

Source of magnetic field effects on the electrocatalytic reduction of CO₂

Thomas C. Player and P. J. Hore

Department of Chemistry, University of Oxford, Physical and Theoretical Chemistry Laboratory, Oxford, United Kingdom

*Author for correspondence: peter.hore@chem.ox.ac.uk

ABSTRACT

We present an analysis of reported magnetic field effects on the yield of formic acid produced by electrocatalytic reduction of carbon dioxide at a nanoparticle tin electrode (Pan *et al.*, *J. Phys. Chem. Lett.* **11** (2020) 48–53). Radical pair spin dynamics simulations are used to show that: (1) the Δg mechanism favoured by Pan *et al.* is not sufficient to explain the observed magneto-current. (2) Field-dependent spin relaxation, resulting from the anisotropy of the g -tensor of CO₂^{•−}, combined with the coherent singlet-triplet interconversion arising from isotropic hyperfine and Zeeman interactions, can quantitatively account for the observed magnetic field effect. (3) Modification of hyperfine interactions by isotopic substitution (¹H → ²H and/or ¹²C → ¹³C) could be used to test both the proposed reaction mechanism and the interpretation presented here.

INTRODUCTION

Conversion of carbon dioxide into small organic molecules is appealing as a way to reduce the accumulation of atmospheric CO₂ and to generate useful chemicals.^{1–7} Pan *et al.* recently reported that the yield of formic acid in the electrocatalytic reduction of CO₂ at a nanoparticle tin electrode could be increased by up to 100% by application of a 900 mT magnetic field.⁸ The authors rationalised this observation as a change in the efficiency of interconversion of the electronic singlet and triplet states of a radical pair comprised of a CO₂^{•−} radical and a hydrogen atom (H[•])

formed by electroreduction of CO_2 and bicarbonate (HCO_3^-), respectively. Figure 1(a) shows the proposed reaction scheme.⁸ The radical pairs are formed in a statistical 3:1 mixture of triplet (total electron spin, $S = 1$) and singlet ($S = 0$). Spin selection rules allow singlet, but not triplet, pairs to combine to produce the diamagnetic formate ion, HCO_2^- . In parallel, the radicals can separate by translational diffusion without reacting. Such “F-pairs” can be sensitive to applied magnetic fields even though they lack the initial spin coherence of the pure singlet or pure triplet states that are usually formed in photochemical reactions. Spin coherence arises in F-pairs from asymmetric reactivity of the singlet and triplet states. The radical pair mechanism provides a solid theoretical basis for quantitative analysis of the quantum spin dynamics that underlie these magnetic field effects.⁹⁻¹⁴

Figure 1(b) shows the change in the electrocatalytic current for CO_2 reduction (referred to as the magneto-current) measured by varying the strength of an applied magnetic field between 0 and 900 mT in a saw-tooth fashion with a period of 55 s.⁸ Peak magneto-currents of 42, 58 and 90% were reported for 0.1, 0.2 and 0.3 M CO_2 -saturated aqueous solutions of KHCO_3 when subjected to a 900 mT magnetic field. The corresponding figures for the increase in the yield of formic acid were 40, 57 and 100%. The sigmoidal shape of Fig. 1(b), with the magnetic field effect tending to saturate at high field, is typical of radical pair reactions.^{9,15,16} The increase in magneto-current and in the amount of formic acid are consistent with a field-induced increase in the efficiency of conversion of triplet pairs into singlets which then react to give HCO_2^- . Pan *et al.*⁸ argued that the magnetic sensitivity was due to a combination of two well-established mechanisms for singlet-triplet interconversion: (a) the Δg mechanism,^{13,17} arising from the difference in the electron Zeeman interactions of the two radicals and (b) the hyperfine mechanism^{13,17} resulting from the magnetic coupling of the electron and the nucleus in H^\bullet . Since the former is expected to become more efficient, and the latter less efficient, at high field, Pan *et al.* argued that the former must be dominant.

