ABSTRACT

KINETICS AND EQUILIBRIA IN THE HYDRATION OF CARBONYL COMPOUNDS

An abstract of a thesis submitted for the Degree of Doctor of Philosophy in the University of Oxford.

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ABSTRACT

A method has been evolved for the study of the kinetics of the dehydration of carbonyl compounds. The basis of this method is shown in the reaction scheme given below:

$$\text{>C(OH)(OH)} \xrightarrow{\text{slow}} \text{>C=O} + H_2O$$

$$\text{>C=O} + \text{scavenger} \xrightarrow{\text{fast}} \text{adduct}$$

The scavengers used were semicarbazide, hydroxylamine, phenylhydrazine and sulphite. Experiments with sulphite as scavenger were followed by titration on an automatic pH stat titrator.

$$\text{>C(OH)(OH)} + SO_3^{=} \longrightarrow \text{>C(}SO_3^{-}\text{)(OH)} + OH^{-}$$

The progress of the reaction with other scavengers was followed by ultra-violet spectrophotometric techniques.

Another reaction scheme suggested by earlier workers[1] as a possible method of studying the kinetics of the dehydration of formaldehyde was investigated and shown both on theoretical and practical grounds to be of no value in providing kinetic data. This scheme was as shown below:

$$H_2C\text{(OH)(OH)} \underset{\text{slow}}{\rightleftharpoons} HCHO + H_2O$$

involatile — volatile ↓ fast → to gas stream

The scavenger techniques were used to study the kinetics of the dehydration of formaldehyde and acetaldehyde. These reactions are subject to general acid-base catalysis. Formaldehyde was studied in detail, a large number of catalysts of varying structures, charge types etc. being investigated[2,3,4]. Acetaldehyde had already been extensively investigated by previous workers. The present work gave

results in good agreement with the earlier work. This work was however of special interest in that recent work by Gruen and McTigue[5] had raised doubts as to the validity of the "thermal maximum" method which had been employed in obtaining the majority of the previous acetaldehyde results.

The results obtained for a wide range of catalysts for formaldehyde conformed with one exception, azide, to two single Brönsted relationships to within log ± 0.5 over sixteen pK units. These relationships were:

Acid catalysis: (12 catalysts studied)

$$\frac{k_A}{p} = 0.46 \left[\frac{qK}{p}\right]^{0.23}$$

Base catalysis: (29 catalysts)

$$\frac{k_B}{q} = 2.0 \times 10^{-4} \left[\frac{p}{qK}\right]^{0.40}$$

where k_A and k_B are the catalytic constants in $l.mole^{-1}\ sec^{-1}$, p and q the statistical factors and K the conventional acid-base strength of the catalyst. The types of catalysts studied included carboxylic acids, nitrogen compounds and inorganic acids, e.g. HF, $H_2AsO_4^-$, H_6TeO_6.

In the light of these catalytic results the general range of validity of the Brönsted relationships is discussed. The effects of statistical factors, steric and charge effects are also reviewed. The formaldehyde results are compared with those from other carbonyl hydration studies. The somewhat anomalous carbon dioxide hydration results of Sharma and Danckwerts[6] are discussed.

The results are also of interest in that they verify some earlier polarographic results[7,8] giving credence to the reliability of the mathematical approximations made in obtaining the polarographic data.

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INTRODUCTION

Many aldehydes and ketones are partly hydrated in aqueous solution according to the equation:

$$>C(OH)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} >C=O + H_2O$$

$$Kd = \frac{k_1}{k_{-1}} = \frac{[>C=O]}{[>C(OH)_2]}$$

The structure of the hydrate as a gem-diol may be demonstrated by Raman spectra and nuclear magnetic resonance.

Several workers have measured these hydration equilibrium constants spectrophotometrically but only in the work of Bell and Clunie (1952)[1], Bell and McDougall (1960)[2] and Gruen and McTigue (1963)[3] has proper attention been given to temperature control and care taken in estimating the extinction coefficient of the unhydrated form in an aqueous medium. Two quantitative nuclear magnetic resonance studies of acetaldehyde by Lombardi and Sogo (1960)[4] and Fujiwara and Fujiwara (1963)[5] have provided results in good agreement with the spectrophotometric work. Results obtained by Matsushima (1963)[6] by Raman intensity measurements in concentrated acetaldehyde solutions show only qualitative agreement. A selection of equilibrium constants are shown in Table 1 below:

TABLE 1

substance	Kd 25°C
[a] formaldehyde	$\sim 10^{-4}$
[b] chloral	3.57×10^{-5} (3), 2.0×10^{-3} (2)
acetaldehyde	0.667 (4), 0.667 (2), 0.809 (5), 1.08 (3).
propionaldehyde	1.45 (3)
monochloroacetone	1.60 (2)
acetone	$> 10^6$ (7)

a. Formaldehyde will be discussed in full in a later section of

this introduction.

b. These results are not directly comparable since the data in reference (2) were obtained in aqueous cyclohexane solutions and that in (3) in aqueous salt solutions.

Kinetic studies of these reactions.

Very little quantitative kinetic work has so far been undertaken. The few results available show that these reactions are subject to general acid-base catalysis, i.e. they have rate constants of the form:

$$k_1 = k_o + k_{H^+}[H^+] + k_{OH^-}[OH^-] + k_A[A] + k_B[B]$$

where k_o is the rate due to catalysis by water molecules and the remaining k's are catalytic constants. Throughout this work first-order rate constants, i.e. k_1, are in sec^{-1} and catalytic constants, k_A and k_B, in $l.mole^{-1}\ sec^{-1}$.

Acetaldehyde is the only carbonyl compound to have been extensively studied, though several workers have investigated formaldehyde polarographically. The main object of this present work was to extend the kinetic data on this compound.

Review of previous work.

Acetaldehyde: Herbert and Lauder (1938)[8] using O^{18} showed that there was a rapid but not instantaneous exchange of oxygen between water and acetaldehyde at room temperature. They postulated that this took place via the hydrate.

Bell and Higginson (1949)[9] studied the dehydration reaction in aqueous acetone at 25°C dilatometrically. It was found to be a first-order reaction showing general acid-base catalysis. 63 catalysts were investigated of which 47 carboxylic acid and phenols conformed to a single Brönsted relationship. The remaining 16 acids of other types showed considerable deviations from this relationship. These deviations were related to an extra change in energy during ionisation due to mesomerism in either the acid or its anion.

Bell and Darwent (1950)[10] investigated the hydration reaction in aqueous solution at 0°C using a dilatometric method. They also found general acid-base catalysis but the high velocity of the reaction restricted the range of catalysts that could be used.

This difficulty was overcome by use of the thermal maximum method devised by Bell and co-workers[11,12]. This method depends on measuring the small temperature changes caused by the heat of reaction. Theoretical expressions were deduced relating Tm, the maximum temperature change in the reaction vessel when heat transfer to its surroundings was taking place, with To the temperature change under adiabatic conditions; thus for a first-order reaction, in which there was no heat of mixing it was found that:

$$T_m/T_o = R^{1/1-R}$$

where $R = k_2/k_1$.

k_2 is the cooling constant governing the rate of heat transfer and k_1 the first-order rate constant for the reaction.

This technique gave results of moderate accuracy and could be used with reactions having half-lives ranging from less than a second to a few minutes.

This method was used by Bell and Clunie (1951)[13] (1952)[14] to investigate the hydration of acetaldehyde at 0°C in solutions of hydrochloric acid and in acetate buffers. These results were used to discount mechanisms involving the simultaneous action of acidic and basic species. Bell, Rand and Wynne-Jones (1956)[15] extended the data on the hydration reaction, working at 25°C. They evaluated catalytic constants for a series of carboxylic acids and pyridines, as well as for water and hydrogen and hydroxyl ions. Their acid catalytic constants were simply related to acidic dissociation constants, though some deviations attributable to steric hindrance were found; e.g. 2:6 lutidinium ion had a low catalytic constant as compared with the 2:4 and 2:5 lutidinium ions. The basic catalysts showed no simple relationship to basic

strength. The authors concluded that in basic catalysis steric effects were predominant. Gruen and McTigue (1963)[16] however explained this anomaly in terms of the formation of appreciable quantities of addition compound between the aldehyde and the catalysing base. They demonstrated the existence of these addition compounds by spectrophotometric measurements. The actual quantities of addition compound formed between propionaldehyde and phosphate and acetate were measured.

Thus if: $C_2H_5CHO + X^- \rightleftharpoons C_2H_5CHOX^- (M^-)$

$$K_X = \frac{[M^-]\,\gamma_M}{[A]\gamma_A[X^-]\gamma_X}$$

They found: $K_X = 0.10$ for acetate
$= 0.45$ for phosphate

Finally Pocker (1960)[17] has reported relative rates of formation and decomposition of acetaldehyde hydrate in water and deuterium oxide. No indication of the technique used was given.

Formaldehyde:

All kinetic studies of this compound have relied on polarographic techniques. Of the two species present in solution CH_2O and $H_2C(OH)_2$ only the former is reducible at a dropping-mercury electrode, thus under suitable conditions of drop rate, concentration etc., the observed polarographic current gives a direct measure of the rate of the process: $H_2C(OH)_2 \longrightarrow CH_2O + H_2O$

The past studies of this reaction are reviewed below: In the first work on this system Jahoda (1935)[18] found the electrode reaction:

$$HCHO + 2H_2O + 2e = CH_3OH + 2OH^-$$

Bieber and Trümpler (1947)[19] showed that the limiting polarographic currents were determined by the rate of dehydration of

methylene glycol when the formaldehyde concentration at the electrode surface decreases in consequence of the electrode reaction. This limiting current was found to be highly dependent on pH and temperature. In buffered solutions the relationship between limiting current and formaldehyde concentration was found to be linear, in unbuffered solutions this was not the case. Vesely and Brdicka (1947)[20] found that the dehydration reaction was subject to acid-base catalysis. They evaluated rate constants using a simplified mathematical treatment. Various workers have since produced many refinements in the mathematics, which have been reviewed in the literature by Lanquist (1955)[21] and Brdicka (1960)[22].

Lanquist[21] and Valenta (1960)[23] have also shown that it is possible to obtain a value for the equilibrium constant of the reaction by studying limiting currents in unbuffered solutions. A knowledge of this constant is very important as any interpretation of the polarographic kinetic data depends directly on its value, unfortunately it is a poorly defined quantity (see Table 2). Spectrophotometric techniques are hampered by the low concentration of the carbonyl compound.

TABLE 2

Kd	Temp.°C	Method	Author	Notes
10^{-4}	20	spectrophotometric	Bieber and Trümpler[24]	A
10^{-3}	25	"	Gruen and McTigue[16]	B
$< 3 \times 10^{-4}$	20	polarographic	Lanquist[21]	
4.37×10^{-4}	20	"	Valenta[23]	
ca.5.5×10^{-4}	30	partial pressures	Hiceto[25]	C

A. Temperature range studied, 54 - 64°C extrapolated to 20°C. 70 cm. silica cells used. The formaldehyde solutions used were 0.87M.

B. Temperature range 25 - 90°C. 1 cm. silica cells. Maximum concentration of formaldehyde > 8M in which solutions polymerisation is very important.

C. He measured formaldehyde partial pressures and assuming ideal gas behaviour evaluated this equilibrium constant.

The polarographic results are given in Table 3, the equilibrium constant being incorporated with the rate constant.

TABLE 3

$K_d k_o$	$K_d k_{H_2BO_3^-}$	$K_d k_{OH^-}$	Author
1.0×10^{-5}	3.8×10^{-3}	1.18	Vesely and Brdicka[20]
1.5×10^{-5}	1.3×10^{-3}	0.58	Brdicka[26]
1.5×10^{-6}	-	-	Lanquist[21]
1.3×10^{-5}	1.3×10^{-3}	0.57	Brdicka[27]

All at 20°C.

Other Carbonyl Compounds: Cohn and Urey (1938)[28] investigated the kinetics of hydration of acetone by observing the rate of exchange of O^{18} between acetone and water at 100°C. Their qualitative results showed that this exchange was catalysed by acids and bases.

Bell and Jensen (1960)[29] studied the kinetics of hydration of s-dichloroacetone spectrophotometrically in a 5% (v/v) water + dioxan mixture. Catalysis by 24 acids and 20 bases was investigated; general relations between acid catalytic constants and acid-base strength were found. In basic catalysis anion bases were about a 1000 times as effective as uncharged bases of the same strength, but within each class the catalytic constant was related to basic strength.

Gruen and McTigue (1963)[16] measured the catalytic constants for the hydrogen ion for acetaldehyde, propionaldehyde, and n- and iso-butyraldehyde using a thermal device. They found the catalytic constant to be almost constant for the homologous series.

Eigen, Kustin and Strehlow (1962)[30] investigated the hydration of pyruvic acid using polarographic and relaxation methods. The system is complicated by ionisation of the acid:

$$CH_3COCOO^- + H_3O^+ \rightleftharpoons CH_3COCOOH + H_2O$$

c_1 ⇅ c_2 ⇅ k_{32}

$$CH_3C(OH)_2COO^- + H^+ \rightleftharpoons CH_3C(OH)_2COOH$$

c_4 c_3

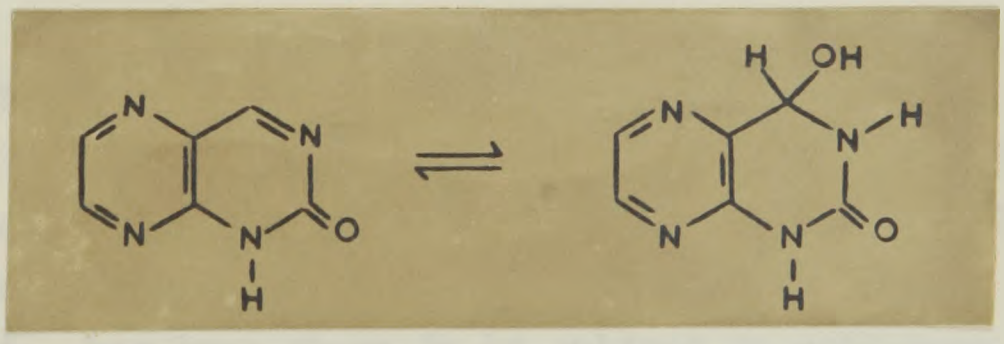
$$k_{32} = k_{32}^{\circ} + k_{32}[H^+] + k_{32}\,C_1 + k_{32}\,C_s$$

where $C_s = C_2 + C_3$ and $C_4 \doteq 0$.

They found the above rate dependence and measured the individual rate constants.

Later work by Strehlow (1962)[31] on pyruvic acid by a pressure-jump relaxation method gave results in good agreement with the earlier work. Some qualitative results were obtained for other ketocarboxylic acids.

Finally, Inoue and Perrin (1962)[32] studied the reversible hydration of 2-hydroxypteridine. This system is exactly analogous to a carbonyl compound with a C = N group replacing the C = O group.



This reaction is subject to general acid-base catalysis. The mechanisms proposed for this reaction are analogous to those for acetaldehyde.

Other Related Reactions.

Carbon Dioxide: Many workers have studied the kinetics of the hydration of carbon dioxide. The early work has been reviewed by Edsall and Wyman (1958)[33] and will not be discussed in detail here.

Eigen, Kustin and Maass (1961)[34] formulated the system:

$$1 \qquad H^+ + HCO_3^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} H_2CO_3 \qquad 2$$

$$k_{13} \quad \Big\uparrow\downarrow k_{31} \qquad k_{23} \Big\uparrow\downarrow \quad k_{32}$$

$$H_2O + CO_2$$

$$3$$

pointing out that the classical formulation:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

was based on an assumed mechanism for which there was no experimental support.

The hydration velocity constant k'_{31}, where $k'_{31} = k_{31} + k_{32}$ was measured by a temperature jump method. Their results are in good agreement with the later work of Ho and Sturtevant (1963)[35] and Gibbons and Edsall (1963)[36] both of whom investigated the system by spectrophotometric stopped-flow techniques.

Above pH 7 hydration also takes place by the reaction:

$$CO_2 + OH^- \rightleftharpoons HCO_3^-$$

Pinsent, Pearson and Roughton (1956)[37] using a rapid thermal method and Sirs (1958)[38] using a stopped-flow conductivity method have produced concordant kinetic results for this reaction. Values of k'_{31} must be corrected for this reaction.

k'_{31} has been shown to be subject to acid-base catalysis by various workers e.g. [39]. Kiese and Hastings (1940)[40] found that a number of ions of weak acids e.g. selenite, arsenite tellurate etc. possess high catalytic powers but no general correlation between ionisation constant and catalytic power was found. Sharma and Danckwerts (1962)[41] have extended this work investigating 25 different catalysts. The 10 anions which had a negatively-charged oxygen atom and

at least one hydroxyl group attached to the same central atom and in which the negative charge is not delocalised formed a single group which obeyed the Brönsted relationship. The other anions were in general weaker catalysts for a given pK. Their results are shown in Figure 1. They also found a variation of the observed catalytic constant with pH for some of the ions studied, see Table 4 below:

TABLE 4

pH =	6.9	7.55	9.0	10.0
		k_B values		
sulphite	2.18	2.3	2.57	0.41
selenite	11.5	15.1	2.63	0.52
hypochlorite	7.45	10.3	13.5	13.5
hypobromite	2680	2020	720	190

They accounted for this effect in terms of the hydration of the ion varying with pH.

Sulphur Dioxide: Eigen, Kustin and Maass[34] evaluated all the rate constants for the scheme:

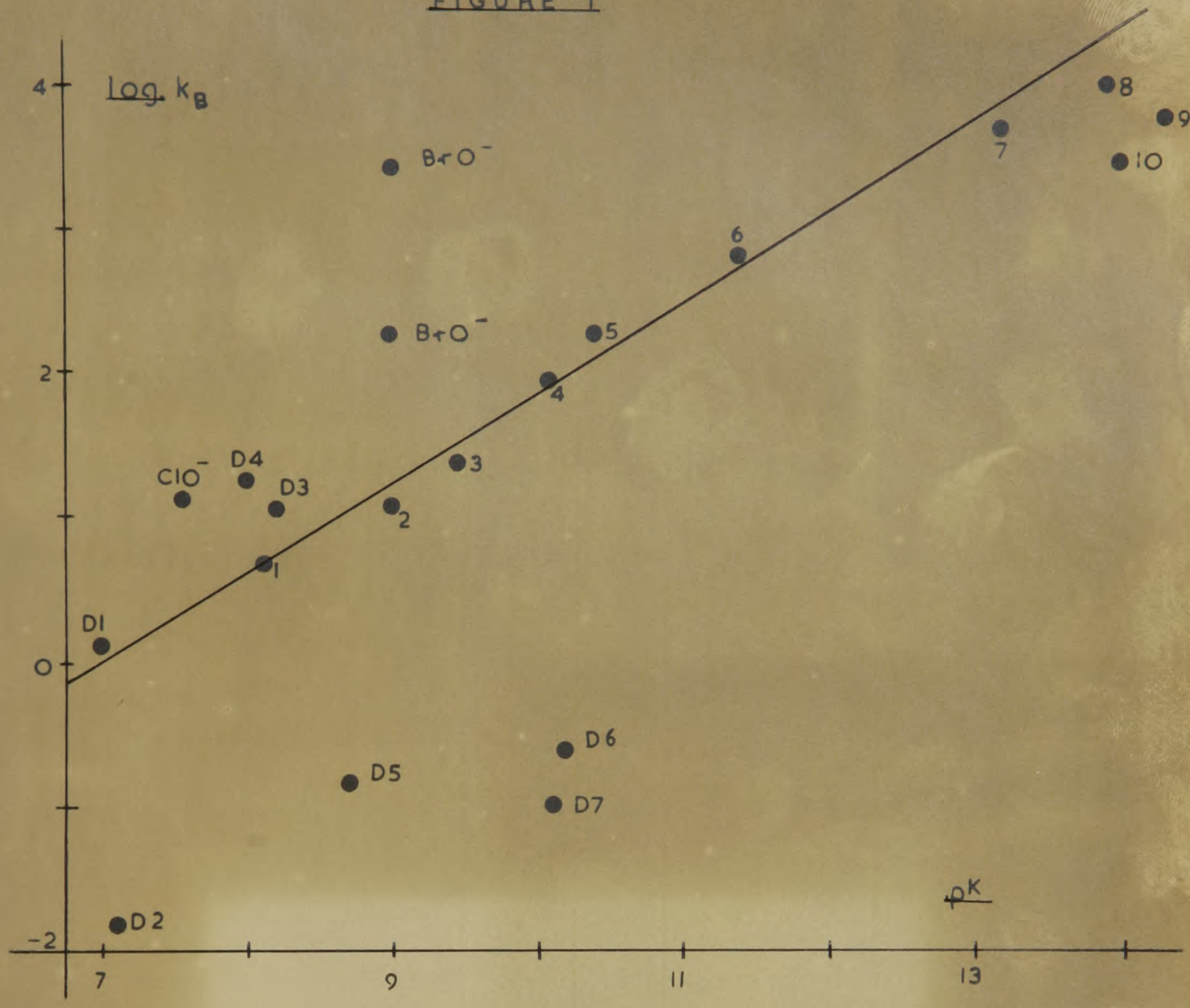
$$H^+ + HSO_3^- \rightleftharpoons H_2SO_3$$
$$\rightleftharpoons \qquad \rightleftharpoons$$
$$SO_2 + H_2O$$

by a temperature-jump method and showed that the dehydration and hydration reactions are much faster than those for carbon dioxide.

The Brönsted Relationships.

All these reactions show general acid-base catalysis and where several catalysts have been investigated they usually obey the classical Brönsted relationships.[42] Written in general terms these are:

FIGURE 1



1. telluric acid
2. germanic acid
3. arsenious acid
4. silic acid
5. chloral hydrate
6. butyl chloral hydrate
7. glyoxal hydrate
8. formaldehyde hydrate
9. acetaldehyde hydrate
10. diacetyl hydrate

D1 sulphite
D2 hydrogen phosphate
D3 selenite
D4 tellurite
D5 phenylarsonate
D6 phenolate
D7 carbonate

also hypobromous and hypochlorous acids shown on figure.

$$k_A/\underline{p} = G_A(\underline{q}K/\underline{p})^{\alpha} \qquad k_B/\underline{q} = G_B(\underline{p}/\underline{q}K)^{\beta}$$

where $0 < \alpha, \beta < 1$

k_A and k_B are the catalytic constants for acidic and basic catalysis and K is the conventional strength of the acid A of the acid-base pair A-B in which A has $\underline{p}$ dissociable protons bound equally firmly to p different atoms and B has $\underline{q}$ equivalent recombination points for the proton. G_A, G_B α and β are constants for a similar series of catalysts, but depend on the nature of the reaction, the solvent and the temperature. These empirical relationships have been rationalised in terms of free energy changes and molecular potential energy curves.[43] Deviations from these relationships due to mesomeric and steric effects are well characterised in many reactions and will be discussed later in this work.

Pedersen (1934)[44] considered the effect of charge on the catalytic power of a species. He produced a set of rules based on arguments concerning the various interactions in a catalytic system, e.g. the relative abilities of charged and uncharged bases to accept a proton and the resulting conjugate acids to lose the proton gained. For base catalysis he concluded that if β (the Brönsted exponent) was sufficiently great (and invariably if $\beta > \frac{1}{2}$) the base having the greater number of positive charges would be the more effective catalyst. Conversely if β was small the greater the number of positive charges the less effective the catalyst. Similar rules were deduced for acid catalysis.

The significance of the statistical factors has recently been discussed by Benson (1958)[45] (1960)[7] he points out that if we compare the free energy changes in a series of similar reactions and interpret the results in terms of molecular structure, we must eliminate accidental symmetry changes. He modifies the Brönsted equations so that:

$$\frac{k_A}{K_{\sigma_A\#}} = G_A \left(\frac{K_A}{K_{\sigma_A}}\right)^{\alpha} \qquad \frac{k_B}{K_{\sigma_B\#}} = G_B \left(\frac{K_B}{K_{\sigma_B}}\right)^{\beta}$$

where K_σ and $K_\sigma\#$ are the ratios of symmetry numbers for the reactant and product species in equilibrium and chemical reaction. These symmetry corrections are those used in statistical mechanics.

Gold (1964)[46] shows that this procedure will lead to an erroneous value if optical isomers are involved in the transition state. He assigns a symmetry number $\frac{1}{2}$ to substances which are an unresolved mixture of enantiomers.

The interpretation of the classical Brönsted relationships has recently been extended by Eigen (1963)[47]. He shows that the equations are the first terms of a Taylor or MacLauren approximation:

$$\log k = f\left[\triangle pK\right] \doteq f(\triangle pK = 0) + \alpha \triangle pK$$

where k is the rate of reaction for two species with pKs differing by $\triangle$pK. Eigen suggests that one might expect the slope of the Brönsted plot α or β, to vary from 0 to 1. Considering a species HA he points out that with strong bases the reaction may be diffusion controlled in which case the pK of the base is of no account and a Brönsted plot would yield a coefficient of 0 with a scatter due to varying diffusion coefficients. On the other hand if HA is transferring a proton to species which are considerably stronger acids than it is then the back reactions will be diffusion controlled and will yield a coefficient of 0; therefore the forward reactions must have a coefficient of 1 apart from the scatter caused by steric and diffusion effects. Between these extreme cases the coefficient can have intermediate values, which over a plot of several pK units might give a scattered straight line. Eigen lists several reactions which fit such a scheme, e.g. in the base-catalysed halogenation of ketones, Bell and co-workers[43] have measured the coefficients of the Brönsted plots for 11 different ketones as the pK of the ketone falls from 20 to 8.3 the coefficient falls regularly from 0.88 to 0.42.

Eigen also mentions a special group of reactions which give better Brönsted plots than expected e.g. the mutarotation of glucose, hydration of acetaldehyde etc. He promised to discuss these reactions in a future paper, so far not forthcoming.

Aims of this work.

1. To produce a direct method enabling the kinetics of the dehydration of formaldehyde to be investigated thus providing a check on the polarographic data.
2. To carry out with formaldehyde a classical Brönsted catalysis treatment using the traditional carboxylic acids etc.
3. To extend the above to cover catalysts of the type used by Sharma and Danckwerts in the hydration of carbon dioxide.
4. To use the above results to test the range of validity of the Brönsted relationships.
5. To investigate any other aldehydes and ketones which might prove accessible with any of the techniques evolved in the main work on formaldehyde.

FORMALDEHYDE (1) Gas Flow.

Bieber and Trümpler[19] in conjunction with their polarographic studies on formaldehyde also carried out a "direct demonstration" of the influence of pH on the dehydration rate of methylene glycol. This was done by employing the dynamic procedure developed by Ledbury and Blair (1925)[48] for measuring formaldehyde partial pressures which involved measurement of the formaldehyde content of an inert gas after passage through a scrubber filled with formaldehyde solution. The rate at which formaldehyde is removed by the gas stream being proportional to the formaldehyde partial pressure under equilibrium conditions. They found that as the rate of gas flow was increased solutions of identical concentration but varying pH showed different values for the rate of CH_2O removal and these were proportional to the variation of the limiting currents with pH as measured by the polarograph. A photostat of their results, the graph, is shown opposite.

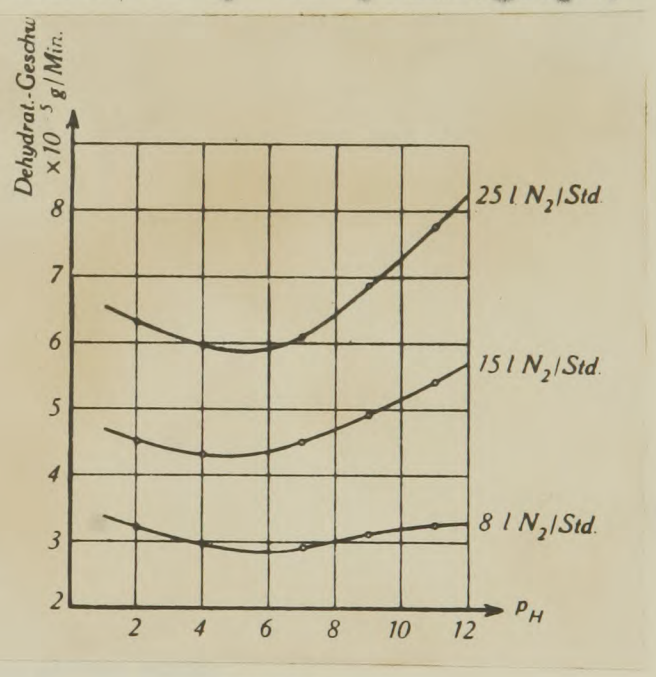


FIGURE 2.

These observations were interpreted in terms of a breakdown of equilibrium conditions at high scrubbing rates, the formaldehyde removal then being determined by the rate of dehydration of the methylene glycol,

i.e. $H_2C(OH)_2 \rightleftharpoons H_2C{=}O + H_2O$

involatile volatile

Their results found support in the original work of Ledbury and Blair who were unable to get satisfactory partial pressure values for formaldehyde solutions at low temperatures with scrubbing rates that had proved satisfactory at ordinary temperatures. Boyd and Logan (1945)[49] in their work on the estimation of free formaldehyde in biological samples by diffusion from the sample to a membrane containing phenylhydrazine solution also found some variation of the rate of diffusion with the pH of the sample. They, however, interpreted their results in terms of the rate of change of the depolymerisation rate of formaldehyde with pH.

In the light of the above work it was hoped to develop one of these gas-flow methods for a quantitative study of the kinetics of the formaldehyde dehydration reaction. To this end the following mathematical analysis was carried out.

Mathematical treatment.

Treating the simplest case, the following equations may be set up:

$$\underset{c(\text{const.})}{H_2C(OH)_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_2O + H_2O$$

$$\underset{x}{CH_2O(\text{aq.})} \overset{K\ \text{equilium}}{\rightleftharpoons} CH_2O(\text{vapour}) \longrightarrow \text{Lost to Gas Stream}$$

Now if v = rate of gas stream in litres/sec.

and V = volume of solution in litres.

we may write:

$$\frac{dx}{dt} = k_1 c - k_{-1} x - \frac{Kv}{V} x$$

Making the steady state assumption and rearranging:

$$x = \frac{k_1 c}{k_{-1} + K\frac{V}{V}}$$

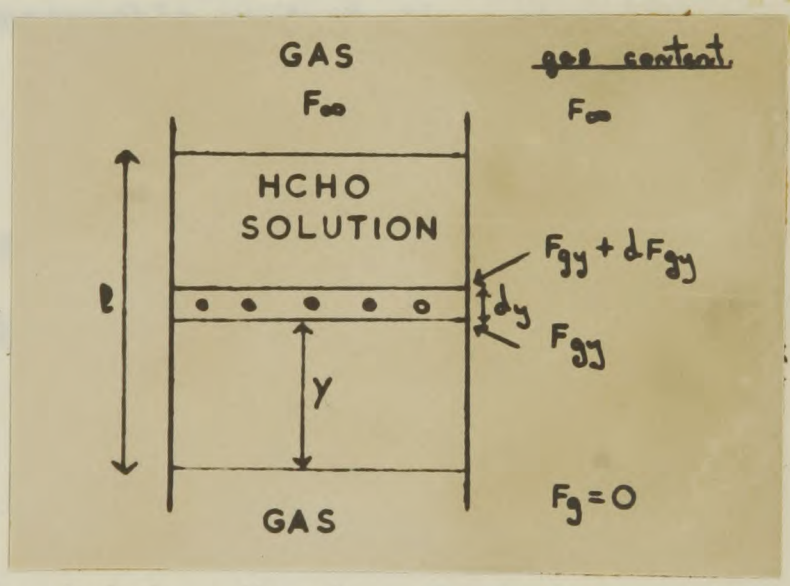
Now as $v \longrightarrow 0$ $\quad x \longrightarrow \frac{k_1 c}{k_{-1}}$

$v \longrightarrow \infty$ $\quad x \longrightarrow 0$

For a reasonable perturbation giving conditions suitable for kinetic measurements k_{-1} must be of comparable magnitude to $K\frac{V}{V}$

i.e. $k_{-1} \approx K\frac{V}{V}$

One can also treat the system in which the bubbles enter the formaldehyde solution with zero formaldehyde content and becomes progressively more concentrated as they pass through the solution attaining complete equilibrium before leaving.



Tube containing the formaldehyde solution.
Cross sectional area = A
Depth = l
Bubbles at height y from entry point on model.

Setting up the same equations as before:

F hydrate $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ F aq. + H_2O
c. const. x_y

F aq. $\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$ F gaseous
F_{gy}

From these two equations may be set up:

$$\frac{dx_y}{dt} = k_1 c + k_{-1} x_y - k_2 x_y - k_{-2} F_{gy}$$

and $$\frac{dF_{gy}}{dt} = k_2 x_y - k_{-2} F_{gy} - \frac{dF_{gy}}{dy} \times \frac{v}{A}$$

where v is the velocity of the gas stream i.e. the bubbles. Applying the steady state assumption, expanding and integrating for F_{gy} one obtains:

$$1 - \frac{F_\infty}{F_{eq}} = e^{-\frac{V}{v}\,\frac{k_{-1}\,k_{-2}}{k_{-1} + k_2}}$$

where $F_{eq} = \frac{k_1 k_2 c}{k_{-1}\,k_{-2}}$

and $V = A\ell$

Now for a reasonable perturbation of equilibrium conditions:

$$\frac{k_{-1}\,k_{-2}}{k_{-1} + k_2}\ \frac{V}{v} \quad \approx \quad 1$$

and for useful kinetic results, i.e. diffusion steps fast, $k_2 \gg k_{-1}$ and expression reduces to that obtained from the other treatment

$$k_{-1} \approx \frac{k_2}{k_{-2}} \cdot \frac{v}{V} \approx K\frac{v}{V}$$

Substituting numerical values in this expression:

From Ledbury and Blair:[48]

$K \simeq 10^{-1}$ with $K_d = 10^{-4}$

and $K \simeq 10^{-2}$ with $K_d = 10^{-3}$

These Kd values represent the extreme values given in the literature (see Table 2, page 5).

Taking values of $k_1 = k_o$ i.e. the most favourable conditions for a kinetic perturbation, one can calculate values of k_{-1}/K. This is done in Table 5 in which the K&ko value is from Brdicka's polarographic work and the other value is that obtained later in this present work.

TABLE 5

	Kd = 10^{-4}		Kd = 10^{-3}	
	k_{-1}	k_{-1}/K	k_{-1}	k_{-1}/K
$K_1 k_o = 1 \times 10^{-5}$	1000	10,000	10	1000
$k_o = 5 \times 10^{-3}$	50	500	5	500

If one takes the values in the bottom line, for a reasonable perturbation $\frac{v}{V} \approx 500$. Thus if the volume of solution V is 1 cc one requires 1800 litres/hour of gas streaming through it to provide useful kinetic results. In the light of these calculations experiments were carried out to repeat Bieber and Trümpler's work.

Experimental.

1. Chemicals and Basic Analytical Techniques.

Formaldehyde: B.D.H. ANALAR formaldehyde solution, containing about 37% w/v. formaldehyde, was used without further purification. Formaldehyde concentrations were estimated by the sodium sulphite method[50] in which excess sodium sulphite is added to the formaldehyde sample and the liberated caustic soda titrated with acid.

$$CH_2O + Na_2SO_3 + H_2O \longrightarrow NaOH + CH_2(NaSO_3)OH$$

Nitrogen: British Oxygen Company cylinders.

