordination.

Case (d) can be further subdivided into (i) Cl → metal charge transfer and (ii) olefin → metal charge transfer. The former is unlikely since Chatt[110] after studying the platinum(II) chloride ammines assigned the Cl → metal charge transfer bands to bands in the region 46,000-50,000cm^{-1}. Changing the other ligand from NH_3 to an olefin will increase the ligand field and also withdraw charge from the platinum, both of which should further raise the energy of these charge transfer bands. Furthermore these bands had extinction coefficients of about 10^4. The latter possibility must remain a possibility since it is impossible at present to decide where the olefin → metal charge transfer bands would occur.

d → d transitions such as are postulated in case (a) normally have extinction coefficients of less than 200[117]. It might be argued that in going from $[PtCl_4^{=}]$ to $[(ol)PtCl_3^{-}]$ the centre of symmetry is removed, thus leaving the Laporte rule, which requires that g states may only combine with u states and vice versa[118], undefined. This results in the bands not being rigorously forbidden, so that their intensities might well be expected to rise. However, in $[(NH_3)PtCl_3^{-}]$ which has the same symmetry as the olefin complexes $[(ol)PtCl_3^{-}]$,

Chatt[110] found no band in the region 30,000-45,000cm^{-1} with an extinction coefficient higher than 118. This suggests that the observed bands cannot be due to d → d transitions.

The possibility that the bands are due to transitions from metal d orbitals to ligand π* orbitals (case (c)) - see figure 32 - is supported by the observation of similar bands in iron(II) complexes with phenanthroline[119]. Like the olefinic ligands under consideration, phenanthroline has empty, low energy, π symmetry orbitals. In the iron(II)-phenanthroline complexes the bands are of lower energy and higher intensity (~10^4) than the present bands. The highly conjugated nature of the ligand will lead to the ligand π* orbitals being of lower energy than in the olefinic ligands, so that the resulting charge transfer bands will be of lower energy. The distance of charge transfer in the iron(II)-phenanthroline system will be much less than in the Pt(II)-olefin system and hence the extinction coefficients in the latter should be much smaller.

In view of the much larger extinction coefficients of the metal → ligand π* transitions it would probably be impossible to see any d → d transitions. Although Ballhausen and Gray[112] indicate that the π* orbital will probably lie above the ~~ligand~~ $d_{x^2-y^2}$ orbital, transitions to the π* orbital will be lowered in energy relative to those to the $d_{x^2-y^2}$ orbital, because the electron-electron repulsions will be

smaller when the electron is in the π^* orbital than when it is in a d-orbital. Thus the charge transfer transitions would probably be comparable in energy to the d → d transitions.

This explanation of the bands as being due to metal d to olefin π^* transitions is supported by the spectra of the complexes trans-$[(P^nPr_3)(\text{piperidine})PtX_2]$ (where X=Cl and Br)[120] where a similar high intensity band is observed and where similar empty π-orbitals are present on the ligand. The position of this band is unaltered when the ligand X is changed from Cl to Br, while other weaker lower energy bands in the spectra are altered, suggesting that this high intensity band is not due to a d → d transition.

Further support is obtained from an approximate calculation by the method of Ballhausen and Gray[112] which indicates that the energy difference between the metal d and ligand π^* orbitals is about 5 electron volts (i.e. about 40,000cm^{-1}). The ionization potential of ethylene is 10.5eV[74], and the separation of the π-bonding and π-antibonding levels in ethylene is 7.6eV[74]. This separation will be increased in the complex. Thus the coulomb energy of the π^* level of complexed ethylene may be estimated at about -3eV. The coulomb energy of the Pt(II) d-orbitals in $[(C_2H_4)PtCl_3^-]$ may be estimated at about -8eV using the spectroscopic data compiled by Moore[121] and assuming that the net charge on the complexed Pt(II) is slightly less than +1. This leaves 5eV or about

40,000cm^{-1} as the difference in energy between the single electron d (Pt(II)) and π^* (C_2H_4) orbitals.

The origin of the three main peaks in the region 30,000-45,000cm^{-1} will now be examined more closely, assuming that they are due to metal d to ligand π^* transitions. The complex [(ol)$PtCl_3^-$] has C_{2v} symmetry, which leads to the following symmetries for the orbitals, which are defined from the axes shown in figure 31.

π^*	b_2
$d_{x^2-y^2}$	a_1
d_{xy}	b_1
d_{z^2}	a_1
d_{yz}	a_2
d_{xz}	b_2

The symmetries of the electric vectors along the axes are:

x	a_1
y	b_1
z	b_2

For a transition to be "allowed", the reducible representation of the product of the lower state, the electric vector and the upper state, when reduced, should contain a_1, the totally symmetric representation[122].

Thus for $d_{xz} \rightarrow \pi^*$ $b_2 \times b_2 \times a_1 = a_1$ ∴ allowed

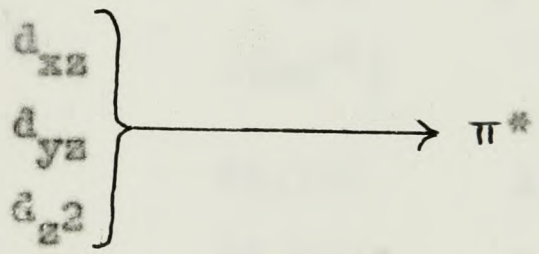
$d_{yz} \rightarrow \pi^*$ $a_2 \times b_2 \times b_1 = a_1$ ∴ allowed

$d_{z^2} \rightarrow \pi^*$ $a_1 \times b_2 \times b_2 = a_1$ ∴ allowed

$d_{xy} \rightarrow \pi^*$ $\left\{ \begin{array}{l} b_1 \times b_2 \times b_1 = b_2 \\ b_1 \times b_2 \times b_2 = b_1 \\ b_1 \times b_2 \times a_1 = a_2 \end{array} \right\}$ ∴ not allowed

Hence group theory predicts three allowed metal d → ligand π^* transitions. The $d_{xy} \rightarrow \pi^*$ transition could occur by a vibronic mechanism, since the vibrational states for square-planar AB_3C are $5a_1$, a_2, $2b_1$ and b_2, in which case it would have a much lower extinction coefficient than the other transitions.

Thus the three strong bands may be assigned to the transitions



A possible way to distinguish between these transitions would be:-

(1) to replace the chloride ligand trans to the olefin by a very different ligand such as water, thus altering the energy of the d_{xz} level relative to the d_{yz} and d_{z^2} levels.

(2) to measure the spectrum in two different solvents of different coordinating power, since a change of solvent should alter the energy of the d_{z^2} orbital more than the

energies of the d_{xz} and d_{yz} orbitals. A suitable alternative to water is difficult to find. Ethanol will dissolve the complex and has no appreciable absorbance below 45,000cm^{-1}. However, it has a very similar ligand field to water. Methyl cyanide dissolves the complex and has a ligand field somewhat greater than water[123], however it absorbs strongly at about 40,000cm^{-1}, leading to spurious peaks[124]. The same objection applies to acetone, which absorbs strongly in the region 35,000-32,000cm^{-1}.

The effect of replacing the chloride ligand trans to ethylene by water is shown in table 23.

TABLE 23

$K^+[(C_2H_4)PtCl_3^-]$ (a)		trans-$[(C_2H_4)PtCl_2(H_2O)]$ (b)		$\Delta\nu$(cm^{-1})
ν(cm^{-1})	ε	ν(cm^{-1})	ε	
41,600	3,220	41,300	1,360	-300
37,700	1,360	38,500	1,150	+800
34,400	750	35,200	710	+800
30,000	250	30,800	150	+800

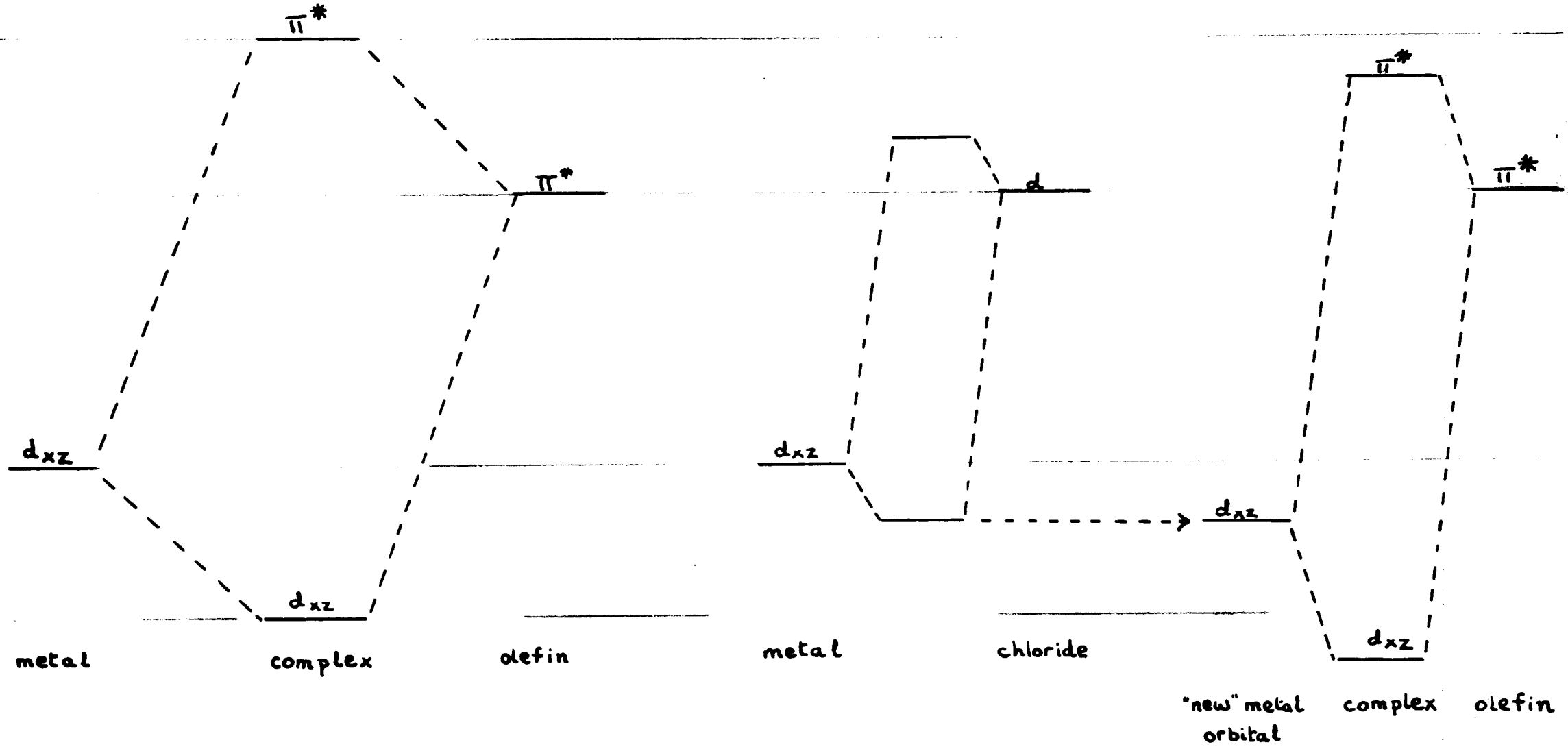
(a) Solution in dilute hydrochloric acid and excess potassium chloride[115] (figure 40).

(b) Solution in dilute sulphuric acid [115] (figure 41).

Since the complex trans-$[(C_2H_4)PtCl_2(H_2O)]$ has C_{2v} symmetry, the "allowed" transitions will be exactly the same

as in Zeise's salt. Since the chloride ligand trans to olefin forms a π-bond primarily with the d_{xz} orbital (the d_{yz} orbital is already involved in π-bond formation with the chloride ligands in the y-direction), the d_{xz} orbital should be lower in energy in $[(C_2H_4)PtCl_3^-]$ relative to $[(C_2H_4)PtCl_2(H_2O)]$ where the ligand trans to ethylene (water) does not form π-bonds. This lowering of the energy of the d_{xz} orbital should also lower the energy of the π^* orbital, since the amount of mixing decreases as the energy separating the component orbitals increases[125]. This is illustrated in figure 33. As a result it is expected that two transitions ($d_{z^2} \rightarrow \pi^*$ and $d_{yz} \rightarrow \pi^*$) will be lower in energy in $[(C_2H_4)PtCl_3^-]$ than in $[(C_2H_4)PtCl_2(H_2O)]$, since the energies of the d_{z^2} and d_{yz} orbitals should be virtually unaffected by a change in the ligand trans to ethylene. In addition one transition ($d_{xz} \rightarrow \pi^*$) is expected to be higher in energy in $[(C_2H_4)PtCl_3^-]$ than in $[(C_2H_4)PtCl_2(H_2O)]$. Since this is observed, the band at 41,600cm^{-1} in Zeise's salt may be assigned to the $d_{xz} \rightarrow \pi^*$ transition.

The effect of a change of solvent on the spectrum of $K^+[(CH_2{=}CH{-}CH_2OH)PtCl_3^-]$ is shown by the results in table 24, which were obtained by Gaussian analysis of the spectra (figures 35 and 36). It can be seen that a change of solvent causes a shift of 1,000cm^{-1} in the peak at 34,800cm^{-1}, but only a shift of 600cm^{-1} in the peak at 38,000cm^{-1}. Since the peak arising from the $d_{z^2} \rightarrow \pi^*$ transition is expected to shift more than



(a) $[(C_2H_4)PtCl_2(H_2O)]$

(b) $[(C_2H_4)PtCl_3^-]$

FIGURE 33

TABLE 24

Spectrum of $K^+[(CH_2{=}CH{-}CH_2OH)PtCl_3^-]$

Aqueous chloride soln.		EtOH soln.		
$\nu(cm^{-1})$	ε	$\nu(cm^{-1})$	ε	$\Delta\nu(cm^{-1})$
41,000	3,325	40,200	2,800	800
38,000	1,780	37,400	1,970	600
34,800	850	33,800	840	1,000
29,800	180.5	29,700	205	100

that due to the $d_{yz} \rightarrow \pi^*$ transition, the peak at 34,800cm^{-1} may be assigned to the former and that at 38,000cm^{-1} to the latter transition. Thus the relative energies of the d-orbitals in platinum(II)-olefin complexes are $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{yz} > d_{xz}$.

The nature of the ligand in the axial position in aqueous chloride solution is uncertain although Milburn[59], from studies of the kinetics of formation of these complexes, has suggested that it is probably water rather than chloride.

The above assignment is given further support by the relative intensities of the bands. The intensity (f) of a band is given approximately by the expression[126]

$$f \approx 4.6 \times 10^{-9} (\varepsilon_{max} \delta\nu_{\frac{1}{2}})$$

where ε_{max} = maximum extinction coefficient and $\delta\nu_{\frac{1}{2}}$ = width of

the band at $\varepsilon = \frac{1}{2}\varepsilon_{max}$. The intensity of a spectral band is given theoretically[126] by

$$f = 1.085 \times 10^{-5} \nu |D|^2$$

where ν is the wavelength of the band (cm^{-1}) and D is the transition moment given by

$$D = \int \Psi_1^* R \Psi_2 d\tau$$

where Ψ_1^* is the wavefunction for the initial state, Ψ_2 is the wavefunction for the final state and R is the dipole vector for all the electrons in the wavefunction. This transition moment has been shown to be proportional to the overlap integral[127]. A consideration of the spacial arrangements of the orbitals - see figure 33 - indicates that the overlap integral $\int \Psi_{d_{xz}} \Psi_{\pi^*} d\tau$ must be larger than either $\int \Psi_{d_{yz}} \Psi_{\pi^*} d\tau$ or $\int \Psi_{d_{z^2}} \Psi_{\pi^*} d\tau$.