However, there are other interactions that could affect the way that $[\text{H}^\bullet \text{CO}_2^{\bullet-}]$ radical pairs respond to an applied magnetic field. Rotational modulation of the anisotropic Zeeman interaction of $\text{CO}_2^{\bullet-}$ ¹⁸⁻²⁰ would lead to electron spin relaxation at a rate that increased quadratically with the

strength of the external field. Enhanced spin relaxation could also result from the spin-rotation interaction in $\text{CO}_2^{\bullet-}$ ^{18,21,22} and from translational modulation of the exchange interaction of the two radicals.^{15,23}

Here we present the results of spin dynamics simulations of the magnetic sensitivity of $[\text{H}^\bullet \text{CO}_2^{\bullet-}]$ radical pairs. This study has three aims: (1) to test the assumption that the Δg mechanism can account for the observed magnetic field effects; (2) to explore the role of spin relaxation; (3) and to see whether isotopic substitution ($^1\text{H} \rightarrow ^2\text{H}$ and/or $^{12}\text{C} \rightarrow ^{13}\text{C}$) could offer additional insight into the mechanism of the reaction and the source of the magnetic field effect.

METHODS

The fraction of $[\text{H}^\bullet \text{CO}_2^{\bullet-}]$ radical pairs that combine to produce formic acid was calculated by numerical solution of a stochastic Liouville equation for the density matrix of a spin system comprising the electron and proton in H^\bullet and the unpaired electron in $\text{CO}_2^{\bullet-}$. Full details are given in the Supplementary Material. The coherent spin dynamics of the radical pair were modelled by means of a spin Hamiltonian, H , containing the isotropic Zeeman interactions of the two electron spins with the applied magnetic field and the isotropic hyperfine interaction in H^\bullet ($a_{\text{H}} = 50.74$ mT²⁴). The Zeeman interactions depend on the strength of the applied field, B , and the g -values of the two radicals ($g_{\text{H}} = 2.0114$,²⁵ $g_{\text{CO}_2} = 2.0007$ ²⁶). Four assumptions were made: (1) that $\text{CO}_2^{\bullet-}$ tumbles sufficiently rapidly that no coherent spin evolution arises from the anisotropic components of its g -tensor; (2) that the average separation of the two diffusing radicals is large enough that there is no net effect of electron spin coupling (i.e. exchange and dipolar interactions) on the coherent spin dynamics; (3) that the nuclear Zeeman interaction in H^\bullet is negligible by virtue of the much smaller magnetic moment of the proton compared to the electron; and (4) that the ^{13}C hyperfine interaction in $\text{CO}_2^{\bullet-}$ can be ignored at natural isotopic abundance (1.1%). The initial state of the radical pair was taken to be a 1:3 mixture of singlet and triplet. The calculations involving isotopologues were identical except for the electron-nuclear interactions. The hyperfine coupling in the deuterium atom is smaller than a_{H} by the ratio of the magnetogyric ratios of the

two nuclei: $a_D = (\gamma_D / \gamma_H) a_H = 7.79$ mT and the isotropic ^{13}C hyperfine coupling in $^{13}\text{CO}_2^{\bullet-}$ is $a_C = 19.93$ mT.²⁷

The reaction steps shown in Fig. 1(a) were modelled using a Haberkorn superoperator, \mathbf{K} ,²⁸ for the spin-selective formation of formic acid from the singlet radical pair (with a first-order rate constant, k_S) and by allowing the radicals in both singlet and triplet states to diffuse apart (with the same first-order rate constant, k_D):

$$\mathbf{K} = \frac{1}{2} k_S (P^S \otimes E + E \otimes P^S) + k_D E \otimes E, \quad (1)$$

where P^S is the singlet projection operator and E is the identity operator. k_S and k_D were treated as variable parameters.

It has long been established that electron spin relaxation can have profound effects on the sensitivity of radical pair reactions to applied magnetic fields.²⁹⁻³² Spin relaxation in $\text{CO}_2^{\bullet-}$ was modelled by one of three mechanisms: (1) generic “random fields” relaxation of the three Cartesian components of the electron spin;³³ (2) singlet-triplet dephasing arising from diffusional modulation of the electron exchange interaction;²³ (3) g -tensor anisotropy, i.e. rotational modulation of the anisotropic electron Zeeman interaction.²⁰ For (1) and (2), a phenomenological relaxation rate constant, w , was varied, along with k_S and k_D , in an attempt to match the calculated yield of formate to the experimental data. For (3), the variable parameter was the rotational correlation time, τ_c , of $\text{CO}_2^{\bullet-}$. The principal components of the g -tensor of $\text{CO}_2^{\bullet-}$, required for mechanism (3), were: $g_{xx} = 2.0032$; $g_{yy} = 1.9975$; $g_{zz} = 2.0014$.²⁶ The three relaxation superoperators were:

$$\mathbf{W}^{(1)} = w \left[\frac{3}{4} E \otimes E - S_{Ax} \otimes \tilde{S}_{Ax} - S_{Ay} \otimes \tilde{S}_{Ay} - S_{Az} \otimes \tilde{S}_{Az} \right], \quad (2)$$

$$\mathbf{W}^{(2)} = w \left[P^S \otimes P^T + P^T \otimes P^S \right], \quad (3)$$

$$\mathbf{W}^{(3)} = \frac{1}{15} \sum_{j=x,y,z} \left(\frac{g_{jj} - g_{\text{iso}}}{g_{\text{iso}}} \right)^2 \omega_0^2 \times \left[3J(\omega_0) \left(\frac{1}{2} E \otimes E - S_{Ax} \otimes \tilde{S}_{Ax} - S_{Ay} \otimes \tilde{S}_{Ay} \right) + 2J(0) \left(\frac{1}{2} E \otimes E - 2S_{Az} \otimes \tilde{S}_{Az} \right) \right]. \quad (4)$$

S_{Aj} ($j = x, y, z$) are the components of the electron spin operator of $\text{CO}_2^{\bullet-}$, the tilde (\sim) indicates the operator transpose, P^S and P^T are the singlet and triplet projection operators, $g_{\text{iso}} = (g_{xx} + g_{yy} + g_{zz})/3$ is the isotropic g -value of $\text{CO}_2^{\bullet-}$, $\omega_0 = g_{\text{iso}} \mu_B B / \hbar$ is the electron Larmor frequency, and the spectral density function is taken to be

$$J(\omega) = \frac{\tau_c}{1 + \omega^2 \tau_c^2}. \quad (5)$$

Only the g -anisotropy mechanism, Eq. (4), depends explicitly on the applied magnetic field, with relaxation expected to be faster at higher fields. Electron spin relaxation in H^\bullet was assumed to be negligible.

The superoperators for the coherent spin dynamics (spin Hamiltonian H), the reactivity of the radicals and their spin relaxation were combined into a Liouvillian, \mathbf{L} ,

$$\mathbf{L} = i(H \otimes E - E \otimes \tilde{H}) + \mathbf{K} + \mathbf{W}^{(k)} \quad (6)$$

from which the fractional yield of formate, Φ_s was calculated (see Supplementary Material) as

$$\Phi_s = \left(\frac{k_s}{4Z} \right) P^S \cdot \mathbf{L}^{-1} \cdot E, \quad (7)$$

where Z is the total number of nuclear spin states.

RESULTS

Hyperfine and Δg mechanisms

We start by exploring whether it is possible to account qualitatively for the increased yield of formate in the presence of an applied magnetic field of up to 900 mT. Many of the simulations

performed in this study predict a pronounced “low field effect”³⁴⁻³⁶ visible as a sharp rise in Φ_S for weak magnetic fields, on the order of a few millitesla. Pan *et al.* did not report such a feature and might have overlooked it had it been present.⁸ We therefore excluded fields weaker than 30 mT from our attempts to match the simulations to the experimental data. We define magnetic field effects (MFEs) as positive or negative, according to whether the product yield, Φ_S , at 900 mT is larger or smaller than that at 30 mT. As mentioned above, Pan *et al.* observed a positive MFE and attributed it to a dominant Δg mechanism.⁸

Initial simulations were performed without spin relaxation, varying the rate constants k_S and k_D over a wide range from 10^3 to 10^{11} s^{-1} . The upper limit was chosen as follows. For there to be a significant magnetic field effect on the $\text{H}^\bullet + \text{CO}_2^{\bullet-}$ reaction, the exchange interaction of the two radicals must not greatly exceed the H^\bullet hyperfine coupling, meaning that the diffusing radicals must, on average, be more than 1.0 to 1.5 nm apart. An estimate of the upper limit on k_S is therefore the reciprocal of the time required for one or both of the radicals to diffuse $\Delta r \approx 1 \text{ nm}$ from this average separation to the contact distance at which they are able to combine to produce HCO_2^- . The translational diffusion coefficients of small molecules in water at room temperature are $< \sim 10^{-9} \text{ m}^2 \text{ s}^{-1}$, so that $k_S \approx D / \Delta r^2 < 10^9 \text{ s}^{-1}$. The magnetic field effect will also be very small if k_D greatly exceeds the frequency of singlet-triplet interconversion, $\gamma_e a_H \approx 9 \times 10^9 \text{ s}^{-1}$. We therefore set the upper limit for both rate constants at 10^{11} s^{-1} .