Acids and Bases: All were ANALAR grade unless a note is added to the contrary.

Sodium hydroxide solutions of the required strength were prepared by washing ANALAR pellets with distilled water. The solutions were protected from the atmosphere with soda-lime tubes.

All acids and bases were standardised against constant boiling-point hydrochloric acid. Occasional cross checks of standard solutions against potassium hydrogen phthalate gave good concordant results.

2. Apparatus.

Volumetric apparatus was standardised by weighing the volume of water delivered at room temperature. All thermometers were standardised against a standard N.P.L. thermometer calibrated for the range used.

3. Gas Flow Experiments.

These experiments were very similar to those carried out by Bieber and Trümpler i.e. a stream of nitrogen saturated with water vapour was bubbled through a solution of formaldehyde of known concentration and the formaldehyde content of the emergent gas stream determined. The solutions of formaldehyde were made up in buffers of varying pHs, and for each buffer experiments were carried out at several flow-rates.

A schematic diagram of the apparatus is shown in Figure 3. The flow of nitrogen from a cylinder was controlled by a needle-valve (1), two large vessels (2) (total capacity 25 litres) served to buffer fluctuations in the flow-rate. A constant flow-rate throughout the apparatus was ensured by holding the water level steady in an open-ended water manometer (3) by means of the needle-valve (1). This manometer consisted of a 10 ft. high outer tube filled with water into which was placed a narrow bore inner tube which was connected to the flow system. An open-ended mercury U-tube manometer (4) was also included in the apparatus.

The main-part of the apparatus was housed in a thermostat tank held at 25.0 ± 0.05°C by a mercury toluene regulator. A series of wash-bottles (6) filled with water served to saturate the gas stream with water vapour. The weight of water/litre of gas, determined by measuring the increase in weight on passing the gas through calcium chloride tubes, compared favourably with that calculated from the known saturated vapour pressure of water.

Various types of bubbling systems were tried. The most satisfactory system was found to be the simplest, with the gas stream entering the solution of formaldehyde held in a test-tube from a narrow bore tube.

Sintered glass bubbling systems gave different flow patterns of the gas through the liquid from one experiment to the next, even though the flow rate was maintained at a constant level. This could be observed visually and was probably due to surface tension effects in the sinters. The result of these changes in flow pattern was to give completely unreproducible results for the apparatus.

The gas from the bubbler passed through two vessels filled with glass wool (8) to remove formaldehyde spray. Three absorption bottles (10) each containing a 1% solution of bisulphite removed any formaldehyde present in the gas stream. The gas leaving the last vessel was collected over water in a reservoir (25 litres capacity) (11). The outlet from this reservoir incorporated a constant head device, the levels in the reservoir and outlet being kept at the same level manually. The liquid displaced by the gas was collected and its volume measured.

Pattern of a Run: 5 cc. of buffer solution, 1 m in formaldehyde, were put in the bubbler. The barometric pressure was read. The values on the nitrogen cylinder were opened and the level of gas in the water manometer taken down to a calculated level to give a flow-rate in the required range. The run was timed from the first appearance of bubbles in the final reservoir. During the run the flow-rate was maintained

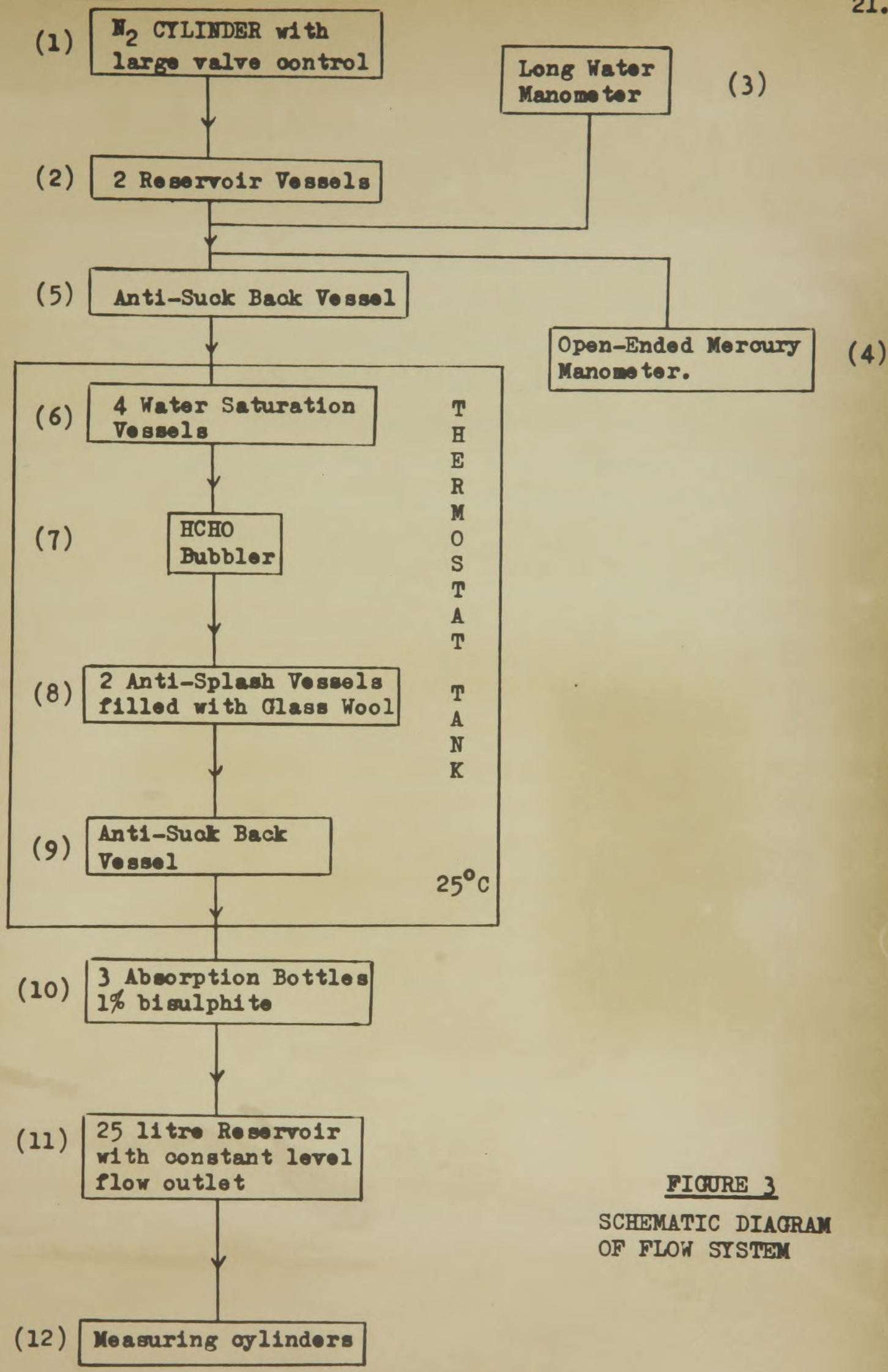


FIGURE 3

SCHEMATIC DIAGRAM OF FLOW SYSTEM

constant with the needle valve and constant-head device continually adjusted to eliminate back pressures.

After a suitable time interval (5 - 20 mins.) the run was terminated by cutting off the gas supply at the "oxygen head" on the nitrogen cylinder. An almost instantaneous cut-off of the gas stream was obtained by taking off all the bottle tops in sequence starting from the one nearest the reservoir and ending with the last water saturation bottle. This procedure eliminated any possible suck-backs between vessels. The anti-suck back vessels were checked for absence of liquid. The average flow-rate during the run was computed from the volume of liquid displaced from the final reservoir and the time of the run.

Analysis: The 1% sodium bisulphite solutions from the scrubbers were analysed for their formaldehyde content using the method of Goldman and Yagoda (1943)[51]. In this method the unreacted bisulphite is destroyed with iodine, the resulting solution is made mildly alkaline and the bisulphite compound is then titrated with iodine. They claim that this method will estimate 1 mg. of formaldehyde in 10 ml. of solution with an accuracy of 1%. This method was checked with standard solutions of formaldehyde before use and shown to give satisfactory results. In all experiments the last absorption bottle contained no formaldehyde, virtually all the formaldehyde content of the gas stream being absorbed by the first absorption vessel.

Results.

pH 1: made up by diluting hydrochloric acid solution

Flow Rate (litres/hour)	8.0	26.0	27.4	29.9	40.8
mg. HCHO/hour	28.5	77.5	83.4	89.2	123

pH 2: made up by diluting hydrochloric acid solution

Flow Rate	7.6	15.3	16.3	22.8	29.8	45.6
mg. HCHO/hour	19.4	40.9	49.6	69.3	93.8	138

pH 3.6: saturated potassium hydrogen tartrate solution

Flow Rate	11.8	24.1	32.0	42.8
mg. HCHO/hour	34.7	63.2	90.3	126

pH 8.5: sodium carbonate buffer as used in analytical technique*

Flow Rate	14.0	26.0	31.0	37.2	40.6	49.0
mg. HCHO/hour	37.5	79.7	100	114	127	142

The results for pH 2 are shown in Fig.4 below.

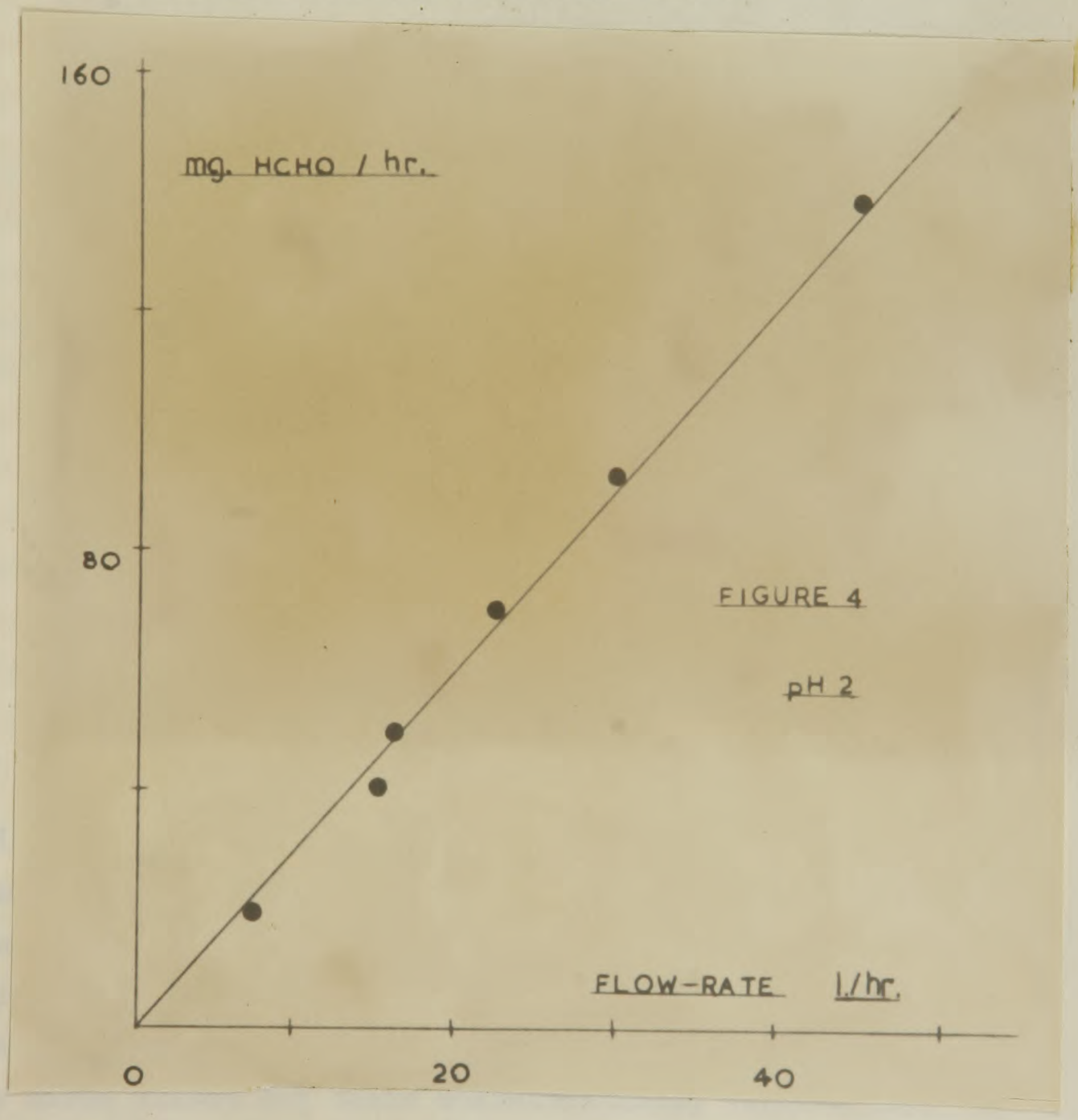


FIGURE 4

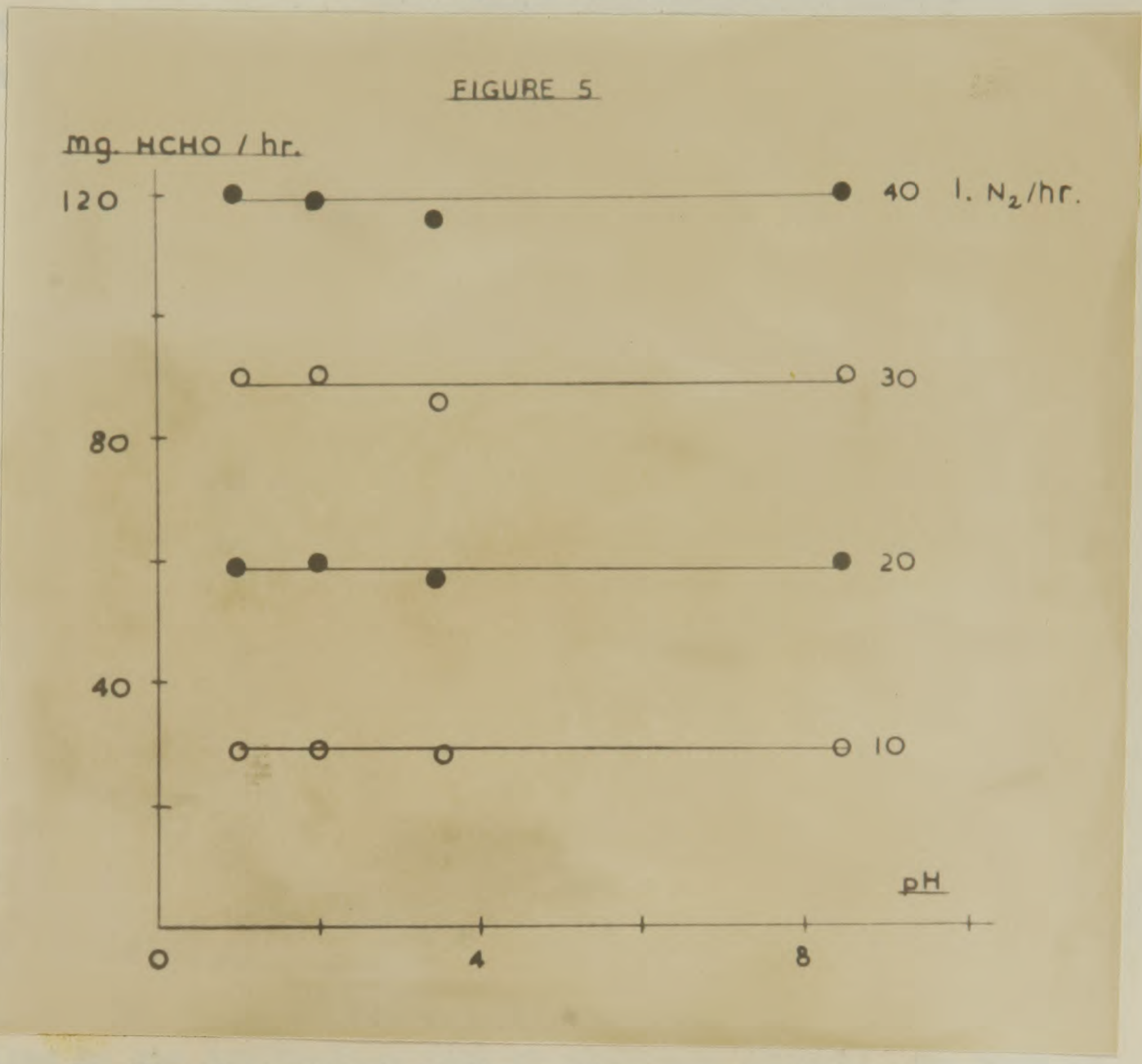
pH 2

* 180 gm Na_2CO_3 to 500 ml water + 20 ml glacial acetic acid. This was diluted by a factor of 10.

Discussion.

The results of the present work are graphed out in the same form as those of Bieber and Trümpler in Figure 5.

FIGURE 5



In direct contrast to the earlier work virtually no variation of the rate of formaldehyde loss with pHis detectable. This is in accord with the mathematical predictions. It would seem from these results that Bieber and Trümpler are either measuring some diffusion effect or the effect of the depolymerisation reaction. A more objective appraisal of their work would have been possible had they given values for their concentrations, volumes etc. The major conclusion for the present work was that no simple gas-flow technique could provide kinetic data for the formaldehyde dehydration reaction.

FORMALDEHYDE (2): Scavenger experiments.

After the failure of the gas flow experiments to provide kinetic data alternative methods were investigated. A scavenging technique in which the reaction scheme set out below was produced appeared to give a simple method of studying the desired kinetics:

$$H_2C(OH)(OH) \overset{\text{slow}}{\rightleftharpoons} HCHO + H_2O$$

$$HCHO + \text{scavenger} \xrightarrow{\text{fast}} \text{adduct}$$

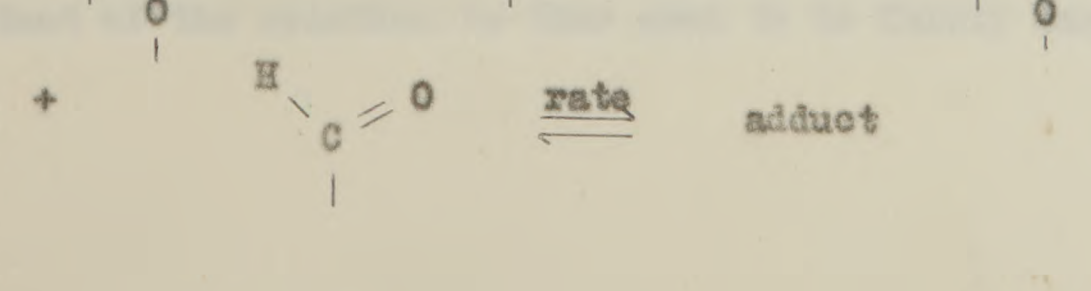
Qualitative preliminary experiments with phenylhydrazine hydroxylamine and semicarbazide hydrochloride showed that all these substances reacted with formaldehyde according to the above scheme giving adducts whose formation could be easily detected and followed by the appearance of their ultra-violet absorption bands. The reaction of formaldehyde with sulphite also conformed to the same pattern:

$$CH_2O + Na_2SO_3 + H_2O \rightleftharpoons NaOH + CH_2(NaSO_3)OH$$

the hydroxide produced being followed by titration on an automatic titrator.

Further credence to the proposed scheme was given by the work of Crowe and Lynch (1949)[52] on the kinetics of the urea-formaldehyde reaction. They found that the rate of this reaction was partially controlled by the dehydration rate of methylene glycol; the rate of anion formation of urea being the other rate-determining process.

A very similar reaction scheme to the present one was evoked by Haas and Kadunce (1962)[53] in their work on the formation of aldose oxime, semicarbazone and hydrazone. Under certain conditions the rate of production of the carbonyl compound was rate-determining.

i.e. 

Ultraviolet Techniques.

Many workers have investigated the formation of compounds of the hydrazone and oxime types. The relevant papers to this present work are summarised below:

Conant and Bartlett (1932)[54] evaluated equilibrium constants, rates of formation and rates of hydrolysis for a number of semicarbazide reactions. They found that the value of the equilibrium constant was markedly affected by acidity since the semicarbazide and semicarbazone were both bases. If the acidity constants of semicarbazide BNH_2 and semicarbazone ANB were defined by the equations:

$$K_R = \frac{[BNH_2][OH_3^+]}{[BNH_3^+]} \qquad K_c = \frac{[ANB][OH_3^+]}{[ANBH^+]}$$

and the true equilibrium constant for the semicarbazone formation:

$$K_o = \frac{[ANB]}{[AO][BNH_2]}$$

the apparent constant K was given by

$$K = K_o \frac{1 + \frac{[OH_3^+]}{K_c}}{1 + \frac{[OH_3^+]}{K_R}}$$

Thus at low acidities $K = K_o$ and at high ones it reached the smaller value of K_oK_R/K_c. The values obtained for acetaldehyde semicarbazone are given below.

	$10^{-3}K_o$	K_c	10^3K_R	K_oK_R/K_c
Acetaldehyde semicarbazone	48	0.078	0.22	135

The extent of the reaction is thus seen to be fairly large even in acid

solution. Unfortunately no results were obtained for formaldehyde semicarbazone.

Their kinetic studies of these reactions showed that they were subject to general acid catalysis, the rate equations for the formation reaction being of the form:

$$\text{Rate} = k\,[AO]\,[BNH_2] \sum k_1\,[HA]$$

The rate data thus exhibited a striking maxima in their pH-rate profile, attributable to the opposing effects of general acid catalysis and the decrease in concentration of the attacking free nitrogen base due to its conversion to the confugate acid at low pH.

Stempel and Schaffel (1944)[55] compared the kinetics and mechanism of the formation of the phenylhydrazone, semicarbazone and oxims of d-carvone and concluded that the three reactions proceeded by the same mechanism.

Jencks (1959)[56] showed that at neutral pHs hydroxylamine and semicarbazide react rapidly with a numberof aldehydes and ketones to form addition compounds which lack the ultra-violet absorption of the original carbonyl compound. These compounds then undergo slow acid-catalysed dehydration to form the oxime or semicarbazone,

$$\text{C=O} + H_2NR \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{C}\begin{matrix}\text{OH}\\ \text{NHR}\end{matrix} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{C=NR} + HOH$$

He concluded that the decrease in the rate of oxime formation at acid pH was due to a transition to a rate-limiting attack of free nitrogen base on the carbonyl compound and was not dependent on general acid catalysis. Dehydrationof the addition complex, addition of water to the oxime or semicarbazone and addition of semicarbazide to the carbonyl group were subject to both specific and general acid catalysis, while the addition of the stronger base, hydroxylamine, to the carbonyl group is specific and catalysed to only a small extent.

Further papers by Jencks and co-workers include the following: Anderson and Jencks (1960)[57]. They investigated the effect of structure, in a series of substituted benzaldehydes, on reactivity in semicarbazone formation. In a discussion of base catalysis in semicarbazone formation, they concluded that this would only be of importance with carbonyl compounds containing strongly electron-withdrawing groups. The oxime reaction would be more susceptible to base-catalysis, but the results so far obtained indicated a higher susceptibility to acid-catalysis.

Cordes and Jencks (1962)[58] showed nucleophilic catalysis in semicarbazone formation. Aniline and several of its derivatives were shown to be much better catalysts than predicted from their pK values. The following reaction sequence was postulated:

$$>C=O + ArNH_2 \xrightarrow{\text{slow}} >C=N-Ar + H_2O$$

$$>C=N-Ar + NH_2NHCONH_2 \xrightarrow{\text{fast}} >C=NNHCONH_2 + ArNH_2$$

The same authors (1962)[59] investigated general acid catalysis in the first stage of semicarbazone formation. For p-chlorobenzaldehyde the Brönsted plot was extended to cover 30 acids of varying structure and charge type.

Present Work.

In the light of the above review the full reaction sequence for the formation of formaldehyde oxime, hydrazone etc. is as shown below, the formation of the oxime being given in the example.

$$H_2C(OH)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HCHO + H_2O \qquad (1)$$

$$NH_3{}^+OH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NH_2OH + H^+ \qquad (2)$$

$$HCHO + NH_2OH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} H_2C\begin{matrix}\diagup OH \\ \diagdown NHOH\end{matrix} \qquad (3)$$

$$H_2C = NOH \qquad (4)$$

For satisfactory kinetic results for the formaldehyde dehydration step (1) the final two stages of this scheme (3) and (4) must go to completion at a rate fast in comparison to the rate of the formaldehyde dehydration reaction. The work of Conant and Bartlett has shown that the position of equilibrium is likely to be very much in favour of the final product. The last two stages of the scheme appear to define an approximate 'useful kinetic' upper and lower pH limit for any scavenger. Within the intermediate range one might expect steps (3) and (4) to be fast enough to play no part in the observed kinetics. At acid pH's step (3) becomes rate determining due to the decreasing concentration of the reactive species and at near neutral pHs the final step (4) would be the rate stage. The object of the early experimental work was to investigate the various scavengers available determining the range of pH over which they could be used and any other factors pertinent to their suitability for use in a more detailed study of the reaction under catalysis by external buffers.

Experimental.

Spectrophotometric apparatus: Two instruments were employed. A Perkin Elmer Spectracord was used when a complete absorption curve of a sample was required. This is an automatic recording spectrophotometer giving a trace of percentage absorbance in the range 200 - 750 mμ.

All quantitative spectrophotometric measurements were made on a Unicam S.P. 500 spectrophotometer. This gives a direct reading of the sample's optical density (D) at any particular wavelength in the range 200 - 1000 mμ. The maker's claim an accuracy of ± 2% for individual readings. On kinetic runs, in which the increase in optical density at a set wavelength was recorded, electronic drifts in the apparatus were minimised and in any set of measurements substantially better than 2% accuracy was achieved. A copper block thermostat was incorporated in the apparatus giving temperature control to ± 0.05°C. The temperature of the block was checked before each set of measurements. All work in this section was at 25.0 ± 0.05°C. 1 cm. silica cells with glass stoppers were employed throughout.

Kinetic work: Buffer solutions of the scavengers were made up either by adding a calculated quantity of acid or alkali to the agent itself, or by titrating to a known pH on the automatic titrator (see next section, page 46). The spectra of the scavengers and their formaldehyde adducts were investigated on the Unicam and Spectracord. From these observations suitable wavelengths and concentrations were chosen for trial kinetic runs.

The method used throughout for Unicam kinetic measurements was to allow (2 cc) samples of the scavenger buffer solutions (the comparison cell and the reaction cell both containing the same solution) to thermally equilibrate in the cell block. The reaction was then initiated by the addition of a small quantity of the aldehyde (0.1 - 0.2 cc) from a calibrated Burroughs-Welcome Agla micro-syringe. After stirring in the block readings were commenced after 15 - 20 secs, taken every 20 secs and continued for about 3 half-lives. The reaction was

considered complete after 6 half-lives. Two methods of evaluating first-order rate constants from the observed data were employed:

1. The normal "infinity value" method.
2. The Guggenheim method.[60]

In cases where both methods were tried good agreement was obtained. Examples of typical first-order rate plots are given later in this section.

Results of Early Work.

Many experiments were carried out with possible scavengers. A selection of the results so obtained will be given with the review of each reagent later in this section.

General Results.

As envisaged each scavenger was of use over a limited range of pH. The limit at low pHs could be extended by increasing the concentration of scavenger. At these pHs below their acid limit scavengers gave lower observed first-order rate constants than expected i.e. if the rate equation was of the form $k_1 = k_o + k_{H^+}[H^+]$ a plot of k_1 against $[H^+]$ tended to fall off as $[H^+]$ was increased beyond the limiting pH. An extreme set of values are shown in Table 6 illustrating the point.

TABLE 6

$10^3[H^+]$	10^3[Semicarb.]	$10^3 k_1$
5.0	8.5	18.0
10.0	8.5	24.7
100	8.5	8.75

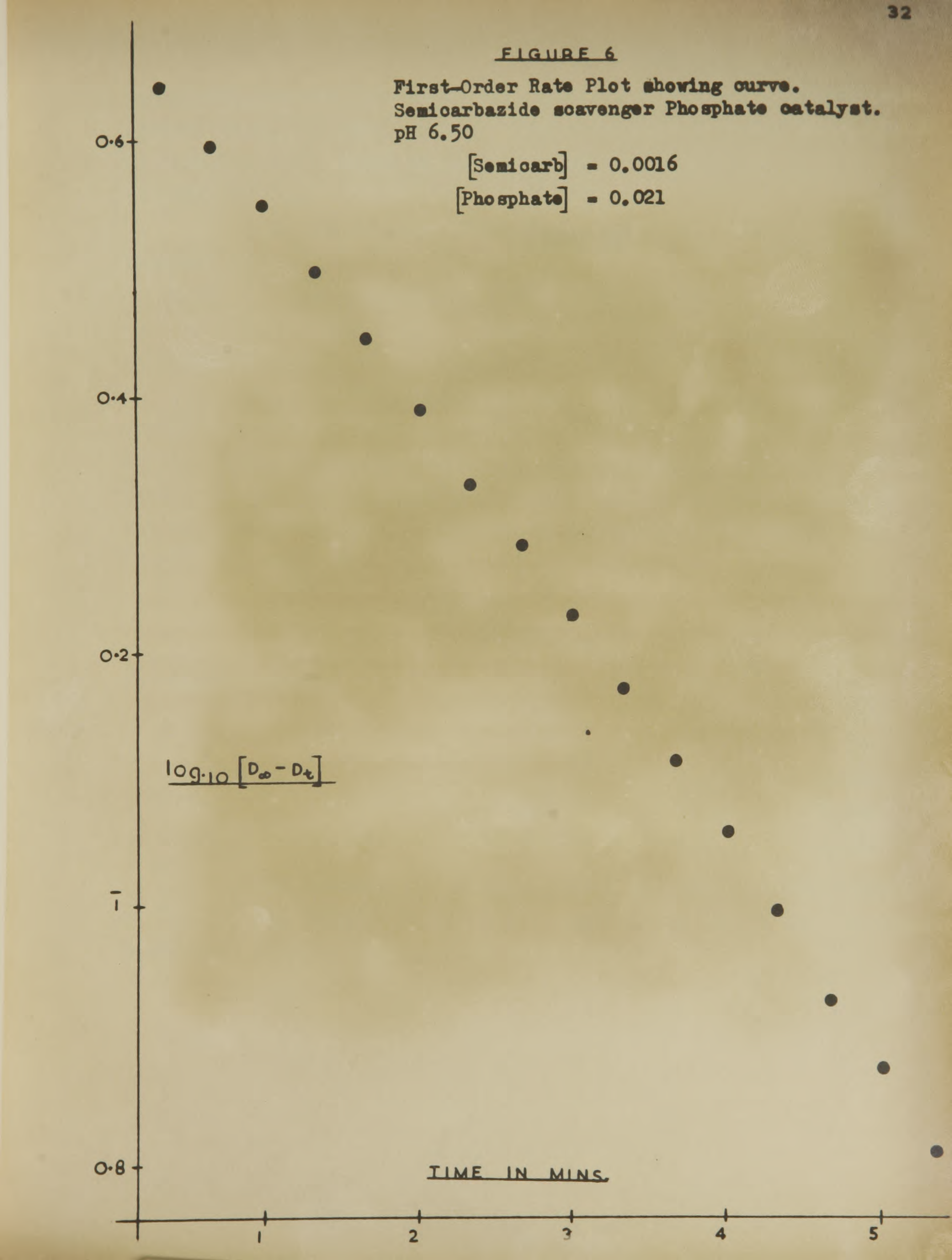
At near neutral pHs curved first-order rate plots were produced due to the final dehydration step playing a part in the observed kinetics, see Figure 6. Curved first-order rate plots were also caused by hydrogen ions produced during the reaction, the adduct species being less strongly

FIGURE 6

First-Order Rate Plot showing curve.
Semicarbazide scavenger Phosphate catalyst.
pH 6.50

[Semicarb] = 0.0016

[Phosphate] = 0.021



protonated than the scavenger, this could change the nature of species present in the reactant mixture. This complication was overcome either by working within the buffer range of the scavenger or by adding an external buffer.

Evidence was also obtained that the final two stages of the reaction scheme:

i.e. HCHO + scavenger $\rightleftharpoons$ final adduct

must go almost to completion. Reaction infinity values remained constant on varying the scavenger concentration which would not be so if the reaction was far from completion. Some examples of infinity values are given in Table 7. In any series of experiments as far as possible exactly the same amount of formaldehyde was added in each run, small variations in the observed infinity values are almost certainly due to experimental errors involved in delivering small samples of formaldehyde from the syringe.

TABLE 7

	$10^6[H^+]$ = 2.14	= 1.07	= 0.54
10^3 [Hydroxylamine]	D_∞	D_∞	D_∞
30.2	0.487	0.503	0.527
60.4	0.490	0.530	0.524
90.6	0.516	0.467	0.516
121	0.499	0.557	0.472
151	0.465	0.516	0.495

Other evidence for completeness of reaction and the validity of the reaction scheme was that under suitable conditions all scavengers tried gave the same value for the water rate k_o.

Review of Reagents.

Semicarbazide.

B.D.H. ANALAR semicarbazide hydrochloride

$K = 2.24 \times 10^{-4}$ (59)

Sketches of the spectra of the pure substance and its formaldehyde semicarbazone c.f. 61 are shown in Figure 7. The semicarbazone spectrum is taken from the final spectrum of a reaction mixture. Kinetic runs were followed either at 230 mμ with a formaldehyde concentration of ca. 5×10^{-5}m. or at 245 mμ with $[HCHO] \simeq 5 \times 10^{-4}$. Unless otherwise stated it may be assumed that the work was at 230 mμ. Infinity values remained constant over several hundred half-lives.

A series of fairly low concentration semicarbazide runs were carried out, the hydrogen ion concentrations in the solutions being calculated from the semicarbazide pK. These results are given in Table 8 and shown graphically in Figure 8. In the final column the observed first-order rate constants have been corrected for the small contribution from semicarbazide catalysis (see later results section, page 74).

TABLE 8

$10^3[H^+]$	10^3[Semicarb.]*	$10^3 k_1$	$10^3 k'_1$
0.57	2.0	6.7	6.6
0.84	4.0	7.7	7.5
0.95	4.9	8.1	7.8
1.38	9.8	9.4	8.8
1.55	10.0	10.3	9.8
1.96	10.0	11.6	11.0
2.65	9.7	13.0	12.4
3.04	9.7	14.4	13.8

* Throughout the rest of this work formulae in brackets denote the concentration of acidic or basic species given, names of substances however include both acidic and basic forms, e.g. $[Semicarb] = [NH_2CONHNH_2] + [NH_2CONHNH_3^+]$

From Figure 8

$$k_o = 5.2 \times 10^{-3}$$

$$k_{H^+} = 2.8$$

From these results and later work with external buffers it was shown that semicarbazide gave good results as a scavenger for the pH range 2.5 - 5.5. Its only disadvantage was that the position of the semicarbazone band was rather low in the ultra-violet range. Many other compounds e.g. aromatic compounds, absorb strongly in this region of the spectrum swamping out the sensitivity of the Unicam and making measurements impossible.

Hydroxylamine.