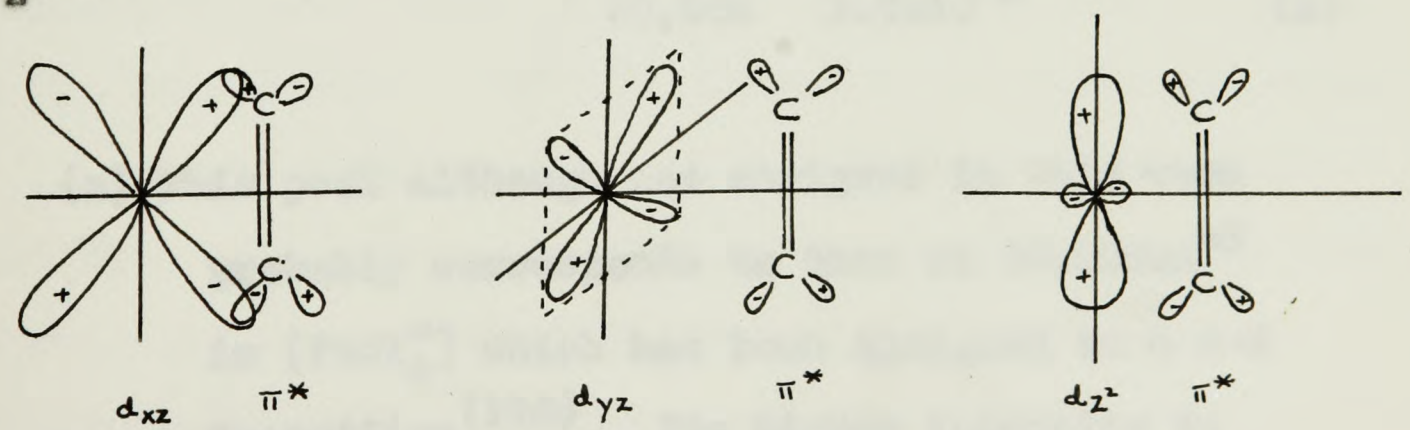


Figure 34

Thus the most intense band is expected to be that arising from the $d_{xz} \rightarrow \pi^*$ transition. This can be seen from table 25 to

TABLE 25

Complex	Peak	Intensity	Assignment
$[(C_2H_4)PtCl_3^-]$	41,600	$6.6(5)\times10^{-2}$	$d_{xz} \rightarrow \pi^*$
	37,700	1.9×10^{-2}	$d_{yz} \rightarrow \pi^*$
	34,400	1.0×10^{-2}	$d_{z^2} \rightarrow \pi^*$
	30,000	4×10^{-3}	(a)
trans-$[(C_2H_4)PtCl_2(H_2O)]$	41,300	2.0×10^{-2}	$d_{xz} \rightarrow \pi^*$
	38,500	1.5×10^{-2}	$d_{yz} \rightarrow \pi^*$
	35,200	$1.0(5)\times10^{-2}$	$d_{z^2} \rightarrow \pi^*$
	30,800	3×10^{-3}	(a)
$[(CH_2{=}CH{-}CH_2OH)PtCl_3^-]$	41,000	5.3×10^{-2}	$d_{xz} \rightarrow \pi^*$
in 1.9M NaCl + 0.1M HCl	38,000	2.4×10^{-2}	$d_{yz} \rightarrow \pi^*$
	34,800	1.5×10^{-2}	$d_{z^2} \rightarrow \pi^*$
	29,800	3.5×10^{-3}	(a)

(a) This peak although not assigned in this work probably corresponds to that at 30,000cm^{-1} in $[PtCl_4^=]$ which has been assigned to a d→d transition[114]. Its higher intensity in these olefin complexes is due to (1) the absence of a centre of symmetry in the complex and (2) intensity borrowed from charge transfer d →π* transitions of the same symmetry.

be consistent with the above assignment. It is obviously not possible to argue qualitatively about the relative magnitudes of the overlap integrals $\int \Psi_{d_{yz}} \Psi_{\pi}^{*} d\tau$ and $\int \Psi_{d_{z^2}} \Psi_{\pi}^{*} d\tau$.

The value of ε_3 at 295mμ

The observed values of ε_3 at 295mμ (33,900cm^{-1}) are shown in table 26. It can be seen that the value of ε_3 is often 770 ± 10. However there are a number of exceptions. In order to try to find an explanation for these exceptions it was necessary to determine whether the positions of the bands had altered and/or whether the extinction coefficients of the bands had altered. Accordingly, the spectra of two complexes with $\varepsilon_3 \approx 770$ ($K^+[(CH_2{=}CH{-}CH_2OH)PtCl_3^-]$ and $[(allNH_3^+)PtCl_3^-]$) and two with $\varepsilon_3 \neq 770$ ($[(butNEt_3^+)PtCl_3^-]$ (ε_3=910) and $[(allPEt_3^+)PtCl_3^-]$ (ε_3=882)) were recorded in a medium of 1.9M sodium chloride and 0.1M hydrochloric acid, and analysed into their component Gaussian curves (figures 35, 37, 38 and 39). Ideally, complexes in which the value of ε_3 was much further removed from 770 than in these two would have been used. However, only one such complex with a reasonably large stability constant was available ($[(allN^nBu_3^+)PtCl_3^-]$ (ε_3=1540)) and this had too low a solubility to enable accurate extinction coefficients to be obtained.

The results, given in table 27, show that the spectra of $K^+[(CH_2{=}CH{-}CH_2OH)PtCl_3^-]$ and $[(allNH_3^+)PtCl_3^-]$ are very similar.

TABLE 26

Extinction coefficients of complexes $[(ol)PtCl_3^-]$ at 295 mμ (ε_3)

Ligand	ε_3
$allNH_3^+$	760
$allNH_2Et^+$	770 (a)
$allNHEt_2^+$	770
$allNEt_3^+$	770 (a)
$allNMe_3^+$	760
$allN^n{-}Pr_3^+$	805
$allN^n{-}Bu_3^+$	1530
$allNH(CH_2)_5^+$	760
$allNH(CH_2)_4^+$	770
$allPEt_3^+$	882 (a)
$allAsEt_3^+$	845 (a)
$butNH_3^+$	890
$butNEt_3^+$	910
$butAsEt_3^+$	920
$pentNH_3^+$	970
$CH_2{=}CH{-}CH(CH_3){-}NH_3^+$	780
$CH_3{-}CH{=}CH{-}CH_2{-}NH_3^+$	760
$CH_2{=}C(CH_3){-}CH_2{-}NH_3^+$	1600
$(CH_3)_2C{=}CH{-}CH_2{-}NH_3^+$	1350
allOH	770
$CH_3CH{=}CH{-}CH_2OH$	760
pentOH	890

(a) Ref. 38

TABLE 27

[(ol)$PtCl_3^-$] Spectra in 1.9M NaCl + 0.1M HCl

(a) $\varepsilon_3 \approx 770$

$K^+[(CH_2{=}CH{-}CH_2OH)PtCl_3^-]$ see figure 35		$[(allNH_3^+)PtCl_3^-]$ see figure 37	
$\nu(cm^{-1})$	ε	$\nu(cm^{-1})$	ε
41,000	3,325	40,900	3,300
38,000	1,780	37,900	1,800
34,800	850	34,700	800
29,800	180.5	30,000	200

(b) $\varepsilon_3 \not\approx 770$

$[(butNEt_3^+)PtCl_3^-]$ see figure 38		$[(allPEt_3^+)PtCl_3^-]$ see figure 39	
$\nu(cm^{-1})$	ε	$\nu(cm^{-1})$	ε
40,800	4,300	40,600	4,300
37,750	1,860	37,600	2,000
34,600	1,000	34,400	920
30,000	266	30,000	240

However, [(butNEt$_3^+$)PtCl$_3^-$] and [(allPEt$_3^+$)PtCl$_3^-$] differ from those in that the three bands in the region 31,000-45,000cm^{-1} are displaced to shorter wavelengths, all within experimental error by the same amount. This suggests that the ligand π^* orbital is lower in energy in those complexes than in those complexes in which $\varepsilon_3 \approx 770$. A very much less likely possibility is that the d_{xz}, d_{yz} and d_{z^2} orbitals are all increased in energy by the same amount. From the list of ε_3 values shown in table 26 it is difficult to find anything in common between the various ligands which give $\varepsilon_3 \approx 770$ or between the ligands which give $\varepsilon_3 \neq 770$.

The effect of a change of temperature on the value of ε_3

The value of ε_3 was found within experimental error to be independent of temperature over the range used in the stability constant studies (303-333°A). As this is a fairly narrow temperature range, it can be accounted for as follows. A decrease in temperature will result in a greater population of lower vibrational levels for the carbon-carbon double-bond, resulting in an increase in the energy of the ligand π^* orbitals[128]. Similarly a decrease in temperature will result in a greater population of lower vibrational levels for the complex, resulting in an increase in the energy of the d-orbitals[128]. Since these two effects are in the same direction any shift of the band maximum will be small. As the

temperature decreases, the band width will also decrease, but the extinction coefficient will increase in such a way as to keep the area of the band, which corresponds to the intensity, constant[128]. Since the measurements were all carried out within 1000cm^{-1} of peaks of half-widths of about 2000cm^{-1} these two effects would be expected to approximately cancel out over the narrow temperature range involved (30°c).

(2) Spectra

The spectra of the platinum-olefin complexes are shown in figures 35 - 41.

The component Gaussian curves were calculated by the method of Chatt[110]. It was assumed that the peaks were symmetrical and that they could be described by the equation,

$$\varepsilon = \varepsilon_{max} \exp.[-a(\nu - \nu_0)^2]$$

where ε = extinction coefficient at wavelength νcm^{-1}, ε_{max} = maximum extinction coefficient (at wavelength ν_0 cm^{-1}) and a = constant. The values of z corresponding to x values lying between 0 and 3, in the expression,

$$z = (2\pi)^{-\frac{1}{2}} \exp.(-\tfrac{1}{2}x^2)$$

were tabulated from mathematical tables[129]. The most intense peak was fitted first. A trial value of ε_{max}, which was

slightly less than the observed ε_{max}, was used to plot the Gaussian curve,

$$\varepsilon = \varepsilon_{max}(2\pi)^{\frac{1}{2}}z = \varepsilon_{max}\exp.(\tfrac{1}{2}x^2).$$

The relation between the value of x and the frequency scale was adjusted to give the best fit of the Gaussian curve to the observed spectrum. The difference between this Gaussian curve and the experimental spectrum was then plotted, and the difference curve analysed into component Gaussian curves as before. The process was repeated until the difference between the extinction coefficient obtained from the sum of the Gaussian curves and the observed spectrum was less than 5%, which was the probable error in the original spectrum.