When the hyperfine interaction in the hydrogen atom was omitted (i.e. $a_H = 0$), so that the Δg mechanism was the only source of singlet-triplet interconversion, the MFE was found to be positive for all combinations of rate constants within the above range. However, when the hyperfine interaction was reinstated and the two g -values replaced by their mean (i.e. $\Delta g = 0$), so that the field-dependence came solely from the hyperfine mechanism, the MFE was always negative. Illustrative simulations can be found in the Supplementary Material. When both mechanisms operated simultaneously (i.e. $a_H = 50.74 \text{ mT}$ and $\Delta g = 0.0107$), the MFE remained negative over the whole range of k_S and k_D values. Contrary to the suggestion of Pan *et al.*,⁸ the Δg mechanism is outweighed by the hyperfine mechanism and the two, acting together, cannot

account for the observed change in the magneto-current. This can be understood in terms of the faster singlet-triplet mixing coming from the hyperfine mechanism, $\gamma_e a_H / 2\pi \approx 1420$ MHz, compared to the Δg mechanism, $\Delta g \mu_B B / h \approx 135$ MHz (when $B = 900$ mT). As there are no other time-independent magnetic interactions in either H^\bullet or $CO_2^{\bullet-}$ that could reverse the dominance of the hyperfine mechanism, it seems likely that electron spin-relaxation is important. This conclusion is supported by the fact that the magneto-current is still increasing at 900 mT (Fig. 1(b)).⁸ Without significant spin relaxation, the magnetic field effect should start to saturate as soon as the field exceeds the ~ 50 mT hyperfine interaction.^{15,37}

Phenomenological spin relaxation

To assess whether random time-dependent local fields (Eq. (2)) or singlet-triplet dephasing (Eq. (3)) could give rise to positive MFEs, we simulated Φ_s for relaxation rate constants, w , between 10^5 and 10^9 s⁻¹, and k_S and k_D in the range 10^3 to 10^{11} s⁻¹, with $a_H = 50.74$ mT and $\Delta g = 0.0107$, as above. Although inclusion of each of these relaxation processes changed the shape of the field-dependence, the MFEs remained strictly negative. Illustrative simulations can be found in the Supplementary Material. This result is not surprising. In magnetic fields comparable to the hyperfine interaction, singlet-triplet interconversion is more efficient than at higher fields where the T_{+1} and T_{-1} triplet states are energetically isolated from the singlet state and therefore much slower to convert to singlet and subsequently react to give the product. Evidently, the two relaxation processes considered above, with their field-independent rate constants, do not qualitatively change that situation. We therefore speculate that a positive MFE on the $H^\bullet + CO_2^{\bullet-}$ reaction might arise from a relaxation process that accelerates as the strength of the magnetic field, B , is increased. More efficient spin-lattice relaxation of the initial population of T_{+1} and T_{-1} triplets to the T_0 state at high field should boost formation of the singlet radical pair state and hence the yield of HCO_2^- .

To explore this possibility, we allowed the rate constant in the random fields relaxation superoperator, Eq. (2), to increase quadratically with the magnetic field: $w = qB^2$. By varying the proportionality constant q between 10^5 and 10^{10} T⁻² s⁻¹, and k_S and k_D between 10^3 and 10^{11} s⁻¹, we did indeed find combinations of the three parameters that gave positive MFEs.