B.D.H. ANALAR hydroxylamine hydrochloride

$K = 1.07 \times 10^{-6}$ (62)

Hydroxylamine hydrochloride itself has virtually no absorption in the near ultra-violet. A trace of the adduct spectrum is shown in Figure 9. Unless otherwise stated experiments were followed at 225 mμ with initial formaldehyde concentrations of ca 2×10^{-3} M. All infinity values remained constant over very long periods. The results of two sets of titrator pH runs are given in Table 9.

TABLE 9

$10^2[NH_3{}^+OH]$*	$10^3 k_1$	
pH 5.00		
4.41	6.06	
13.3	8.12	Shown graphically
24.1	9.98	in Figure 11A.
36.5	12.5	Intercept = 5.3×10^{-3}
48.7	14.8	
pH 6.00		
1.38	5.60	
2.39	6.55	Plotted in Figure 11B
5.90	7.80	Intercept = 5.2×10^{-3}
8.60	9.16	
13.3	11.4	

* This has been calculated from the hydroxylamine concentration, pK and pH.

FIGURE 7

Sketches of Spectra.

I. Semicarbazide Hydrochloride.
II. Formaldehyde Semicarbazone.

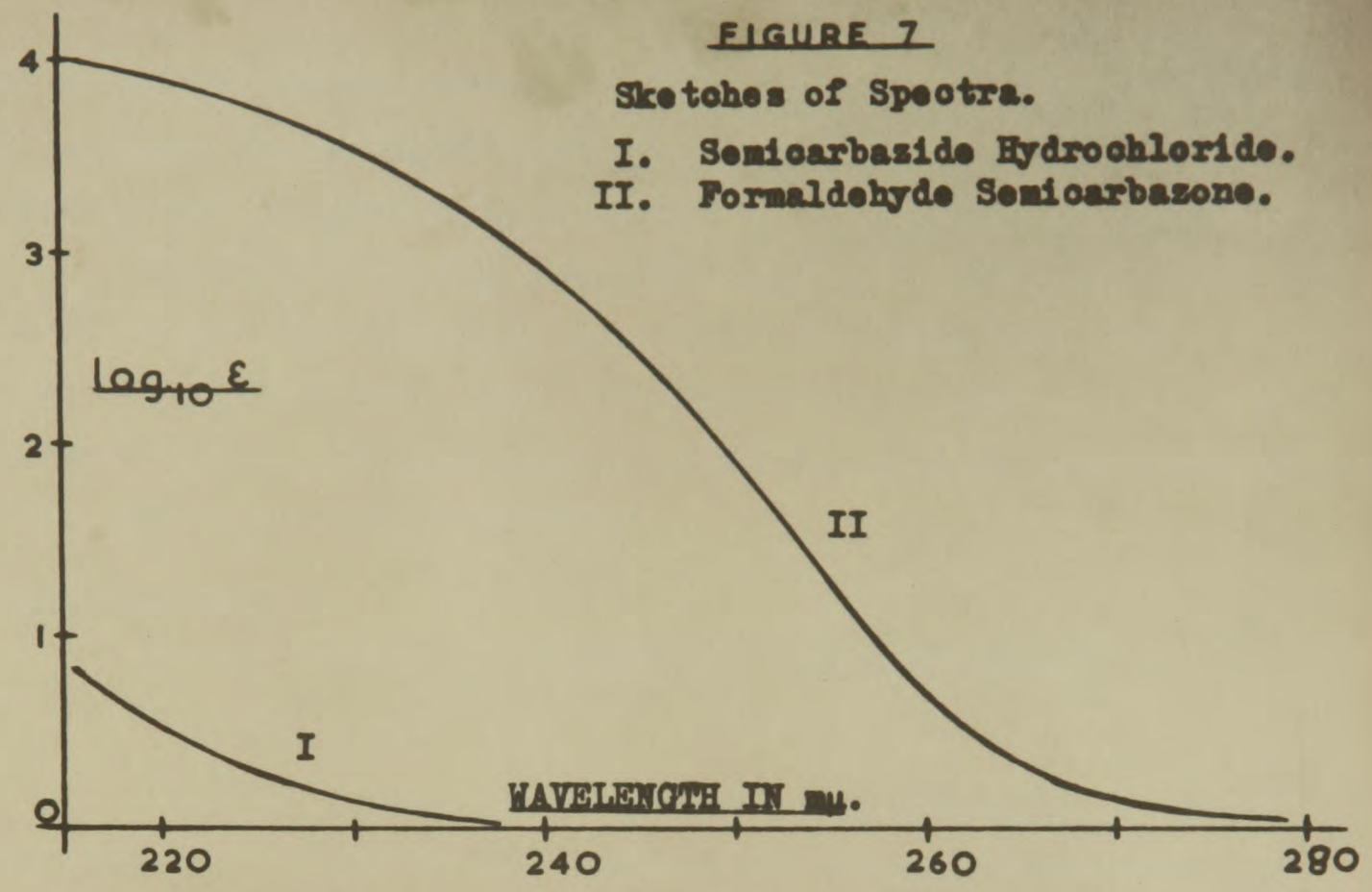
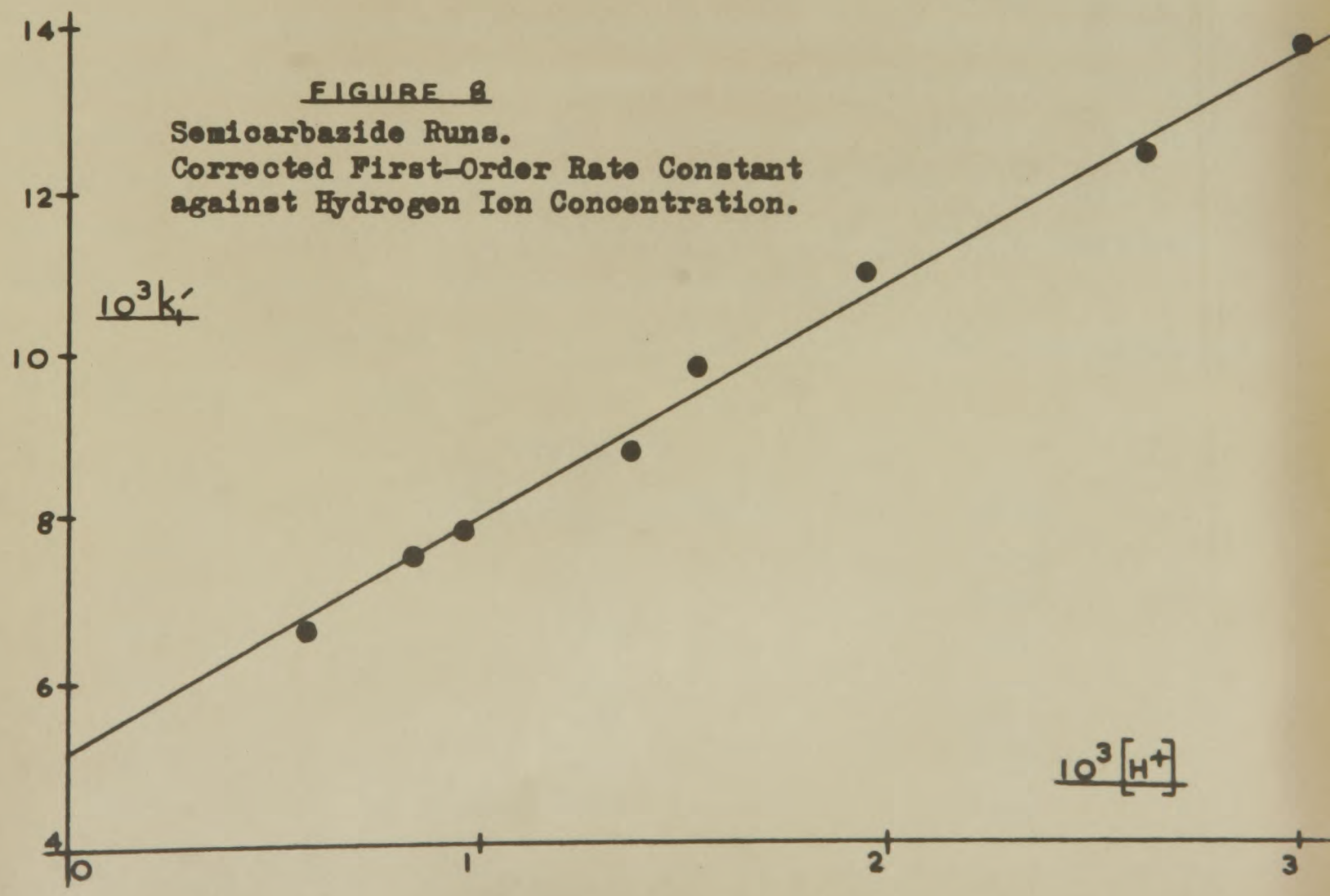


FIGURE 8

Semicarbazide Runs.
Corrected First-Order Rate Constant
against Hydrogen Ion Concentration.



These intercept values correspond to k_o values as any contribution from hydrogen ion catalysis will be negligible at the pHs used. These k_o results are in good agreement with those obtained for semicarbazide.

Hydroxylamine had a useful range as a scavenger from pH 4.5 - 6.5. Its disadvantages were that the oxime band was even lower down in the ultra-violet than the semicarbazone band and its intensity was rather low making much higher concentrations of scavenger necessary than in the semicarbazide system.

Phenylhydrazine.

B.D.H. ANALAR phenylhydrazine hydrochloride.

$K = 1.86 \times 10^{-6}$ (63)

Phenylhydrazine itself absorbs very strongly in the ultra-violet; a trace of the spectrum of its cation is shown in Figure 10 c.f. 67, as is the adduct band formed on adding a small amount of phenylhydrazine hydrochloride to a large excess of formaldehyde. This high phenylhydrazine absorption severely reduced the sensitivity of the Unicam, making accurate readings difficult. There appeared to be much overlap and too small a change of intensity in going from the original phenylhydrazine to the hydrazone band to provide a suitable wavelength for study, i.e. a wavelength at which the hydrazone absorbed strongly and the phenylhydrazine little. Phenylhydrazine was thus rejected as a scavenger for later work.

The results of some of the low concentration phenylhydrazine runs are given in Table 10.

TABLE 10

$10^5[H^+]$	10^3 [Phenylhydrazine]	$10^3 k_1$
0.65	1.89	5.16
1.2	1.44	5.39
1.8	1.93	5.39
3.9	1.93	5.30
3.9	3.78	5.51
9.7	1.44	5.86
11.0	1.93	5.57

FIGURE 9

Sketch of the Spectrum of Formaldehyde Oxime.

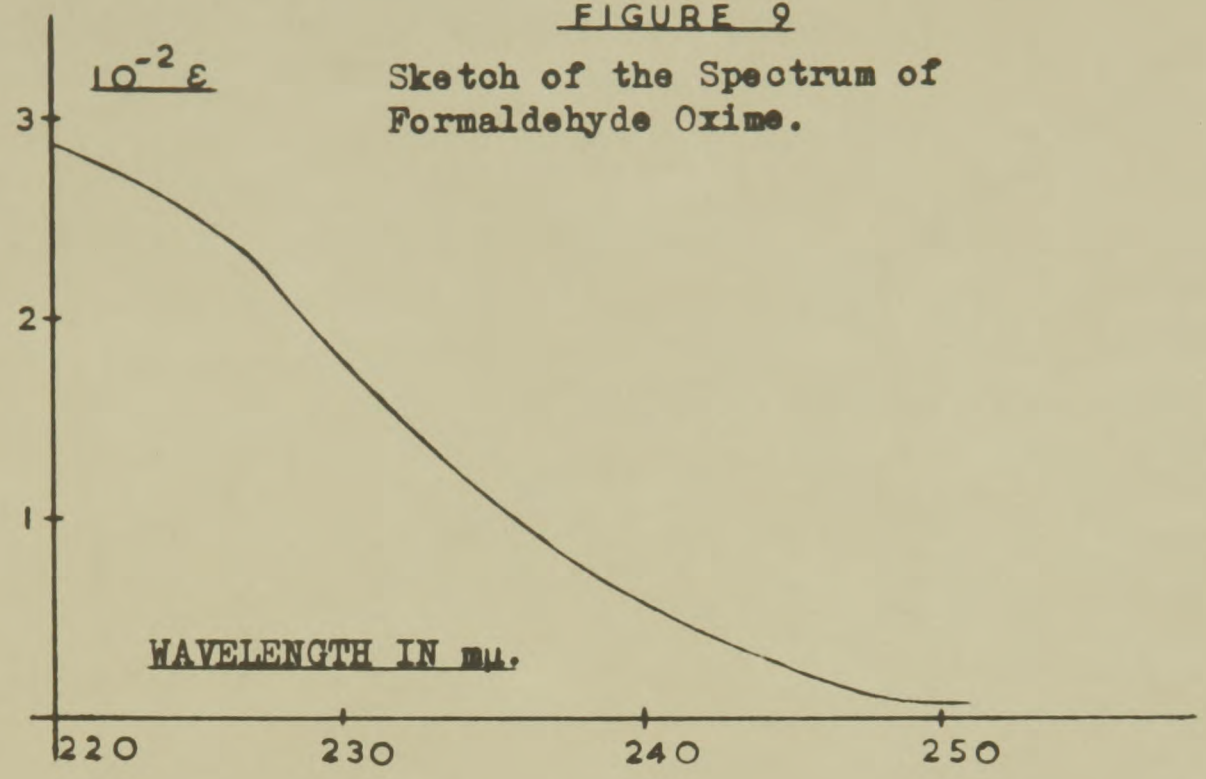


FIGURE 10

Sketches of spectra of
I. Phenylhydrazine
II. Formaldehyde hydrazone
both in acid solution

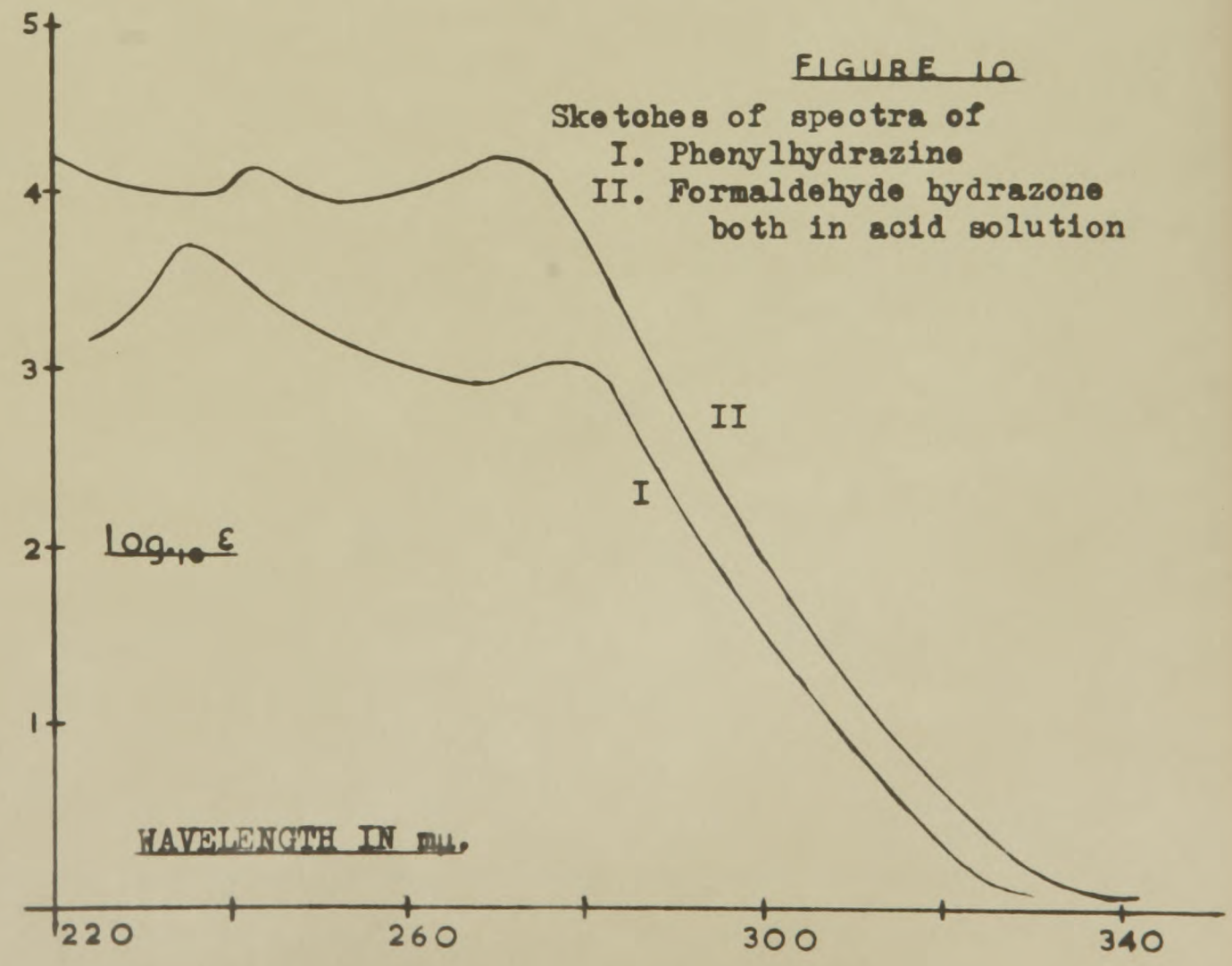
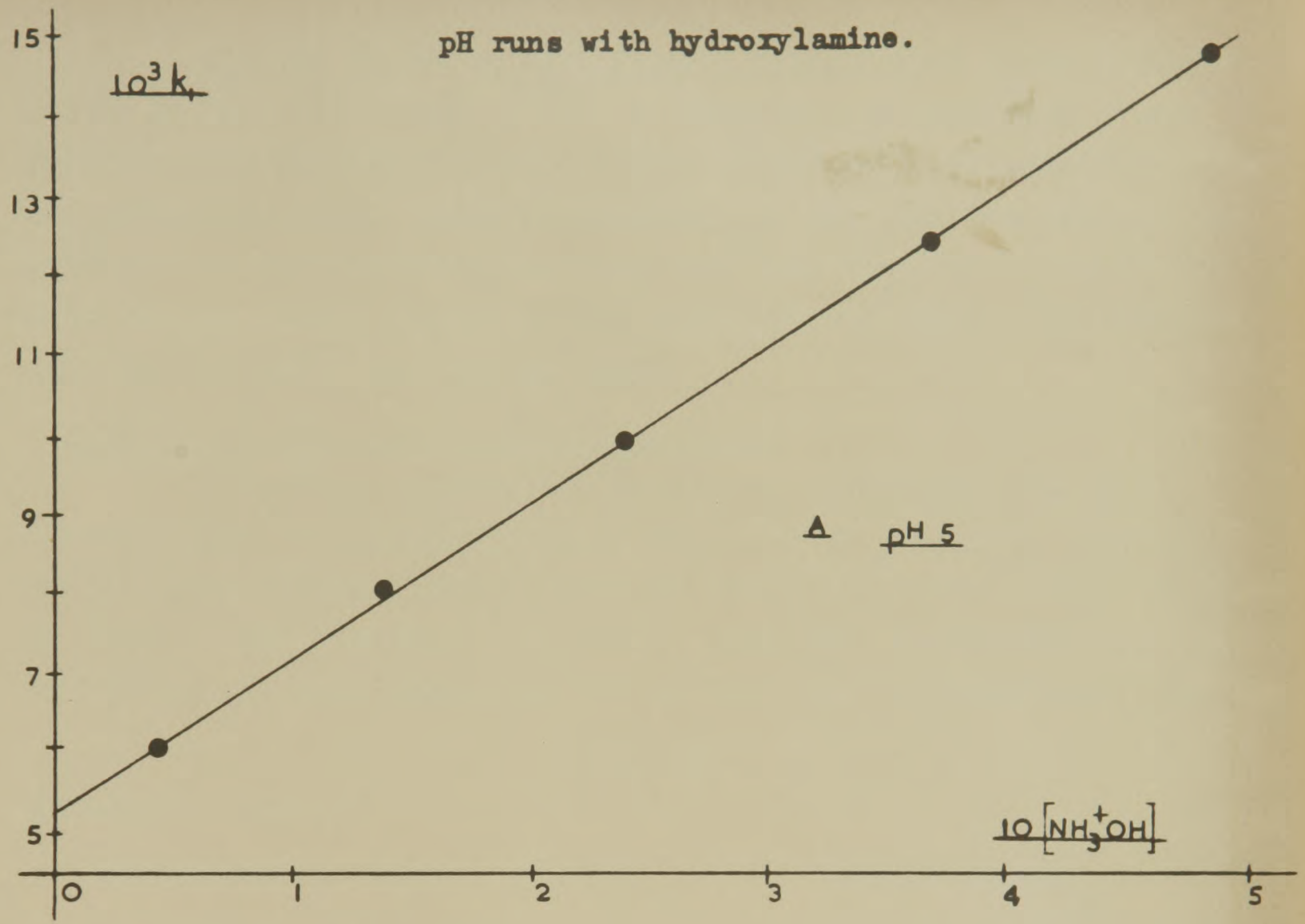
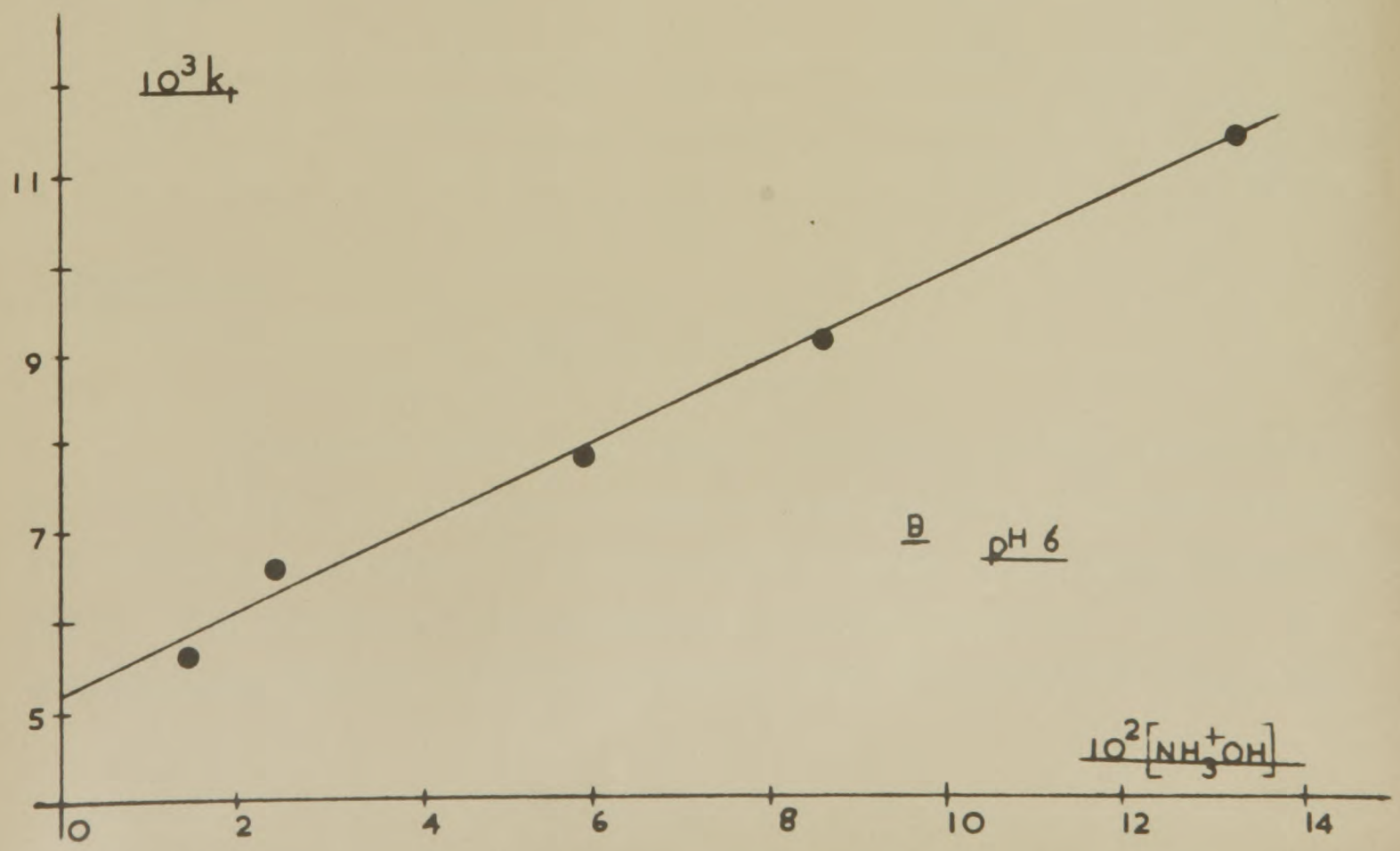


FIGURE II

pH runs with hydroxylamine.





All are at 290 mμ with initial formaldehyde concentrations of ca. 10^{-4}m. Later results confirm that no catalytic contribution to the observed rate from the phenylhydrazine itself would be expected at the concentrations used. With the exception of the last two results, the hydrogen ion concentrations employed are such that the k_1 values are equal to k_o. These results are in good agreement with those obtained with semicarbazide and hydroxylamine.

p-nitro and 2:4 dinitro-phenylhydrazines.

Both these substances appeared to suffer from the same disadvantages as phenylhydrazine. Some data on the D.N.P. spectra of formaldehyde obtained from a paper by Braude and Jones (1945)[64] is given in Table 11 illustrating this point. A further disadvantage was the low solubility of these compounds. No serious work was undertaken with them.

TABLE 11

Spectra in alcohol:

formaldehyde D.N.P.		D.N.P. itself	
λ_{max} mμ	$10^{-2}\varepsilon_{max.}$	$\lambda_{max.}$	$10^{-2}\varepsilon_{max.}$
225	185	219	120
256	120	258	95
348	230	350	145
		415	60

Hydrazine.

B.D.H. ANALAR hydrazine sulphate

$K_2 = 1.18 \times 10^{-8}$ (65)

Hydrazine itself has little absorption in the ultra-violet. It reacts with formaldehyde to give a band starting at about 250 mμ and showing no maximum within the Unicam range. Runs were followed at 235 mμ with initial formaldehyde concentrations of ca. 10^{-4} m. No satisfactory results could be obtained with this compound since the

observed infinity values slowly decreased with time; scans of the complete adduct spectrum showing this decrease to occur for the whole band. A series of "infinity value" readings are shown in Table 12.

TABLE 12

Reaction Time in Hours.	Optical Density 235 mμ.
0.5	0.363
6	0.346
18	0.322
24	0.300
40	0.253

In view of the above complications no quantitative work was undertaken with this compound, but qualitatively the results were of the correct order of magnitude, e.g. hydrazine sulphate solution made up to pH 6.20 on the titrator, samples run on the Unicam.

[Hydrazine]	$10^3 k_1$
0.041	5.00
0.081	5.44

These first-order rate constants were calculated by Guggenheim plots taken from the first two half-lives of the reaction, thus minimising the effect of any slow downward drift of the infinity value.

Thiosemicarbazide.

B.D.H. Laboratory Reagent

$K = 2.82 \times 10^{-3}$

This ionisation constant was determined by potentiometric titration on the automatic titrator. The introduction of the sulphur atom made the compound more acidic as would be expected from a comparison with other similar sulphur oxygen analogues, see Table 13.

TABLE 13

	pK		pK
semicarbazide	3.65	urea	0.1
thiosemicarbazide	2.55	thiourea	-0.96

Thiosemicarbazide absorbs very strongly in the ultra-violet, λmax. 235 mμ, log ε = 4.08. [67] This made Unicam work difficult, but it was found possible to carry out experiments at 290 mμ with initial formaldehyde concentrations of ca. 10^{-4}m and thiosemicarbazide concentrations of up to 0.05m. Within the pH-range studied, pH 3-5, the final dehydration stage of the reaction scheme was too slow to be excluded from the observed kinetics. At pHs less than 3 general acid catalysis would almost certainly have made this stage fast but the onset of hydrogen ion catalysis in the formaldehyde dehydration reaction would have made this reaction too fast to study on the Unicam. Thiosemicarbazide was thus rejected as a scavenger for future work.

Sulphite Techniques.

Relatively little work has been undertaken on these reactions, previous work is reviewed below.

Stewart and Donnally (1932)[68] carried out a series of experiments on the rate of dissociation of benzaldehyde sodium bisulphite. They found that the rate of this process changed with changing hydrogen ion concentration reaching a minimum at pH 1.8. Further work by the same authors (1932)[69] showed that the value of the equilibrium constant was strongly pH dependent. Specific reaction rates of sulphite and bisulphite ions with benzaldehyde were evaluated and it was concluded that the addition reaction proceeded almost exclusively via the sulphite ion.

Skrabal and Skrabal (1936)[70] investigated the formaldehyde-bisulphite reaction. They proposed the following kinetic scheme:

$$CH_2O + H_2SO_3 \xrightarrow{k_0} CH_2(OH)SO_3^- + H^+$$

$$CH_2O + HSO_3^- \xrightarrow{k_1} CH_2(OH)SO_3^-$$

$$CH_2O + SO_3^= + H_2O \xrightarrow{k_2} CH_2(OH)SO_3^- + OH^-$$

having the rate equation:

$$\frac{d\left[CH_2(OH)SO_3^-\right]}{dt} = \left[0.004\left[H_2SO_3\right] + 0.24\left[HSO_3^-\right] + 7100\left[SO_3^=\right]\right]\left[CH_2O\right]$$

Thus here again the sulphite ion was by far the most important species in the addition.

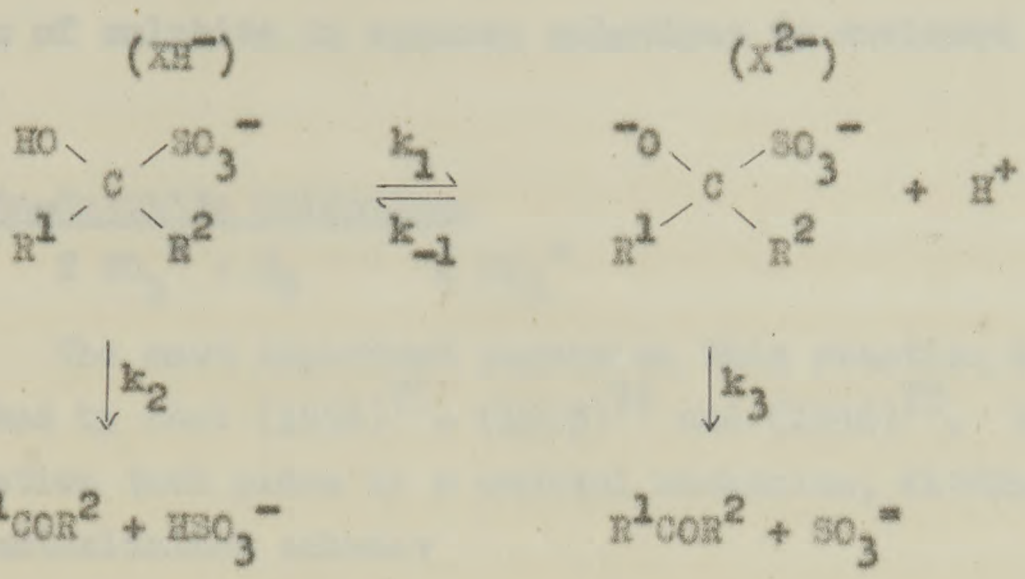
They also measured the equilibrium constant of the reaction:

$$H_2C(OH)_2 + SO_3^= \rightleftharpoons CH_2(OH)SO_3^- + OH^-$$

finding $$K = \frac{\left[CH_2(OH)SO_3^-\right]\left[OH^-\right]}{\left[H_2C(OH)_2\right]\left[SO_3^=\right]} = 0.80$$

Blackadder and Hinshelwood (1958)[72] measured the kinetics of decomposition of several bisulphite addition compounds. Their kinetic

representation was as follows:



so that the rate of decomposition of the bisulphite adduct, assuming a small stationary value in the doubly charged species (X^{2-}), is given by the equation:

$$\text{rate} = k_2\left[XH^-\right] + \frac{k_1 k_3 \left[XH^-\right]}{k_{-1}\left[H^+\right] + k_3}$$

Relevance to Present Work.

Assuming that the reaction proceeds completely through the sulphite ion; the following scheme may be set up for the present work.

$$H_2C(OH)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_2O + H_2O$$

$$HSO_3^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} SO_3^{=} + H^+$$

$$H_2O + CH_2O + SO_3^{=} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CH_2(OH)SO_3^- + OH^-$$

The data of Skrabal and Skrabal suggested that suitable conditions could be found under which the rate of formation of the bisulphite adduct would be fast in comparison to the rate of dehydration of formaldehyde and the reaction would also go almost to completion. Work was therefore undertaken using an automatic titrator to elucidate

the most favourable conditions for further work. Some work on the oxidation of sulphite in aqueous solutions is reviewed in the next section.

Bisulphite-Sulphite Oxidation.

$$2\,SO_3^{=} + O_2 \longrightarrow 2\,SO_4^{=}$$

The most important papers on this reaction have been contributed by Abel (1951)[73], (1955)[74] and (1956)[75]. He showed that the oxidation took place by a radical mechanism, fitting into the general autoxidation scheme:

$$O_2 + A^{-} \longrightarrow AOO^{-}$$

$$AOO^{-} + X \longrightarrow 2\,O^{-} + X^{+} + A$$

$$A + X \longrightarrow X^{+} + A^{-}$$

For the bisulphite-sulphite oxidation reaction the hydroxide ion was the preferred electron donor, A^{-}, and X represented the bisulphite ion, HSO_3^{-}.

Abel treated the kinetics of the reaction theoretically, deriving an expression relating the effect of hydrogen ion concentration to the rate of sulphite oxidation:

$$-\frac{d([HSO_3^{-}] + [SO_3^{=}])}{dt} = g\frac{[HSO_3^{-}]}{\sqrt{H^{+}}}$$

The catalytic constant g contains all the free radical terms etc. This expression was shown to fit the earlier data of Fuller and Crist (1941).[76]

One result of interest for the present work was that this equation predicts a maximum rate of oxidation at a pH corresponding to the pK of sulphite-bisulphite.

Later work on the reaction has been carried out and reviewed by Schroeter (1961)[77], and (1963)[78]. His results are in good agreement with those of Abel. He lists compounds which have been shown to act as

inhibitors in the reaction, the concentrations used being in the range 10^{-6} - 10^{-4}m. These were acids, alcohols, amines, amides, aldehydes, alkaloids, ketones, indoles, phenols, inorganic anions such as arsenite, antimonite, phosphite and cyanide, and finally the ammonium cation. He concludes that 'possibly many other classes of organic compounds will measurably inhibit the rate of oxidation in very low concentration.' In contrast, heavy metal ions in parts per million can be detected by observing their catalytic effect on the rate of oxidation.

These species which inhibited the reaction were the types of compounds envisaged as catalysts for the formaldehyde dehydration reaction. This obviously augered well for investigations with sulphite as scavenger.

The Titrator.