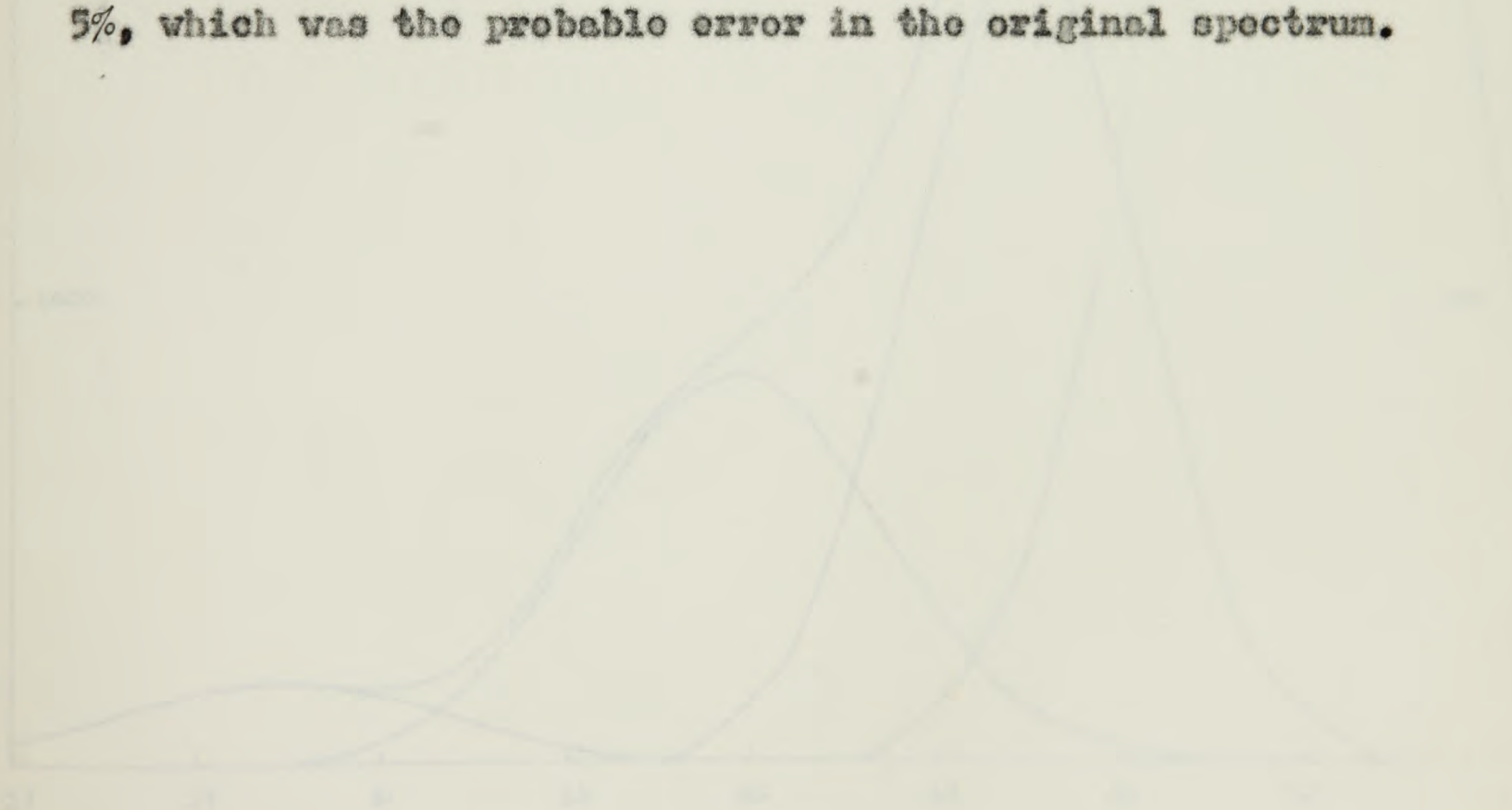


FIGURE 35

$K^+[(allyl\ alcohol)PtCl_3^-]$ in 1·9 M NaCl + 0·1 M HCl

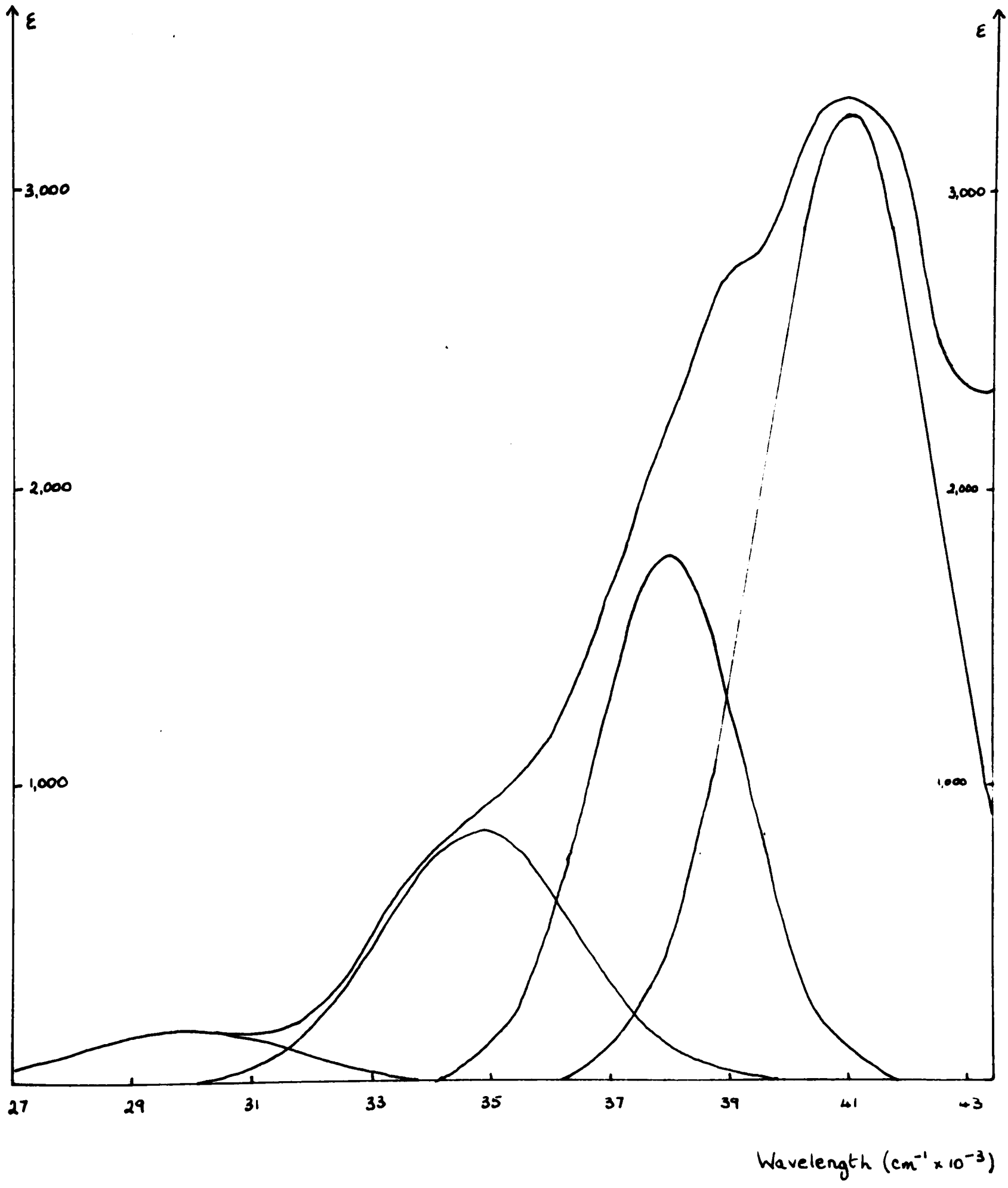


FIGURE 35

$K^+[(\text{allyl alcohol})PtCl_3^-]$ in ethanol

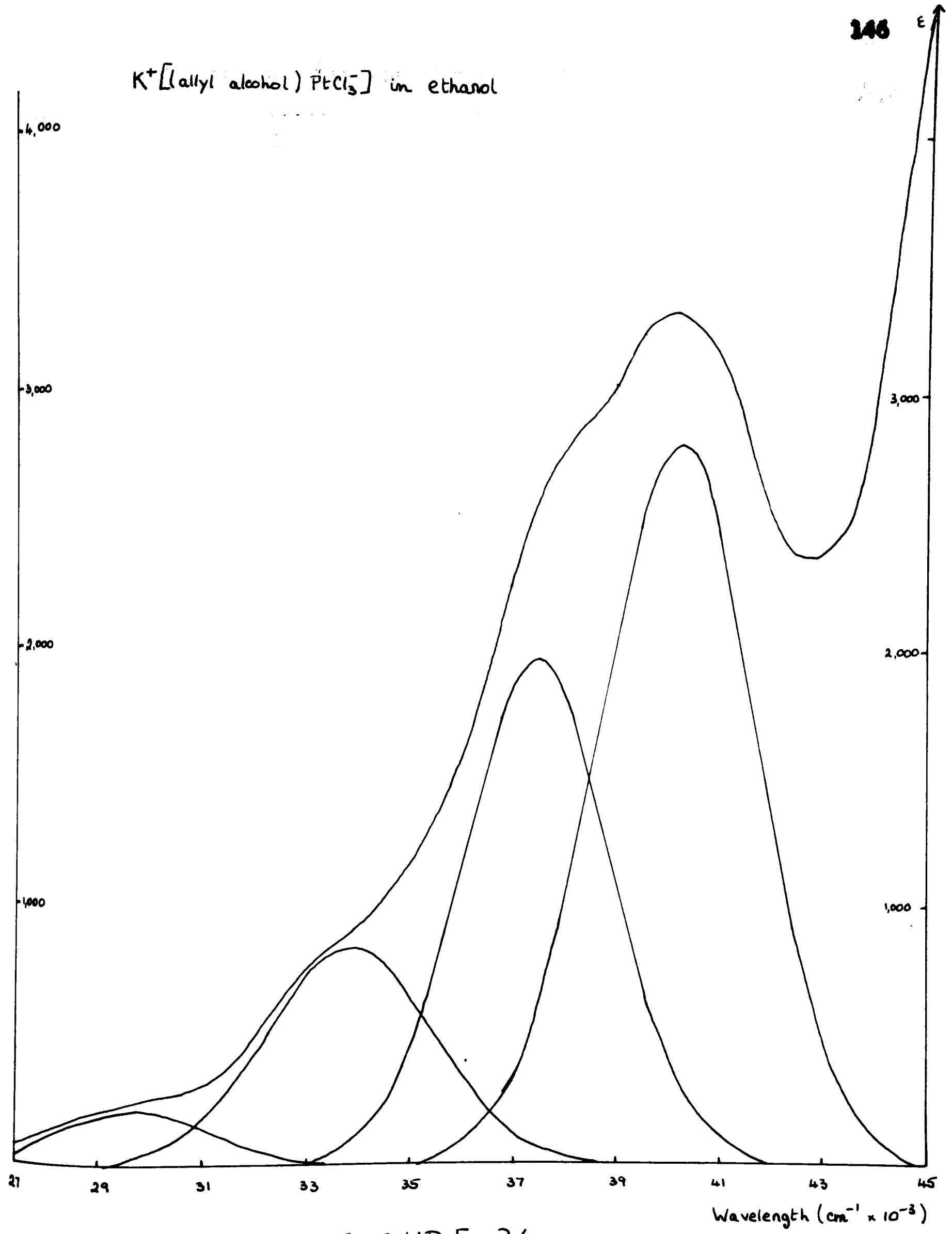


FIGURE 36

$[(all\,NH_3^+)PtCl_3^-]$ in 1·9 M NaCl + 0·1 M HCl

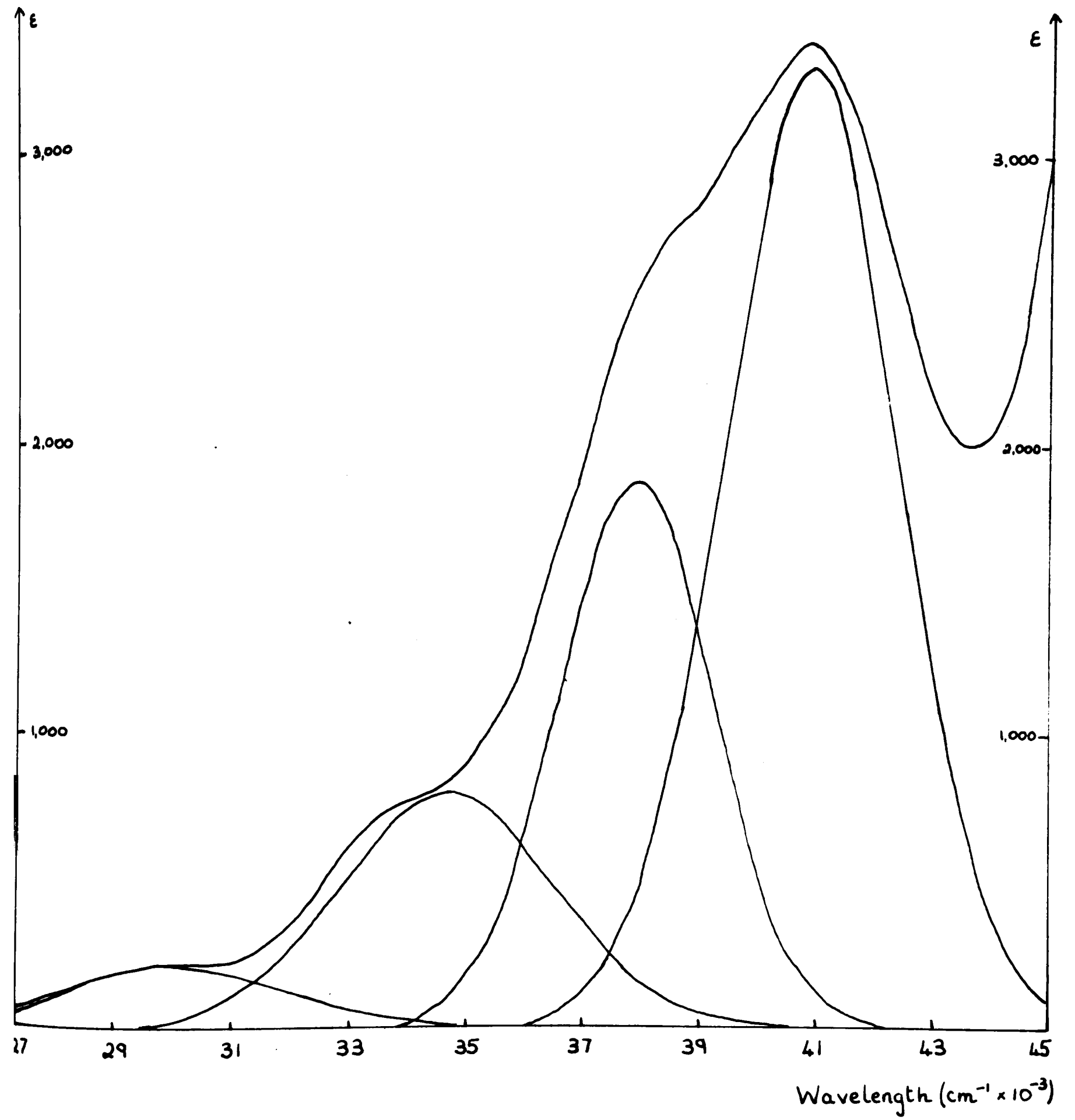


FIGURE 37

$[(but NEt_3^+)PtCl_3^-]$ in 1·9M NaCl + 0·1M HCl

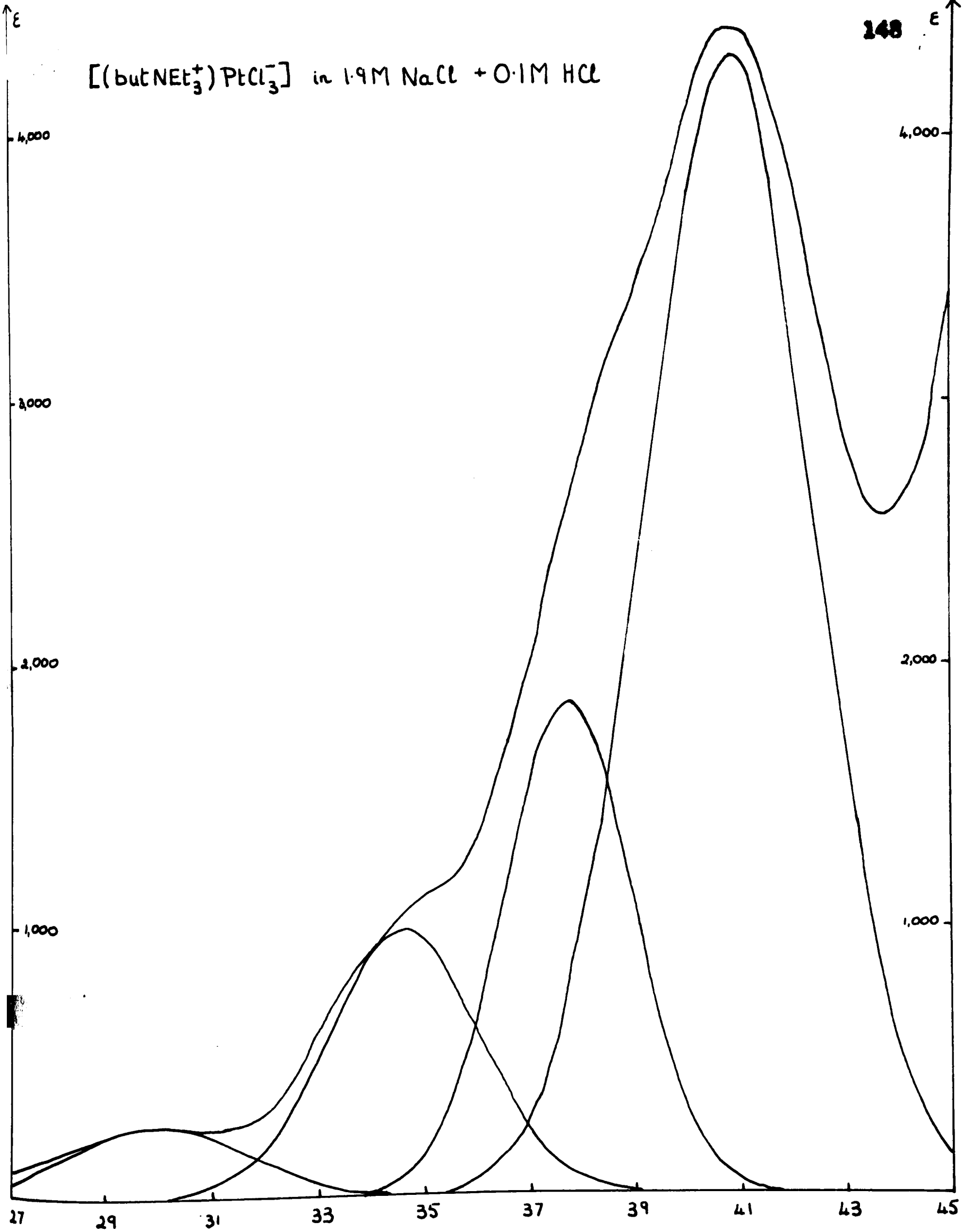


FIGURE 38

$[(allPEt_3^+)PtCl_3^-]$ in 1·9M NaCl + 0·1M HCl

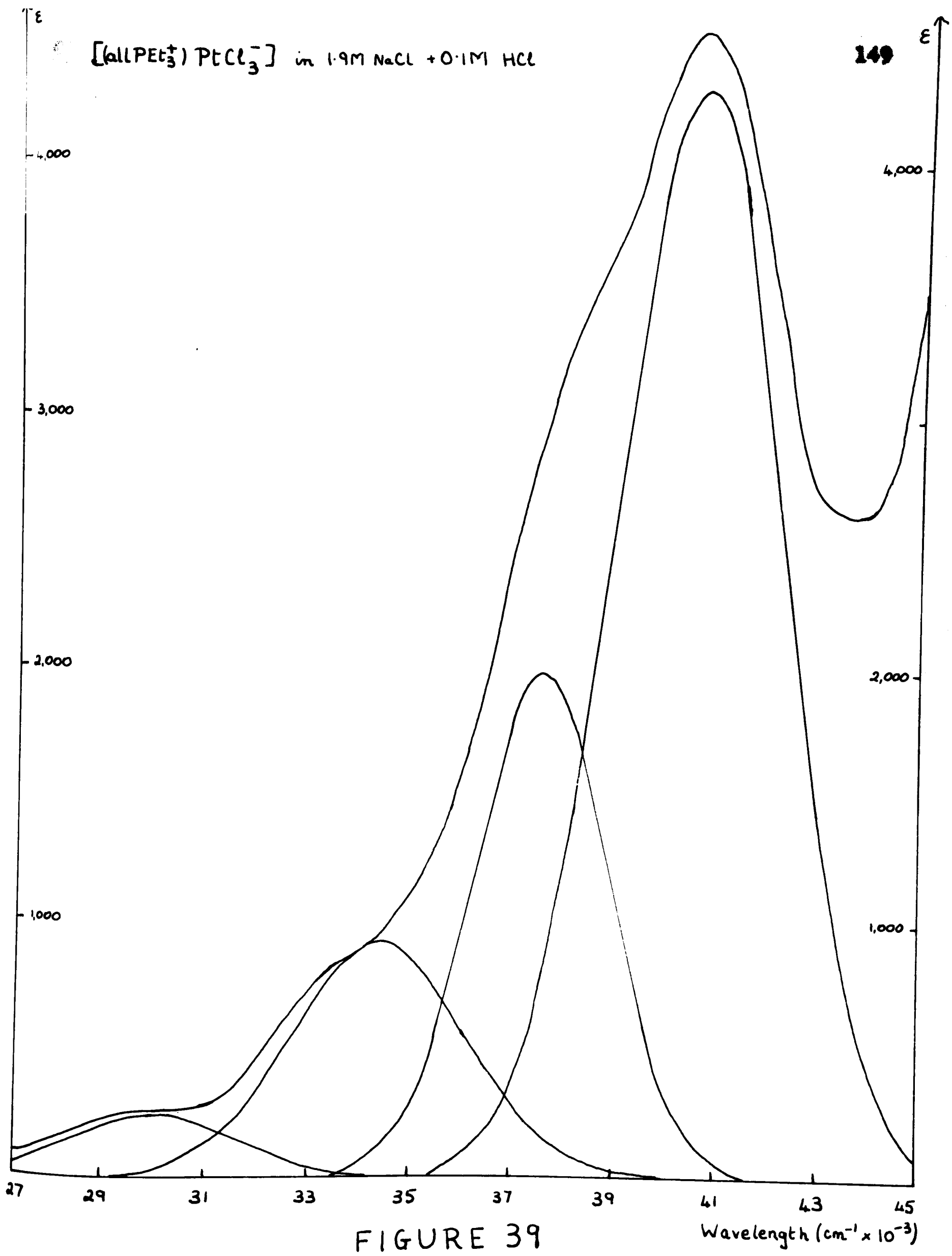


FIGURE 39

$K^+[(C_2H_4)PtCl_3^-]$ in dilute hydrochloric acid

(Lokken and Martin[115])

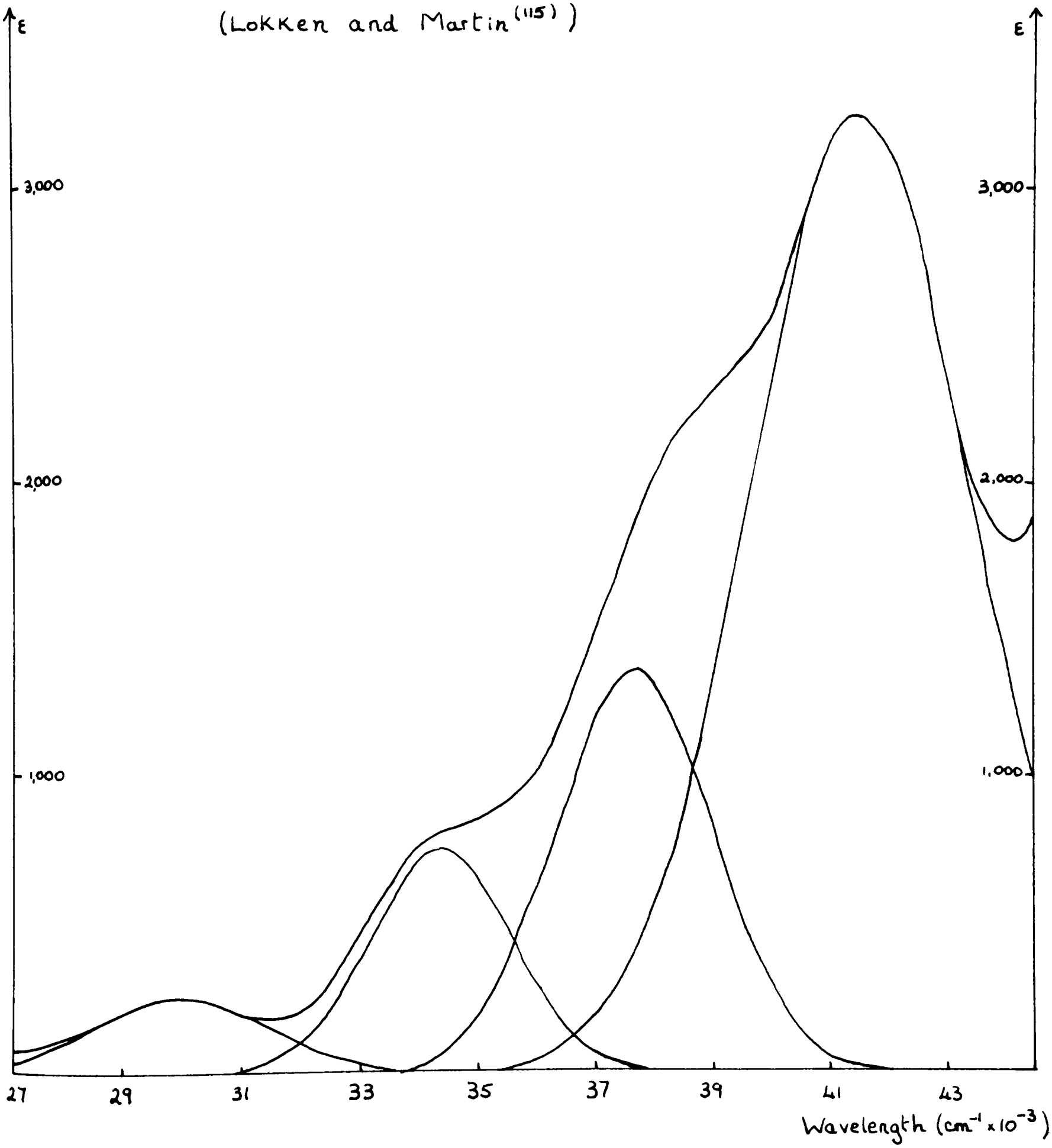


FIGURE 40

$[(C_2H_4)PtCl_2(H_2O)]$ in dilute sulphuric acid

(Lokken and Martin[115])

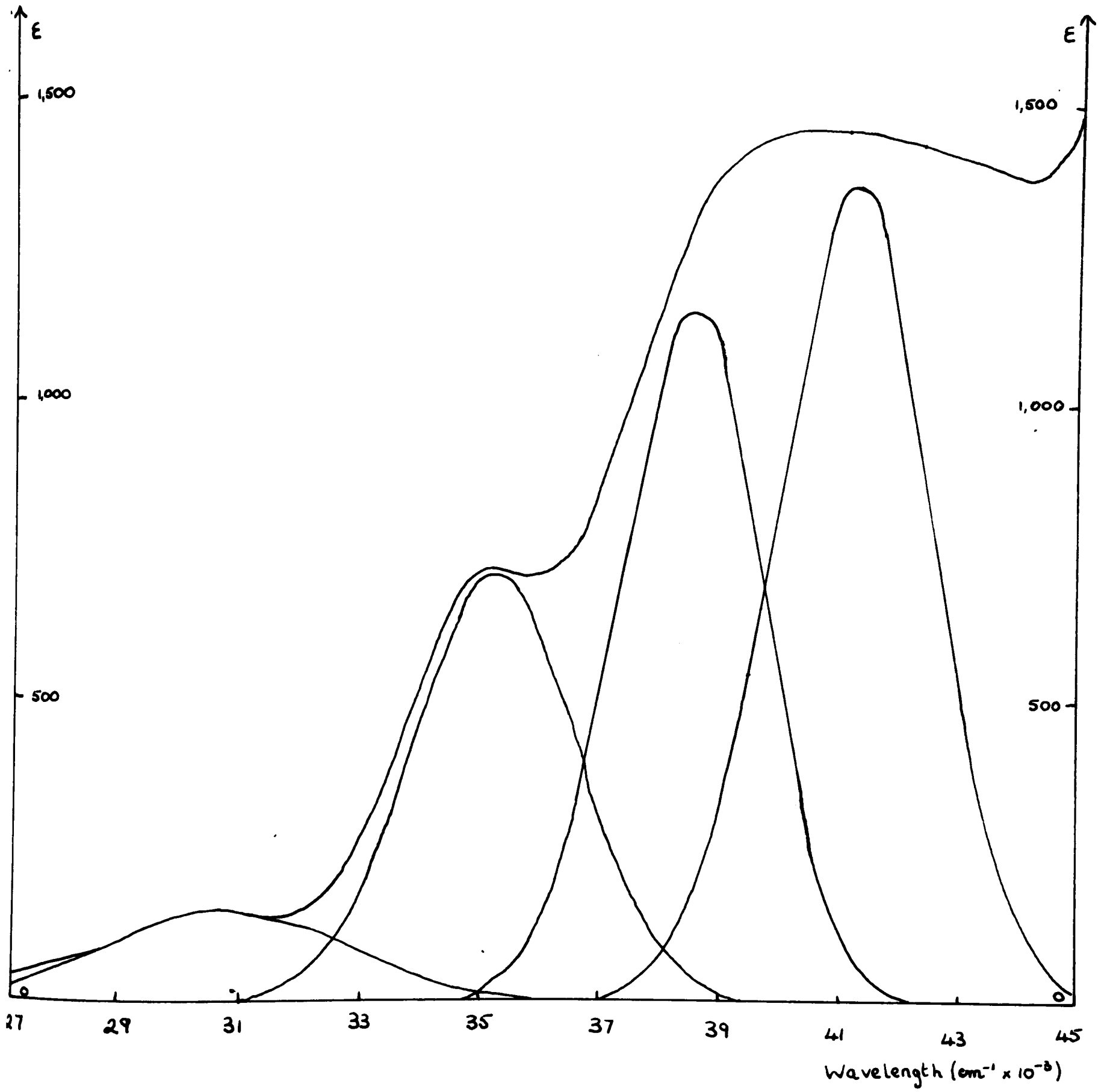


FIGURE 41

CHAPTER 7

Experimental Section

Preparation of the Ligands

Analyses All analyses in this section are recorded to one place of decimals except for 0.05, in accordance with the Chemical Society's Handbook for Authors.(130)

Molar Quantities Molar quantities are given to two decimal places only.

Allylammonium perchlorate Commercial allylamine (19g; 0.33 moles) was treated with perchloric acid (27.3ml of 72%; 0.33 moles). The product was recrystallised twice from a mixture of ethanol and ether. Yield 26.55g i.e. 42% (Found: C,23.2; H,5.2; N,8.8. Calc. for $C_3H_8ClNO_4$; C,22.9; H,5.1; N,8.9%).

N-Trialkylallylammonium perchlorate A mixture of the trialkylamine (0.15 moles) and allyl bromide (0.15 moles) was refluxed in benzene (150 ml) for one hour (trimethylamine), for four hours (tri-n-propylamine) and for two days (tri-n-butylamine). The product was extracted with water and treated with sodium perchlorate (0.18 moles) solution. The

white precipitate was recrystallised twice from ethanol.

N-Trimethylallylammonium perchlorate Yield 58%. Found: C,36.1; H,7.1; N,6.5. $C_6H_{14}ClNO_4$ requires C,36.1; H,7.1; N,7.0%. A solution made up from this product gave a slight opalescence with silver nitrate due to a trace of bromide ion. This was removed by adding excess silver perchlorate solution (0.1N), digesting on a hotplate for twenty minutes and then filtering through an AGx4 sinter. The filtrate was acidified with dilute perchloric acid, and then hydrogen sulphide, which had been passed through two gas wash-bottles, one containing distilled water, to remove any hydrochloric acid spray, was bubbled through. The precipitated silver sulphide was filtered off through an AGx4 sinter. A brisk stream of nitrogen was passed through the filtrate while it was heated and stirred on a hotplate for half-an-hour. The solution was finally filtered through a Whatman 42 filter paper and standardised for acidity and concentration of ammonium salt by the method on page 21.

N-Tri-n-propylallylammonium perchlorate Yield 45%. Found: C,50.65; H,9.2; N,4.8. $C_{12}H_{26}ClNO_4$ requires C,50.85; H,9.25; N,4.9%. A test with silver nitrate showed the absence of halide ion.