g-tensor anisotropy relaxation

Encouraged by the last result, we turned to the *g*-tensor anisotropy mechanism, Eq. (4), in which the field-dependence of the relaxation superoperator can be derived from the properties of the $\text{CO}_2^{\bullet-}$ radical. Once again, Φ_s was calculated using $a_H = 50.74$ mT and $\Delta g = 0.0107$. Agreement between the predictions of the model and the experimental data were sought by optimising the value of τ_c , for integer values of $\log_{10}(k_s)$ and $\log_{10}(k_D)$ between 3 and 11, using a least-squares fitting procedure. Simulations of

$$\frac{\Phi_s(B) - \Phi_s(30 \text{ mT})}{|\Phi_s(900 \text{ mT}) - \Phi_s(30 \text{ mT})|} \quad (8)$$

were compared with the experimental data (Fig. 1(b)). Satisfactory agreement was found for 17 sets of the three parameters, summarised in Table 1. Four of them correspond to short-lived radical pairs with long rotational correlation times: $k_s = 10^{10}$ or 10^{11} s^{-1} , $k_D = 10^9$, 10^{10} or 10^{11} s^{-1} , and $\tau_c \geq 1 \text{ } \mu\text{s}$. The remainder have $10^6 < k_s < 10^{11} \text{ s}^{-1}$, $10^3 < k_D < 10^5 \text{ s}^{-1}$, and τ_c between ~ 1 ps and 15 ps. We discuss the interpretation of these results in the following section.

		$\log_{10}(k_s)$					
		6	7	8	9	10	11
$\log_{10}(k_D)$	3	1.25	0.61	0.61	0.64	0.65	0.65
	4	—	8.9	4.6	5.4	5.7	5.7
	5	—	—	—	—	12.4	14.2
	6–8	—	—	—	—	—	—
	9	—	—	—	—	—	1.0*
	10	—	—	—	—	10.3*	9.1*
	11	—	—	—	—	—	65*

Table 1. Optimised values of the rotational correlation time, τ_c , for combinations of rate constants k_s and k_D (in s^{-1}) that predict magnetic field effects in agreement with the experimental data of Pan *et al.*⁸ The units of τ_c are picoseconds apart from the asterisked entries which are in microseconds. Spin relaxation was modelled by means of the *g*-tensor anisotropy mechanism. Missing entries in

the table indicate combinations of k_S and k_D for which satisfactory fits to the data could not be obtained. The shaded area highlights the most credible values of the three parameters (see below).

Figure 2 shows the magnetic field effect on $[^1\text{H}^\bullet \text{ } ^{12}\text{CO}_2^{\bullet-}]$ (and its isotopologues, discussed below) calculated for two of the sets of parameter values in Table 1. Like the other entries in Table 1, both show satisfactory agreement with the (scaled) magneto-current data.

Spin-rotation relaxation

A second relaxation mechanism that depends on the electronic g -tensor arises from the interaction of the electron spin with the rotational angular momentum of the radical. The relaxation superoperator for this mechanism has the same form as the random fields superoperator, Eq. (2), with the rate constant, w , given by:

$$w = \frac{1}{9\tau_c} \sum_{j=x,y,z} (g_{jj} - g_e)^2 \quad (9)$$

where $g_e \approx 2.0023$ is the free-electron g -value.^{21,22} With this mechanism in place of g -tensor anisotropy, the simulated MFEs were uniformly negative for $10^3 < k_S, k_D < 10^{11} \text{ s}^{-1}$ and $1 \text{ ps} < \tau_c < 1 \text{ } \mu\text{s}$. Apart from a few cases in which the MFEs were very small ($< 1\%$), the same was true when the two relaxation mechanisms were allowed to operate simultaneously.

To summarise, we were able to satisfactorily model the magneto-current using g -tensor anisotropy as the spin relaxation mechanism but not with spin-rotation or with g -tensor anisotropy and spin-rotation acting together.

Isotopologous reactions

Isotopic substitution affects radical pair reactions principally via the changes in hyperfine interactions associated with the different magnetic moments of the isotopes.³⁸ In the case of $\text{H}^\bullet + \text{CO}_2^{\bullet-} \rightarrow \text{HCO}_2^-$, in which a covalent bond is formed in a reaction with little or no activation energy, mass isotope effects should be very small and magnetic isotope effects should dominate.