Measurements and control of pH were performed with equipment supplied by the Radiometer Company of Copenhagen consisting essentially of:

A titrator (type TTTlc)
Syringe Burette (type SBUla)
Titrigraph (Syringe Burette Recorder type SBR2c)

The titrator acted as a direct reading pH-meter which could be read to ± 0.02 units. Kinetic runs on the sulphite reaction were followed at constant pH by means of the titrigraph and syringe burette. Acid was added from the syringe sufficient to keep the reactant mixture at the desired pH, and the quantity added per unit time was plotted out on a chart by the titrigraph. The chart speeds were checked with a Smith's timer stop clock and showed no significant deviations from the rates specified by the suppliers. The reaction was carried out in a double-wall pyrex vessel with a close-fitting lid. This was maintained at a constant temperature by pumping water from a thermostat tank through the outer jacket. Further details concerning the assembly and operation of the automatic titrator used in this work may be obtained from the book by Bates (1964)[79] entitled "Determination of pH".

Experimental Methods.

B.D.H. ANALAR sodium sulphite and potassium metabisulphite ($K_2S_2O_5$) were used throughout.

$$K_1 = 1.72 \times 10^{-2} \qquad (80)$$
$$K_2 = 6.24 \times 10^{-8}$$

Because of the tendency of sulphite solutions to oxidise all solutions were made up with "boiled-out" water. Fresh solutions were made up before each series of runs.

In all except the earliest runs the acid used to start the hydroxide produced in the reaction was metabisulphite, statting with this had the advantage of keeping both the pH and the concentration of sulphite in the reaction mixture constant.

Reaction: $CH_2O + H_2O + SO_3^{=} \rightleftharpoons CH_2(SO_3^{-})OH + OH^{-}$

Statting Solution: $\frac{1}{2}(H_2O + S_2O_5^{=}) \equiv SO_3^{=} + H^{+}$

This simplified the observed kinetics since the sulphite term in the rate equations, which was a fairly large term, was kept constant throughout any experiment.

The usual conditions for any experiment were:

pH 7.5 - 8.5
sulphite concentration $5 \times 10^{-2} - 10^{-3}$m
initial formaldehyde concentration ca. 2×10^{-3}m.

Under this range of conditions Skrabal and Skrabal's work predicts almost complete reaction. This was confirmed in two ways:

1. The consumption of the statting metabisulphite in any run corresponded almost exactly to the amount of formaldehyde added to initiate the reaction mixture.
2. The "infinity values" in any series of experiments were constant and independent of the amount of sulphite added.

A typical set of infinity values are given in Table 14 as an example.

TABLE 14

$10^3[SO_3^=]$	% of syringe used in stat.	
7.92	62	
15.8	62	pH of statt = 7.62
23.8	60	For further details
31.7	58	of these runs, see
39.6	55.5	results section, p. 81

The pH "limits" (7.5 - 8.5) were defined as follows: Work was only attempted at alkaline pHs since the ultra-violet techniques appeared to cover the acid pH range fairly adequately. Runs in strongly acid media were in any case precluded by the necessity of keeping the final stage of the reaction scheme fast.

i.e. $CH_2O + SO_3^= + H_2O \longrightarrow CH_2(OH)SO_3^- + OH^-$

In the alkaline range the lower limit of pH ca 7.5 was set by sulphite oxidation problems. All sulphite solutions gradually became more acidic on standing. Qualitative experiments appeared to give results in agreement with Abel's predictions i.e. a maximum rate of oxidation in the region of the sulphite pK. This rate of oxidation was dependent on the care taken in making up the "boiled-out" solutions and the rate and type of stirring in the reaction vessel. Several experiments were carried out bubbling nitrogen through the reaction mixture; unfortunately this procedure made the titrator's reading somewhat unstable and so was not continued. The effect of this slow oxidation on the observed readings was to produce infinity values which were too low, the hydrogen ion produced by the oxidation "statting" the reaction, the rate plots obtained in these experiments showing distinct curvature. The envisaged difficult tasks of completely degassing all solutions, excluding light etc. were found to be unnecessary as at higher pHs oxidative problems became less severe. Thus above pH 7.5 "boiled-out" solutions of sulphite buffers remained at constant pH for relatively long periods. The excellent results obtained using

the titrator indicated that within the pH range specified oxidation of the sulphite during an experiment was so slow that it in no way complicated the observed kinetics. The stability of the sulphite during a run might well be due to the inhibiting effect of the formaldehyde added on the oxidation reaction. The addition of other buffers to the system, e.g. phosphate, tellurate etc., in the later work appeared to enhance the sulphite stability considerably making kinetic experiments very easy.

The upper limit of pH 8.5 was set by the magnitude of hydroxide ion catalysis in the formaldehyde dehydration reaction, this reaction becoming too fast for the titrator. If the titrator lost control of a pH-stat it had little chance of regaining it for a chain reaction was set up with the hydroxide ion produced producing more reaction which produced more hydroxide etc., etc. A buffer, be it the sulphite within its buffer range or another species, helped to keep the reaction under control, the buffer capacity damping down swings in pH thus making it easier for the titrator to follow the reaction.

Experimental Procedure.

The sulphite buffer (25 ml) was allowed to thermally equilibrate in the reaction vessel. The titrator was adjusted to stat at the desired pH. In the case of an accurately made up buffer this was at the exact pH of the buffer. The reaction was initiated by squirting a small amount (ca 0.5 cc) of formaldehyde solution from an 'Agla' syringe into the reaction vessel.

A sample titrator trace is shown on the next page, Figure 12. Details of the buffer concentrations used are given in the main results section, page 67. The horizontal scale measures time, the gap between each vertical line representing a 15 sec. unit. The vertical scale gives the amount of statting solution added; the scale denoting percentage of the syringe added. Examples of first-order rate plots obtained are given in Figure 13. The results obtained with sulphite buffer solutions are given in the main results section, page 81.

FIGURE 12

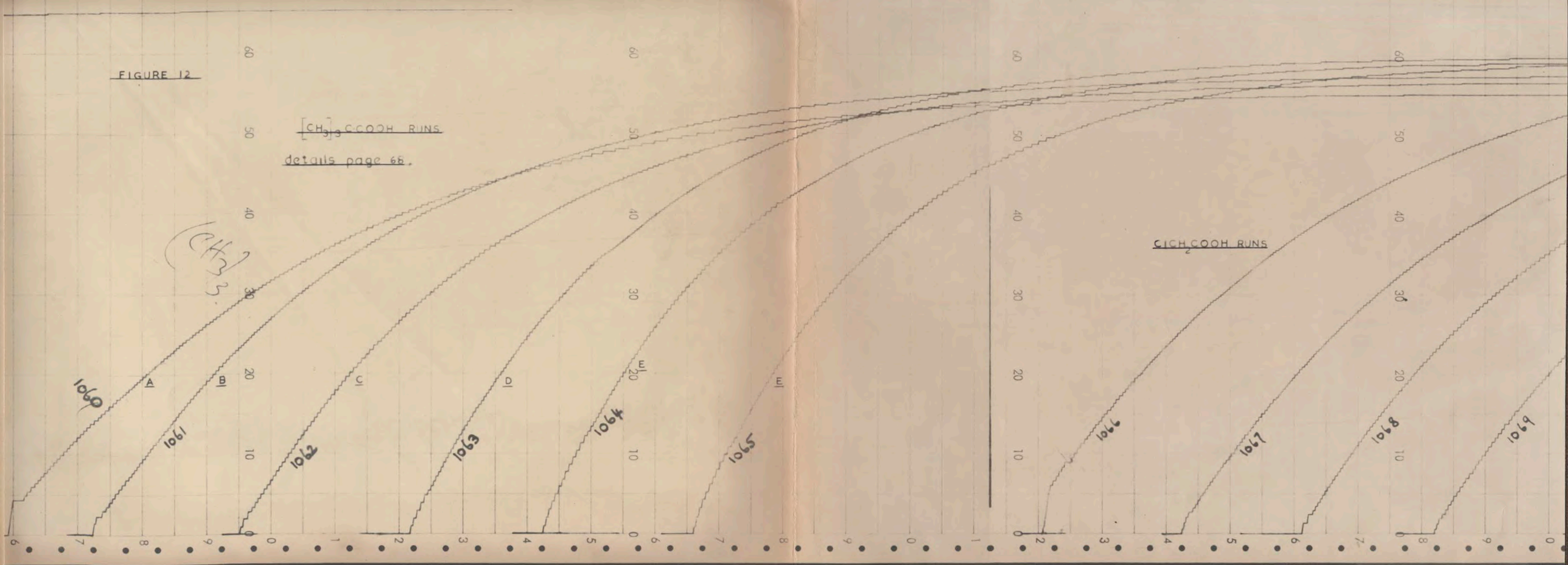
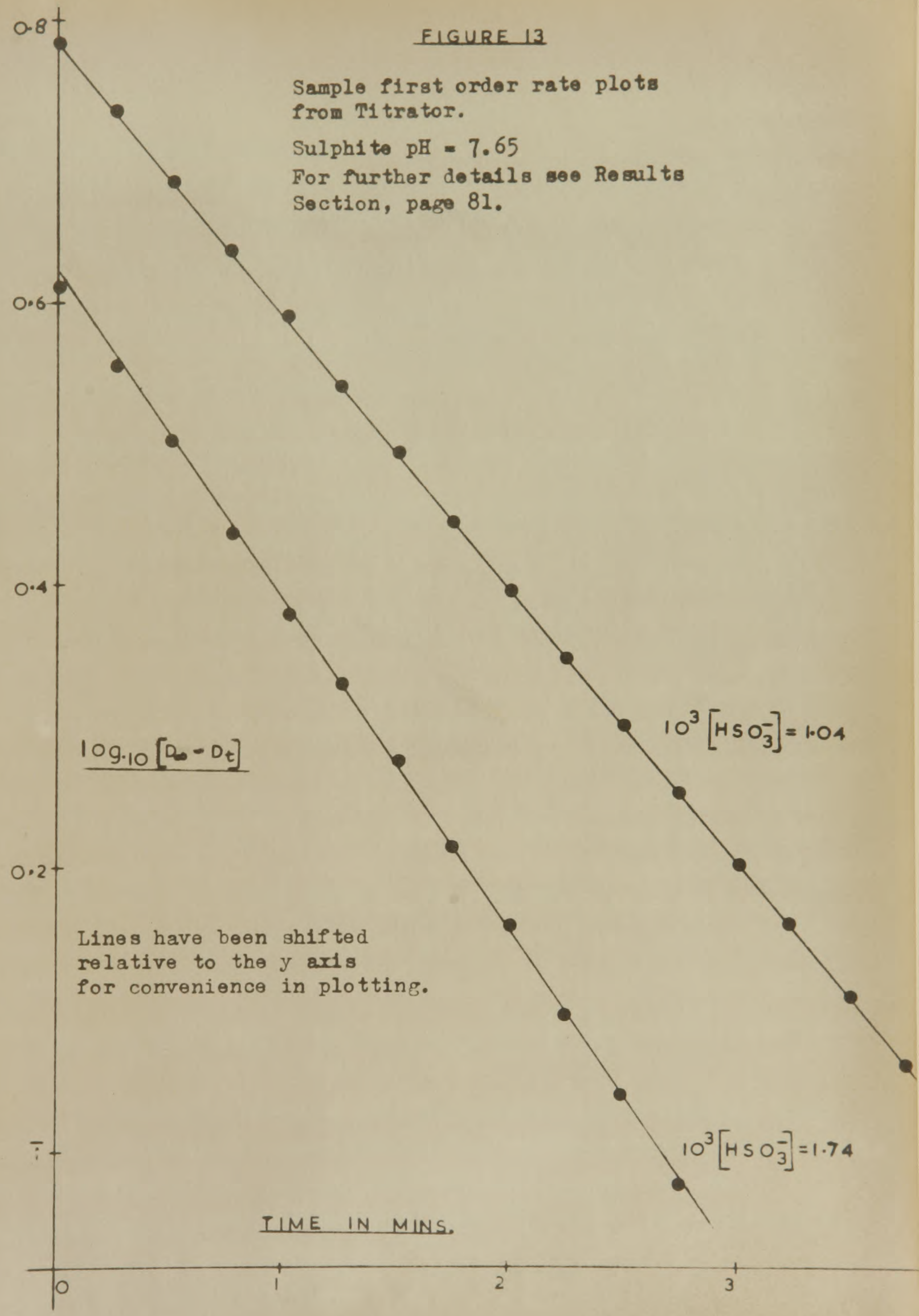

[CH3]3CCOOH RUNS
details page 68.
ClCH2COOH RUNS
1060
1061
1062
1063
1064
1065
1066
1067
1068
1069
A
B
C
D
E
60
50
40
30
20
10
0

FIGURE 13

Sample first order rate plots from Titrator.

Sulphite pH = 7.65

For further details see Results Section, page 81.



External Buffers.

Methods with Buffer Solutions.

Theory: As has already been mentioned the rate constant for the dehydration of formaldehyde is of the form:

$$k_1 = k_o + k_{H^+}[H^+] + k_{OH^-}[OH^-] + \sum k_A[A] + \sum k_B[B]$$

The above expression may be simplified for the specific case of catalysis by a buffer solution consisting of a single weak acid HA and its sodium salt A^- and putting in:

$$\frac{[H^+]\,[A^-]}{[HA]} \cdot \frac{f_{H^+}f_{A^-}}{f_{HA}} = K \quad ; \quad [H^+]\,[OH^-]\,f_{H^+}f_{OH^-} = K_w$$

where K and K_w are the thermodynamic equilibrium constants and the f's activity coefficients. Thus:

$$k_1 = k_o + \frac{k_{H^+}}{f_1} K \frac{[HA]}{[A^-]} + \frac{k_{OH^-}}{f_2} \cdot f_1 \frac{K_w}{K} \frac{[A^-]}{[HA]}$$

$$+ [HA]\left[k_{HA} + k_{A^-}\frac{[A^-]}{[HA]}\right]$$

where $f_1 = \frac{f_{H^+}\, f_{A^-}}{f_{HA}}$. $\qquad f_2 = f_{H^+}\, f_{OH^-}$

Now $\frac{[HA]}{[A^-]} = r$ the buffer ratio of the weak acid.

$$k_1 = k_x + [HA]\left[k_{HA} + \frac{k_{A^-}}{r}\right]$$

where $k_x = k_o + k_{H^+} \cdot \frac{K}{f_1} \cdot r + k_{OH^-}\frac{K_w}{K}\,\frac{1}{r}\,\frac{f_1}{f_2}$.

Thus if a series of runs are carried out at constant ionic strength, in which the acid concentration is varied but the buffer ratio kept constant, on plotting the rate constant against the acid concentration, a straight line with slope $k_{HA} + \frac{k_{A^-}}{r}$ and intercept k_x

should be obtained; and if a number of such series are carried out a plot of the slopes of these graphs against $\frac{1}{r}$ should be linear of slope k_{A^-} and intercept k_{HA}.

From the polarographic data in any solution either $k_{H^+}[H^+]$ or $k_{OH^-}[OH^-]$ may make a significant contribution to the observed velocity but not both. Thus in acid solution:

$$k_x = k_o + k_{H^+} \frac{K}{f_1} r$$

A plot of these intercepts against $[H^+]$ should give a straight line plot of slope k_{H^+}/f_1 and intercept k_o, thus to evaluate k_{H^+} one only needs to know f_1.

Activity Coefficients.

To enable a sufficient range of acid concentrations to be used, the ionic strength of the buffer solutions was kept fixed at 0.2 by the addition of calculated amounts of sodium chloride.

Wherever possible the methods used in evaluating activity coefficients were the same as those employed by Bell, Rand and Wynne-Jones[15] in their work on the catalysed hydration of acetaldehyde. Thus for carboxylic acid buffers in which $[H^+] = \frac{Kr}{f_1}$ some results of Larsson and Adell (1931)[81] have been used. They showed that $\frac{1}{f_1}$ has a value close to 1.75 for a number of carboxylic acids in various chloride solutions of I = 0.2 and this value has been used throughout this present work. In buffer solutions of nitrogen bases, where $r = \frac{[BH^+]}{[B]}$ the corresponding expression is $[H^+] = \frac{Kr\, f_{BH^+}}{f_{H^+}\, f_B}$. Here Bell, Rand and Wynne-Jones consider it a good approximation to put the activity factor equal to unity, so that $[H^+] = Kr$.

For inorganic species, which were not included in the acetaldehyde work, one of the normal Debye-Hückel equations[79] was used in evaluating hydrogen ion concentrations

i.e. $$-\log f = \frac{0.51\, n^2 \sqrt{I}}{1 + 1.5\sqrt{I}}$$

Thus for the system:

$$HA^{n-} + H_2O \rightleftharpoons A^{(n+1)-} + H_3O^+$$

$$-\log[H^+] = pK - \log r + \frac{0.51\sqrt{I}}{1 + 1.5\sqrt{I}}\left[n^2 - (n+1)^2 - 1\right]$$

It should be noted that the titrator reads $[H^+]\ f_{H^+}$.

Hydroxide ion concentrations were calculated in the usual way from the expression:

$$K_w = [H^+][OH^-]\ f_{H^+}\ f_{OH^-} = 10^{-14}$$

Experimental.

Stock solutions were made up by weight and the standardisation checked by titration. Two procedures were followed in making up reaction mixtures.

Procedure 1: In this the catalysing acid or base was used within its buffer range, a solution of known buffer ratio being prepared. The scavenger was made up in a solution of exactly the same pH, by diluting with a calculated amount of acid or alkali. The pHs of the two solutions were checked using the titrator as a pH meter. The titrator was standardised with buffers of known pH before these measurements. Known amounts of the catalyst stock solution were added to a fixed volume of the scavenger and the reaction mixture brought to constant ionic strength (I = 0.2) by the addition of a calculated amount of salt solution.

The observed rate constants contained terms in the scavenger e.g. for hydroxylamine hydrochloride

$$k_1 = k_o + k_{H^+}[H^+] + k_{NH_3^+OH}[NH_3^+OH] + k_{NH_2OH}[NH_2OH]$$
$$+ k_A[A] + k_B[B]$$

These terms in the scavenger remained effectively constant

throughout any series of experiments, and were usually negligibly small compared to the other terms in the equation. In any case they could be computed from the runs with the scavengers themselves and subtracted out. The values of k_o, k_{H^+}, k_A and k_B were obtained by the methods given in the theoretical section.

Procedure 2: In this substances were used well outside their buffer range so that they could be treated as being completely in either their acidic or basic form. Scavenger and catalyst solutions were made up and titrated to approximately the same pH on the titrator. In these runs the rate expression, e.g. for a base with a sulphite scavenger, is of the form:

$$k_1 = k'_x + k_B[B]$$

where $k'_x = k_o + k_{OH^-}[OH^-] + k_{HSO_3^-}[HSO_3^-] + k_{SO_3^=}[SO_3^=]$

A value of k_B may be obtained directly from a plot of k_1 against [B].

In most sets of runs with both procedures instead of increasing the catalyst concentration in successive experiments, an experiment at high catalyst concentration was followed by one at low concentration and that by one at medium concentration and so on. Thus any error introduced by "ageing" of the solutions was more or less cancelled out when the mean line was drawn through all the points on a plot of observed rate constants against catalyst concentration.

Both of these procedures will be illustrated in the acetic acid results, page 57.

The following factors were taken into account in the choice of catalysts and the conditions used to study them:

1. The pK of the catalyst. The range suitable for study was pK 2 - 9.5. At pHs outside this range the reaction was too fast to study and the catalytic constants of species with pK 2 - 9.5 which could be studied within the pH range 2 - 9.5 were too small to be measured with any accuracy.
2. The solubility of the catalyst. Many substances e.g. substituted benzoic acids and phenols could only be studied in the basic (soluble) form.

3. The catalyst's stability and reactivity with the scavenger.
4. The position and intensity of the catalyst's ultraviolet absorption bands.
5. Ionic strength considerations in many cases limited the range of catalyst concentrations available for study.

Criterion for Good Run.

If the following conditions were obeyed it was assumed that no side-reactions were taking place.

1. Good first-order rate plots, a few typical plots obtained with tellurate buffers are shown on pages 85 and 86 .
2. Guggenheim and infinity value plots giving the same rate-constants.
3. The infinity value remaining constant for many half-lives after the completion of the reaction.
4. The infinity value being of the expected value in the light of earlier work.
5. Good straight line plots for (1) observed first-order rate constants against catalyst concentration, (2) slopes of these plots against reciprocal of buffer ratio.
6. No change in pH on mixing the catalyst and scavenger and allowing to stand.

Notes on Results Section.

1. Definitions:

c_A = concentration of acidic constituent of buffer, mole/l.
c_B = concentration of basic constituent.
r = buffer ratio acid / base .
k_1 = first-order velocity constant, sec^{-1}.
k_a, k_b = catalytic constants in l. $mole^{-1}$ sec^{-1}.
K = acid dissociation constant.

2. Most velocity constants given are the mean of two determinations.
3. If no reference is given with dissociation constants they have been taken from "Dissociation Constants of Organic Acids in Aqueous Solution."[82]
4. Melting-points were measured on a Kofler block. Literature melting-points have been taken from the "Handbook of Chemistry and Physics."[83]

Results.

GROUP A: Organic acids studied in the ultraviolet and on the titrator.

Acetic acid

B.D.H. ANALAR acetic acid

$K = 1.75 \times 10^{-5}$

Ultraviolet runs

The results for buffer ratio 1.5 are given in full as an illustration of the reproducibility of the experiments: the results for the remaining buffer ratios are summarised.

$$r = \frac{[CH_3COOH]}{[CH_3COO^-]} = \frac{c_A}{c_B} = 1.5$$

$$[H^+] = 4.59 \times 10^{-5}$$

$$[HCHO] = 5 \times 10^{-5}$$

Wavelength used = 230 mμ

[Semicarb.] $= 1.80 \times 10^{-3}$

Run	$10^3 c_A$	$10^3 k_1$
291	9.86	5.76
294	19.7	6.28
295	29.6	6.71
292	39.4	7.50
296	49.3	8.22

[Semicarb.] $= 0.74 \times 10^{-3}$

Run	$10^3 c_A$	$10^3 k_1$
307	9.86	5.72
308	19.7	6.24
309	29.6	6.87
310	39.4	7.47
311	49.3	7.80

The averaged k_1 values are plotted in Figure 14A. against their corresponding c_A values.

$$\text{Slope} = k_A + \frac{k_B}{1.5} = 0.0588$$

$$\text{Intercept} = k_o + k_{H^+}[H^+] + k_{A'}[NH_2CONHNH_3^+] + k_{B'}[NH_2CONHNH_2]$$

$$= 5.13 \times 10^{-3}$$

r = 1.00

$[H^+] = 3.06 \times 10^{-5}$

$[\text{Semicarb.}] = 0.98 \times 10^{-3}$

$10^3 c_A$	$10^3 k_1$	
8.18	5.70	
16.4	6.26	Plotted in Figure 14B.
24.5	6.80	slope = 0.0607
32.7	7.27	intercept = 5.17×10^{-3}
40.9	7.70	

r = 0.500

$[H^+] = 1.53 \times 10^{-5}$

$[\text{Semicarb.}] = 1.41 \times 10^{-3}$

$10^3 c_A$	$10^3 k_1$	
5.48	5.65	
11.0	6.24	Plotted in Figure 14C.
16.4	6.65	slope = 0.0927
21.9	7.17	intercept = 5.14×10^{-3}
27.4	7.68	

The results for the other two buffer ratios studied are presented in the form which will be used throughout the rest of this chapter.

r = 0.333

$[H^+] = 1.02 \times 10^{-5}$

$[\text{Semicarb.}] = 2.34 \times 10^{-3}$

$10^3 c_A$		0	4.09	8.18	12.3	16.4	20.4
$10^3 k_1$	obs.	5.18	5.68	6.17	6.51	6.97	7.52
	calc.	5.11	5.64	6.08	6.54	6.99	7.44

slope = 0.1115

The first observed value (underlined) represents the intercept of the "c_A vs. k_1" graph. The calculated value below this is obtained by evaluating:

$$k_o + k_{H^+}[H^+] + k_A,[NH_2CONHNH_3^+] + k_B,[NH_2CONHNH_2]$$

in this case = 5.11×10^{-3} other terms small

= 5.11×10^{-3}

The other calculated values are obtained by adding to the intercept value the increments due to the catalytic effects of the buffer species present. The k_A and k_B used in these calculations being the final values obtained for the species concerned.

e.g. $c_A = 4.09 \times 10^{-3}$

$10^3 k_1$ calc. = intercept + $k_A[CH_3COOH] + k_B[CH_3COO^-]$

= $5.18 + [0.043 \times 4.09] + [0.0224 \times 12.3]$

= 5.64

In all cases the agreement between observed and calculated values is within ± 5%.

r = 0.250

$[H^+] = 7.7 \times 10^{-6}$

[Semicarb.] = 1.95×10^{-3}

$10^3 c_A$		0	3.29	6.58	9.86	13.2	16.4
$10^3 k_1$	obs.	<u>5.14</u>	5.57	6.04	6.39	6.72	7.37
	calc.	5.11	5.58	6.01	6.45	6.89	7.32

slope = 0.1339

Figure 15 shows a plot of the slopes obtained for these five buffer ratios against the reciprocal of their buffer ratios.

slope = k_B = 0.0234

intercept = k_A = 0.043

Titrator runs.

These runs are tabulated in an analogous way to those from the ultra-violet work. The pH given is that read off the titrator scale. The calculated values:

$$k'_x = k_o + k_{OH^-}[OH^-] + k_{SO_3^=}[SO_3^=] + k_{HSO_3^-}[HSO_3^-]$$

are evaluated for acetate but not the other "procedure 2" sets of runs. This is for the following reasons:

1. In many cases the titrator pH was not accurately standardised before the runs. An error in the observed pH would alter all the terms except k_o magnifying the error in the calculated k'_x value.

2. k_{OH^-}, is not a well defined constant, see page 88.

[Sulphite] = 0.0037 pH = 7.60

$10^3 c_B$	0	40.0	80.0	120	160
$10^3 k_1$ obs.	6.48	7.35	8.19	9.06	9.83
calc.	6.70	7.38	8.27	9.17	10.1

Plotted in Figure 16A.

slope = k_B = 0.0216

[Sulphite] = 0.0034 pH = 7.81

$10^3 c_B$	0	47.3	94.5	142	189
$10^3 k_1$ obs.	7.39	8.26	9.45	10.6	11.6
calc.	7.18	8.45	9.51	10.6	11.6

Plotted in Figure 16B.

k_B = 0.0222

Final values: k_A = 0.043 k_B = 0.0224

The k_B value is obtained by averaging the three k_B values. With some of the other buffer systems the k_B is computed solely from the titrator runs as this appears to be the more reliable technique.

FIGURE 14

Plot of observed first order rate constant k_1, against concentration of acidic constituent of catalyst solution c_A for several acetic acid buffer ratios.

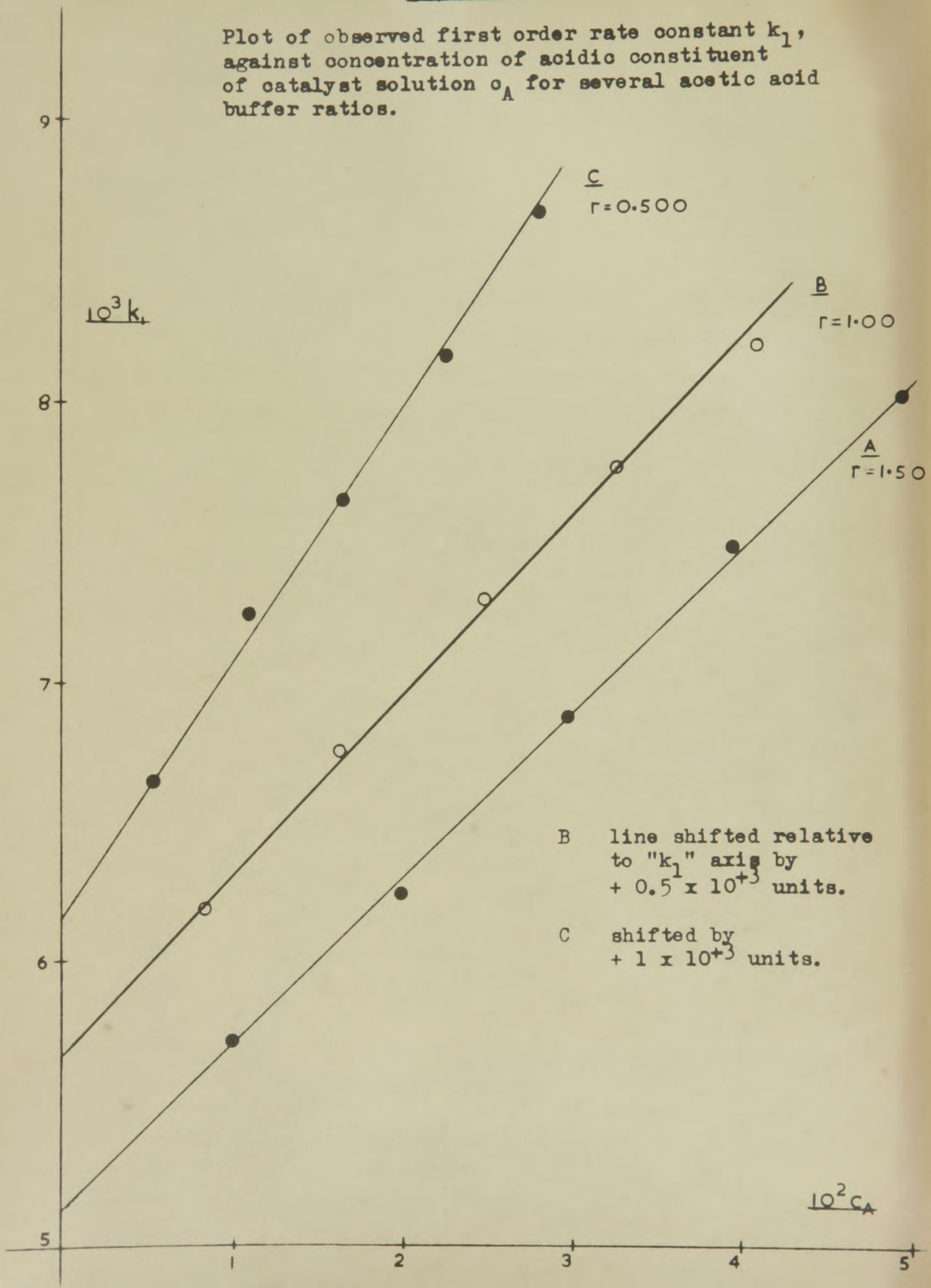


FIGURE 15

Plot of slope of "σ_A vs k_1" plot. against reciprocal of buffer ratio for acetic acid.

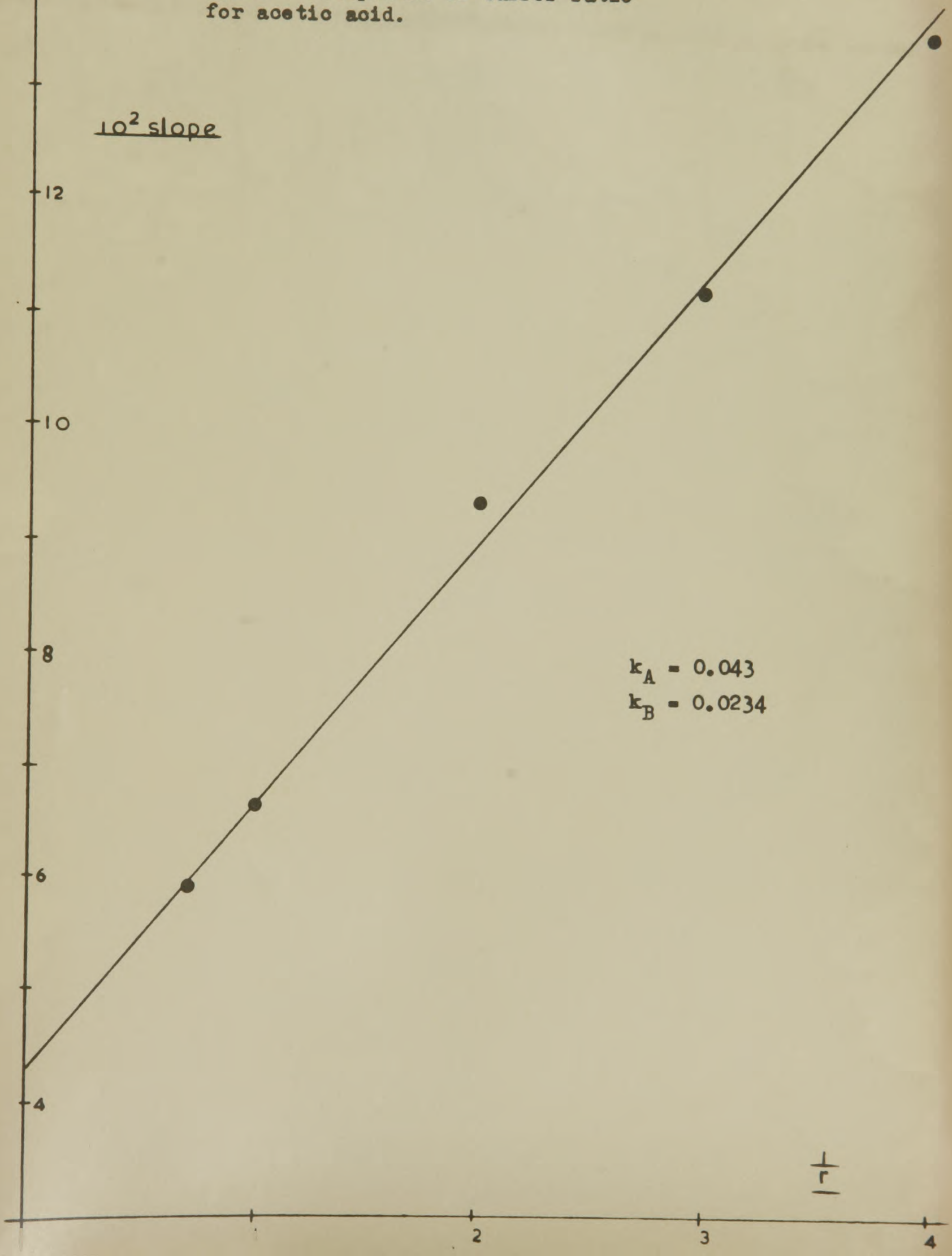
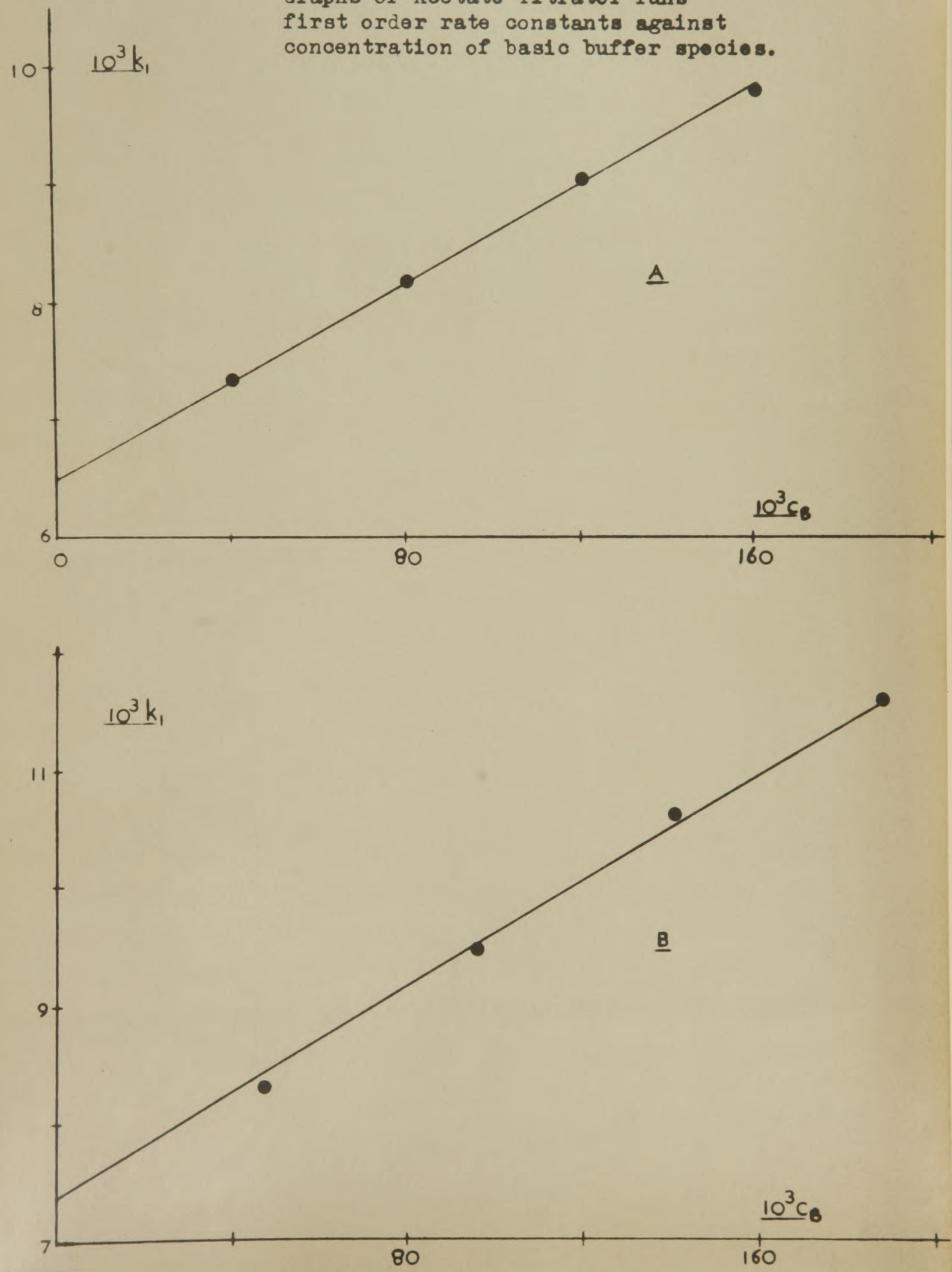


FIGURE 16

Graphs of Acetate Titrator runs first order rate constants against concentration of basic buffer species.