N-Tri-n-butylallylammonium perchlorate Yield 33%. Found: C,54.9; H,9.4; N,4.8. $C_{15}H_{32}ClNO_4$ requires C,55.3; H,9.9; N,4.3%. A test with silver nitrate showed the absence of halide ion.

Triethylphosphine and triethylarsine[85]

These two ligands were prepared by the same method. A solution of ethyl magnesium bromide in ether under nitrogen was prepared by slow addition of ethyl bromide (190 ml; 2.7 moles) in dry ether (500 ml) to a well stirred mixture of magnesium (60g; 2.5 moles) in dry ether (750 ml). When the addition, which took two hours, was complete, the mixture was gently refluxed for half an hour.

The reaction mixture was then cooled in an acetone/carbon dioxide bath to a point where it could just be stirred vigorously. A solution of phosphorus trichloride (96.15g; 0.7 moles) or arsenic trichloride (126.9g; 0.7 moles) in dry ether (500 ml) was added dropwise over a period of five hours and the mixture then allowed to warm up to room temperature, with stirring, overnight.

The Grignard solution was then hydrolysed by slow addition of a cold de-oxygenated solution of ammonium chloride (500g) in water (2 litres). The two layers were separated under nitrogen by siphoning off the ether layer and a little of the water layer into a large separating funnel. The ether layer was dried over anhydrous sodium sulphate under nitrogen. The ether was decanted off and distilled under nitrogen.

Triethylphosphine	b.p. 128-9°c
	Yield 23.2g i.e. 28.1%
Triethylarsine	b.p. 45-47°c/20mm Hg
	Yield 64.3g i.e. 56.8%.

Both products were sealed under nitrogen in weighed ampoules.

3-buten-1-ol[131]

A solution of allylmagnesium bromide in dry ether under nitrogen was prepared by slow addition of a solution of allyl bromide (350g; 2.9 moles) in dry ether (800 ml) to a well-stirred mixture of magnesium (110g; 9.6 moles) in dry ether (2500 ml). The reaction was initiated by adding a test-tube of ethylmagnesium bromide in dry ether. Once the reaction had started, indicated by a cloudiness in solution, the reaction vessel was surrounded by an ice-bath to prevent the formation of biallyl. After all the allyl bromide had been added, which took four hours, the mixture was stirred for a further hour to ensure that the reaction was complete.

Gaseous formaldehyde, which was prepared by heating paraformaldehyde (140g; 4.66 moles) in a bolt-head flask at 200°c, was passed in a stream of nitrogen through a wide (12.5mm) lagged tube into the Grignard reaction vessel. Vigorous mechanical stirring was used and the flask was well cooled in an ice-bath during this stage. The formaldehyde was passed in over a period of two hours; stirring became difficult after one hour.

After stirring overnight the reaction mixture was hydrolysed. Ammonia solution (20ml; 0.880) was run in slowly to bind the excess formaldehyde as hexamethylene tetramine and prevent acetal formation. Dilute hydrochloric acid (1500ml; 2N) was then added slowly with cooling.

The two layers were separated and the ether layer dried over anhydrous potassium carbonate. The ether was removed by distillation and the product distilled at atmospheric pressure. b.p. 112.5-114°c (Lit[131] 113.5°c). Yield 89.3g i.e. 43%.

4-Chloro-but-1-ene[132]

A mixture of 3-buten-1-ol (64.8g; 0.90 moles) and pyridine (3 ml; 0.04 moles) was cooled in a flask at 0°c. Thionyl chloride (114g; 0.96 moles) was added slowly with vigorous stirring over a period of three hours. After stirring for a further hour the product was distilled at atmospheric pressure b.p. 72-80°c. This was washed with water (50ml), 10% sodium carbonate solution (50ml) and finally two more portions of water. After drying over calcium chloride, distillation gave 45.4g (i.e. 55.8%) of 4-chloro-but-1-ene. b.p. 74-76°c (Lit[132] 75°c).

4-Bromo-but-1-one[133]

A mixture of 3-buten-1-ol (63.2g; 0.88 moles) and pyridine (12.75ml; 0.20 moles) was run slowly into well stirred phosphorus tribromide (27.8ml; 0.29 moles) in a flask surrounded by an ice-bath. A white solid, which was filtered off before the mixture was distilled, precipitated out towards the end of the reaction. Once the addition was complete the mixture was distilled, during which the product in the flask became bright orange and deposited a bright orange solid. The product,

which boiled in the range 99-114°c, was neutralised with potassium hydroxide and well washed with water. After drying over calcium chloride the product was distilled off. b.p. 98-99°c (Lit[133] 98.5-99°c) Yield 54.86g i.e. 56.6%.

N-Triethylbut-3-enylammonium perchlorate

All attempts to prepare this compound from 4-chloro-but-1-ene failed. A solution of triethylamine (18.2g; 0.18 moles) and 4-bromo-but-1-ene (24.25g; 0.18 moles) in benzene (100ml) was refluxed gently for two days. The white precipitate (22.4g i.e. 53% yield) which formed was filtered off, dried and dissolved in the minimum volume of water. A saturated solution of sodium perchlorate (15g; 0.11 moles) was added and the white precipitate which formed filtered off and recrystallised from ice-cold n-propanol. Yield 15g i.e. 33% (Found: C,46.1; H,8.6; N,5.3. $C_{10}H_{22}ClNO_4$ requires C,47.0; H,8.7; N,5.5%).

As-Triethylbut-3-enylarsonium perchlorate

As with the ammonium salt above, all attempts to prepare this compound from 4-chloro-but-1-ene failed. It was prepared by gently refluxing a solution of triethylarsine (19.05g; 0.12 moles) and 4-bromo-but-1-ene (15.9g; 0.12 moles) in benzene (100ml) under nitrogen for two days. Yield 9.7g i.e. 26.5%. The final product was obtained by a method identical to that described above. Yield 6.6g i.e. 18%. Found: C,37.6; H,6.6; As,23.7. $C_{10}H_{22}AsClO_4$ requires C,38.25; H,7.0; As,23.7%).

4-Penten-1-ol

(1) Tetrahydrofurfuryl Chloride[134]

A mixture of freshly distilled tetrahydrofurfuryl alcohol (408g; 4.0 moles) and freshly distilled pyridine (348g; 4.4 moles) was well stirred in a flask surrounded by an ice-bath. Thionyl chloride (500g; 4.2 moles) was added slowly over a period of six hours. After three hours the heavy white precipitate which formed caused difficulty in stirring; later, stirring became easier. After stirring overnight at room temperature the mixture was extracted into dry ether (7x500ml), leaving a dark solid material behind. The ether was distilled off and the product then distilled under vacuum. b.p. 28-30°c/8mm Hg. (Lit[134] 41-42°c/11mm Hg or 47-48°c/15mm Hg). Yield 301g i.e. 63%.

(2) 4-penten-1-ol

A mixture of powdered sodium (112g; 4.86 moles) in dry ether (700ml) was vigorously stirred under nitrogen. A few ml of a solution of tetrahydrofurfuryl chloride (301g; 2.5 moles) in dry ether (300ml) was added and a vigorous reaction set in, as indicated by refluxing of the ether, and the solution became slightly blue. Once the reaction had obviously started the flask was cooled in ice and the remainder of the tetrahydrofurfuryl chloride solution added dropwise with vigorous stirring over a period of six hours.

After stirring overnight the product was hydrolysed with a saturated solution of water in ether (1000ml), the flask

being surrounded by an ice-bath. The hydrolysis was completed using iced-water (200ml). The two layers were separated and the ether layer dried over anhydrous magnesium sulphate. After removing the ether by distillation, the product was factionally distilled. b.p. 134-137°c (Lit[134] 134-137°c). Yield 127.3g i.e. 61%.

5-Chloropent-1-ene

This was prepared by a method similar to that described above for 4-chlorobut-1-ene. 4-Penten-1-ol (69.45g; 0.805 moles) and pyridine (3ml; 0.04 moles) were treated with thionyl chloride (98.9g; 0.83 moles) giving 5-chloropent-1-ene. b.p. 104-106°c (Lit[135] 104-105°c). Yield 68.8g i.e. 81.6%.

N-allylpiperidine[136]

A solution of allyl bromide (30g; 0.23 moles) in benzene (40ml) was run slowly into a well-stirred solution of piperidine (45g; 0.53 moles) in benzene (60ml) in a flask surrounded by an ice-bath. During the addition a white precipitate of piperidine hydrobromide was formed. When the addition was complete the mixture was stirred for an hour and a half at 50°c, then cooled in an ice-bath and filtered. The filtrate was then fractionally distilled giving N-allylpiperidine. b.p. 149-151°c (Lit[136] 151-152°c). Yield 16.31g i.e. 56.6%.

N-allylpyrrolidine[137]

This was prepared by a method similar to that used for N-allylpiperidine. Pyrrolidine (32.8g, 0.46 moles) and allyl bromide (30g; 0.23 moles) gave N-allylpyrrolidine. b.p.

128-129°c (Lit[137] 129-130°c). Yield 8.0g i.e. 31.2%.

N-diethylallylamine[138]

Allyl chloride (52g; 0.68 moles) was added slowly to a well-stirred solution of diethylamine (100g; 1.36 moles) in benzene (100ml) at room temperature. When the addition was complete the mixture was refluxed for two hours, cooled and extracted into excess dilute hydrochloric acid. The aqueous layer was separated off, neutralised and extracted with ether. The ether layer, after drying over anhydrous potassium carbonate, was fractionally distilled giving N-diethylallylamine b.p. 111-112°c (Lit[138] 111°c). Yield 25.2g i.e. 34%. Found: C,74.2; H,13.1; N,12.4. Calc. for $C_7H_{15}N$; C,74.3; H,13.4; N,12.4%).

Preparation of 1-chloro-3-methyl-but-2-ene[139]

Dry hydrogen chloride gas was bubbled slowly for six hours through a solution of isoprene (68.5g; 1.0 moles) in ether (25ml) in a flask surrounded by a cold water bath. After standing at room temperature overnight the solution was slowly distilled until the liquid temperature reached 85°c. It was then held at this temperature for two hours. The reason for this is that two or possibly three isomers are formed initially. The isomer required is the most stable isomer and also the highest boiling. The other isomer of importance is the 2-chloro-isoprene which boils at 80°c. The product was then distilled off. b.p. 108-110°c (Lit[139] 112°c). Yield 57.45g i.e. 55%.

Gabriel Phthalimide Synthesis of amines[132]

A number of amines were prepared from the corresponding chloro-compounds by Gabriel phthalimide syntheses. A typical method is described below.

A mixture of equivalent amounts of potassium phthalimide and the chloro-compound in dimethylformamide (250ml) was stirred at 120°c for four hours and at 145°c for a further hour. The hot mixture was poured on to finely crushed ice (300g) and after standing for a few minutes the precipitate was filtered off, well washed with water and dried in a vacuum dessicator over calcium chloride. Yields were generally 95% or better.

The phthalimide derivative was gently refluxed in ethanol (200ml) with a slight excess of hydrazine hydrate for two hours. A thick precipitate formed. After cooling, an excess of hydrochloric acid (6M) was added and the mixture gently refluxed for one hour. After cooling the mixture was filtered at atmospheric pressure through a large (42cm) filter paper. The filtrate was evaporated to dryness on a rotary evaporator, treated with excess potassium hydroxide (5M) and extracted with ether. The ether layer was fractionally distilled to give the amine in about 15-20% yield.

3-butenylamine

Prepared as above from 4-chlorobut-1-ene. b.p. 76-78°c. (Lit[132] 75-77°c). Yield 15%.

4-pentenylamine

Prepared as above from 5-chloropent-1-ene. b.p. 104-105°c (Lit[140] 105-106°c). Yield 15%.

trans-Crotylamine

Prepared as above from crotyl chloride. b.p.84-86°c (Lit 85-86°c[141], 83-84°c[131]). Yield 17%. The product exhibited infra-red bands at 1080, 1045 and 963cm^{-1} confirming that it was the trans-isomer[131]. Bands at 1625, 1342, 1316 and 1055cm^{-1} diagnostic of the cis-isomer[131] were absent.

3-methyl-but-2-enylamine

Prepared as above from 1-chloro-3-methyl-but-2-ene, except that the phthalimide derivative was prepared at 100°c only. b.p. 108-110°c (Lit[141] 110.5°c). Yield 14%.

2-methyl-prop-2-enylamine

Prepared as above from 1-chloro-2-methyl-prop-2-ene. b.p. 78-80°c (Lit[142] 77-82°c). Yield 22%. A small sample was treated with concentrated hydrochloric acid, and the white crystalline product isolated and dried under high vacuum. Melting-point 186-186.5°c (with decomposition). (Found: C,44.6; H,9.7; N,12.8. $C_4H_{10}ClN$ requires C,44.65; H,9.4; N,13.0%).

1-methyl-prop-2-enylamine

Prepared as above from 1-chloro-1-methyl-prop-2-ene. b.p. 64-66°c (Lit[141] 64°c). Yield 13%. A solution containing a little of the amine in petroleum ether (b.p.40-60°c)

was treated with dry hydrogen chloride gas. The white crystalline precipitate formed was filtered off and dried under high vacuum. (Found: C,44.5; H,9.5; N,12.8. $C_4H_{10}ClN$ requires C,44.65; H,9.4; N,13.0%).

3-chloro-prop-2-enylammonium chloride(143)

A mixture of potassium phthalimide (136g; 0.735 moles), 1:3-dichloropropene (81g; 0.735 moles) and dimethylformamide (500ml) was stirred at 60-95°c for five hours. After cooling, the mixture was treated with water (750ml) and the solid filtered off, well washed with water and dried under vacuum. Yield 126g i.e. 76.9%.

The phthalimide derivative (126g; 0.57 moles) and hydrazine hydrate (34.5ml; 0.69 moles) were gently refluxed in methanol (450ml) for two hours. After cooling to room temperature hydrochloric acid (250ml, 7M) was added and the slurry refluxed with stirring for two hours. The warm slurry was filtered and the precipitate well washed with a mixture of hot water (1000ml) and methanol (200ml). The filtrate was evaporated to dryness on a rotary evaporator. The product was dissolved in the minimum volume of water, made alkaline with potassium hydroxide and the free amine extracted into petroleum ether (b.p. 40-60°c) (5x50ml). The petroleum ether was separated off and dried over anhydrous calcium chloride. Dry hydrogen chloride gas was bubbled through and the white crystalline material obtained filtered off and dried

under high vacuum. Melting point 200-210°c (with decomposition) (Lit[143] 209-210°c). Yield 21.0g i.e. 29%. (Found: C,28.0; H,5.5; N,9.9. Calc. for $C_3H_7Cl_2N$; C,28.1; H,5.5; N,10.9%).

2-Chloro-prop-2-enylammonium chloride

Prepared in exactly the same way as 3-chloro-prop-2-enylamine above from 2,3-dichloro-prop-1-ene. Yield 17.5%. (Found: C,28.3; H,5.6; N,10.8. Calc. for $C_3H_7Cl_2N$; C,28.1; H,5.5; N,10.9%).

Propylammonium perchlorate

A solution of perchloric acid (66ml of 60%; 0.61 moles) in water (35ml) was added slowly to a solution of propylamine (36g; 0.61 moles) in water (50ml) in a flask surrounded by an ice-bath. The aqueous solution was evaporated to dryness on a rotary evaporator and the white crystalline product recrystallised from a mixture of ethanol and ether. Yield 65.5g i.e. 67.5%. (Found: C,22.4; H,6.2; N,8.6. Calc. for $C_3H_{10}ClNO_4$: C,22.6; H,6.3; N,8.8%).

Butylammonium perchlorate

Butylammonium perchlorate was prepared by the same method from butylamine (44.5g; 0.61 moles) and perchloric acid (66ml of 60%; 0.61 moles). Yield 68.5g i.e. 65%. (Found: C,27.2; H,7.1; N,7.2. Calc. for $C_4H_{12}ClNO_4$: C,27.7; H,7.0; N,8.1%).

Allyl alcohol

Commercial allyl alcohol was redistilled using a 12" vacuum jacketted fractionating column. b.p. 96°c (Lit[144] 96.6°c).

Crotyl alcohol

Commercial crotyl alcohol was redistilled using a 12" vacuum jacketted fractionating column. b.p. 120-120.5°c (Lit[145] 120-121°c). The product was shown from its infra-red spectrum to be the trans-isomer[145]. Thus it exhibited three small peaks at 1290, 1310 and 1335cm^{-1}, and the peaks at 865 and 900cm^{-1} had relative intensities of 1:3 both of which are consistent with the trans-isomer. Peaks at 1053 and 1031 and a pronounced shoulder at 869cm^{-1} diagnostic of the cis-isomer, were absent.

n-Propanol

Commercial n-propanol was redistilled using a 12" vacuum jacketted fractionating column. b.p. 96°c (Lit[146] 97.2°c).

n-Butanol

Commercial n-butanol was redistilled using a 12" vacuum jacketted fractionating column. b.p. 117°c (Lit[147] 116°c).

Preparation of the Complexes

All the complexes described in this section were prepared by the following method. A solution of the free amine, or ammonium salt, in dilute hydrochloric acid (2N) was prepared. An equivalent quantity of potassium tetrachloroplatinate(II) was dissolved in dilute hydrochloric acid (2N) and this solution filtered into the amine solution. The mixture was heated for about five minutes at 80°c and then allowed to stand. The yellow crystalline product obtained was filtered off, washed with water and dried in vacuo.

Trichloro(allylammonium)-platinum(II) Yield 73%. Found: C,10.25; H,2.4; N,3.65; Pt,54.2. Calc. for $C_3H_8Cl_3NPt$ requires C,10.0; H,2.2; N,3.9; Pt,54.3%.

Trichloro(N-trimethylallylammonium)-platinum(II) Yield 70%. Found: C,18.6; H,3.6; N,3.4; Pt,48.3. $C_6H_{14}Cl_3NPt$ requires C,18.0; H,3.5; N,3.5; Pt,48.6%.

Trichloro(N-tri-n-propylallylammonium)-platinum(II) Yield 68%. Found: C,30.1; H,5.4; N,3.2; Pt,40.3. $C_{12}H_{26}Cl_3NPt$ requires C,29.7; H,5.4; N,2.9; Pt,40.2%.

Trichloro(N-tri-n-butylallylammonium)-platinum(II) Yield 75%. Found: C,33.95; H,6.15; N,2.6. $C_{15}H_{32}Cl_3NPt$ requires C,34.1; H,6.1; N,2.65%.

Trichloro(N-triethyl-but-3-enylammonium)-platinum(II) Yield 71%. Found: C,26.0; H,4.8; N,3.1: Pt,42.5. $C_{10}H_{22}Cl_3NPt$ requires C,26.2; H,4.8; N,3.1; Pt,42.6%.