Chloracetic acid.

B.D.H. ANALAR chloracetic acid

$K = 1.359 \times 10^{-3}$

Ultraviolet runs.

$r = 0.500$

$[H^+] = 11.9 \times 10^{-4}$

$[\text{Semicarb.}] = 8.4 \times 10^{-4}$

$10^3 c_A$		0	3.40	6.80	10.2	13.6	17.0
$10^3 k_1$	obs.	7.28	7.68	8.13	8.52	8.90	9.48
	calc.	7.25	7.71	8.13	8.56	8.98	9.41

$r = 0.333$

$[H^+] = 7.92 \times 10^{-4}$

$[\text{Semicarb.}] = 1.45 \times 10^{-3}$

$10^3 c_A$		0	2.55	5.10	7.65	10.2	12.8	15.3
$10^3 k_1$	obs.	6.70	6.95	7.43	7.65	8.11	8.39	8.70
	calc.	6.54	7.03	7.36	7.70	8.03	8.36	8.69

$r = 0.250$

$[H^+] = 5.94 \times 10^{-4}$

$[\text{Semicarb.}] = 1.31 \times 10^{-3}$

$10^3 c_A$		0	2.66	5.33	10.7	13.4	16.0	21.3
$10^3 k_1$	obs.	6.30	6.65	7.05	7.71	7.93	8.30	9.03
	calc.	6.18	6.66	7.02	7.74	8.10	8.46	9.17

$r = 0.200$

$[H^+] = 4.76 \times 10^{-4}$

$[\text{Semicarb.}] = 9.9 \times 10^{-4}$

$10^3 c_A$		0	3.18	6.37	12.7	15.9	19.1
$10^3 k_1$	obs.	6.00	6.43	6.89	7.57	8.19	8.54
	calc.	5.97	6.45	6.89	7.76	8.23	8.67

$k_A = 0.116$

$k_B \doteq 0.004$

Titrator runs.

[Sulphite] = 0.0031 pH = 7.90

$10^3 c_B$	0	58.3	117	175	233
$10^3 k_1$ obs.	7.10	7.34	7.63	7.88	8.06
calc.		7.38	7.65	7.92	8.20

k_B = 0.0045

[Sulphite] = 0.0041 pH = 7.80

$10^3 c_B$	0	50.5	101	152	202
$10^3 k_1$ obs.	6.86	7.10	7.39	7.53	7.82
calc.		7.10	7.34	7.57	7.81

k_B = 0.0048

Average k_B = 0.0047

Final values: k_A = 0.116, k_B = 0.0047

Formic acid.

B.D.H. ANALAR formic acid

$K = 1.77 \times 10^{-4}$

Ultraviolet runs.

r = 2.00

$[H^+] = 6.19 \times 10^{-4}$

[Semicarb.] $= 1.09 \times 10^{-3}$

$10^3 c_A$	0	4.14	8.28	12.4	16.6	20.7
$10^3 k_1$ obs.	6.04	6.33	6.80	7.16	7.42	7.86
calc.	6.22	6.39	6.75	7.10	7.46	7.81

r = 1.00

$[H^+] = 3.10 \times 10^{-4}$

[Semicarb.] $= 1.42 \times 10^{-3}$

$10^3 c_A$	0	6.22	12.4	18.6	24.9	31.1	37.3
$10^3 k_1$ obs.	5.46	5.94	6.64	7.15	7.56	8.26	8.70
calc.	5.67	6.04	6.61	7.19	7.76	8.34	8.91

r = 0.500

$[H^+] = 1.55 \times 10^{-4}$

$[\text{Semicarb.}] = 1.60 \times 10^{-3}$

$10^3 c_A$	0	4.12	8.23	12.4	16.5	20.6	24.7
$10^3 k_1$ obs.	5.46	5.87	6.33	6.79	7.20	7.65	7.92
calc.	5.39	5.90	6.33	6.77	7.20	7.66	8.07

r = 0.333

$[H^+] = 9.29 \times 10^{-5}$

$[\text{Semicarb.}] = 1.40 \times 10^{-3}$

$10^3 c_A$	0	6.18	12.4	18.5	24.7	30.9
$10^3 k_1$ obs.	5.31	6.01	6.68	7.32	8.06	8.73
calc.	5.28	6.05	6.78	7.52	8.25	8.79

r = 0.200

$[H^+] = 6.19 \times 10^{-5}$

$[\text{Semicarb.}] = 1.52 \times 10^{-3}$

$10^3 c_A$	0	4.10	8.20	12.3	16.4	20.5	24.6
$10^3 k_1$ obs.	5.24	5.88	6.37	7.04	7.42	8.14	8.60
calc.	5.22	5.84	6.44	7.03	7.63	8.23	8.83

$k_A = 0.079$

$k_B = 0.012$

Titrator runs.

$[\text{Sulphite}] = 0.0038$ pH = 7.84

$10^3 c_B$	0	50.0	100	150	200
$10^3 k_1$ obs.	7.00	7.77	8.35	9.12	9.58
calc.		7.67	8.34	9.01	9.68

$k_B = 0.0135$

$[\text{Sulphite}] = 0.0062$ pH = 7.65

$10^3 c_B$	0	40.5	81.0	122	162
$10^3 k_1$ obs.	6.86	7.46	7.92	8.54	9.02
calc.		7.40	7.95	8.49	9.03

$k_B = 0.0132$

Average $k_B = 0.0134$

Final values: $k_A = 0.079$, $k_B = 0.0134$

Trimethylacetic acid.

B.D.H. Laboratory Reagent. This was recrystallised from water and dried in vacuo over phosphorus pentoxide. The purity was checked by titration.

$K = 8.91 \times 10^{-6}$

Ultraviolet runs.

$r = 10.0$

$[H^+] = 1.56 \times 10^{-4}$

[Semicarb.] = 0.0101 245mμ

$10^3 c_A$	0	44.5	89.0	134	178
$10^3 k_1$ obs.	5.95	7.05	8.40	9.60	10.2
calc.	5.66	7.16	8.37	9.58	10.8

$r = 2.70$

$[H^+] = 4.21 \times 10^{-5}$

[Semicarb.] = 0.0013 230mμ

$10^3 c_A$	0	11.0	22.1	44.2	66.2	88.3
$10^3 k_1$ obs.	5.07	5.49	5.80	6.53	7.36	8.04
calc.	5.11	5.44	5.81	6.54	7.28	8.01

$r = 0.822$

$[H^+] = 1.35 \times 10^{-5}$

[Semicarb.] = 0.0014 230mμ

$10^3 c_A$	0	3.39	6.78	13.6	20.3	27.1
$10^3 k_1$ obs.	5.14	5.27	5.54	5.97	6.10	6.55
calc.	5.11	5.32	5.49	5.85	6.20	6.55

$r = 0.411$

$[H^+] = 6.76 \times 10^{-6}$

[Semicarb.] = 0.0012 230mμ

$10^3 c_A$	0	8.15	16.3	24.5	32.6
$10^3 k_1$ obs.	5.02	5.60	6.18	6.78	7.28
calc.	5.11	5.67	6.31	6.96	7.60

$k_A = 0.025$

$k_B = 0.021$

Titrator runs.

[Sulphite] = 0.0028 pH = 7.73

$10^3 c_B$	0 [A]	49.8 [B]	99.5 [C]	149 [D]	199 [E]
$10^3 k_1$ obs.	6.62	7.71	8.82	9.70	11.1
calc.		7.73	8.83	9.94	11.0

k_B = 0.0218

[Sulphite] = 0.0058 pH = 7.59

$10^3 c_B$	0	42.5	85.0	128	170
$10^3 k_1$ obs.	6.62	7.47	8.45	9.42	10.4
calc.		7.56	8.51	9.45	10.4

k_B = 0.0226

Average k_B = 0.0222

Final values: k_A = 0.025, k_B = 0.0222.

GROUP B: Aliphatic and aromatic acids investigated only on the titrator.

Salicylate.

B.D.H. ANALAR salicylic acid

$K = 1.05 \times 10^{-3}$

[Sulphite] = 0.0033 pH = 7.60

$10^3 c_B$	0	45.3	90.5	136	181
$10^3 k_1$ obs.	6.16	6.30	6.74	6.93	7.06
calc.		6.40	6.63	6.87	7.10

$k_B = 0.0052$

Phenoxyacetate.

L. Light and Co. Laboratory Reagent. M.P. 99.5 - 101°C Lit. 99°C.

$K = 6.75 \times 10^{-4}$

[Sulphite] = 0.0029 pH = 7.82

$10^3 c_B$	0	54.0	108	162	216
$10^3 k_1$ obs.	6.33	6.62	6.96	7.26	7.53
calc.		6.64	6.95	7.25	7.56

$k_B = 0.0057$

p-nitrobenzoate.

B.D.H. Laboratory Reagent. M.P. 237.5 - 238.5°C Lit. 242°C.

$K = 3.61 \times 10^{-4}$

[Sulphite] = 0.0029 pH = 7.82

$10^3 c_B$	0	45.8	91.5	137	183
$10^3 k_1$ obs.	6.57	6.91	7.25	7.44	7.78
calc.		6.88	7.19	7.50	7.81

$k_B = 0.0068$

Glycollate.

Sodium glycollate B.D.H. Laboratory Reagent.

$K = 1.48 \times 10^{-4}$

[Sulphite] = 0.0025 pH = 7.57

$10^3 c_B$	0	53.5	107	161	214
$10^3 k_1$ obs.	5.93	6.48	7.25	7.78	8.56
calc.		6.60	7.27	7.94	8.61

[Sulphite] = 0.0064 pH = 7.80

$10^3 c_B$	0	49.3	98.5	148	197
$10^3 k_1$ obs.	7.28	7.68	8.59	9.12	9.74
calc.		7.90	8.51	9.13	9.74

k_B = 0.0125

o-toluate.

B.D.H. Laboratory Reagent. M.P. 104.5 - 105.5°C Lit. 104°C.

$K = 1.24 \times 10^{-4}$

[Sulphite] = 0.0022 pH = 7.75

$10^3 c_B$	0	41.8	83.5	125	167
$10^3 k_1$ obs.	6.75	7.20	7.68	7.98	8.35
calc.		7.17	7.59	8.00	8.42

k_B = 0.0100

o-methoxy-benzoate.

B.D.H. Laboratory Reagent. M.P. 100.5 - 103°C Lit. 100°C.

$K = 8.06 \times 10^{-5}$

[Sulphite] = 0.0079 pH = 7.65

$10^3 c_B$	0	40.8	81.5	122	163
$10^3 k_1$ obs.	7.24	7.73	8.59	9.12	9.79
calc.		7.86	8.49	9.11	9.73

k_B = 0.0153

Benzoate.

B.D.H. Laboratory Reagent. M.P. 121.5 - 122°C Lit. 122°C.

$K = 6.30 \times 10^{-5}$

[Sulphite] = 0.0019 pH = 7.71

$10^3 c_B$	0	55.3	111	166	221
$10^3 k_1$ obs.	6.23	7.00	7.63	8.21	9.03
calc.		6.93	7.64	8.34	9.04

k_B = 0.0127

Oxalate.

B.D.H. ANALAR sodium oxalate

$K_2 = 5.41 \times 10^{-5}$

[Sulphite] = 0.0038 pH = 7.84

$10^3 c_B$	0	22.8	45.5	68.3	91.0
$10^3 k_1$ obs.	7.00	7.44	8.16	8.54	9.26
calc.		7.60	8.19	8.79	9.38

[Sulphite] = 0.0047 pH = 7.75

$10^3 c_B$	0	16.0	32.0	48.0	64.0
$10^3 k_1$ obs.	6.67	7.15	7.58	8.06	8.50
calc.		7.09	7.51	7.92	8.34

$k_B = 0.0261$

Phenylacetate.

B.D.H. Laboratory Reagent recrystallised from water.
M.P. 76 - 76.5°C. Lit. 76.7°C.

$K = 4.88 \times 10^{-5}$

[Sulphite] = 0.0031 pH = 7.90

$10^3 c_B$	0	51.0	102	153	204
$10^3 k_1$ obs.	7.10	7.73	8.69	9.60	10.2
calc.		7.89	8.67	9.46	10.2

[Sulphite] = 0.0041 pH = 7.80

$10^3 c_B$	0	55.0	110	165	220
$10^3 k_1$ obs.	6.53	7.39	8.16	9.17	9.98
calc.		7.38	8.23	9.07	9.92

$k_B = 0.0154$

p-toluate.

B.D.H. Laboratory Reagent M.P. 181.5 - 182°C. Lit. 180°C.

$K = 4.24 \times 10^{-5}$

[Sulphite] = 0.0079 pH = 7.65

$10^3 c_B$	0	56.0	112	168	224
$10^3 k_1$ obs.	7.24	8.06	8.92	9.73	10.6
calc.		8.09	8.94	9.79	10.6

$k_B = 0.0152$

Cinnamate.

B.D.H. Laboratory Reagent M.P. 133 - 133.5°C. Lit 133°C.

$K = 3.65 \times 10^{-5}$

[Sulphite] = 0.0019 pH = 7.71

$10^3 c_B$	0	47.5	95.0	143	190
$10^3 k_1$ obs.	6.23	6.86	7.82	8.64	9.41
calc.		7.02	7.82	8.61	9.40

$k_B = 0.0167$

GROUP C: A phenol measured on the titrator.

Pentachlorophenol.

B.D.H. Laboratory Reagent. This was recrystallised from benzene. M.P. 189°C. Lit. 191°C.

$K = 5.5 \times 10^{-6}$ (84)

[Sulphite] = 0.0029 pH = 8.13

$10^3 c_B$	0	19.8	39.6	59.3	79.1
$10^3 k_1$ obs.	8.35	8.69	9.21	9.60	10.2
calc.		8.78	9.22	9.65	10.1

$k_B = 0.0219$

GROUP D: Nitrogen compounds.

Semicarbazide Hydrochloride.

B.D.H. ANALAR semicarbazide hydrochloride

$K = 2.24 \times 10^{-4}$ (59)

Wavelength = 245mμ $[HCHO] = 5 \times 10^{-4}$

r = 1.00

$[H^+] = 2.24 \times 10^{-4}$

$10^3 c_A$	0	15.8	31.5	47.3	63.0	78.8
$10^3 k_1$ obs.	5.30	6.50	7.15	8.34	9.27	10.3
calc.	5.51	6.30	7.29	8.29	9.28	10.3

r = 0.50

$[H^+] = 1.12 \times 10^{-4}$

$10^3 c_A$	0	4.93	9.86	19.7	29.6	39.4	49.3
$10^3 k_1$ obs.	5.20	5.59	5.95	6.62	7.15	8.06	8.38
calc.	5.31	5.54	5.87	6.54	7.21	7.88	8.55

r = 0.333

$[H^+] = 7.5 \times 10^{-5}$

$10^3 c_A$	0	9.20	18.4	27.6	36.8	46.0
$10^3 k_1$ obs.	5.10	5.76	6.46	7.08	7.71	8.45
calc.	5.25	5.77	6.44	7.11	7.78	8.45

$k_A = 0.0585$, $k_B = 0.0048$

Azide.

B.D.H. Laboratory Reagent

$K = 2.8 \times 10^{-5}$ (85)

[Sulphite] = 0.0031 pH = 7.94

$10^3 c_B$	0	113	225
$10^3 k_1$ obs.	7.68	8.01	8.16
calc.		7.91	8.13

[Sulphite] = 0.0032 pH = 7.89

$10^3 c_B$	0	50.0	100	150	200
$10^3 k_1$ obs.	7.33	7.63	7.57	7.82	7.77
calc.		7.43	7.53	7.63	7.73

$k_B \simeq 0.002$

The azide ion has such a low catalytic power that its catalytic constant cannot be measured with any accuracy.

Pyridine.

B.D.H. ANALAR pyridine

$K = 6.03 \times 10^{-6}$ (86)

$[Sulphite] = 0.0051$ pH = 8.00

$10^3 c_B$	0	75.5	151	227	302
$10^3 k_1$ obs.	8.21	9.45	10.6	11.9	13.1
calc.		9.34	10.5	11.6	12.7

$[Sulphite] = 0.0048$ pH = 7.87

$10^3 c_B$	0	55.0	110	165	220
$10^3 k_1$ obs.	7.96	8.78	9.31	9.85	11.2
calc.		8.78	9.60	10.4	11.2

$k_B = 0.0149$

Hydroxylamine hydrochloride.

B.D.H. ANALAR hydroxylamine hydrochloride

$K = 1.07 \times 10^{-6}$ (62)

Wavelength = 230mμ $[HCHO] \simeq 2.5 \times 10^{-3}$

r = 10.0

$[H^+] = 1.07 \times 10^{-5}$

$10^3 c_A$	0	37.0	74.0	111	148	185
$10^3 k_1$ obs.	5.08	5.91	6.60	7.45	8.45	9.26
calc.	5.11	5.92	6.76	7.60	8.43	9.27

r = 2.00

$[H^+] = 2.14 \times 10^{-6}$

$10^3 c_A$	0	20.2	40.4	60.6	80.8	101
$10^3 k_1$ obs.	5.18	5.90	6.78	7.20	8.10	8.77
calc.	5.11	5.89	6.61	7.32	8.04	8.75

r = 1.00

$[H^+] = 1.07 \times 10^{-6}$

$10^3 c_A$	0	15.1	30.2	45.3	60.4	75.5
$10^3 k_1$ obs.	5.10	5.95	6.61	7.64	8.14	9.03
calc.	5.11	5.87	6.64	7.42	8.19	8.96

$\mu = 0.50$

$[H^+] = 0.54 \times 10^{-6}$

$10^3 c_A$	0	10.1	20.2	30.3	40.4	50.5
$10^3 k_1$ obs.	5.05	5.80	6.79	7.37	8.57	9.01
calc.	5.11	5.88	6.72	7.55	8.39	9.22

$k_A = 0.0195$, $k_B = 0.0316$

GROUP E: Inorganic compounds.

Sulphate.

B.D.H. ANALAR sodium sulphate.

K_2 = 0.0103 (87)

[Sulphite] = 0.0048 pH = 7.70

$10^3 c_B$	0	39.6	79.2
$10^3 k_1$ obs.	6.48	6.72	7.05
calc.		6.74	7.00

[Sulphite] = 0.0101 pH = 7.50

$10^3 c_B$	0	43.1	86.1
$10^3 k_1$ obs.	7.92	8.16	8.54
calc.		8.20	8.49

k_B ≐ 0.0066

This value is of limited accuracy in view of the low catalytic effect. The concentrations of sulphate which could be used were limited by ionic strength considerations.

Fluoride.

Sodium fluoride B.D.H. Laboratory Reagent extra pure.

$HF \rightleftharpoons H^+ + F^-$ $K_1 = 6.71 \times 10^{-4}$ (88)

$HF + F^- \rightleftharpoons HF_2^-$ $K_2 = 3.96$

In these experiments F^- is the only species present to any appreciable extent.

[Sulphite] = 0.0048 pH = 7.98

$10^3 c_B$	0	57.3	115	172	229
$10^3 k_1$ obs.	8.25	9.10	10.1	11.3	12.3
calc.		9.26	10.3	11.3	12.3

[Sulphite] = 0.0048 pH = 7.70

$10^3 c_B$	0	33.5	67.0	101	134
$10^3 k_1$ obs.	6.77	7.40	7.90	8.45	9.12
calc.		7.36	7.96	8.55	9.14

[Sulphite] = 0.0109 pH = 7.50

$10^3 c_B$	0	41.8	83.5	125	167
$10^3 k_1$ obs.	7.78	8.55	9.45	9.93	11.0
calc.		8.52	9.26	10.0	10.7

k_B = 0.0177

Cacodylic acid.

Sodium cacodylate B.D.H. Laboratory Reagent.

$$K_B = \frac{[(CH_3)_2 \text{ As OOH.H}^+]}{[H_3O^+][(CH_3)_2AsOOH]} = 37.3 \qquad (89)$$

$$K_A = \frac{[H_3O^+][(CH_3)_2AsOO^-]}{[(CH_3)_2AsOOH]} = 5.33 \times 10^{-7}$$

[Semicarb.] = 0.0089 pH = 4.00 245mμ

$10^3 c_A$	0	29.3	58.5	87.8	117
$10^3 k_1$ obs.	5.95	6.62	7.80	8.45	9.60
calc.		6.86	7.77	8.67	9.58

[Semicarb.] = 0.0073 pH = 4.30 245mμ

$10^3 c_A$	0	36.0	72.0	108	144
$10^3 k_1$ obs.	5.76	6.86	8.01	9.13	10.4
calc.		6.88	7.99	9.11	10.2

k_A = 0.031

[Sulphite] = 0.0036 pH = 7.80

$10^3 c_B$	0	15.1	30.1	45.2	60.2
$10^3 k_1$ obs.	6.71	8.40	10.2	11.7	13.6
calc.		8.41	10.1	11.8	13.5

[Sulphite] = 0.0048 pH = 7.98

$10^3 c_B$	0	10.4	20.8	31.1	41.5
$10^3 k_1$ obs.	8.30	9.60	10.6	11.6	13.1
calc.		9.47	10.6	11.8	13.0

k_B = 0.113

Phosphite.

Sodium phosphite B.D.H. Laboratory Reagent

K_1 = 0.031 - 0.021 (90)

$K_2 = 1.5 \times 10^{-7}$

[Semicarb.] = 0.0094 pH = 4.00 245mμ

$10^3 c_A$	0	18.7	37.4	56.0	74.7
$10^3 k_1$ obs.	5.95	6.81	7.68	8.49	9.21
calc.		6.77	7.60	8.42	9.24

[Semicarb.] = 0.0078 pH = 4.50 245mμ

$10^3 c_A$	0	17.2	34.3	51.5	68.6
$10^3 k_1$ obs.	5.39	6.20	6.91	7.72	8.35
calc.		6.15	6.90	7.66	8.41

k_A = 0.044

[Sulphite] = 0.0015 pH = 7.95

$10^3 c_B$	0	8.93	17.9	26.8	35.7
$10^3 k_1$ obs.	6.91	8.64	10.7	12.6	14.2
calc.		8.85	10.8	12.7	14.7

[Sulphite] = 0.0048 pH = 8.04

$10^3 c_B$	0	3.58	7.15	10.7	14.3
$10^3 k_1$ obs.	8.74	9.69	10.4	11.2	12.0
calc.		9.52	10.3	11.1	11.8

k_B = 0.217

Arsenate.

B.D.H. ANALAR sodium arsenate

$K_1 = 5.62 \times 10^{-3}$

$K_2 = 1.70 \times 10^{-7}$ (91)

$K_3 = 2.95 \times 10^{-12}$

[Semicarb.] = 0.0101		pH = 4.00		245mμ	
$10^3 c_A$	0	11.3	22.7	34.0	45.3
$10^3 k_1$ obs.	5.95	6.86	7.53	8.64	9.60
calc.		6.85	7.74	8.64	9.53

[Semicarb.] = 0.0051		pH = 4.50		245mμ	
$10^3 c_A$	0	12.8	25.5	38.3	51.0
$10^3 k_1$ obs.	5.34	6.43	7.29	8.40	9.60
calc.		6.35	7.36	8.36	9.37

$k_A = 0.079$

[Sulphite] = 0.0030		pH = 7.90			
$10^3 c_B$	0	4.40	8.80	13.2	17.6
$10^3 k_1$ obs.	6.72	7.83	9.29	10.5	12.1
calc.		8.01	9.30	10.6	11.9

[Sulphite] = 0.0048		pH = 8.04			
$10^3 c_B$	0	3.70	7.40	11.1	14.8
$10^3 k_1$ obs.	8.74	9.98	10.7	12.0	12.8
calc.		9.83	10.9	12.0	13.1

$k_B = 0.293$

Sulphite.

B.D.H. ANALAR sodium sulphite

$K_1 = 1.72 \times 10^{-3}$ (80)

$K_2 = 6.24 \times 10^{-8}$

r = 0.234 pH calc. = 7.42

$[OH^-] = 3.65 \times 10^{-7}$ pH obs. = 7.37

$10^3 c_A$	0	1.73	3.45	5.18	6.90	8.63
$10^3 k_1$ obs.	5.50	7.21	8.44	9.95	12.1	13.8
calc.	5.70	7.12	8.74	10.4	12.0	13.6

r = 0.166 pH calc. = 7.57

$[OH^-] = 5.14 \times 10^{-7}$ pH obs. = 7.57

$10^3 c_A$	0	1.45	2.90	4.35	5.80	7.25
$10^3 k_1$ obs.	5.90	7.85	9.85	12.2	13.3	15.6
calc.	5.93	7.82	9.74	11.7	13.6	15.5

r = 0.137 pH calc. = 7.65

$[OH^-] = 6.23 \times 10^{-7}$ pH obs. = 7.62

$10^3 c_A$	0	0.35	0.70	1.04	1.39	1.74
$10^3 k_1$ obs.	5.75	6.38	6.72	7.43	7.90	8.89
calc.	6.12	6.31	6.87	7.43	7.99	8.54

r = 0.098 pH calc. = 7.80

$[OH^-] = 8.70 \times 10^{-7}$ pH obs. = 7.81

$10^3 c_A$	0	0.26	0.53	0.79	1.06	1.32
$10^3 k_1$ obs.	5.80	6.43	6.86	7.48	8.31	8.85
calc.	6.52	6.39	6.99	7.58	8.17	8.76

r = 0.082 pH calc. = 7.88

$[OH^-] = 1.04 \times 10^{-6}$ pH obs. = 7.90

$10^3 c_A$	0	0.71	1.43	2.14	2.86	3.57
$10^3 k_1$ obs.	5.80	7.70	9.64	11.7	13.8	15.7
calc.	6.79	7.72	9.63	11.5	13.5	15.4

$k_A \doteq 0$, $k_B = 0.22$

The poor agreement between the observed intercept values and the calculated values is probably due to the additive effect of errors introduced (1) in the extrapolation of the observed intercept values and (2) by the k_{OH^-} value used in the calculation, see page 88 .
The other observed and calculated values show good internal consistency.

Phosphate.

B.D.H. ANALAR mono- and disodium hydrogen phosphates

$K_1 = 7.5 \times 10^{-3}$

$K_2 = 6.2 \times 10^{-8}$

$K_3 = 2 \times 10^{-13}$

[Semicarb.] = 0.0089 pH = 4.00 245mμ

$10^3 c_A$	0	8.80	17.6	26.4	35.2
$10^3 k_1$ obs.	5.95	6.84	7.53	8.37	9.15
calc.		6.73	7.50	8.28	9.05

[Semicarb.] = 0.0103 pH = 4.50 245mμ

$10^3 c_A$	0	8.80	17.6	26.4	35.2
$10^3 k_1$ obs.	5.86	6.53	7.42	8.25	8.80
calc.		6.64	7.41	8.19	8.96

r = 10.0

$[H^+] = 2.14 \times 10^{-6}$

[Hydroxylamine] = 0.0303

$10^3 c_A$	0	8.90	17.8	26.7	35.6
$10^3 k_1$ obs.	5.80	6.88	7.68	8.75	9.83
calc.	5.82	6.90	8.00	9.09	10.2

r = 5.00

$[H^+] = 1.07 \times 10^{-6}$

[Hydroxylamine] = 0.0223

$10^3 c_A$	0	7.23	14.5	21.7	28.9
$10^3 k_1$ obs.	5.53	6.53	7.59	8.87	9.86
$10^3 k_1$ calc.	5.68	6.73	7.93	9.15	10.3

r = 0.169

$[OH^-] = 5.13 \times 10^{-7}$ pH calc. = 7.57

[Sulphite] = 0.0033 pH obs. = 7.58

$10^3 c_B$	0	7.98	16.0	23.9	31.9
$10^3 k_1$ obs.	6.16	8.93	12.0	15.3	19.0
calc.	6.39	9.38	12.6	15.8	19.0

r = 0.088

$[OH^-] = 10.0 \times 10^{-7}$ pH calc. = 7.86

[Sulphite] = 0.0056 pH obs. = 7.80

$10^3 c_B$	0	3.09	6.17	9.25	12.3	15.4
$10^3 k_1$ obs.	7.35	8.59	9.98	11.0	12.2	13.7
calc.	7.89	8.58	9.80	11.0	12.3	13.5

$k_A = 0.088$, $k_B = 0.39$

Tellurate.

B.D.H. ANALAR telluric acid.

$K_1 = 2.0 \times 10^{-8}$ (93)

$K_2 = 1.1 \times 10^{-11}$

[Semicarb.] = 0.0386		pH = 4.30		245mμ	
$10^3 c_A$	0	36.0	72.0	108	144
$10^3 k_1$ obs.	5.76	6.90	7.97	9.21	10.1
calc.		6.84	7.92	9.00	10.1

[Semicarb.] = 0.0162		pH = 4.50		245mμ	
$10^3 c_A$	0	39.3*	78.5*	118	157*
$10^3 k_1$ obs.	5.39	6.57	7.43	9.02	9.98
calc.		6.57	7.75	8.93	10.1

$k_A = 0.030$

r = 0.826

$[OH^-] = 6.05 \times 10^{-7}$ pH calc. = 7.64

[Sulphite] = 0.0026			pH obs. = 7.60		
$10^3 c_A$	0	2.16	4.31	6.47	8.62
$10^3 k_1$ obs.	6.20	7.34	8.45	9.72	10.7
calc.	6.61	7.44	8.68	9.92	11.2

r = 0.500

$[OH^-] = 10.0 \times 10^{-7}$ pH calc. = 7.86

[Sulphite] = 0.0053			pH obs. = 7.90		
$10^3 c_A$	0*	1.72*	3.44	5.16	6.88*
$10^3 k_1$ obs.	8.01	9.93	11.8	13.0	14.9
calc.	7.77	9.60	11.2	12.8	14.4

$k_B = 0.45$

* The first-order rate plots used in obtaining these values are shown in Figures 17 and 18. These plots are typical examples of the standard of plot obtained throughout this work.