Trichloro(As-triethyl-but-3-enylarsonium)-platinum(II)

Yield 69%. Found: C,22.7; H,4.2; As,13.95; Pt,36.7.

$C_{10}H_{22}AsCl_3Pt$ requires C,23.4; H,4.3; As,14.45; Pt,37.6%.

Trichloro(N-allylpiperidinium)-platinum(II) Yield 61%.

Found: Pt,45.8. Calc. for $C_8H_{15}Cl_3NPt$: Pt,45.6%.

Trichloro(N-allylpyrrolidinium)-platinum(II) Yield 60%.

Found: Pt,47.6. Calc. for $C_7H_{13}Cl_3NPt$: Pt,47.2%.

Trichloro(trans-crotylammonium)-platinum(II) Yield 60%.

Found: Pt,52.2. Calc. for $C_4H_{10}Cl_3NPt$: Pt,52.2%.

A suspension of the complex in water was treated with excess potassium cyanide solution to liberate the free amine, which was extracted into petroleum ether/(b.p. 40-60°c). The petroleum ether layer was dried over anhydrous potassium carbonate and then treated with dry hydrogen chloride gas. The crotylammonium chloride, which was precipitated, was filtered off and dried in vacuo. The product exhibited bands in the infra-red at 1077, 1045 and 962cm^{-1} confirming that it was the trans-isomer[131]. Bands at 1625, 1342, 1316 and 1055cm^{-1} diagnostic of the cis-isomer[131] were absent.

Trichloro(2-methyl-prop-2-enylammonium)-platinum(II) Yield 53%.

Found: Pt,52.6. Calc. for $C_4H_{10}Cl_3NPt$: Pt,52.2%.

Trichloro(1-methyl-prop-2-enylammonium)-platinum(II) Yield 57%.

Found: Pt,52.4. Calc. for $C_4H_{10}Cl_3NPt$: Pt,52.2%.

Trichloro(3-chloro-prop-2-enylammonium)-platinum(II)

Attempts to prepare this complex led to a product which was not identified. Found: Pt,40.7. Calc. for $C_3H_7Cl_4NPt$: Pt,49.5%.

Trichloro(3-methyl-but-2-enylammonium)-platinum(II)

All attempts to prepare this complex failed to yield any product.

Potassium Trichloro(allyl alcohol)-platinum(II)

A solution of potassium tetrachloroplatinate(II) (2g; 0.005 moles) in water (10ml) was added to a solution of allyl alcohol (0.6g; 0.01 moles) in water (10ml). The resulting solution was evaporated to dryness in a dessicator over caustic soda flakes (8 days). The yellow crystalline solid was well-washed with ether, and then extracted into acetone and further recrystallised from acetone, using a rotary evaporator to avoid raising the temperature of the solution above 25°c. Yield 20%. Found: Pt,48.7. Calc. for $C_3H_6Cl_3KOPt$, Pt,48.9%.

Gas Chromatography Study of the Reaction between 3-buten-1-ol and Potassium Tetrachloroplatinate(II)

The gas chromatograph, which was constructed in this laboratory by Howell and Chiswell[148] had a column packed with embacel, which had been treated with hexamethyldisilazine to remove free -OH groups, and then coated with silicone oil.

A solution of potassium tetrachloroplatinate(II) (4g; 0.01 moles) in dilute hydrochloric acid (50ml; 0.2M) was filtered into a solution of 3-buten-1-ol (1.7g; 0.024 moles) and the mixture heated for ninety minutes at 78°c. A sample was withdrawn, cooled and treated with benzene followed by a solution of potassium cyanide to liberate any butadiene and 3-buten-1-ol present in the form of a complex. The benzene layer was separated and a sample (2μl) passed through the column. Further samples (2μl) of hydrogen cyanide in benzene, 3-buten-1-ol in benzene and butadiene in benzene were run to identify the peaks. A peak at 3.15cm corresponded to butadiene. Final confirmation of this was obtained by adding a trace of butadiene to the reaction mixture, when the peak identified as being due to butadiene was augmented in height, whilst the other peaks were unaltered in height.

A solution of 3-buten-1-ol (1.7g; 0.024 moles) in dilute hydrochloric acid (50ml; 0.2M) and benzene (25ml) was

heated in a stoppered flask at 78°c. Samples were withdrawn after one hour and five hours and passed through the gas chromatograph. Neither showed any trace of butadiene.

Analyses

All analyses for platinum and arsenic were repeated three times. The wavelengths given are average values. The actual position of the peak was redetermined each time the analysis was carried out.

Platinum

The complexes were analysed for platinum using the colorimetric method based on stannous chloride described by Sandell[149] and used previously by the author[150]. The complexes were broken down by boiling with 5ml of a 50:50 mixture of concentrated nitric and perchloric acids. The residue was then boiled down twice with concentrated hydrochloric acid (5ml), and dissolved in concentrated hydrochloric acid (5ml). This solution was transferred to a 250ml volumetric flask and made up to the mark with water. 25ml of this solution was pipetted into a 100ml volumetric flask. Concentrated hydrochloric acid (9.5ml) and stannous chloride solution (20ml) were added and the volume made up with distilled water. After standing for twenty minutes the absorbances were measured at 403mμ against a blank containing hydrochloric acid and stannous chloride. The concentration of platinum was read off from a calibration curve prepared using Johnson-Matthey 'Specpure' ammonium tetrachloroplatinate(II).

Stannous chloride solution

AnalaR stannous chloride dihydrate (230g) was dissolved in AnalaR concentrated hydrochloric acid (325ml) and the solution made up to 1 litre with distilled water.

Arsenic

Analysis for arsenic was carried out using the heteromolybdenum blue method originally described by Magnusson[151]. As described previously by the author[150], samples of about 10mg were accurately weighed out and heated for about two hours with ammonium vanadate (20mg) and concentrated perchloric acid (5ml). After cooling, water was added and the solutions were warmed until clear. The solutions were transferred to 500ml volumetric flasks, the volume being made up with water. 5ml samples were pipetted into 25ml flasks and ammonium molybdate solution (5ml) and hydrazine sulphate solution (2ml) were added from burettes. After making up to nearly 25ml, the flasks were placed in a boiling water-bath for fifteen minutes to develop the blue colour. After cooling and making up to the mark, the absorbance was measured at 840mμ against a blank containing the reagents. The concentration of arsenic was read off from a calibration curve prepared using AnalaR sodium arsenate ($Na_2HAsO_4.7H_2O$).

Ammonium molybdate solution

Ammonium molybdate (1.5g) was dissolved in a mixture of concentrated sulphuric acid (15ml) and distilled water (80ml).

Hydrochloric acid (100ml; 3.0N) was added and the solution made up to 375ml.

Hydrazine sulphate solution

A 0.05% solution in distilled water was made up.

Carbon, Hydrogen and Nitrogen

These elements were determined by Dr. A. Bernhardt, Max Planck Institut, Mülheim(Ruhr), W. Germany.

Physical Measurements

(a) Ultra-violet and visible spectra

The absorbance values for the stability constant measurements were obtained on a Unicam SP 500 spectrophotometer. The spectra reported in chapter 6 were recorded on a Unicam SP 700 spectrophotometer.

(1) Unicam SP 500 spectrophotometer

The Unicam SP 500 spectrophotometer was fitted with an Adkins thermostatted cell-housing, which had a temperature stability of $\pm$ 0.2°c. At 295mμ, the wavelength used for most of the measurements, the slit width was 0.4mm for the first half of the work and 0.22mm for the second half. The decrease in slit width occurred after the hydrogen lamp had been replaced. At these slit widths the stray light should be negligible. The wavelength calibration of the instrument was checked at intervals using the hydrogen lines at 656.3mμ and 486.1mμ. No appreciable drift was observed over a period of two years. The absorbance calibration was checked once during the period of work using the standard filters supplied by Unicam. It was exact, within the limits of accuracy of the instrument.

The silica cells used for measuring the absorbance values were stored in fresh chromic acid, and well washed with distilled water immediately before use. The cells were

marked so that they were always used the same way round. Any error which might arise from multiple internal reflections was not considered, as it was found that solutions obeyed the Lambert-Beer law in various sizes of cell (2mm, 5mm and 1cm).

From experience with analytical calibration curves the accuracy of the instrument was known to be about 0.5%.

(2) Unicam SP 700 spectrophotometer

The Unicam SP 700 spectrophotometer is a double-beam pen-recording instrument. The absorbance values recorded on this machine have an accuracy of about 4%. The wavelength values have a repeatability of $\pm 50cm^{-1}$.

(b) Infra-red spectra

All the infra-red spectra reported on p.90 were recorded on a Perkin-Elmer model 237 infra-red spectrometer. The solid samples were prepared as mulls in nujol and hexachlorobutadiene and pressed between sodium chloride plates. The liquid samples were run as liquid films. All the spectra were calibrated at $1603cm^{-1}$ and $1495cm^{-1}$ using a polystyrene film. Using this technique the machine had a repeatability of $\pm 1.5cm^{-1}$.

The results reported on p. 79 were recorded on a Unicam SP 200 infra-red spectrometer, due to a breakdown of the Perkin-Elmer 237.

(c) pH measurements

The pH titrations were performed using a Pye, Model 79 pH meter, fitted with a combined glass electrode and reference calomel electrode (Pye Ingold - type 401 $E_o(7)$).

(d) Thermometers

Two thermometers, one reading from 0°c to 50°c in tenths and the other from 40°c to 70°c in tenths, were used to measure the temperature of the water-bath. Both were calibrated against standard N.P.L. thermometers.

(e) Determination of the Solvation energy of Allyl Alcohol

(1) Heat of solution

A two pint thermos flask was thoroughly cleaned out, dried and fitted with a thermometer calibrated in tenths of a degree. Distilled water (500ml) was added to the flask and its temperature recorded. Allyl alcohol (50ml), initially at the same temperature as the water was then added and the flask swirled to ensure complete mixing. The maximum temperature, which was reached after one minute, was read with the aid of a magnifying glass. The rate of cooling of the solution was then observed and found to be 0.5°c in 30 minutes. In view of the low rate of cooling no correction was applied. A control experiment with ethyl alcohol was also made.

Allyl alcohol			Ethyl alcohol		
Initial temp.	Final temp.	.°.Rise	Initial temp.	Final temp.	.°.Rise
20.50°c	22.60°c	2.10°c	20.45°c	24.00°c	3.55°c
20.55°c	22.65°c	2.10°c	20.80°c	24.40°c	3.60°c

From these results the heats of solution of ethyl and allyl alcohols were calculated, allowing for the thermal capacity of the thermos flask (34.1 cals/degree). The heat of solution of 1 mole of allyl alcohol in 32.5 moles of water was 1.61 Kcals, and for ethyl alcohol 2.31 Kcals. The value for ethyl alcohol is in good agreement with the values given by Lange[152], who reports the heat of solution as 1.75 Kcals/mole in 10 moles of water and 2.49 Kcals/mole in 200 moles of water.

(2) Solvation energy of allyl alcohol

Brieglob[81] notes that the solvation energy is obtained from the sum of the latent heat of evaporation and the heat of solution. Lange[152] gives the latent heat of evaporation of allyl alcohol as 9.45 Kcals/mole. Hence the solvation energy of allyl alcohol is about 11 Kcals/mole.

APPENDIX I

(1) Computer Programme for the Calculation of Platinum-Olefin Stability Constants

The Algol programme FAJAM20 was used to calculate the platinum-olefin stability constants. The meanings of the symbols used in the programme are given after the programme.

```
FAJAM20
   CALCULATION OF STABILITY CONSTANTS→

begin
     integer i,form,h;
     real Pt,B,D,b,d,E,F,G,C1,H,I,J,j;
     real array A1,A2,Un,C1,C2,K1,K2[1:13];
     open (20);
     open (30);
     for i:=1 step 1 until 13 do
     begin
          A1[i] := read (20);
          A2[i] := A1[i]-0.001
     end;
     Pt:=read(20);
     C1:=read(20);
     b:=read(20);
     d:=read(20);
     for i := 1 step 1 until 13 do Un[i] := read (20);
     B:=bXPt;
     for i := 1 step 1 until 13 do
     begin
          C1[i] := A1[i] - B;
          C2[i] := A2[i] - B
     end;
     for j := 650 step 10 until 1150 do
     begin
          D:=j-b;
          for i := 1 step 1 until 13 do
          begin
               E:=C1[i]/D;
               F:=Pt-E;
               G:=F/d;
               H:=EXC1;
```

```
        I:=H/G;
        J:=Un[i]-E;
        K1[i]:=I/J;
        E:=C2[i]/D;
        F:=Pt-E;
        G:=F/d;
        H:=EXC1;
        I:=H/G;
        J:=Un[i]-E;
        K2[i]:=I/J
end;
write text (30,[j*=*]);
write (30,format([ndddc]),j);
write text (30,[[3s]K1[7s]K2[c]]);
form:= format([nddddd.ddssss]);
for i := 1 step 1 until 13 do
begin
        write text (30,[[c]]);
        write (30,form,K1[i]);
        write(30,form,K2[i])
end;
comment This section refines the value of the parameter
j (the extinction coefficient of the platinum olefin
complex) by a least squares treatment;
begin
        real MIN,N,P,S,T,X,Y,Z,t;
        real array L,M,Q,R,U,V,W[1:13];
        for i := 1 step 1 until 13 do L[i] := K1[i] - K2[i];
        MIN := L[1];
        for h := 2 step 1 until 13 do
                if L[h] < MIN then MIN := L[h];
        for i := 1 step 1 until 13 do
                M[i] := MIN/L[i];
        N:=0;
        for i := 1 step 1 until 13 do N := N+M[i];
        P:= 13/N;
        for i := 1 step 1 until 13 do
        begin
                Q[i] := M[i]XP;
                R[i] := Q[i]XK1[i]
        end;
        S:=0;
        for i := 1 step 1 until 13 do S := S+R[i];
        T:=S/13;
        for i := 1 step 1 until 13 do
        begin
                U[i] := T-K1[i];
                V[i] := Q[i]XU[i];
                W[i] := V[i]↑2
```

```
                end;
                X:=0;
                for i := 1 step 1 until 13 do X:=X+W[i];
                Y:=X/13;
                Z:= sqrt(Y);
                t:= (Z/T)X100;
                write text (30,[K*=*]);
                write (30,format([nddddd.ddss]),T);
                write text (30,[t*=*]);
                write (30,format([nddd.ddccc]),t)
            end;
        end;
        close (20);
        close (30)
end →
```

List of symbols for FAJAM20

Symbol	Meaning
A1[i]	Absorbance of flask i
A2[i]	(Absorbance of flask i) - 0.001
b	ε_1'
B	$\varepsilon_1' \times [Pt]_T$
C1	$A1 - \varepsilon_1'[Pt]_T/(K_2/[Cl^-] + 1)$
C1	$[Cl^-]$
d	$1 + K_2/[Cl^-]$
D	$\varepsilon_3 - \varepsilon_1'/(K_2/[Cl^-] + 1)$
E	$[(ol)PtCl_3^-]$
F	$[Pt]_T - [(ol)PtCl_3^-]$
G	$[PtCl_4^=]$
H	$[(ol)PtCl_3^-][Cl^-]$
I	$[(ol)PtCl_3^-][Cl^-]/[PtCl_4^=]$

Symbol	Meaning
j	ϵ_3
J	$[ol]_T - [(ol)PtCl_3^-]$
K1[i]	Value of K_1 for the i^{th} flask calculated from A1[i]
K2[i]	Value of K_1 for the i^{th} flask calculated from A2[i]
L	ΔK
M	r
N	$\sum_1^{13} r$
P	$\left\{\sum_1^{13} r\right\}/13$
Pt	Total concentration of platinum i.e. $[Pt]_T$
Q	R_i
R	K_iR_i
S	$\sum_1^{13} K_iR_i$
t	$\sigma\%$
T	$\left\{\sum_1^{13} K_iR_i\right\}/13 = \bar{K}_1$
U	$\bar{K}_1 - K_i$
Un[i]	$[ol^+]_T$ in flask i

Symbol	Meaning
V	$R_i\lvert\bar{K} - K_i\rvert$
W	$(R_i\lvert\bar{K} - K_i\rvert)^2$
X	$\sum_{1}^{13} (R_i\bar{K} - K_i)^2$
Y	σ^2
Z	σ

Data

The programme FAJAM20 requires the following data in the order given

(1) Absorbance readings for flasks 1 to 13.

(2) Total platinum concentration (moles/litre).

(3) Total chloride concentration (moles/litre).

(4) Apparent extinction coefficient of $[PtCl_4^{=}]$ -

see p. 40.

(5) The value of the constant $(K_2/[Cl^-] + 1)$ at the temperature used.

(6) Olefin concentrations (moles/litre) for flasks 1 to 13.

Output

The programme gives the output in the following form, which is for the N-allylpiperidinum ion, for ϵ_3 values every ten units from 650 to 1150.

$\varepsilon_3 = 760$

K1	K2
439.60	427.46
453.14	446.35
434.46	428.78
433.01	428.64
442.60	438.83
431.37	428.05
436.13	433.05
438.17	435.26
434.50	431.73
437.24	434.55
437.45	434.82
436.16	433.58
439.45	436.88

K = 437.29 T = 0.82

K1 is the "true stability constant" for each flask. K2 is the artificial stability constant obtained by subtracting 0.001 absorbance units from the observed absorbance, which is required for a least-squares treatment of the errors.

K is the mean stability constant obtained by the least-squares procedure. T is the standard deviation (%).

(2) Computer Programme for the Calculation of Silver-Olefin Stability Constants

The Algol programme FAJAM50 was used to calculate the silver-olefin stability constants. The meanings of the symbols used in the programme are given after the programme.

```
FAJAM 50
CALCULATION OF STABILITY CONSTANTS FOR SILVER OLEFIN SYSTEMS →

begin
     integer i,form,j;
     real Ag,a,b,c,d,e,f,g,h;
     real array A,E,F,G1,G2,K1,K2 [1:10];
     open (20);
     open (30);
     for i:= 1 step 1 until 10 do
          A[i] := read (20);
     for i:= 1 step 1 until 10 do
          E[i] := read (20);
     for i := 1 step 1 until 10 do
          F[i] := read (20);
     for i := 1 step 1 until 10 do
     begin
          G1[i] := E[i] + F[i];
          G2[i] := G1[i] - 0.01
     end;
     Ag := read (20);
     for i := 1 step 1 until 10 do
     begin
          a:= G1[i]/59.157;
          b:= 2.303Xa;
          c:= exp(b);
          d:= 1/c;
          e:= 1 - d;
          f:= AgXe;
          g:= A[i] - f;
          h:= gXd;
          K1[i] := e/h;
          a:= G2[i]/59.157;
          b:= 2.303Xa;
          c:= exp(b);
          d:= 1/c;
          e:= 1-d;
          f:= AgXe;
          g:= A[i] -f;
          h:= gXd;
          K2[i] := e/h
```

```
end;
write text (30, [[3s] K1 [12s] K2 [c]]);
form := format ([nddd.ddddssss]);
for i := 1 step 1 until 10 do
begin
     write text (30, [[c]]);
     write (30, form, K1[i]);
     write (30, form,K2[i])
end;

comment Calculation of the standard deviation;

begin
     real MIN, N,P,S,T,X,Y,Z,t;
     real array L,M,Q,R,U,V,W[1:10];
     for i := 1 step 1 until 10 do
          L[i] := K1[i] - K2[i];
     MIN := L[1];
     for j := 2 step 1 until 10 do
          if L[j] < MIN then MIN := L[j];
     for i := 1 step 1 until 10 do
          M[i] := MIN/L[i];
     N:= 0;
     for i := 1 step 1 until 10 do
          N := N + M[i];
     P := 10/N;
     for i := 1 step 1 until 10 do
     begin
          Q[i] := M [i] X P;
          R[i] := Q[i] X K1[i]
     end;
     S:= 0;
     for i := 1 step 1 until 10 do
          S := S + R[i];
     T := S/10;
     for i := 1 step 1 until 10 do
     begin
          U[i] := T - K1[i];
          V[i] := Q[i] X U[i];
          W[i] := V[i]↑2
     end;
     X := 0;
     for i := 1 step 1 until 10 do
          X := X + W [i];
     Y := X/10;
     Z := sqrt (Y);
     t := (Z/T) X 100;
```

```
            write text ( 30, [ K*=*]);
            write (30, format ([nddddd.ddddssss]),T);
            write text (30, [ t*=*]);
            write (30, format ([nddddd.ddddcc]),t)
        end;
        close (20);
        close (30);
end →
```

List of symbols for FAJAM50

Symbol	Meaning
A	Total ligand concentration (moles/litre) for a given reading.
E	Emf observed using an unsaturated ligand
F	Emf observed using a saturated ligand
G1	Sum of emfs i.e. E + F
G2	(E + F) - 0.01
Ag	Total silver concentration (moles/litre)
a	$(\Delta E/(RT/\mathcal{F}))x2.303 = \log_{10}(1/\alpha_o)$
b	$2.303a = \ln(1/\alpha_o)$
c	$1/\alpha_o$
d	α_o
e	$1 - \alpha_o$
f	$B(1 - \alpha_o) = B - b$
g	$A - 1(B - b) = a$
h	$a\alpha_o$

The symbols used in the second half of the programme have exactly the same meaning as in FAJAM20.

Data

The programme FAJAM50 requires the following data in the order given.

(1) Ligand concentration in moles/litre for each reading.

(2) Emf (mV) observed when the unsaturated ligand is used.

(3) Emf (mV) observed when the saturated ligand is used.

(4) Total silver concentration in moles/litre.

Output

The programme gives the output in the following form which was obtained for the crotylammonium ion at a silver concentration of 0.005M.

K1	K2		
1.2771	1.2412		
1.2748	1.2552		
1.2881	1.2740		
1.2895	1.2782		
1.2782	1.2685		
1.2875	1.2789		
1.2805	1.2727		
1.2845	1.2773		
1.2845	1.2778		
1.2806	1.2742	K = 1.2831	T = 0.2958%

K1 is the "true stability constant" obtained for each reading. K2 is the artificial stability constant obtained by subtracting 0.01mV from the observed reading, which is required for a least-squares treatment of the results. K is the mean stability constant obtained by the least-squares procedure. T is the standard deviation (%).

APPENDIX II

Experimental readings for platinum-olefin stability constants

The experimental readings for each of the systems studied are recorded below. The layout of the readings is as follows:

A1	A11	Un4
A2	A12	Un5
A3	A13	Un6
A4	Pt	Un7
A5	C1	Un8
A6	b	Un9
A7	d	Un10
A8	Un1	Un11
A9	Un2	Un12
A10	Un3	Un13
K=	σ=	ε_3=

where A1 = absorbance of flask 1, Un1 = concentration of olefin in flask 1, Pt, C1, b and d have the meanings given on p.180, K_1 = calculated stability constant and ε_3 = value of ε_3 at which the standard deviation (σ) is a minimum.

(1) $allNH_3^+$ at 44.0°c

0.068;	0.328;	0.0004077;
0.1035;	0.347;	0.0005242;
0.1205;	0.364;	0.0006407;
0.1525;	0.0009919;	0.0007572;
0.1835;	1.9847;	0.0008737;
0.212;	30.24;	0.0009902;
0.238;	1.0211;	0.001107;
0.263;	0.0001165;	0.001223;
0.285;	0.0002330;	0.001340;
0.309;	0.0002912;	0.001456;
K_1=1737	σ=0.59%	ε_3=760

(2) allNH$_3^+$ at 30.2°c

0.075;	0.393;	0.0004100;
0.1195;	0.416;	0.0005271;
0.1415;	0.435;	0.0006443;
0.183;	0.0009964;	0.0007626;
0.220;	1.9956;	0.0008785;
0.257;	25.09;	0.0009957;
0.289;	1.0123;	0.001113;
0.3195;	0.0001183;	0.001230;
0.345;	0.0002343;	0.001347;
0.3715;	0.0002928;	0.001464;
K_1=2829	σ=0.77%	ε_3=760

(3) allNHEt$_2^+$ at 45.3°c

0.100;	0.4345;	0.001694;
0.159;	0.452;	0.002178;
0.1865;	0.468;	0.002662;
0.233;	0.0009919;	0.003146;
0.275;	1.9847;	0.003630;
0.3105;	30.24;	0.004114;
0.350;	1.0211;	0.004598;
0.370;	0.0004840;	0.005082;
0.393;	0.0009679;	0.005565;
0.4155;	0.001210;	0.006049;
K_1=551.5	σ=1.53%	ε_3=770

(4) allNHEt$_2^+$ at 30.0°c

0.077;	0.371;	0.0008457;
0.1215;	0.390;	0.001087;
0.144;	0.4075;	0.001329;
0.183;	0.0009976;	0.001571;
0.218;	1.9956;	0.001812;
0.249;	26.06;	0.002054;
0.2795;	1.0292;	0.002295;
0.3075;	0.0002416;	0.002537;
0.330;	0.0004833;	0.002779;
0.3505;	0.0006041;	0.003020;
K_1=864.7	σ=0.64%	ε_3=770

(5) allNMe$_3^+$ at 60.0°c

0.117;	0.330;	0.005477;
0.1355;	0.346;	0.006086;
0.168;	0.361;	0.006695;
0.198;	0.0009849;	0.007912;
0.212;	1.9706;	0.009129;
0.224;	32.49;	0.01035;
0.251;	1.0292;	0.01156;
0.275;	0.002434;	0.01278;
0.295;	0.003043;	0.01400;
0.313;	0.004260;	0.01521;
K_1=117.0	σ=0.63%	ϵ_3=760

(6) allNMe$_3^+$ at 44.5°c

0.089;	0.3775;	0.003698;
0.137;	0.3935;	0.004754;
0.159;	0.408;	0.005811;
0.198;	0.0009918;	0.006868;
0.234;	1.9847;	0.007924;
0.265;	33.78;	0.008981;
0.289;	1.0211;	0.01004;
0.315;	0.001056;	0.01109;
0.338;	0.002113;	0.01215;
0.3585;	0.002641;	0.01321;
K_1=173.3	σ=0.62%	ϵ_3=760

(7) allNMe$_3^+$ at 30.0°c

0.104;	0.4475;	0.003718;
0.1705;	0.464;	0.004781;
0.198;	0.4775;	0.005843;
0.248;	0.0009974;	0.006906;
0.289;	1.9956;	0.007968;
0.326;	24.56;	0.009030;
0.358;	1.0123;	0.01009;
0.3815;	0.001062;	0.01115;
0.404;	0.002125;	0.01222;
0.4285;	0.002656;	0.01328;
K_1=258.6	σ=0.79%	ϵ_3=760

(8) allN-Pr_3^+ at 60.0°c

0.0435;	0.134;	0.0008273;
0.054;	0.1415;	0.001064;
0.0595;	0.149;	0.001300;
0.0695;	0.0009846;	0.001536;
0.0795;	1.9706;	0.001773;
0.0885;	33.52;	0.002009;
0.0985;	1.0292;	0.002245;
0.107;	0.0002364;	0.002482;
0.116;	0.0004727;	0.002718;
0.125;	0.0005909;	0.002954;
K_1=131.1	σ=0.61%	ε_3=805

(9) allN-Bu_3^+ at 60.0°c

0.128;	0.276;	0.0008723;
0.138;	0.291;	0.0009969;
0.160;	0.306;	0.001121;
0.180;	0.0009851;	0.001246;
0.200;	1.97056;	0.001308;
0.220;	26.28;	0.001371;
0.240;	1.0292;	0.001433;
0.2495;	0.0005607;	0.001495;
0.2595;	0.0006230;	0.001620;
0.265;	0.0007477;	0.001744;
K_1=307.6	σ=0.96%	ε_3=1530

(10) all$NH(CH_2)_4^+$ at 60.0°c

0.094;	0.430;	0.001445;
0.1535;	0.445;	0.001858;
0.180;	0.4605;	0.002271;
0.224;	0.0009853;	0.002684;
0.272;	1.9706;	0.003096;
0.302;	26.25;	0.003509;
0.332;	1.0292;	0.003922;
0.359;	0.0004129;	0.004335;
0.385;	0.0008257;	0.004748;
0.409;	0.001032;	0.005161;
K_1=648.6	σ=1.40%	ε_3=770

(11) $\underline{allNH(CH_2)_5^+ \text{ at } 60.0^\circ c}$

0.0715;	0.3365;	0.001307;
0.1145;	0.353;	0.001681;
0.1305;	0.370;	0.002054;
0.165;	0.0009845;	0.002428;
0.199;	1.9706;	0.002801;
0.2245;	26.25;	0.003174;
0.252;	1.0292;	0.003548;
0.2765;	0.0003735;	0.003921;
0.297;	0.0007469;	0.004295;
0.318;	0.0009337;	0.004668;
K_1=437.3	σ=0.82%	ε_3=760

(12) $\underline{butNH_3^+ \text{ at } 60.0^\circ c}$

0.0895;	0.460;	0.0005149;
0.142;	0.483;	0.0006620;
0.169;	0.506;	0.0008092;
0.2195;	0.0009851;	0.0009563;
0.266;	1.9706;	0.001103;
0.307;	27.92;	0.001262;
0.345;	1.0292;	0.001398;
0.378;	0.0001471;	0.001545;
0.4105;	0.0002942;	0.001692;
0.439;	0.0003678;	0.001839;
K_1=2038	σ=1.16%	ε_3=890

(13) $\underline{butNH_3^+ \text{ at } 44.5^\circ c}$

0.0825;	0.464;	0.0004033;
0.137;	0.488;	0.0005186;
0.1615;	0.511;	0.0006338;
0.212;	0.0009919;	0.0007490;
0.256;	1.9847;	0.0008643;
0.300;	25.20;	0.0009795;
0.3395;	1.0211;	0.001095;
0.374;	0.0001152;	0.001210;
0.408;	0.0002305;	0.001325;
0.437;	0.0002881;	0.001440;
K_1=3017	σ=0.71%	ε_3=890

(14) $\underline{butNH_3^+ \text{ at } 30.0^\circ c}$

0.071;	0.408;	0.0002704;
0.114;	0.435;	0.0003476;
0.1355;	0.4585;	0.0004249;
0.176;	0.0009972;	0.0005021;
0.215;	1.9956;	0.0005794;
0.252;	26.07;	0.0006566;
0.2865;	1.0123;	0.0007339;
0.3215;	0.00007725;	0.0008111;
0.3515;	0.0001545;	0.0008884;
0.382;	0.0001931;	0.0009656;
K_1=4396	σ=0.62%	ε_3=890

(15) $\underline{butNEt_3^+ \text{ at } 60.0^\circ c}$

0.1205;	0.618;	0.0005421;
0.204;	0.6405;	0.0006969;
0.2405;	0.660;	0.0008518;
0.313;	0.0009849;	0.001007;
0.376;	1.9706;	0.001162;
0.432;	31.57;	0.001316;
0.4805;	1.0292;	0.001471;
0.527;	0.0001549;	0.001626;
0.560;	0.0003097;	0.001781;
0.5905;	0.0003872;	0.001936;
K_1=4449	σ=1.02%	ε_3=910