FIGURE 17

First-Order Rate Plots for Tellurate Titrator Runs
r = 0.50

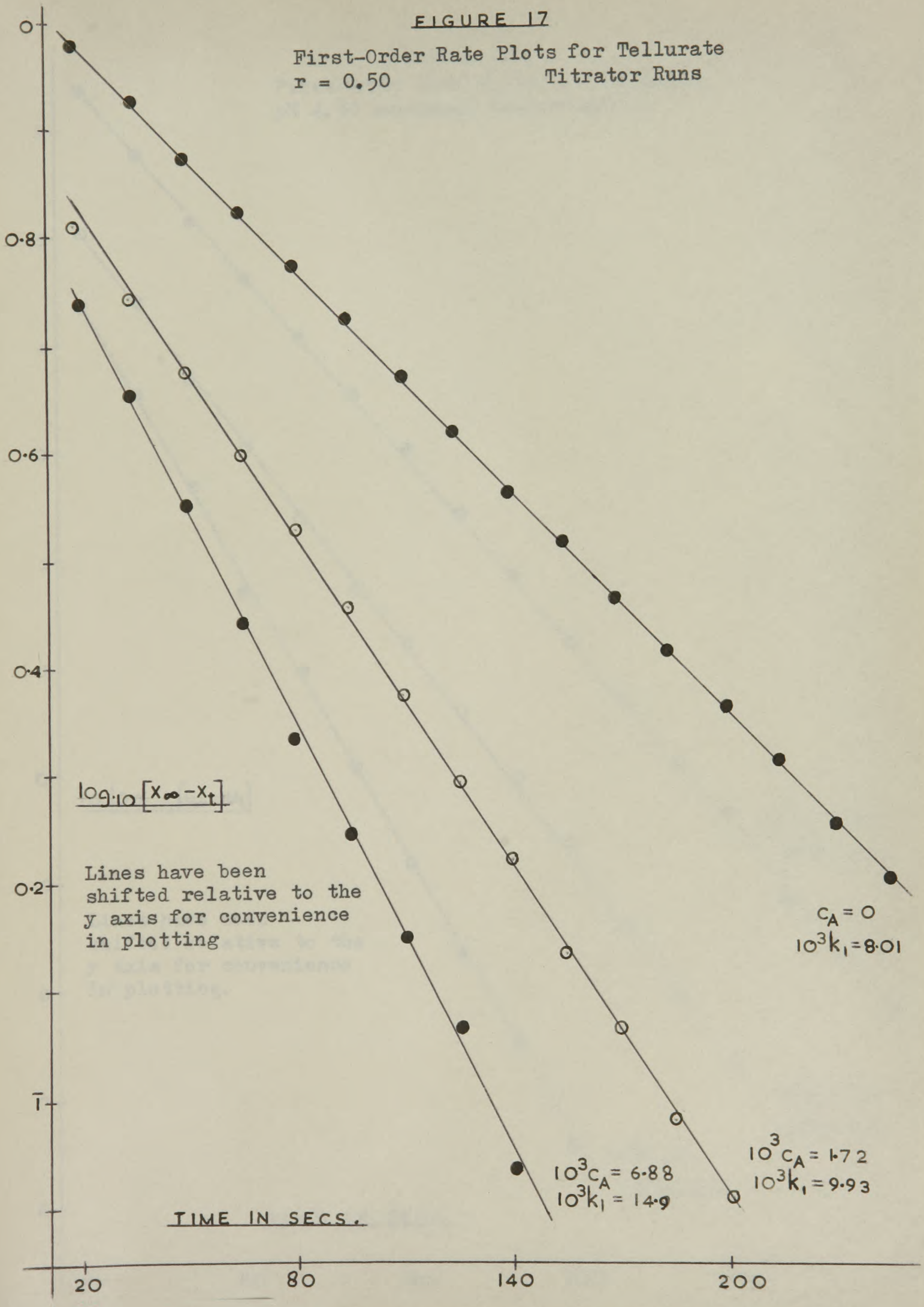
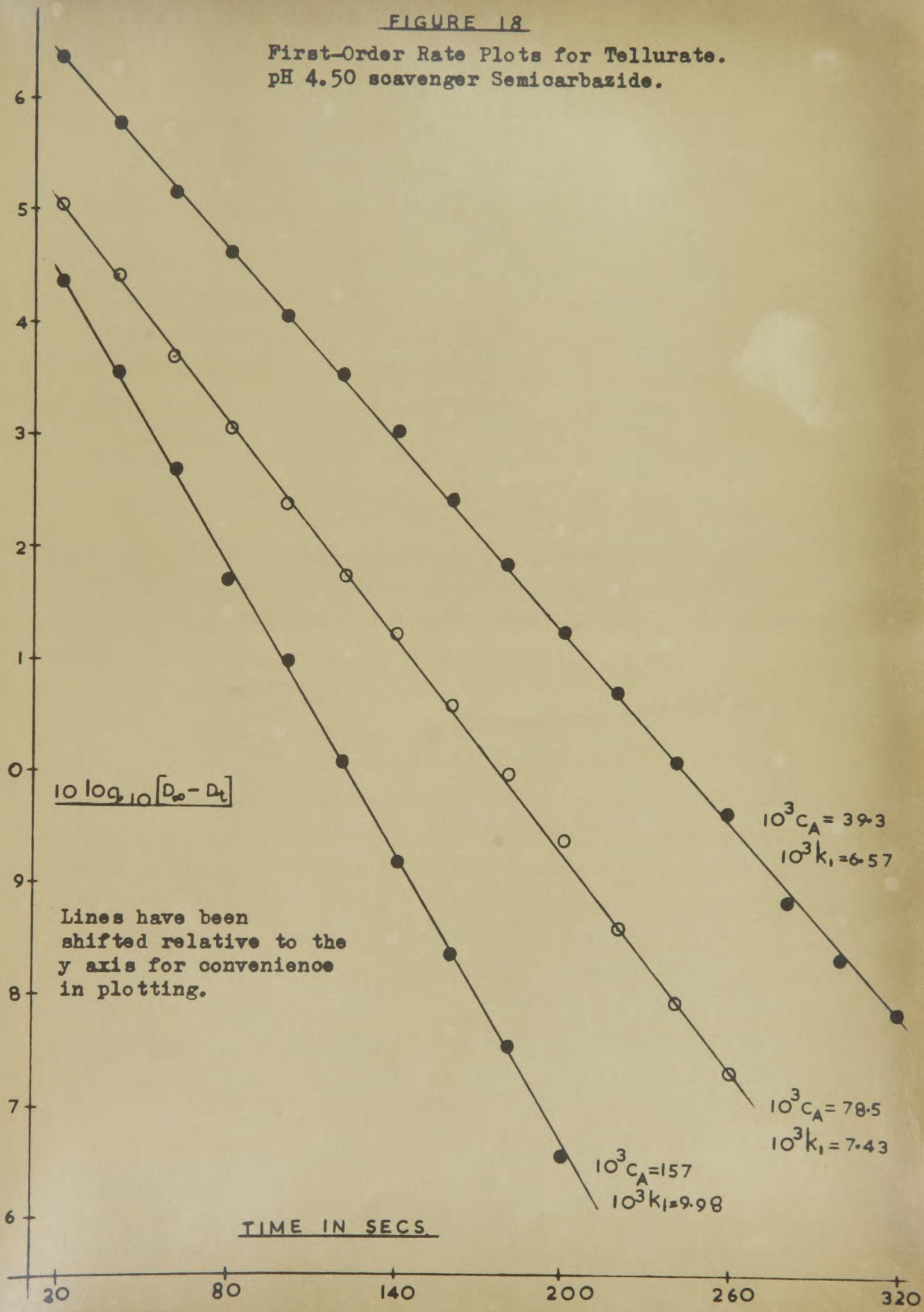


FIGURE 18

First-Order Rate Plots for Tellurate.
pH 4.50 scavenger Semicarbazide.



Borate.

B.D.H. ANALAR boric acid.

$K_1 = 6.2 \times 10^{-10}$ (94)

$K_2 = 1.8 \times 10^{-13}$

[Semicarb.] = 0.0094 pH = 4.00 245mμ

$10^3 c_A$	0	118	237	355
$10^3 k_1$ obs.	5.95	6.62	7.20	7.82
calc.		6.52	7.09	7.65

[Semicarb.] = 0.0162 pH = 4.50 245mμ

$10^3 c_A$	0	122	244	367
$10^3 k_1$ obs.	5.39	5.90	6.53	6.96
calc.		5.98	6.57	7.15

$k_A = 0.0048$

This value is of limited accuracy due to uncertainties regarding the species present in the concentrated solution required to obtain a measurable effect.

r = 10.0

$[OH^-] = 1.61 \times 10^{-6}$ pH calc. = 8.07

[Sulphite] = 0.0023 pH obs. = 8.09

$10^3 c_A$	0	5.75	11.5	17.3	23.0
$10^3 k_1$ obs.	7.87	9.50	11.5	13.4	15.2
calc.	8.23	9.65	11.4	13.2	15.0

r = 4.45

$[OH^-] = 3.62 \times 10^{-6}$ pH calc. = 8.42

[Sulphite] = 0.0020 pH obs. = 8.44

$10^3 c_A$	0	3.00	6.00	9.00	12.0
$10^3 k_1$ obs.	11.2	13.2	15.0	17.6	19.5
calc.	11.4	13.3	15.4	17.5	19.5

r = 2.77

$[OH^-] = 5.81 \times 10^{-6}$ pH calc. = 8.63

[Sulphite] = 0.0015 pH obs. = 8.63

$10^3 c_A$	0	2.88	5.76	8.64
$10^3 k_1$ obs.	15.5	18.6	21.2	24.2
calc.	14.8	18.7	21.8	25.0

$k_B = 3.05$

Discussion.

1. Evaluation of k_o, k_{H^+} and k_{OH^-}.

k_o: In the buffer solution experiments, the intercepts of the plots of rate constant against c_A have the value:

$$k_o + k_{H^+} K\, r/f_1 \equiv k_o + k_{H^+}[H^+]$$

The intercepts from acetic acid, trimethylacetic acid and hydroxylamine hydrochloride are effectively k_o values as very little catalytic contribution would be expected from hydrogen ion at the pHs used. These intercepts when collected and averaged give:

$$k_o = 5.1_1 \times 10^{-3}\ \text{sec}^{-1}$$

All values averaged were within ± 2% of this mean value.

k_{H^+}: This was evaluated from systems in which hydrogen ion catalysis was important. In Figure 19 the intercepts from chloracetic acid, formic acid and semicarbazide hydrochloride are graphed out against the corresponding hydrogen ion concentrations; the slope giving the k_{H^+} value:

$$k_{H^+} = 1.8\ \text{l.mole}^{-1}\ \text{sec}^{-1}.$$

k_{OH^-}: The only catalytic system studied in which catalysis from OH^- makes a really significant contribution to the observed rate is borate. In other systems the hydroxide contribution is small and of the same order of magnitude as the sulphite value making an exact assessment of the contribution difficult. In Figure 20 the borate-buffer intercepts minus their sulphite ion contributions are graphed out against the calculated hydroxide ion concentrations. These intercepts have the value

$$k_o + k_{OH^-}\ \frac{K_w}{K_r} \cdot \frac{f_1}{f_2} \equiv k_o + k_{OH^-}[OH^-]$$

and from Figure 20: $k_o = 1620\ \text{l.mole}^{-1}\ \text{sec}^{-1}$.

This is probably not a very accurate value but is almost certainly of the right order of magnitude. The calculated sulphite intercepts would suggest that this value is somewhat too high.

FIGURE 19

Evaluation of k_{H^+}

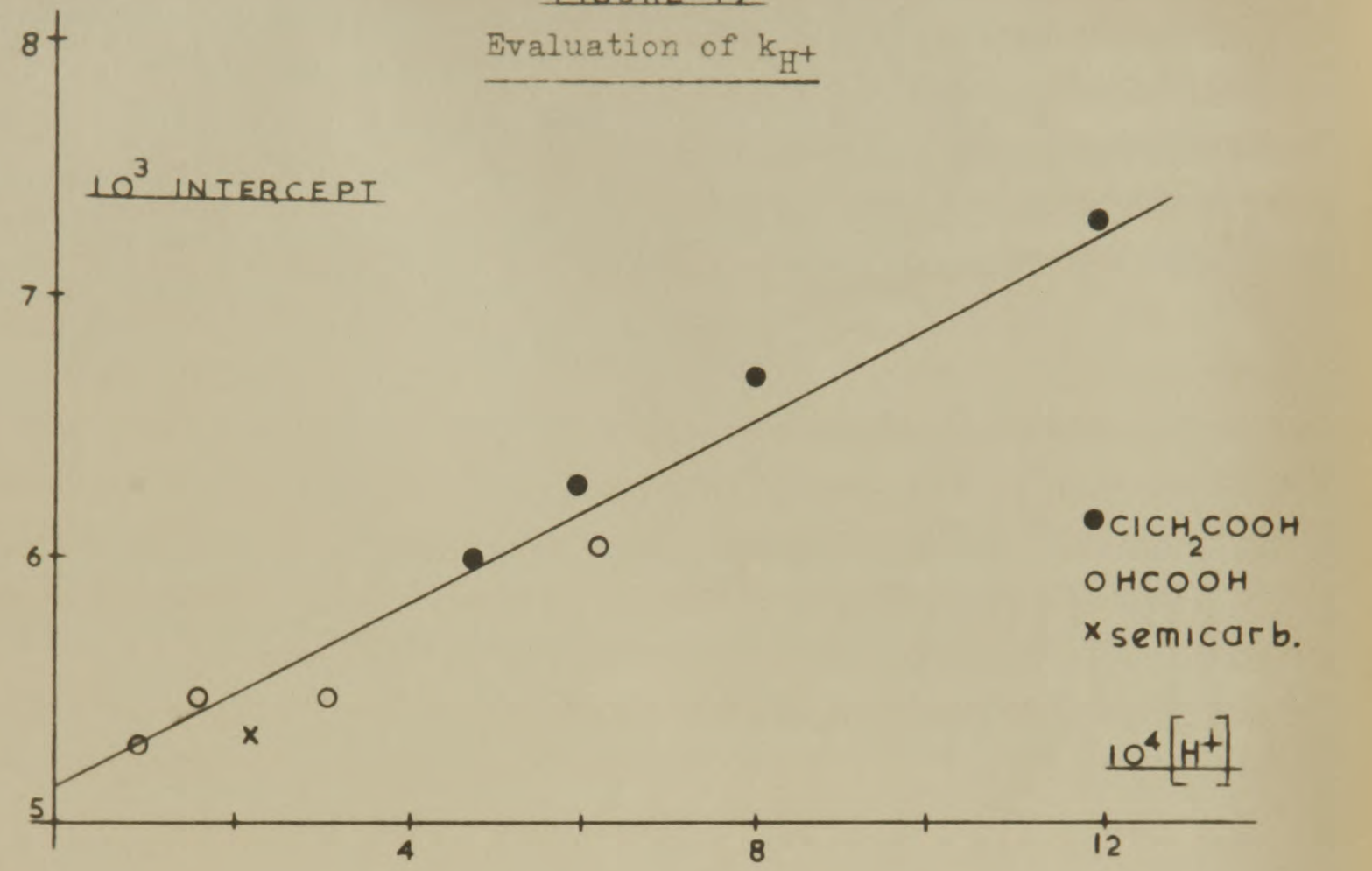
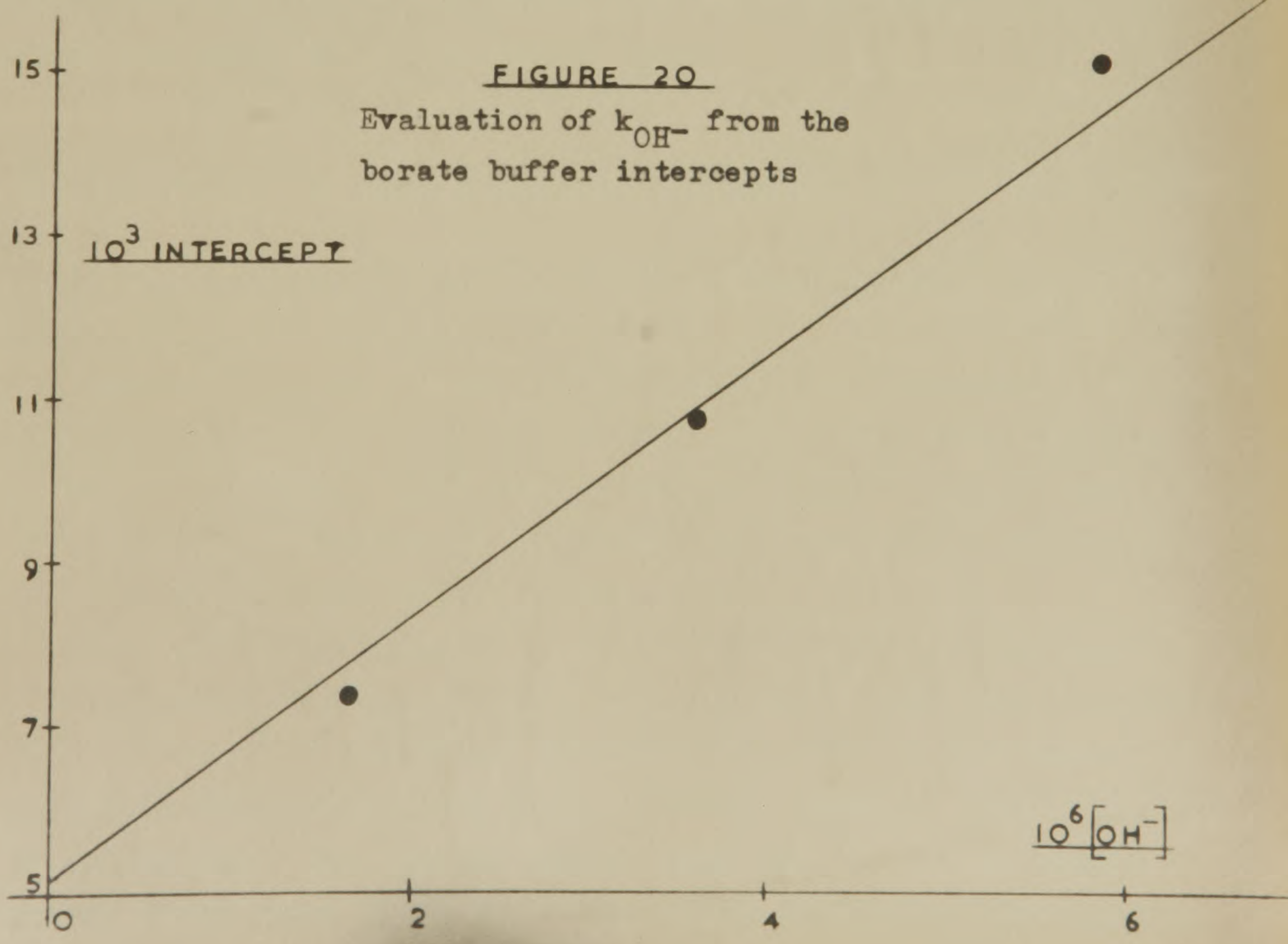


FIGURE 20

Evaluation of k_{OH^-} from the borate buffer intercepts



Comparison with other work on the Formaldehyde Reaction:

During the course of this present work some very similar work was published in Comptes Rendus by Hénaff (1963)[95]. Very few experimental details were given in the paper, but almost certainly he used techniques identical to those already described in this work. His results, given for 20°C, were:

$20^{\circ}C$ $\quad k_o = 4.5 \times 10^{-3}$

$k_{OH^-} = 770$

$k_{H^+} = 2.0$

One must assume that these results are at approximately zero ionic strength, the paper giving no guidance on this point.

He also gave an activation energy for the uncatalysed reaction of 14.8 kcal. If this value is used to correct Hénaff's k_o value to 25°C the following value is obtained:

$25^{\circ}C$ $\quad k_o = 6.9 \times 10^{-3}$

which compares reasonably favourably with the value obtained in this work from the early low concentration runs:

i.e. $\quad k_o = 5.3 \times 10^{-3}$

The discrepancy of ca. 25% between the two results may be due to several causes:

1) Small inaccuracies in the temperature control in both sets of work might contribute an error.
2) The activation energy given by Hénaff might be inaccurate. In the original paper[95] no indication of the temperature range employed to obtain it is given. In a private communication[66] Hénaff states that this activation energy was evaluated from two sets of measurements at 20°C and 1°C with hydroxylamine at pH 4.2.
3) Hénaff found that experiments with hydroxylamine, semicarbazide etc. gave first-order rate constants about 8% lower than those obtained from the sulphite reaction. He attributed this to involvement of the final dehydration step of the reaction scheme. This might well be so, at some pHs, but the present work has shown that over a fairly large range of pH the ultra-violet scavengers give kinetic

results independent of this final stage, and in the pH range used by Hénaff (pH 2 - 9)[66] he would have found conditions in which the final step was fast in comparison to the formaldehyde dehydration step. A more probable reason for his non-agreement could be a failure to allow for catalytic contributions from the scavengers themselves. In his private communication[66] he gives the maximum concentrations of the scavengers used as: $[\text{sulphite}] = 9 \times 10^{-3}$, $[\text{hydroxylamine}] = 45 \times 10^{-3}$ and $[\text{semicarbazide}] = 25 \times 10^{-3}$. At these concentrations a significant contribution to the observed rate would be expected from catalysis by the scavenger species themselves. It is thus not surprising that Hénaff's results are somewhat higher than those obtained in the present work.

One other point of interest in the French work was that he evaluated a theoretical expression for the rate of sulphite reaction. Taking the scheme:

$$H_2C(OH)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HCHO \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} {}^{-}O - CH_2 - SO_3^{-} \qquad [SO_3^{=}]$$

he calculated that:

$$\text{rate of reaction} = k_1 \left[\frac{1}{1 + k_{-1}/k_2 [SO_3^{=}]} \right] [H_2C(OH)_2]$$

Experimental results gave k_{-1}/k_2 a value of 1.3×10^{-6} mole litre^{-1}. Thus under all the experimental conditions used in this present work the term $k_{-1}/k_2 [SO_3^{=}]$ was very small and the equation:

$$\text{rate} = k_1 [H_2C(OH)_2]$$

entirely applicable.

Polarographic work: The results of polarographic work on this reaction were given in Table 3, page 6. The final two lines of this table are reproduced on the following page:

$K_d k_o$	$K_d k_{H_2BO_3^-}$	$K_d k_{OH^-}$	Author
1.5×10^{-6}	-	-	Lanquist[21]
1.3×10^{-5}	1.3×10^{-3}	0.57	Brdicka[27]

All at 20°C.

The most accurate value of K_d appears to be that obtained by Valenta[23] i.e. $K_d = 4.37 \times 10^{-4}$ at 20°C. This was obtained polarographically using short triangular pulses, thus minimising further formaldehyde hydrate dissociation. It also seems reasonable in that it is mid-way between the two extreme spectrophotometric values. If this K_d value is put into the polarographic data the results in Table 15 are obtained.

TABLE 15.

k_o	$k_{H_2BO_3^-}$	k_{OH^-}	Source
3.4×10^{-3}	-	-	Lanquist
3.0×10^{-2}	3.0	1300	Brdicka
4.5×10^{-3}	-	770	Hénaff
3.3×10^{-3}	2.0	1060	Author

The author's catalytic constants have been corrected with Hénaff's activation energy. This activation energy was obtained for the water rate, but in applying it to the other constants no substantial inaccuracies are likely to be produced. c.f. 121

Apart from the k_o value of Brdicka the scavenger and polarographic results are in good agreement. This anomalous k_o value may be due to errors in extrapolation. In the buffer solutions used the water contribution was only a small proportion of the observed rate; thus making an accurate determination of k_o difficult. Lanquist's k_o value was obtained from a series of low concentration phosphate buffers made up to pH 7. Some other results of Lanquist's, Table 16, also show reasonable agreement.

TABLE 16

Electrolyte:pH		k_1 Lanquist	k_1 calc.
0.010M Na_2CO_3	9.54	0.069	0.046
	10.44	0.41	0.31
	10.88	0.64	0.85

The value of $k_{CO_3^=}$ used in evaluating k_1 calc. was estimated from the Brönsted plot Figure 21 page 97 . It was corrected to 20°C with Henaff's activation energy.

Carbonyl Addition Reactions: In the light of the present work it is obvious that many other reactions of aldehydes and ketones will proceed via the free carbonyl group. Some other reactions in which rate-contributing aldehyde dehydrations might be encountered are reviewed below:

1. Cyanohydrin formation: no kinetic experiments with formaldehyde have been undertaken so far. Work with acetaldehyde[96] shows the reaction to be mechanistically very similar to semicarbazone formation etc.

2. Borohydride reduction:

$$>C=O + H_4B^- \rightleftharpoons >C<_{OBH_3^-}^{H}$$

Brown and Tchikawa (1957)[97] found a good linear free-energy relationship between the equilibrium constants for the dissociation of cyanohydrins and the rate constants for the reactions of cyclanones with sodium borohydride. This is obviously attributable to the similarity of the two reactions. It would be very interesting if a future worker could investigate the borohydride reduction of some hydrated carbonyl compounds.

3. Dimedone: Its reaction with formaldehyde was investigated by Spencer and Henshall (1955)[98]. The pH-rate profile was shown to be very similar to that for semicarbazide formation. Under the conditions used the formaldehyde dehydration was fast in comparison to the dimedone reaction.

4. Amides: Many workers[e.g. 99] have investigated their reaction with formaldehyde, reaction rates for both possible steps are slow in comparison to the dehydration step.
5. Ammonia:[e.g. 114,119.] The remarks concerning amides apply equally well to this compound. The reaction is even more complicated there being more possibilities for further reaction.

Catalytic constants.

The catalytic constants given in the results section are collected in the following tables. Various types of Brönsted plot obtained from them are shown in Figures 21-26.

GROUP A:

Carboxylic acids:

acid	K	k_a	k_b
chloroacetic	1.36×10^{-3}	0.116	0.0047
formic	1.77×10^{-4}	0.079	0.0134
acetic	1.75×10^{-5}	0.043	0.0224
trimethylacetic	8.91×10^{-6}	0.025	0.0222

For these compounds p = 1, q = 2

GROUP B:

Acids on the titrator

acid	K	k_B
salicylic	1.05×10^{-3}	0.0052
phenoxyacetic	6.75×10^{-4}	0.0057
p-nitrobenzoic	3.61×10^{-4}	0.0068
glycollic	1.48×10^{-4}	0.0125
o-toluic	1.24×10^{-4}	0.0100
o-methoxybenzoic	8.06×10^{-5}	0.0153
benzoic	6.30×10^{-5}	0.0127
oxalic (K_2)	5.41×10^{-5}	0.0261
phenylacetic	4.88×10^{-5}	0.0154
p-toluic	4.24×10^{-5}	0.0152
cinnamic	3.65×10^{-5}	0.0167

For oxalate p = 1, q = 4, for the rest p = 1, q = 2.

GROUP C:

A phenol on the titrator

phenol	K	k_B
pentachlorophenol	5.5×10^{-6}	0.0219

p = 1, q = 1.

GROUP D:

Nitrogen compounds

acid	p	q	K	k_a	k_b
semicarbazide	1	1	2.24×10^{-4}	0.0585	0.0048
hydrazoic	1	2	2.8×10^{-5}	-	(0.002)
pyrindinium	1	1	6.0×10^{-6}	-	0.0149
hydroxylammonium	1	1	1.07×10^{-6}	0.0195	0.0316

GROUP E:

Inorganic compounds

acidic species	p	q	K	k_a	k_b
HSO_4^-	1	4	1.03×10^{-2}	-	0.0066
HF	1	1	6.71×10^{-4}	-	0.0177
$(CH_3)_2AsOOH$	1	2	5.39×10^{-7}	0.031	0.113
$H_2AsO_4^-$	2	3	1.7×10^{-7}	0.079	0.293
$H_2PO_3^-$	1	3	1.5×10^{-7}	0.044	0.217
HSO_3^-	1	3	6.24×10^{-8}	-	0.22
$H_2PO_4^-$	2	3	6.2×10^{-8}	0.088	0.39
H_6TeO_6	6	1	2.0×10^{-8}	0.030	0.45
* H_3BO_3	3	1	6.2×10^{-10}	0.0048	3.05
* $HB(OH)_4$	1	4	6.2×10^{-10}	0.0048	3.05

* The structure of borate will be discussed on page 112.

GROUP F:

The collected water, hydrogen ion and hydroxide ion catalytic constants.

acid	p	q	K	k_a	k_b
H_3O^+	1	1	* 55.5	1.8	9.2×10^{-5}
H_2O	1	1	1.8×10^{-16}	9.2×10^{-5}	1620

* See below.

The Acid Strength of H_3O^+.

The figure 55.5 is usually given for the acid strength of H_3O^+, this being the number of formula weights of H_2O in a litre of water. This procedure is open to objection both because of the high concentrations involved, and because of the associated nature of water. Bell (1943)[100] attempted to obtain a more reliable estimate of the acid strength of H_3O^+. He assumed that the molecules in liquid water could

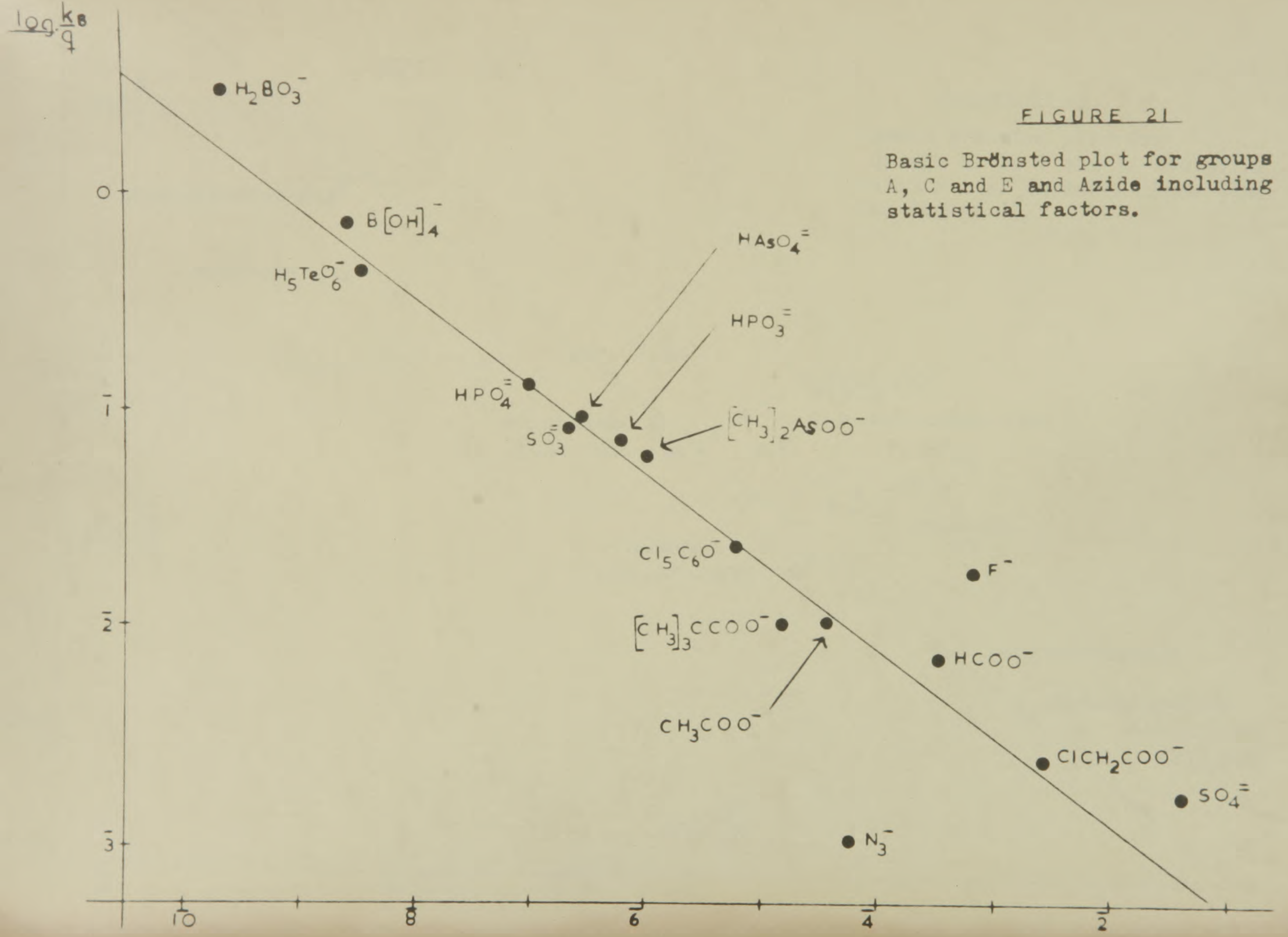


FIGURE 21

Basic Brönsted plot for groups A, C and E and Azide including statistical factors.

FIGURE 22

Basic Brönsted plot for Groups A, B, C and D. including statistical factors. Same line as Figure 21.

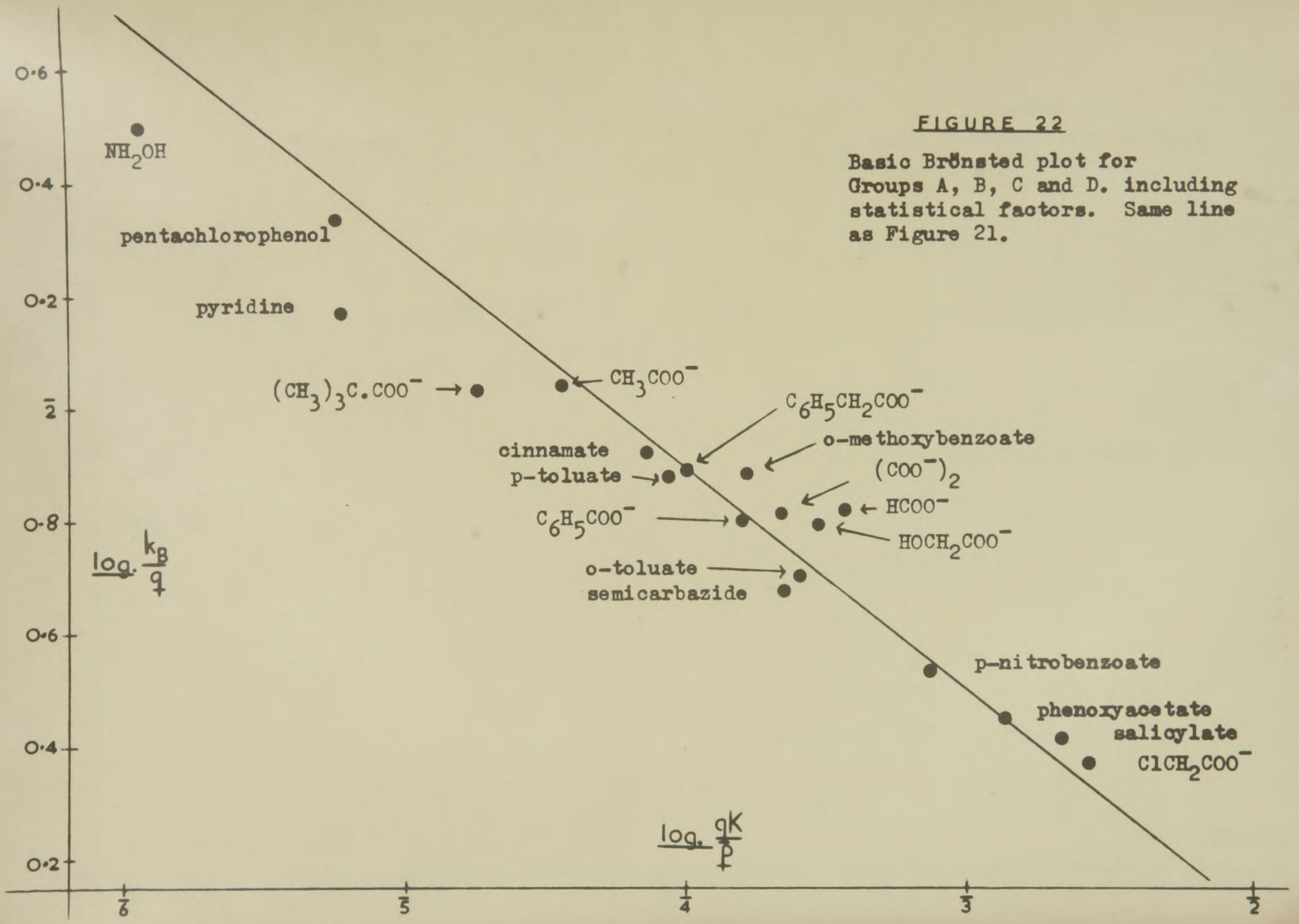


FIGURE 23

Basic Brönsted plot without statistical factors.