(16) $\underline{butNEt_3^+ \text{ at } 44.8^\circ c}$

0.0825;	0.4595;	0.0002730;
0.131;	0.4885;	0.0003510;
0.1545;	0.514;	0.0004290;
0.200;	0.0009914;	0.0005070;
0.2435;	1.9847;	0.0005849;
0.2855;	32.78;	0.0006629;
0.325;	1.0211;	0.0007409;
0.3625;	0.00007799;	0.0008189;
0.3965;	0.0001560;	0.0008969;
0.4305;	0.0001950;	0.0009749;
K_1=5911	σ=0.45%	ε_3=910

(17) $\underline{\text{butNEt}_3^+ \text{ at } 30.0^\circ\text{c}}$

0.059;	0.337;	0.0001647;
0.0915;	0.363;	0.0002117;
0.107;	0.387;	0.0002588;
0.1385;	0.0009972;	0.0003058;
0.1685;	1.9956;	0.0003529;
0.199;	26.39;	0.0004000;
0.229;	1.0123;	0.0004470;
0.257;	0.00004729;	0.0004941;
0.285;	0.00009411;	0.0005411;
0.311;	0.0001176;	0.0005882;
K_1=7778	σ=0.77%	ε_3=910

(18) $\underline{\text{butAsEt}_3^+ \text{ at } 60.0^\circ\text{c}}$

0.1305;	0.664;	0.0005577;
0.222;	0.683;	0.0007171;
0.2645;	0.705;	0.0008764;
0.341;	0.0009849;	0.001036;
0.4125;	1.9706;	0.001195;
0.472;	31.53;	0.001354;
0.5295;	1.0292;	0.001514;
0.568;	0.0001593;	0.001673;
0.602;	0.0003187;	0.001832;
0.637;	0.0003984;	0.001992;
K_1=5459	σ=1.65%	ε_3=920

(19) $\underline{\text{butAsEt}_3^+ \text{ at } 44.8^\circ\text{c}}$

0.087;	0.4955;	0.0002809;
0.140;	0.525;	0.0003611;
0.1655;	0.5525;	0.0004413;
0.215;	0.0009914;	0.0005216;
0.262;	1.9847;	0.0006018;
0.308;	32.29;	0.0006821;
0.351;	1.0211;	0.0007623;
0.390;	0.00008025;	0.0008426;
0.430;	0.0001605;	0.0009228;
0.463;	0.0002006;	0.001003;
K_1=7014	σ=0.70%	ε_3=920

(20) $\underline{\text{butAsEt}_3^+ \text{ at } 30.0^\circ\text{c}}$

0.0555;	0.3105;	0.0001412;
0.084;	0.334;	0.0001816;
0.0985;	0.3575;	0.0002219;
0.1265;	0.0009972;	0.0002623;
0.1545;	1.9956;	0.0003026;
0.1815;	26.07;	0.0003430;
0.2085;	1.0123;	0.0003833;
0.235;	0.00004035;	0.0004237;
0.2605;	0.00008070;	0.0004640;
0.286;	0.0001009;	0.0005044;
K_1=8962	σ=0.43%	ε_3=920

(21) $\underline{\text{pentNH}_3^+ \text{ at } 60.0^\circ\text{c}}$

0.100;	0.527;	0.0008610;
0.1705;	0.540;	0.001107;
0.201;	0.560;	0.001353;
0.263;	0.0009849;	0.001599;
0.306;	1.9706;	0.001845;
0.360;	26.28;	0.002091;
0.400;	1.0292;	0.002337;
0.439;	0.0002460;	0.002583;
0.4695;	0.0004920;	0.002829;
0.499;	0.0006150;	0.003075;
K_1=1124	σ=2.51%	ε_3=970

(22) $\underline{CH_3\text{-}CH\text{=}CH\text{-}CH_2\text{-}NH_3^+ \text{ at } 60.2^\circ\text{c}}$

0.0635;	0.2815;	0.001856;
0.095;	0.297;	0.002386;
0.110;	0.311;	0.002916;
0.137;	0.0009847;	0.003447;
0.1635;	1.9706;	0.003977;
0.1845;	29.96;	0.004507;
0.2085;	1.0292;	0.005038;
0.2285;	0.0005303;	0.005568;
0.2485;	0.001060;	0.006098;
0.2635;	0.001326;	0.006628;
K_1=209.3	σ=0.67%	ε_3=760

(23) $CH_3-CH=CH-CH_2-NH_3^+$ at 44.5°c

0.077;	0.3445;	0.001869;
0.1185;	0.3625;	0.002403;
0.139;	0.378;	0.002937;
0.1745;	0.0009918;	0.003471;
0.2055;	1.9847;	0.004005;
0.2365;	29.74;	0.004540;
0.2615;	1.0211;	0.005074;
0.2865;	0.0005341;	0.005608;
0.3095;	0.001068;	0.006142;
0.328;	0.001335;	0.006676;
K_1=303.7	σ=0.64%	ϵ_3=760

(24) $CH_3-CH=CH-CH_2-NH_3^+$ at 30.0°c

0.089;	0.4135;	0.001878;
0.145;	0.4325;	0.002415;
0.179;	0.4475;	0.002951;
0.215;	0.0009974;	0.003488;
0.2545;	1.9956;	0.004025;
0.290;	22.56;	0.004561;
0.3205;	1.0123;	0.005098;
0.348;	0.0005366;	0.005634;
0.3735;	0.001073;	0.006171;
0.396;	0.001342;	0.006708;
K_1=450.4	σ=1.66%	ϵ_3=760

(25) $CH_2=CH-CH(CH_3)-NH_3^+$ at 60.0°c

0.084;	0.3635;	0.0008273;
0.126;	0.381;	0.001064;
0.1455;	0.3995;	0.001300;
0.1825;	0.0009849;	0.001536;
0.216;	1.9706;	0.001773;
0.247;	36.55;	0.002009;
0.273;	1.0292;	0.002246;
0.2995;	0.0002364;	0.002482;
0.3205;	0.0004728;	0.002718;
0.344;	0.0005909;	0.002955;
K_1=803.8	σ=0.72%	ϵ_3=780

(26) $CH_2=CH-CH(CH_3)-NH_3^+$ at 45.3°c

0.100;	0.443;	0.0008332;
0.157;	0.461;	0.001071;
0.1835;	0.478;	0.001309;
0.231;	0.0009919;	0.001547;
0.272;	1.9847;	0.001785;
0.3095;	35.29;	0.002024;
0.345;	1.0211;	0.002262;
0.3735;	0.0002393;	0.002500;
0.4005;	0.0004761;	0.002738;
0.422;	0.0005952;	0.002976;
K_1=1282	σ=0.65%	ϵ_3=780

(27) $CH_2=CH-CH(CH_3)-NH_3^+$ at 30.0°c

0.1145;	0.5265;	0.0008378;
0.191;	0.5455;	0.001077;
0.2245;	0.5615;	0.001317;
0.2875;	0.0009976;	0.001556;
0.341;	1.9956;	0.001795;
0.3875;	26.06;	0.002035;
0.4245;	1.0123;	0.002274;
0.4565;	0.0002394;	0.002513;
0.4825;	0.0004788;	0.002753;
0.5065;	0.0005985;	0.002992;
K_1=2194	σ=0.88%	ϵ_3=780

(28) $CH_2=C(CH_3)-CH_2-NH_3^+$ at 60.0°c

0.087;	0.1295;	0.03069;
0.0915;	0.133;	0.03261;
0.096;	0.137;	0.03453;
0.1005;	0.0009849;	0.03645;
0.104;	1.9706;	0.03837;
0.109;	29.45;	0.04028;
0.1115;	1.0292;	0.04220;
0.115;	0.02494;	0.04412;
0.120;	0.02686;	0.04604;
0.125;	0.02877;	0.04796;
K_1=3.18	σ=0.82%	ϵ_3=1600

(29) $(CH_3)_2C{=}CH{-}CH_2{-}NH_3^+$ at 60.0°c

Only 6 flasks were used instead of the normal 13. The absorbance values quoted are those obtained after subtracting the absorbance due to the free ligand (see p.53).

0.06625;	0.0009978;	0.02272;
0.07035;	1.9706;	0.02575;
0.07545;	29.06;	0.02878;
0.08055;	1.0292;	0.03181;
0.08415;		0.03484;
0.08975;		0.03787;
K_1=2.58	σ=0.84%	ε_3=1350

(30) Allyl alcohol at 60.0°c

0.0855;	0.597;	0.0008769;
0.193;	0.614;	0.001127;
0.280;	0.626;	0.001378;
0.3525;	0.0009846;	0.001629;
0.420;	1.9706;	0.001879;
0.469;	26.25;	0.002130;
0.508;	1.0292;	0.002380;
0.531;	0.0001253;	0.002631;
0.561;	0.0003758;	0.002881;
0.580;	0.0006264;	0.003132;
K_1=3890	σ=2.41%	ε_3=770

(31) Allyl alcohol at 44.5°c

0.204;	0.609;	0.0008471;
0.289;	0.6225;	0.001089;
0.3405;	0.6305;	0.001210;
0.427;	0.0009917;	0.001331;
0.4935;	1.9847;	0.001452;
0.5205;	42.86;	0.001573;
0.5415;	1.0211;	0.001694;
0.566;	0.0003025;	0.001815;
0.581;	0.0004841;	0.001936;
0.598;	0.0006051;	0.002057;
K_1=7250	σ=0.83%	ε_3=770

(32) Allyl alcohol at 30.0°c

0.153;	0.598;	0.0004259;
0.189;	0.6185;	0.0005482;
0.2245;	0.6365;	0.0006693;
0.292;	0.0009979;	0.0007910;
0.354;	1.9956;	0.0009120;
0.412;	40.08;	0.001034;
0.463;	1.0123;	0.001156;
0.506;	0.0001825;	0.001278;
0.541;	0.0002434;	0.001399;
0.572;	0.0003042;	0.001521;
K_1=13011	σ=1.42%	ε_3=770

(33) Crotyl alcohol at 60.0°c

0.122;	0.546;	0.0008050;
0.203;	0.562;	0.001035;
0.240;	0.574;	0.001265;
0.307;	0.0009858;	0.001495;
0.362;	1.9706;	0.001725;
0.4065;	26.37;	0.001955;
0.4415;	1.0292;	0.002185;
0.475;	0.0002300;	0.002415;
0.501;	0.0004600;	0.002645;
0.5245;	0.0005750;	0.002875;
K_1=3008	σ=1.22%	ε_3=760

(34) 4-penten-1-ol at 60.0°c

0.130;	0.621;	0.0008159;
0.220;	0.628;	0.001049;
0.262;	0.641;	0.001282;
0.331;	0.0009846;	0.001515;
0.394;	1.9706;	0.001748;
0.449;	26.28;	0.001981;
0.497;	1.0292;	0.002215;
0.5305;	0.0002331;	0.002448;
0.561;	0.0004662;	0.002681;
0.590;	0.0005828;	0.002914;
K_1=2525	σ=2.86%	ε_3=890

APPENDIX III

Experimental readings for silver-olefin stability constants

The readings obtained for the silver-olefin stability constants are recorded below. Column 1 contains the ligand concentrations (moles/litre), column 2 the emf (mV) observed when the unsaturated ligand is used, column 3 the emf (mV) observed when the saturated ligand is used and column 4 the total silver concentration in moles/litre. The calculated stability constant (K) and the standard deviation (σ) are given below the readings.

(1) $CH_2=CH-CH_2NH_3^+$ v. 0.01M Ag^+

0.01114;	0.304;	0.058;	
0.02075;	0.559;	0.107;	
0.02912;	0.770;	0.153;	
0.03648;	0.940;	0.203;	
0.04299;	1.142;	0.245;	
0.04880;	1.268;	0.285;	
0.05401;	1.382;	0.319;	
0.05872;	1.504;	0.351;	
0.06298;	1.617;	0.378;	
0.06687;	1.736;	0.403;	0.009869;

K = 1.292 σ = 1.21%

(2) $\underline{CH_2=CH-CH_2NH_3^+}$ v. ~ 0.005M Ag^+

0.01110;	0.305;	0.055;	
0.02070;	0.575;	0.107;	
0.02900;	0.780;	0.150;	
0.03640;	0.9735;	0.202;	
0.04290;	1.1475;	0.243;	
0.04860;	1.2925;	0.282;	
0.05380;	1.420;	0.3175;	
0.05860;	1.5475;	0.350;	
0.06280;	1.6375;	0.376;	
0.06670;	1.7255;	0.403;	0.0049345;

K = 1.304 σ = 0.67%

(3) $\underline{CH_3-CH=CH-CH_2NH_3^+}$ v. ~ 0.01M Ag^+

0.01112;	0.302;	0.055;	
0.02070;	0.557;	0.105;	
0.02905;	0.773;	0.150;	
0.03639;	0.952;	0.200;	
0.04289;	1.125;	0.238;	
0.04868;	1.260;	0.2775;	
0.05388;	1.374;	0.311;	
0.05858;	1.485;	0.341;	
0.06283;	1.594;	0.3675;	
0.06671;	1.704;	0.393;	0.009869;

K = 1.279 σ = 0.55%

(4) $\underline{CH_3-CH=CH-CH_2NH_3^+}$ v. ~ 0.005M Ag^+

0.01112;	0.305;	0.055;	
0.02070;	0.560;	0.107;	
0.02905;	0.788;	0.150;	
0.03639;	0.971;	0.200;	
0.04289;	1.125;	0.238;	
0.04868;	1.275;	0.2775;	
0.05388;	1.393;	0.311;	
0.05858;	1.512;	0.341;	
0.06283;	1.615;	0.3675;	
0.06671;	1.701;	0.393;	0.0049345;

K = 1.283 σ = 0.30%

(5) $CH_2=CH-CH_2OH$ v. ~0.01M Ag^+

0.01116;	4.900;	0.059;	
0.02079;	8.820;	0.111;	
0.02917;	11.815;	0.1565;	
0.03653;	14.245;	0.1975;	
0.04306;	16.240;	0.238;	
0.04888;	17.920;	0.274;	
0.05410;	19.350;	0.3075;	
0.05881;	20.600;	0.338;	
0.06308;	21.660;	0.364;	
0.06698;	22.620;	0.3885;	0.009869;

Result on p.116

(6) $CH_2=CH-CH_2OH$ v. ~0.005M Ag^+

0.01116;	5.353;	0.059;	
0.02079;	9.327;	0.111;	
0.02917;	12.441;	0.156;	
0.04306;	16.911;	0.238;	
0.04888;	18.583;	0.274;	
0.05410;	19.823;	0.307;	
0.05881;	21.238;	0.338;	
0.06308;	22.325;	0.364;	
0.06698;	23.261;	0.388;	0.0049345;

Result on p.116

(7) $CH_3-CH=CH-CH_2OH$ v. ~0.01M Ag^+

0.01116;	1.963;	0.060;	
0.02079;	3.584;	0.112;	
0.02917;	4.940;	0.157;	
0.03653;	6.049;	0.197;	
0.04306;	7.013;	0.232;	
0.04888;	7.881;	0.263;	
0.05410;	8.601;	0.292;	
0.05881;	9.267;	0.323;	
0.06308;	9.847;	0.354;	
0.06698;	10.359;	0.386;	0.009869;

Result on p.116

(8) $CH_3-CH=CH-CH_2OH$ v. ~0.005M Ag^+

0.01127;	2.013;	0.060;	
0.02099;	3.750;	0.112;	
0.02946;	5.122;	0.158;	
0.03690;	6.300;	0.199;	
0.04349;	7.288;	0.234;	
0.04936;	8.123;	0.265;	
0.05464;	8.894;	0.296;	
0.05939;	9.569;	0.326;	
0.06371;	10.140;	0.358;	
0.06764;	10.712;	0.394;	0.0049345;

Result on p.116

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