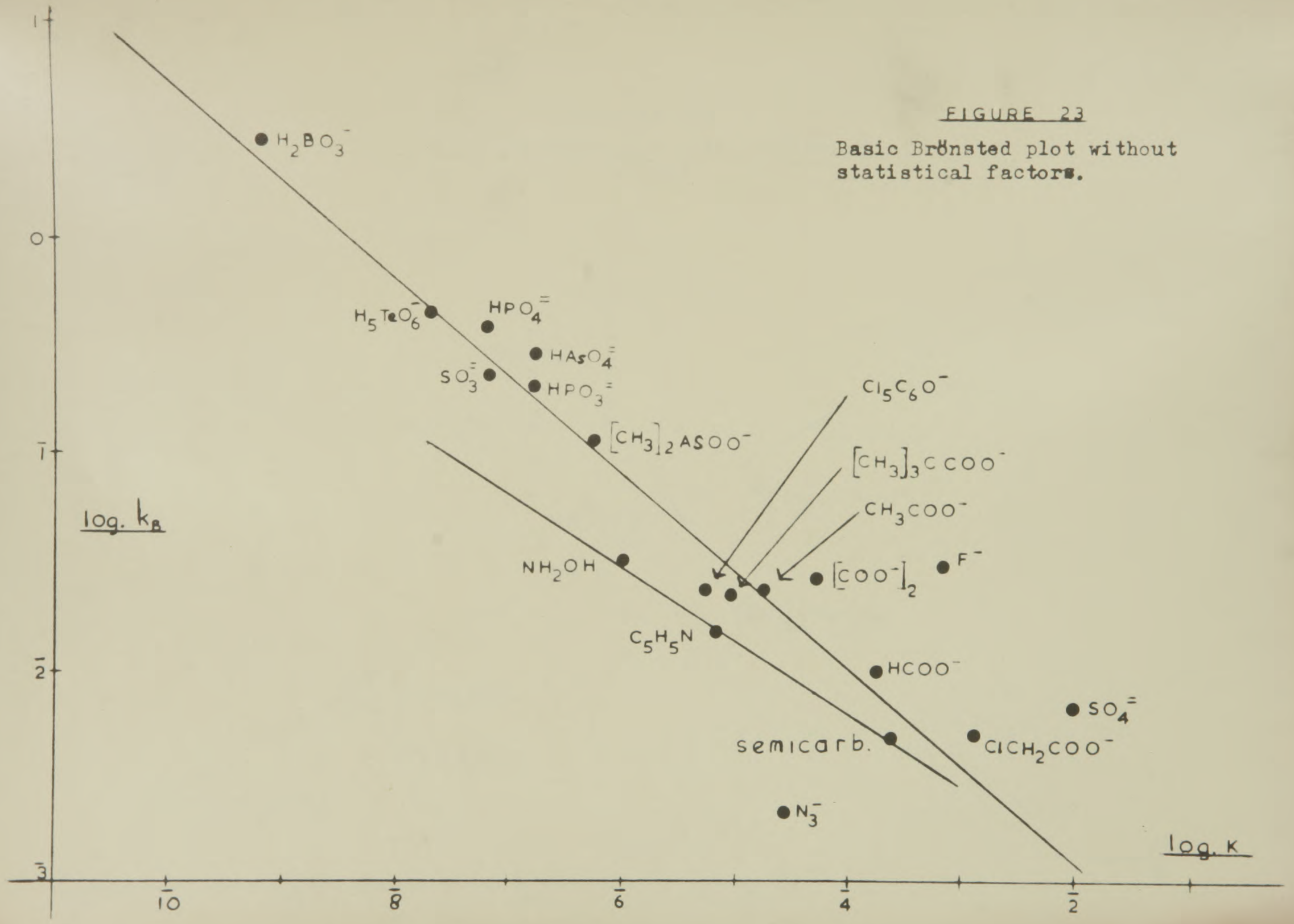
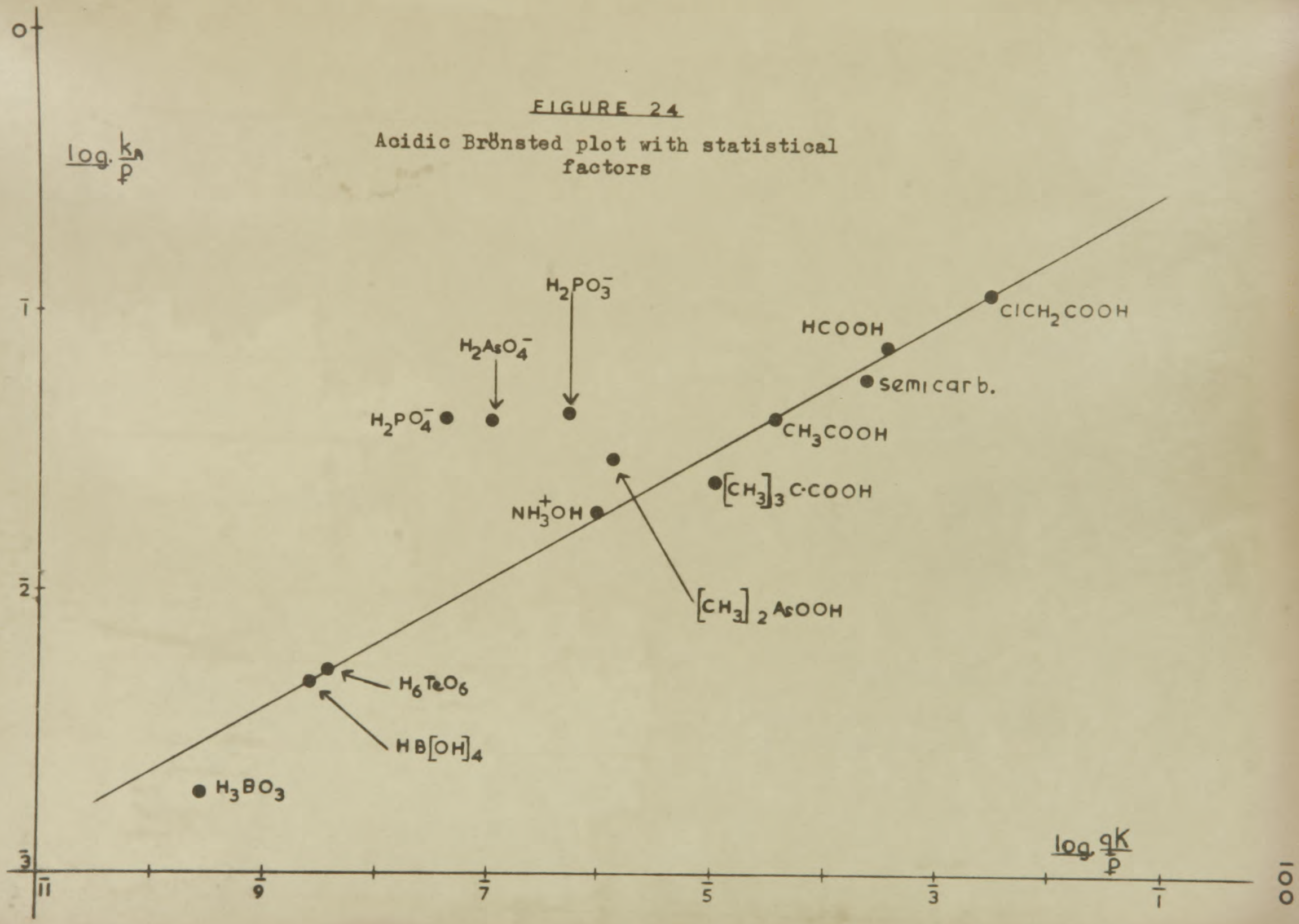


FIGURE 24

Acidic Brönsted plot with statistical factors



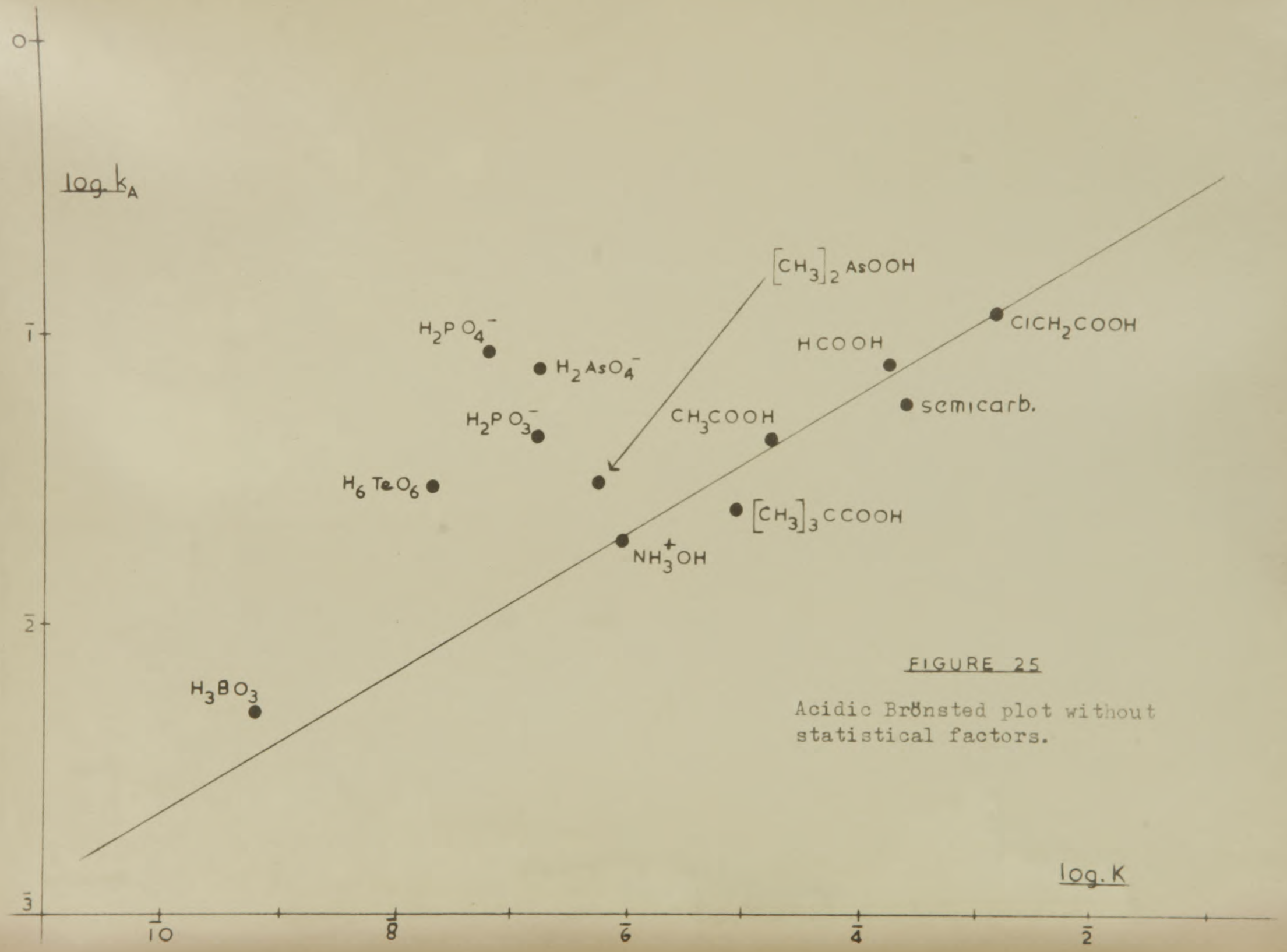


FIGURE 25

Acidic Brönsted plot without statistical factors.

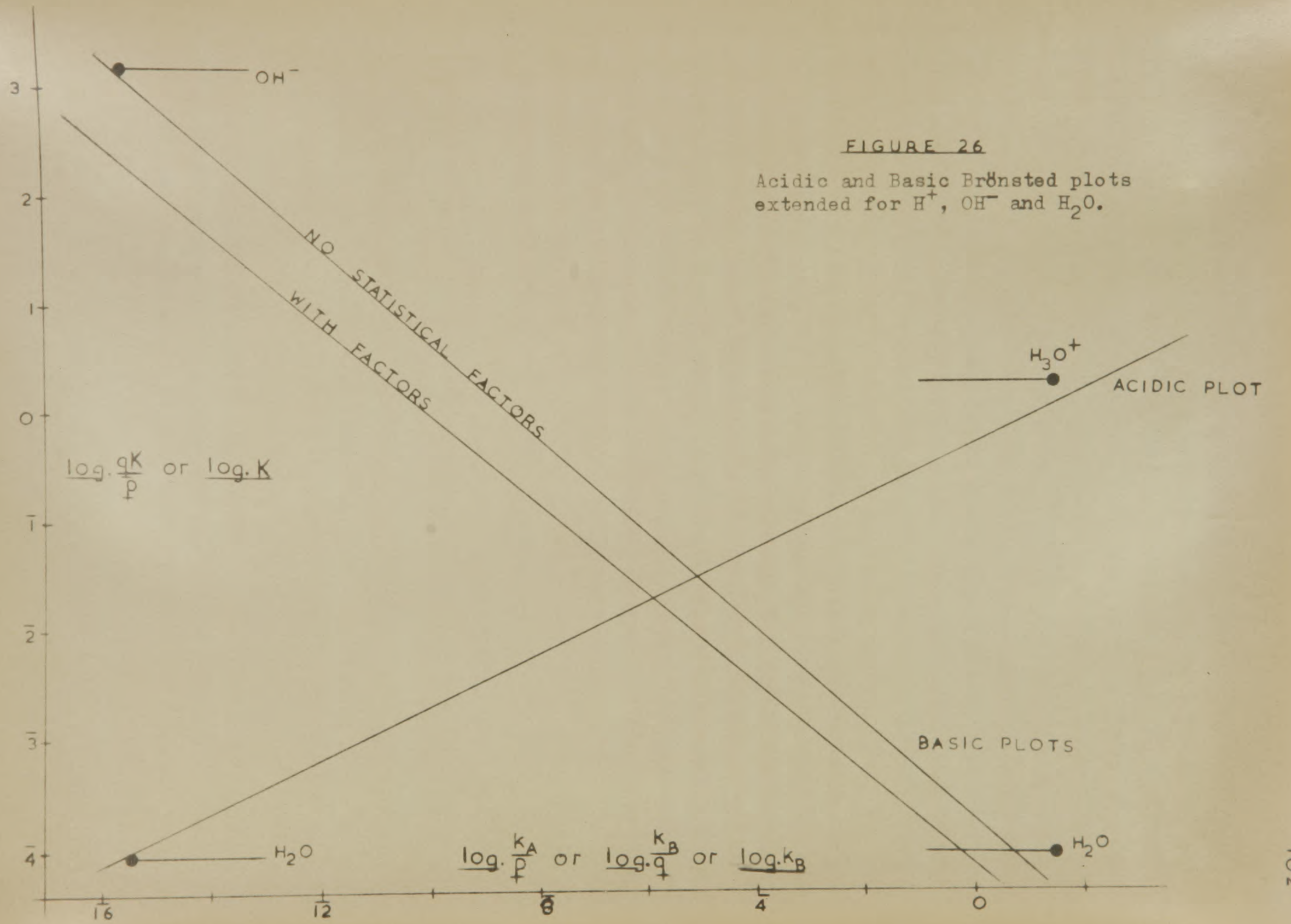


FIGURE 26

Acidic and Basic Brönsted plots extended for H^+, OH^- and H_2O.

be divided sharply into two classes, those which were associated, and those which were free. If the concentration of the latter was $[H_2O^*]$ then the product $f^*[H_2O^*]$ would be more suitable for the strength of H_3O^+. From solubility and freezing point data for water in various solvents, an approximate figure of 0.1 was suggested for this product. This figure, though probably nearer the "true" acid strength of H_3O^+ may best, perhaps, be regarded as the lower limit of this "dissociation constant". This range of dissociation constants is shown on the Brönsted plot, Figure 26, which has been extended to cover catalysis by H_2O, H^+ and OH^-.

The Bronsted Plots.

The formaldehyde dehydration reaction gives good acidic and basic Brönsted plots over large pK ranges. Water falls near the line so that no differentiation between it acting as either a base or an acid, or both, can be made. The plots will be discussed in relation to the following headings:

1. General range of validity of the Bronsted relationships.
2. Eigen curvature.
3. Charge effects.
4. Statistical factors.
5. Steric effects.
6. Deviations from the plots.
7. Comparison with (a) other organic carbonyl hydration reactions (b) Cordes and Jencks'[59] work.
8. Discussion of Sharma and Danckwerts'[41] carbon dioxide hydration studies.
9. Conclusions.

Range of Validity of Bronsted Expressions.

$$k_A/p = G_A\left[\frac{qK}{p}\right]^{\alpha} \qquad k_B/q = G_B\left[\frac{p}{qK}\right]^{\beta}$$

The original statement of the Bronsted relations was that

G_A, G_B, α and β were constants for a similar series of catalysts (see page 11). The operative word in this formulation is "similar". The present work shows that for the formaldehyde dehydration reaction this expression covers catalysts of several different types; even compounds containing different types of atom bonded to the proton i.e. N-H, O-H and H-F, show only small deviations from the mean lines. Apart from the oximes, enols and nitroparaffins which present notable exceptions, this general validity of the Brönsted relations is equally apparent in the other organic carbonyl hydration reactions studied. Eigen curvature permitting, this general applicability of the expressions to a wide variety of species e.g. carboxylic acids, inorganic acids, amines, etc., is found in many reactions. The only system studied so far which shows large deviations with a wide range of compounds is the carbon dioxide hydration reaction. In other reactions large deviations from the relations are very much the exception. This is fairly surprising when one considers that the Brönsted relationships are almost entirely empirical and even in Eigen's terms are only "crude first approximations". Some of the more recent general acid-base catalysis studies are tabulated out below showing the smallness of deviations and the very good general applicability of the Brönsted relationships.

Kresge and Chiang (1961):[101] acid-catalysed hydrogen exchange in 1,3,5-trimethoxybenzene-2-t. Their results are listed below: $\alpha = 0.52$.

catalyst.	log. deviation
H_3O^+	+ 0.03
CH_2FCO_2H	+ 0.20
HCOOH	- 0.15
CH_3COOH	+ 0.11
$H_2PO_4^-$	+ 0.03
NH_4^+	- 0.40
H_2O	+ 0.23

Bell and Spencer (1959):[102] base-catalysed bromination of ethyl nitroacetate.

β = 0.66, 6 carboxylate anions, pyridine and α-picoline obey a single Brönsted relationship to within log. deviation ± 0.2.

Jencks and Carriuolo (1961):[103] base-catalysed hydrolysis of ethyl dichloroacetate. β = 0.47, H_2O, $HCOO^-$, CH_3COO^-, pyridine, succinate, 4-picoline, $HPO_4^=$ and imidazole give a good plot.

No statistical factors were used. Aniline the only other species studied shows a deviation of - 0.5.

Lifshitz and Perlmutter-Hayman (1962):[104] basic hydrolysis of chlorine. $H_2O + Cl_2 \longrightarrow HOCl + Cl^- + H^+$ β = 0.54, CH_2ClCOO^-, $HCOO^-$, $SO_4^=$, $CHCl_2COO^-$, $HPO_4^=$ and H_2O obey a single relationship to within log. ± 0.2.

2. Eigen curvature:[47] The formaldehyde dehydration reaction gives a good Brönsted plot over "too large" a pK range; it falls in Eigen's special group (see page 13). The other reactions in this group are the hydration of acetaldehyde and s-dichloroacetone and the mutarotation of glucose. The position of k_{OH^-} on the base-catalysed Brönsted plot is specially significant for if curvature occurs this should fall well below the calculated value. The only case before the present work where this was not so was in the base-catalysed mutarotation of glucose, see Table 17.

TABLE 17

	k_{OH^-} obs.	k_{OH^-} calc.
Dehydration of Formaldehyde	1.6×10^3	2.2×10^2*
Mutarotation of Glucose[105]	3.8×10^3	7.4×10^2
cf. Decomposition of Nitramide[105]	1.0×10^6	1.0×10^9
Iodination of Acetone[105]	1.5×10^1	5.2×10^4

* This value is taken from plot with statistical factors.

The explanation of the "straightness" of the special group's Brönsted plots probably lies in their involvement of the solvent in the transition state, see mechanism page 120 . The reaction mechanisms

proposed for the carbonyl hydration reactions involve a formal termolecular stage. This fairly complicated transition state requiring orientation of three species means that limiting diffusion conditions are never approached and the slope of the Brönsted plot maintains a constant value.

3. Charge effects: The results of the early general acid-base catalysis studies showed a marked dependence on the charge carried by the catalyst. Some results obtained for the decomposition of nitramide[105] are shown below illustrating this point.

Bases with two negative charges: $k_B/q = 2.07 \times 10^{-5}\left[\frac{p}{qK}\right]^{0.87}$

Uncharged bases: $k_B/q = 1.70 \times 10^{-4}\left[\frac{p}{qK}\right]^{0.75}$

Bases with two positive charges: $k_B/q = 7.8 \times 10^{-3}\left[\frac{p}{qK}\right]^{0.82}$

These and many other early results were in accord with the predictions of the Pedersen charge rules.[44]

The formaldehyde dehydration reaction appears to be fairly insensitive to charge effects. The small deviations which could conceivably be attributed to charge effects are unfortunately not in agreement with the Pedersen charge rules. Thus in basic catalysis, $\beta = 0.40$. Thus it is a difficult system to classify since it falls on Pedersen's border-line. This border-line is defined by the phrase: 'if β is sufficiently large and always if $\beta > \frac{1}{2}$'. If β is taken as small the behaviour of the uncharged nitrogen bases relative to carboxylic acid anions can be attributed to a 'Pedersen' charge effect. This however can hardly be counted a satisfactory application of the charge rule. No other data on charge effects in base-catalysed carbonyl hydrations are available for comparison.

In acid catalysis, $\alpha = 0.23$. Here in applying the charge rules α must obviously be taken as small. The high values of

$H_2PO_4^-$, $H_2PO_3^-$ and $H_2AsO_4^-$ and the slightly low values of the positively charged nitrogen compounds are definitely against the predictions of the charge rules.

This insensitivity to charge effects was also shown in the work of Bell, Rand and Wynne-Jones[15] on the hydration of acetaldehyde. Their acidic Brönsted plot showed pyridinium ions and carboxylic acids falling on the same line. This lack of charge effects is equally apparent in recent general acid-base catalysis studies tabulated on page 104, and in the semicarbazone formation work of Cordes and Jencks[59], see page 117.

4. Statistical Factors: In Figures 21 - 26 Brönsted plots are given with and without statistical factors included. In the basic catalysis plot little improvement in the scatter is produced by the introduction of these factors. Some justification for statistical factors may be found in the position of pentachlorophenol; its position relative to the carboxylic acids being definitely improved by the inclusion of a statistical correction. Oxalate in which the two groups are fairly independent obviously justifies at least half of its factor of $q = 4$. The slope of the basic plot is slightly steeper in the plot with no statistical corrections.

$\beta = 0.40$ with statistical factors included.

$\beta = 0.45$ without.

This is due to the higher pK inorganic species having the higher statistical corrections e.g. telluric acid $p = 6$, $q = 1$, sulphite $p = 1$, $q = 3$ as against the carboxylic acids $p = 1$, $q = 2$. One point of interest is that the k_{OH^-} value falls much nearer the line on the plot without statistical factors, see Figure 26. The acidic Brönsted plot is slightly improved by the inclusion of statistical factors, the inorganic species grouping slightly nearer the line.

The use of Benson's statistical factors[45] would make little difference to the plots as in nearly every case they are identical with the "classical" statistical factors used. The main conclusion from the

present work is that the errors introduced by the omission of statistical factors are small in comparison to the deviations produced by other effects. The only real requirement for statistical corrections appears to be with compounds containing several distinct functional groups.

5. Steric effects: The existence of steric effects in the formaldehyde dehydration reaction is not very well defined. Possible steric effects are of several types.

A. Classical steric hindrance: This blocks off lines of approach and makes the formation of the transition state difficult. This accounts for the low catalytic constant of α-picoline as compared to γ-picoline in the hydration of acetaldehyde.[15]

The low value for trimethylacetate might be due to this type of steric hindrance. A direct measure of the blocking effect of the t-butyl group is given by a comparison of the proton decomposition and recombination rates of acetic and trimethylacetic acids. These have been measured by Albery and Bell (1963)[106]. Their values are shown in Table 18.

TABLE 18

	k_d sec^{-1}	k_r m^{-1} sec^{-1}
acetic acid	9.1×10^5	5.2×10^{10}
trimethylacetic acid	1.42×10^5	1.53×10^{10}

This type of proton jump reaction is however not quite comparable to the present case. Any argument based on lines of approach is at least partially invalidated by the solvent cage effect. This probably means that once the molecules get together they stay together for considerable periods colliding several times until they eventually achieve the correct orientation for reaction.

B. Positive steric effects: Bell, Gelles and Möller (1949)[107] in their work on the halogenation of ketones and esters, showed that the proximity of two large groups could give positive deviations. This

lowers the energy of the transition state as when the reactant species are closer together they will cause the separation of fewer solvent molecules than when they are further apart. This factor would tend to stabilise the transition state. This effect may be increased by Van der Waals forces between the groups. Effects of this type might easily account for many of the observed deviations from the Brönsted relations, but could hardly be very important in this reaction, formaldehyde hydrate being a relatively small molecule.

6. Deviations: Before discussing the more notable deviations from the Brönsted plots it must be stated that there is rarely a simple explanation for any deviation. One has only to compare the efficiency of a catalyst in several similar reactions to be convinced of this. The random occurrence of these small deviations is not surprising in view of the considerable number of factors upon which catalyst efficiency may depend: (a) the equilibrium constant for the formation of the hydrogen-bonded complex between the catalyst and substrate, (b) the amount of polarisation of the carbonyl group by the catalyst which facilitates attack by the nucleophilic reagent, (c) the rate of proton transfer between the catalyst and substrate. Thus while these properties may be individually correlated with the acidity of the catalyst, the overall catalytic efficiency may be somewhat different for different types of acids.

Basic catalysis: This plot seems to show a dependence on the type of atom that the proton is bonded to, Figures 21 - 23. Thus fluoride falls high, 24 compounds containing oxygen bonds obey the relation:

$$k_B/q = 2.00 \times 10^{-4}\left[\frac{p}{qK}\right]^{0.40}$$

to within $\pm$ 0.4 log units. 3 nitrogen bases fall within the range just specified, but consistently low obeying the relation:

$$k_B/q = 2.24 \times 10^{-4}\left[\frac{p}{qK}\right]^{0.35}$$

Finally azide falls very low and is obviously in a special category. Classical charge effects having been ruled out it appears that the Brönsted relation is just not adequate to cope accurately with the

changes in the shapes of the energy curves for the N-H, O-H and F-H bonds.

The following deviations will be discussed individually.

species	log. deviation*
N_3^-	ca. -1
F^-	+ 0.63
$SO_4^=$	+ 0.33
$(CH_3)_3COO^-$	- 0.17
$HCOO^-$	+ 0.15

* all log. deviations are taken from the plots including statistical factors.

Azide: This showed such a large negative deviation that it was impossible to measure its catalytic constant with any accuracy. The N_3^- ion is somewhat analogous to a nitro-compound in that it has several resonance forms:

$$\overset{-}{N} = \overset{+}{N} = N^- \longleftrightarrow {}^-N - \overset{+}{N} \equiv N \longleftrightarrow N \equiv \overset{+}{N} - \overset{=}{N}$$

and requires much electronic rearrangement in going to hydrazoic acid.

Unfortunately no other studies of azide catalysis have been undertaken. Hydrazoic acid was one of the catalysts investigated in the reaction of semicarbazide with p-chlorobenzaldehyde[59]. In this work hydrazoic acid fell on the line with the carboxylic acids.

Fluoride: This shows a fairly large positive deviation. Catalysis by the fluoride ion has been discussed by Bell and McCoubrey (1956)[108]. They point out that since no electronic rearrangement is involved in ionisation it might be expected to resemble acids such as oximes which are more powerful catalysts than carboxylic acids of the same pK. This however is not a legitimate comparison since the proton is attached to a different kind of atom. Basing their arguments on the bond energies of the H-F and H-O bonds and the electron affinities of fluorine and oxygen they concluded that the fluorine acid will usually have a lower

catalytic power than the corresponding carboxylic acid. Their results for five different reactions are shown in Table 19.

TABLE 19

Reaction	k_T - log. deviation*	β
Decomposition of nitramide	+ 0.17	0.76
Bromination of ethyl acetoacetate	- 0.25	0.59
Bromination of ethyl cyclopentanone 2-carboxylate	- 0.29	0.58
Iodination of acetonylacetone	+ 0.16	0.89
Iodination of acetone	- 0.13	0.88

* No statistical corrections were made.

From the above Table 19 it is clear that an accurate prediction of fluoride's catalytic efficiency be it high or low is quite impossible.

In the present work it could conceivably be the fluoride ion's lack of steric requirements which gives it some of its high catalytic effect (cf. trimethylacetate falling low, formate slightly high).

Sulphate: This shows a small positive deviation. This deviation may be suspect in view of the very small catalytic effect measured. Again this species has no steric requirements.

Trimethylacetate and Formate: These two species are the most and least sterically hindered of the carboxylic acids studied. Their deviations could be due to a 'lines of approach' effect or a difference in solvent structure round the two groups. A comparison of the deviations shown by trimethylacetate and formate in the other carbonyl hydration reactions studied is given on page 116.

Acidic catalysis: Of the 12 catalysts studied all except three obey the relation:

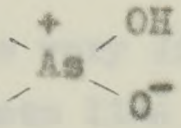
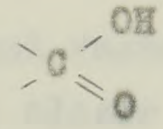
$$k_A/p = 0.457\left[\frac{qK}{p}\right]^{0.23}$$

to within $\pm$ 0.2 log units.

The following substances showing significant deviations will be discussed individually.

substance	log. deviation
$(CH_3)_2AsOOH$	+ 0.20
$H_2PO_3^-$	+ 0.44
$H_2AsO_4^-$	+ 0.56
$H_2PO_4^-$	+ 0.68

Cacodylic acid: This small positive deviation may be due to some form of semi-polar bond participation:

e.g.  as against 

This slight change of bond type is too big a change in structure for the Brönsted relation to hold. A similar small positive deviation, + 0.4, is shown in the Bell and Darwent work[10] on the hydration of acetaldehyde. One other possible explanation of this high catalytic effect could be that this compound is catalysing via simultaneous operation of both its acidic and basic functions. It is difficult to postulate a satisfactory mechanism on this interpretation. A check on the basic Brönsted plot shows that it is not possible to explain this high catalytic effect in terms of the species acting as a base for its first ionisation constant.

$H_2PO_3^-$, $H_2AsO_4^-$ and $H_2PO_4^-$: The cacodylic acid remarks apply equally well to these compounds. $H_2AsO_4^-$ and $H_2PO_4^-$ also show positive deviations of the same order of magnitude in the reaction of semicarbazide with p-chlorobenzaldehyde, see next section.

Borate: This falls near the mean lines in both the acidic and basic plots. In several other reactions e.g. bromination of ethyl malonate[43], borate has a very low catalytic effect. This has been attributed to the structure of the borate ion in aqueous solution. Raman spectra shows it to exist as $B(OH)_4^-$ rather than $B(OH)_2O^-$. Thus if boric acid exists in aqueous solution as H_3BO_3, $B(OH)_4^-$ can only act as a proton acceptor by

simultaneous loss of a water molecule. The present work suggests that the acid exists in solution in the following form:

$H_2O - \underset{\underset{OH}{|}}{\overset{OH}{|}}{B} - OH$. Raman spectra investigations might verify this point.

On this basic Brönsted plot including statistical factors, Figure 21, two species are shown:

$H_2BO_3^-$ with $p = 3$, $q = 1$

$B(OH)_4^-$ $p = 1$, $q = 4$

in spite of the very different statistical factors both points fall close to the mean line, $B(OH)_4^-$ being the closer point. On the acidic plot the two possible species are again shown $HB(OH)_4$ again falling somewhat closer to the mean line than H_3BO_3.

7a. Comparison with other Carbonyl Hydration Reactions:

The following similarities have already been noted:

a) good plots over large pK ranges

b) lack of Eigen curvature

c) insensitivity to catalyst charge type.

Deviations from the mean lines and the slopes of these lines will now be discussed.

Deviations from the Plots: These systems show few large deviations from the Brönsted plots. These are produced by "unusual" catalytic species. Comparison and discussion of the minor deviations found with different carbonyl compounds are not very valuable in view of the range of solvents used, see Table 20.

Solvent effects have been discussed by Bell in his book, "Acid-Base Catalysis".[105] Changes in solvent alter both catalytic constants and ionisation constants. Some examples of the effect of solvent on catalytic constants obtained from work on the decomposition of nitramide are given in Table 21.[105]

TABLE 20

Reaction	Solvent	Dielectric constant
Acid catalysed dehydration of acetaldehyde.[9]	92.5% acetone 7.5% water	22.8
Acid-base catalysis of hydration of s-dichloroacetone.[29]	95% dioxan 5% water	5.6
Acid-base catalysis of hydration of acetaldehyde.[15]	water	78.5

TABLE 21

Catalyst	Water	m-cresol	isoamyl alcohol
	ε = 78.5	ε = 13	ε = 5.7
aniline	0.97	0.146	0.033
dichloracetate ion	0.0010	0.0118	0.063
benzoate ion	0.36	5.4	17.0

Bell states that in any series of acids of the same charge type, 'the relative strength is approximately independent of solvent.' pKs measured in water have been used by Bell and Higginson[9] in their work on acetaldehyde and by Bell and Jensen[29] with s-dichloroacetone. This may be the cause of some of the minor deviations and discrepancies between plots.

One compensating factor in the present comparison is that the "local" medium of the catalyst or aldehyde in the dioxan-water and aqueous acetone solvents used might well be analogous to that in aqueous solution, the species hydrogen bonding preferentially to the water. Longer range effects would however be very different in the different solvents.

The medium also has a small effect on the slope of Brönsted plot, also investigated for the decomposition of nitramide, see Table 22.[105]

TABLE 22

Slope β

Solvent	ε	Anions	Amines
Water	78.5	0.80	0.75
m-cresol	13	0.78	0.84
i-amyl alcohol	5.7	0.83	0.92
anisole	4.4	-	0.64

Recent work by Caldin and Peacock (1955)[109] on the nitramide decomposition catalysed by dimethylaniline in a variety of solvents at several temperatures is of interest in that it has shown that simple electrostatic theory is quite inadequate to explain solvent effects.

One of the major deviations in the acetaldehyde and s-dichloroacetone work which might be attributed to a medium effect and gives some measure of the possible effect is given below:

Catalyst: saccharin	log. deviation
s-dichloroacetone	- 0.8
acetaldehyde	+ 0.55

Trimethylacetic and formic acids showed the largest minor deviations in the formaldehyde work. Their logarithmic deviations in the various systems are shown in Table 23.

TABLE 23

Base catalysis:

	Trimethylacetate	Formate	
Reaction	log. deviation	log. deviation	β
Mutarotation of glucose	- 0.20	+ 0.04	0.40
Hydration of s-dichloroacetone*	0	+ 0.15	0.5
Formaldehyde	- 0.17	+ 0.15	0.40
Acid catalysis:			α
s-dichloroacetone*	+ 0.2	- 0.1	0.27
Dehydration of acetaldehyde**	+ 0.3	- 0.2	0.56
Hydration of acetaldehyde	0	+ 0.05	0.54
Formaldehyde	- 0.1	+ 0.02	0.23

* dioxan-water ** aqueous acetone

One would expect deviations to be the same, as the equilibrium constant of the reaction must have a constant value.

These deviations are all too small to permit valuable discussion.

Slopes of the Plots: The slopes of the basic Brönsted plots are tabulated in Table 24.

TABLE 24

Reaction	β	ref.
Dehyd. formaldehyde	0.40	present work
Hyd. acetaldehyde	0.43	10
Hyd. s-dichloroacetone	0.5	29
Mutarotation of glucose	0.40	105

These slopes all have similar values as would be expected from a series of such similar reactions. The pKs of the carbonyl compounds which have been measured are formaldehyde 13.27 and acetaldehyde 13.57.[111] which are consistent with the above β values.

In Table 25 the acidic catalysis slopes are given.

TABLE 25

Reaction	α	ref.
Dehyd. formaldehyde	0.23	present work
Dehyd. acetaldehyde	0.56	9
Hyd. "	0.54	15
" "	0.37	10
Hyd. s-dichloroacetone	0.27	29
Mutarotation of glucose	0.3	105

The acidic catalysis slopes with the notable exception of acetaldehyde again have very similar values. It is very difficult to see any theoretical reason for this high acetaldehyde value. There does however appear to be some uncertainty concerning the exact acetaldehyde value, as the Bell and Darwent results[10] give a substantially lower value than the other work. It is tempting to suggest that the high value obtained by Bell and Higginson[9] was in part due to a medium effect, c.f. Table 20, page 114. The results of Bell, Rand and Wynne-Jones[15] are somewhat suspect in view of Gruen and McTigue's objections to the thermal maximum method used in their work. These objections will be discussed in a later section.

7b. Cordes and Jencks' semicarbazide work:[59] They studied general acid-catalysis in the attack of semicarbazide on p-chlorobenzaldehyde. 30 acids were investigated of which ten acids had catalytic constants three to fivefold greater than predicted by the Brönsted plot (slope 0.25). These abnormally effective catalysts were $H_2PO_4^-$ (log. deviation 0.7), $H_2AsO_4^-$ (deviation 0.4), hydroxamic acids, substituted ammonium ions and the pyridinium ion. The plot was linear over the range studied, 12 pK units; H_3O^+ fell on the line. The results showed no charge effects, species of the types A^-, A° and A^+ all falling above the mean line. If statistical factors were not included the results showed no significant alteration in the degree of scatter. This reaction thus gives a Brönsted plot which is qualitatively very similar to that found for acidic catalysis in the present work.

8. Discussion of Carbon Dioxide Work: The work of Sharma and Danckwerts[41] is the only carbonyl hydration study to show very large deviations from the Brönsted plot, (deviations of up to ± 3 log units). Their plot is shown in the introduction, page 10 . On a naive view one would expect this reaction to give results comparable with those from the organic carbonyl hydration reactions especially so if one accepts the recent report by Pocker and Meany (1964)[110] which states that carbonic anhydrase accelerates the hydration of acetaldehyde. This enzyme's only previously known function was to catalyse the reaction between carbon dioxide and water.

Sharma and Danckwerts' main finding was that compounds containing the $^{-}O\diagdown_{X}\diagup OH$ grouping, where the negative charge is not delocalised by resonance, formed a single Brönsted group and in general were better catalysts than other inorganic anions. Special catalysis by compounds of this type is not apparent in the work with aldehydes and ketones. In the present work tellurate falls in line with the carboxylic acids on the basic plot and sulphite, another species expected to give a high value on the Sharma and Danckwerts' picture, again falls in line with the other species. Also in the Bell and Higginson* work on acetaldehyde chloral hydrate falls on the mean Brönsted line; and in the Bell and Jensen* studies on s-dichloroacetone it shows a negative deviation of ca 0.3 log units. Thus if one accepts the Sharma and Danckwerts' results one must conclude that the carbon dioxide hydration reaction proceeds by a very different mechanism to that postulated for the organic carbonyl hydrations, i.e. for basic catalysis rate step:

$$B^{-} + H_2O + RCHO \rightleftharpoons BH + RCH(OH)O^{-}$$

It is conceivable that some mechanism involving both of the carbon dioxide's oxygen atoms in the transition state might give the very specific catalytic results they obtain. It is however very difficult to

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* In the original papers an inaccurate pK value for chloral hydrate was used. Thus in the Bell and Higginson paper it was reported that chloral hydrate showed a positive deviation + 0.7. If the pK value of Bell and Onwood (1962)[111] is used no deviation is found.

suggest a plausible reaction scheme for this reaction. It might have been easier to explain their results were they approaching diffusion controlled conditions. Their plot has a slope of 0.56 and shows no marked tendency to Eigen curvature.

In the light of the above it is very tempting to suggest that these authors may have been measuring some gaseous diffusion phenomenon. They studied the pressure drop over the catalytic solutions. This requires the following system to be set up:

$$CO_2 \text{ (gaseous)} \overset{\text{fast}}{\rightleftharpoons} CO_2 \text{ (aqueous)}$$

$$CO_2 \text{ (aqueous)} + H_2O \overset{\text{slow}}{\rightleftharpoons} HCO_3^- + H^+$$

The first step could well be rate-contributing in the apparatus used. The second step in this reaction scheme is relatively fast.

$$\text{Rate} = \left[k_o + k_B[B]\right][CO_2]$$

$$k_o = 0.02 \text{ sec}^{-1}$$

i.e. $t_{\frac{1}{2}}$ for uncatalysed reaction = 35 secs.

If the first stage was rate-contributing one might envisage the wide range of rates found as being due to surface tension effects, specific surface effects with some of the catalysts adsorbed in the surface layer etc. This type of slow gaseous/liquid diffusion was noted in Roughton and Booth's work.[112] They studied the carbon dioxide hydration by a very similar method to that employed by Sharma and Danckwerts. In their paper they state that: 'Diffusion between the gas and liquid phases tends to become the limiting factor as the reaction velocity increases'.

9. Conclusions: The main inference from the present work is that one should not expect too much from the Brönsted relationships. The relationships are simple and semi-empirical; it would thus be very surprising if they exactly rationalised the complex systems they are applied to. The present reaction shows a remarkable tendency to obey these expressions. In many ways it was rather disappointing that the same type of behaviour that was shown in the hydration of carbon dioxide was not found. The author finds himself taking the somewhat negative attitude that only really large deviations, ca 1 log units, from these plots are worth considering in any theoretical detail. Any literature survey of general acid-base catalysis studies will show that very few simple correlations exist between the efficiencies of catalysts in several different reactions.

Steric and charge effects are similarly not directly comparable. To a first approximation one would expect these effects to be allowed for in the pKs of the species concerned, but obviously in some reactions they become very important. Provided these limitations are recognised these relationships fit the experimental data exceedingly well.

Mechanism.

The mechanisms proposed by Bell and co-workers[9,10,15] for the hydration of acetaldehyde appear to be applicable to the present work. They are as follows:

Acid catalysis:

$$HB + H_2C(OH)_2 \rightleftharpoons H_2C\begin{matrix}OH\\OH_2^+\end{matrix} + B^- \qquad (1)$$

$$B^- + H_2C\begin{matrix}OH\\OH_2^+\end{matrix} \rightleftharpoons HB + H_2O + HCHO \qquad (2)$$

Basic catalysis:

$$B^- + H_2C(OH)_2 \rightleftharpoons H_2C\begin{matrix}OH\\O^-\end{matrix} + HB \qquad (3)$$

$$HB + H_2C\begin{matrix}OH\\O^-\end{matrix} \rightleftharpoons HCHO + H_2O + B^- \qquad (4)$$

Of these four steps, (1) and (3) involve simple proton transfers and are almost certainly extremely rapid. The rate-determining steps thus become (2) and (4) which involve greater structural changes. Bell and Darwent[10] have shown that the reverse termolecular reactions cannot be split into two successive bimolecular steps while the overall reaction continues to show general acid-base catalysis. No other satisfactory mechanisms have been put forward for carbonyl hydration reactions.

These mechanisms are exactly analogous to those proposed for several other reactions:

1. The mutarotation of glucose.[113]
2. The semicarbazide reaction.[59]
3. Cyanohydrin formation.[96]
4. The formation of aldehyde ammonia compounds.[114]
5. Reaction of formaldehyde with amides.[99]

These mechanisms and some of the other mechanisms proposed for the carbonyl hydration reaction and the evidence for and against them will now be discussed.

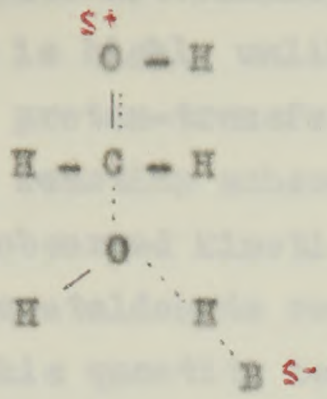
Acid Catalysis.

Gruen and McTigue[16] draw attention to an additional mechanism for the acid-catalysed reaction:

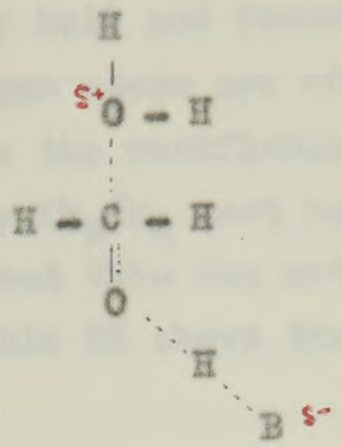
$$HB + H_2C(OH)_2 \rightleftharpoons H_2COH^+ + H_2O + B^- \qquad (5)$$

$$H_2COH^+ \rightleftharpoons HCHO + H^+ \qquad (6)$$

in which step (5) is the slow catalysed step followed by a rapid proton transfer (6). The rate-determining transition states for this mechanism (I) and that suggested by Bell et al. (II) are as shown below.



(I)



(II)

Gruen and McTigue pointed out that their results, showing that the hydrogen ion catalytic constants were almost constant in the homologous series, CH_3CHO, C_2H_5CHO, C_3H_7CHO (normal and iso), were consistent with either mechanism. This was because both mechanisms required the addition of a proton to the carbonyl-oxygen atom and the nucleophilic addition of water to the carbonyl-carbon atom; increasing the length of the hydrocarbon chain would increase the partial negative charge on both the carbonyl-carbon and the oxygen and this would affect the rate of the proton addition and water addition in opposite directions.

Another mechanism proposed by Gibert (1954)[115] also involved protonated intermediates of the type $H_2C{=}O\overset{+}{H}$. His reaction scheme was:

$$H^+ + H_2C(OH)_2 \rightleftharpoons (H_2CHOH)^+ + H_2O$$

$$H_2C(OH)_2 \rightleftharpoons (H_2CHOH)^+ + OH^-$$

$$OH^- + (H_2COH)^+ \overset{\substack{H_2O \\ H_3O^+ \\ HOAc \\ OAc^-}}{\rightleftharpoons} HCHO + H_2O$$

This scheme will only lead to general acid-base catalysis provided that reactions of the type:

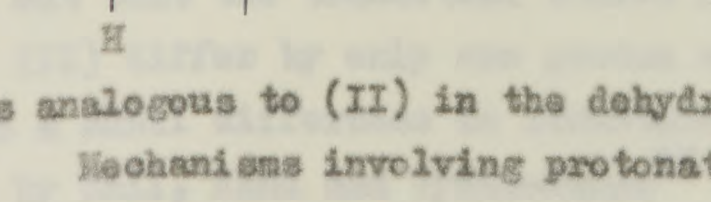
$$(H_2COH)^+ + B^- \rightleftharpoons HCHO + HB$$

are rate-determining. Bell, Rand and Wynne-Jones[15] point out that this is highly unlikely as work by Bell and Pearson (1953)[116] had shown that proton-transfers between oxygen atoms are effectively instantaneous. This reaction scheme also leads to the verifiable prediction that for the observed kinetics the quantity Kk_b/k_a must have a constant value. The acetaldehyde results showed that this was not so, large variations in this quantity being found. Table 26 shows the same to be true for formaldehyde.

TABLE 26

Acid	K	$10^6 Kk_b/k_a$
H_3O^+	55.5	284
chloroacetic	1.36×10^{-3}	55
semicarbazide	2.24×10^{-4}	18
formic	1.77×10^{-4}	30
acetic	1.75×10^{-5}	9
trimethylacetic	8.91×10^{-6}	8
hydroxylammonium	1.07×10^{-6}	1.7
cacodylic	5.39×10^{-7}	2.0
telluric	2.0×10^{-8}	0.3
boric	6.2×10^{-10}	0.4

Support for the Bell mechanism is found in the related work on acid catalysis of semicarbazone formation in a series of substituted benzaldehydes by Cordes and Jencks.[59] They produced fairly conclusive evidence for the transition state:



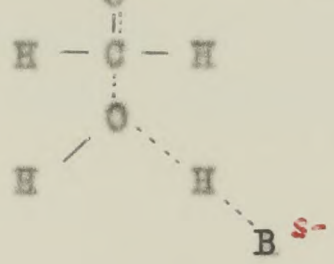
which is analogous to (II) in the dehydration reaction.

Mechanisms involving protonated aldehydes as intermediates were invalidated in the following way. They evaluated second-order rate constants from the known basicities of the benzaldehydes for the

hypothetical mechanism involving attack of semicarbazide on the protonated benzaldehydes. For p-nitrobenzaldehyde the second-order rate constant required was 2.7×10^{12} m^{-1} sec^{-1} which was an order of magnitude higher than diffusion controlled reactions in aqueous solution (the second-order rate constant for reaction of hydrated proton with hydroxide ion is 1.4×10^{11} m^{-1} sec^{-1}).[118] The calculated second-order rate constants for the other substituted benzaldehydes were all lower than that obtained for p-nitrobenzaldehyde. If these rate constants were plotted against σ^+-substituent constants a good straight line was obtained which would not have been so if diffusion conditions were being approached by the more reactive substrates.

Base Catalysis.

The transition state in the rate-determining step for the base catalysed reaction may be represented as (III), the only mechanism proposed being Bell's.



(III)

Gruen and McTigue's work.[16]

They showed the formation of appreciable quantities of addition compounds between the aldehyde and the catalysing bases in the reaction mixtures used for "thermal maximum" determinations. They pointed out that the transition states for acidic and basic catalysis (II and III) differ by only one proton and found it difficult to explain how such a small difference in structure could lead to the steric effects invoked by Bell, Rand and Wynne-Jones[15] to explain their base catalysis results. The present work provides a good basic Brönsted plot

reinforcing Gruen and McTigue's objection to the thermal maximum method's results. In the scavenger system used in this work, no complications would be expected from side reactions of the aldehyde with the catalysing bases for as the free carbonyl compound is produced it reacts with the more reactive scavenger molecule. It is also of interest that the dilatometric results of Bell and Darwent[10] give a good basic Brönsted plot for the acetaldehyde hydration reaction.

ACETALDEHYDE

Previous work on this compound has already been reviewed in the introduction. It was thought of interest to check the earlier "thermal maximum" fast reactor results by one of the scavenger techniques evolved for formaldehyde. This study would be of special value in that Gruen and McTigue's work,[16] showing the formation of appreciable quantities of addition compounds in these systems, had cast doubts on the validity of the "thermal maximum" method's results for this reaction. This work would also show the applicability of the scavenger techniques to aldehydes other than formaldehyde, acetaldehyde posing some difficulties since it was only 50% hydrated. Finally a co-worker in the author's laboratory was engaged on a nuclear magnetic resonance study of the kinetics of the acetaldehyde hydration reaction and this proposed work offered an opportunity of comparing these three different experimental techniques in the measurement of the same quantities.

Experimental:

Chemicals: B.D.H. Acetaldehyde was redistilled in an atmosphere of nitrogen directly before used. Solutions were analysed by the sulphite method.

Kinetic runs:

The technique was exactly analogous to that used for formaldehyde. Experiments were carried out in acetate buffers, the scavenger used being semicarbazide hydrochloride. The scavenger concentration was such that no catalytic contribution to the observed rate constant would be expected from it. In several experiments the scavenger concentration was in fact varied, verifying the above hypothesis. Runs were followed on the UNICAM at 236 mμ, the acetaldehyde concentration employed being approximately 5×10^{-5}m. A plot of a typical run is shown in Figure 27. The unhydrated species reacted with the scavenger before readings could be commenced. Readings started at 15 secs. and taken every 10 secs for 2-3 half-lives produced a normal

FIGURE 27

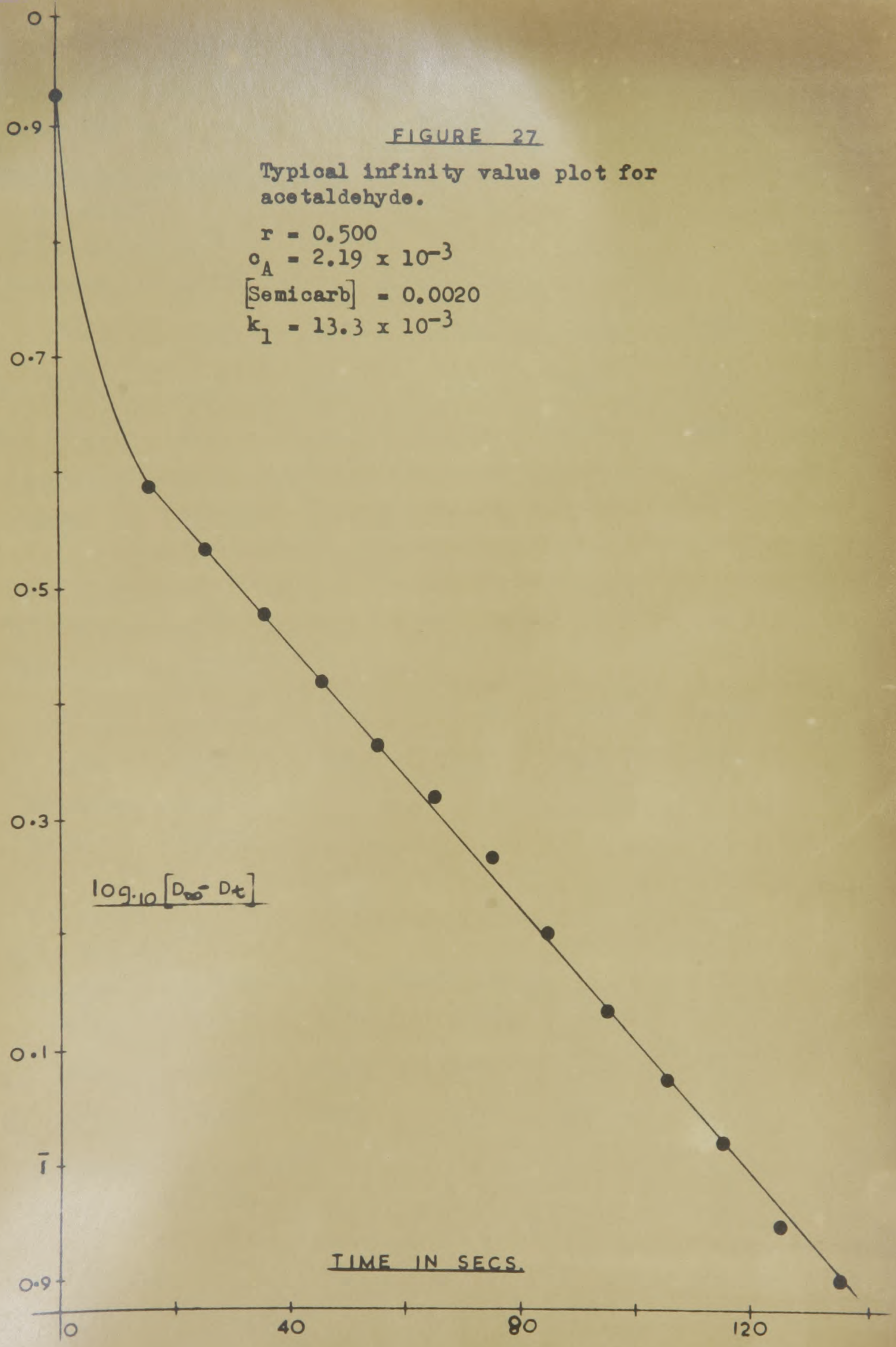
Typical infinity value plot for acetaldehyde.

r = 0.500

$c_A = 2.19 \times 10^{-3}$

[Semicarb] = 0.0020

$k_1 = 13.3 \times 10^{-3}$



first-order rate plot corresponding to a rate determining dehydration step. The ionic strength was kept constant throughout at 0.2.

Results for Acetate Buffers.

r = 0.500

$[H^+] = 1.53 \times 10^{-5}$

[Semicarb.] = 0.0020 for 1., 0.0049 for 2.

	$10^3 c_A$	1.09	2.19	3.28	4.38	5.47
1.	$10^3 k_1$	12.6	13.3	14.1	14.5	14.8
2.	$10^3 k_1$	12.4	13.7	13.9	14.8	15.4

Intercept = 12.1×10^{-3}

Slope = 0.585

r = 0.333

$[H^+] = 1.02 \times 10^{-5}$

[Semicarb.] = 0.0052

$10^3 c_A$	0.82	1.64	2.46	3.28	4.11
$10^3 k_1$	10.4	10.7	11.4	12.1	12.5

Intercept = 9.70×10^{-3}

Slope = 0.706

r = 0.250

$[H^+] = 7.7 \times 10^{-6}$

[Semicarb.] = 0.0029 for 1., 0.0071 for 2.

	$10^3 c_A$	1.64	3.28	4.93	6.57	8.21
1.	$10^3 k_1$	8.87	10.0	11.7	13.2	13.9
2.	$10^3 k_1$	9.04	10.8	11.5	12.7	14.4

Intercept = 7.75×10^{-3}

Slope = 0.792

r = 0.200

$[H^+] = 6.1 \times 10^{-6}$

[Semicarb.] = 0.0052

$10^3 c_A$	0.55	1.10	1.64	2.19	2.74
$10^3 k_1$	7.94	8.30	8.64	9.56	9.90

Intercept = 7.30×10^{-3}

Slope = 0.949

These results are shown graphically in Figure 28. In Figure 29 the intercepts from Figure 28 are plotted against the corresponding hydrogen ion concentrations and in Figure 30 the slopes are graphed against the reciprocals of the buffer ratios. The results were found to fit the equation:

$$k_1 = 0.0037 + 565[H^+] + 0.35[CH_3COOH] + 0.11[CH_3COO^-] \ .$$

Discussion.

The thermal maximum method gives rate constants k* which are the sum of the forward and backward rate-constants.

So that: $k_1 = k^* \frac{1}{1 + K_d}$

Bell, Rand and Wynne-Jones[15] found that for acetate buffers k* obeyed the equation:

$$k^* = 0.0079 + 930[H^+] + 0.47[CH_3COOH] + 0.157[CH_3COO^-]$$

In Table 27 below various values of K_d are taken and the catalytic constants for the forward rate alone are calculated.

FIGURE 28

Plot of observed first-order rate constants against concentration of acidic constituent for several buffer ratios.

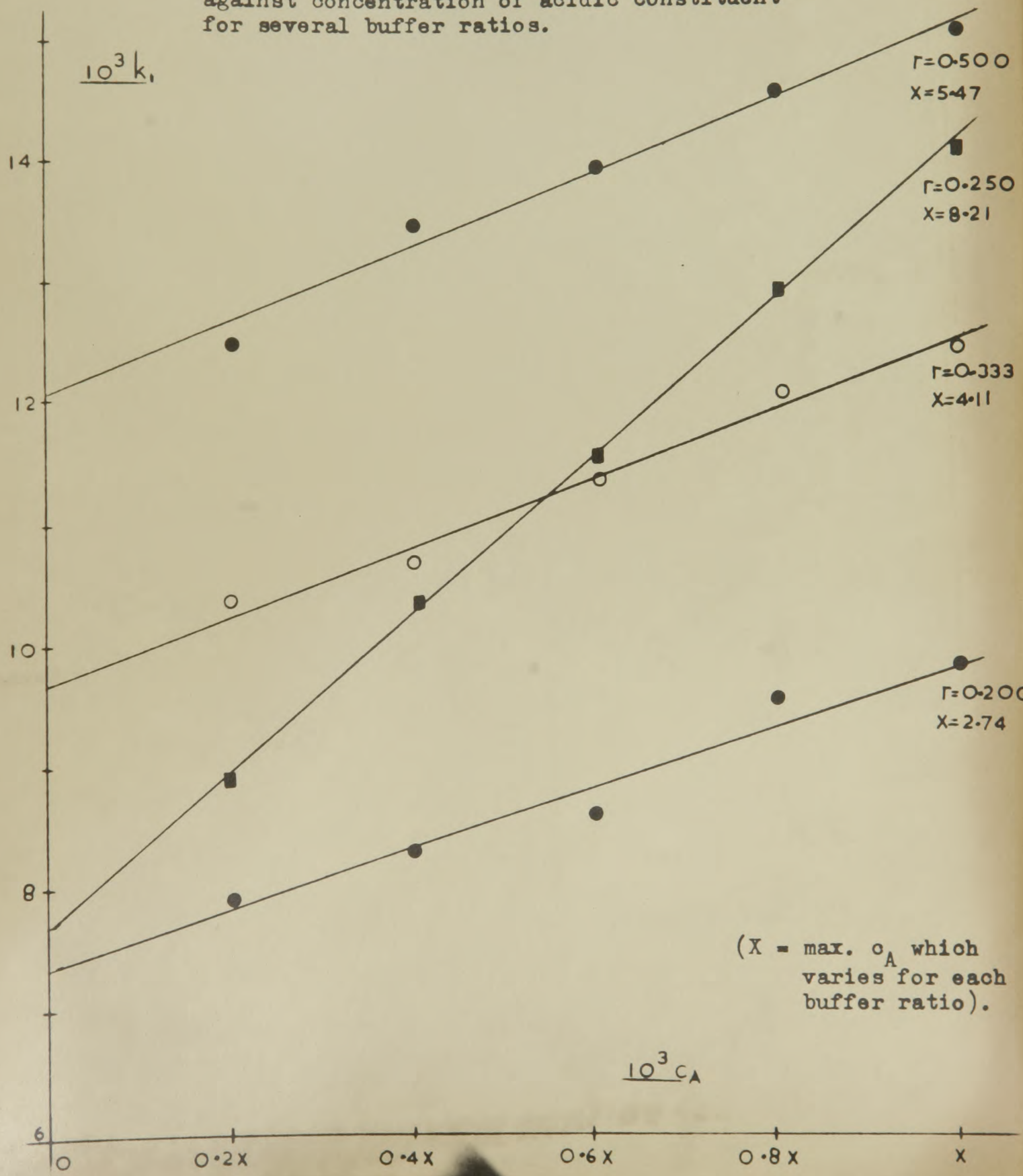


FIGURE 29

Graph of collected intercepts ($k_o + k_{H^+}[H^+]$) against $[H^+]$.

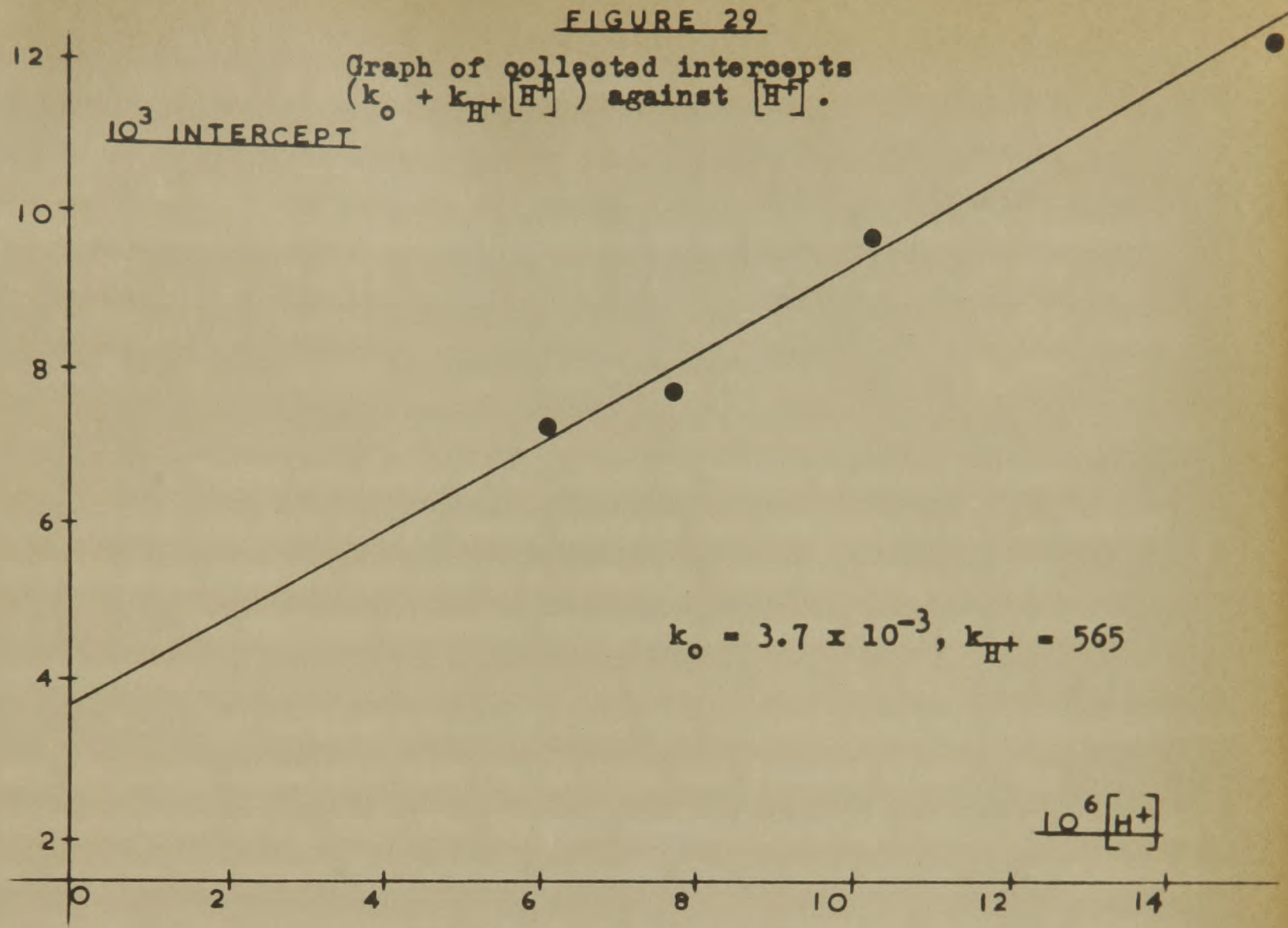


FIGURE 30

Plot of slopes against reciprocals of buffer ratios.

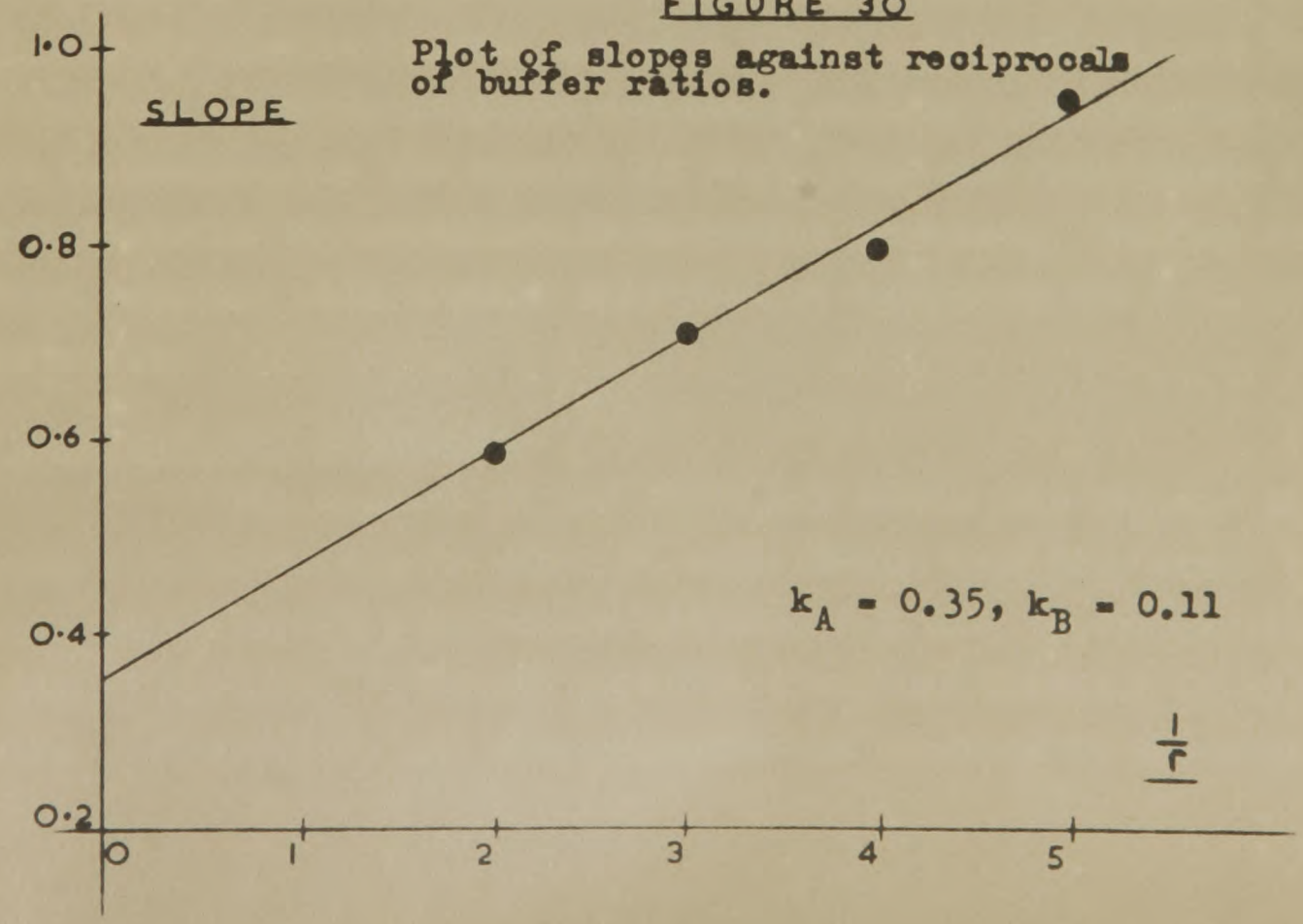


TABLE 27

K_d	k_o	k_{H^+}	k_A	k_B
This work	0.0037	565	0.35	0.11
0.667	0.0047	558	0.28	0.094
0.809	0.0044	514	0.26	0.087
1.08	0.0038	447	0.23	0.076

Gruen and McTigue's[16] thermal maximum results gave $k_{H^+} = 1400$ for I = 0. If their results are corrected to I = 0.2 by introducing Larsson and Adell's activity factor[81] $k^*_{H^+} = 800$.

No nuclear magnetic resonance results have so far been forthcoming.

The results obtained from the thermal maximum determinations are in rough agreement with those from the present work. The introduction of K_d into the thermal maximum results makes it difficult to assess the exact difference between the values given by the different methods. The closeness of the results would suggest that for acetate at least the formation of nucleophilic addition compounds of the type proposed by Gruen and McTigue plays only a small part in the thermal maximum's observed kinetics. With other catalytic species the formation of these addition compounds must be more important if one is to rationalise the results of Bell, Rand and Wynne-Jones for base catalysis in the acetaldehyde hydration reaction. Further studies of this reaction with a wider selection of catalysts would be of great interest.

Other carbonyl compounds:

The success of the scavenger techniques evolved in this work with acetaldehyde makes it seem likely that they could be used in many other carbonyl hydration studies, e.g. for the dehydration of chloral hydrate. A recent paper by Chang and Ulbricht (1958)[120] states that semicarbazide and thiosemicarbazide condense in the cold with

chloral hydrate with the elimination of one molecule of water. Two drawbacks to the sulphite technique might be found in other studies (1) in slow reactions oxidation problems would cause difficulties, (2) some of the halogen substituted carbonyl compounds are known to decompose fairly rapidly in alkaline solution. Some of the other possible scavenger species mentioned in the formaldehyde discussion might prove valuable in future work.

As has already been shown in the introduction to this thesis very little work has been carried out on these carbonyl hydration reactions. Table 1, page 1, shows many other aldehydes and ketones to be considerably hydrated in solution. The measurement of substituent effects in the carbonyl hydration reaction would obviously be of great interest. The present work appears to open the way for these studies.

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