Figures 2(a) and (b) show MFEs calculated for $[\text{H}^\bullet \text{CO}_2^{\bullet-}]$ radical pairs in which hydrogen has been replaced by deuterium, or ^{12}C by ^{13}C , or both. Deuterium has a hyperfine coupling ~ 6.5 times smaller than hydrogen, and ^{13}C substitution in $\text{CO}_2^{\bullet-}$ introduces a hyperfine coupling of 19.93 mT.²⁷ In Fig. 2(a), the MFEs of all three isotopologues of $[\text{H}^\bullet \text{CO}_2^{\bullet-}]$ are biphasic, initially decreasing and then increasing when $B > 200\text{-}300$ mT. For the set of parameters chosen for Fig. 2(b), the MFE remains monophasic and is significantly larger for $^2\text{H}^\bullet$ than for $^1\text{H}^\bullet$.

DISCUSSION

Table 1 summarises the results of our attempts to account for the magneto-current reported by Pan *et al.*⁸ including hyperfine and Δg mechanisms of singlet-triplet interconversion in the radical pair, $[\text{H}^\bullet \text{CO}_2^{\bullet-}]$. Good agreement with the data was achieved for certain values of the three parameters, k_s , k_D and τ_c , provided the dominant electron spin relaxation pathway in $\text{CO}_2^{\bullet-}$ is rotational modulation of the anisotropic Zeeman (g -tensor) interaction. But which, if any, of the 17 entries in Table 1 are credible? A lower bound on τ_c for $\text{CO}_2^{\bullet-}$ can be obtained from the Stokes-Einstein equation for the rotational diffusion of a sphere of radius a in a medium of viscosity η at temperature T ,

$$\tau_c = \frac{4\pi\eta a^3}{3k_B T}. \quad (10)$$

Taking $a \approx 150$ pm for CO_2 , $\eta \approx 10^{-3}$ kg m⁻¹ s⁻¹ for water at $T = 298$ K, Eq. (10) gives $\tau_c \approx 3.4$ ps. Therefore we can probably discount the top row of Table 1 ($k_D = 10^3$ s⁻¹) in which $\tau_c \approx 1$ ps. The four entries in the bottom right hand corner of Table 1 are also improbable, for two reasons. First, the values of k_s (10^{10} and 10^{11} s⁻¹) exceed by some margin the above-estimated upper limit on the rate constant for production of formate, $D/\Delta r^2 \approx 10^9$ s⁻¹. Second, the expression used for the relaxation superoperator, Eq. (4), is unlikely to be valid for rotational correlation times as long as 1 μ s which do not satisfy the conditions for motional narrowing. It therefore seems reasonable to exclude the final two columns of Table 1.

We are therefore left with the shaded area in Table 1, i.e. $\tau_c \approx 5\text{-}10$ ps, $k_D \approx 10^4 \text{ s}^{-1}$, $k_S \approx 10^7\text{-}10^9 \text{ s}^{-1}$ as the conditions most likely to be realistic. The small value of k_D and the much larger value of k_S may be understood by reference to Fig. 3 which shows the field-dependence of the spin-lattice relaxation rate of $\text{CO}_2^{\bullet-}$ predicted by the g -tensor anisotropy mechanism,¹⁹

$$R = \frac{1}{5} \sum_{j=x,y,z} \left(\frac{g_{jj} - g_{\text{iso}}}{g_{\text{iso}}} \right)^2 \left[\frac{\omega_0^2 \tau_c}{1 + \omega_0^2 \tau_c^2} \right], \quad (11)$$

with $\tau_c = 1, 5$, and 25 ps. For all three correlation times relaxation is faster at higher field, as required for a positive MFE. Without efficient spin-lattice relaxation at high field, radical pairs initially in the T_{+1} and T_{-1} states (50% of the total) can never produce HCO_2^- . Strongly field-dependent spin-lattice relaxation of the kind shown in Fig. 3 transfers population from the unreactive T_{+1} and T_{-1} states to T_0 which mixes coherently with the singlet state which then gives HCO_2^- . This process is most efficient when $\omega_0 \tau_c \approx 1$, i.e. $\tau_c \approx 6.3$ ps and $R_{\text{max}} \approx 6.7 \times 10^4 \text{ s}^{-1}$ when $B = 900$ mT. It is no coincidence, therefore, that this estimate of τ_c falls within the range of τ_c values in the shaded region of Table 1. Nor is it surprising that k_D must be as slow as $\sim 10^4 \text{ s}^{-1}$ (Table 1): if k_D is not smaller than R_{max} , the T_{+1} and T_{-1} pairs will separate before they can relax to T_0 .

The small value of k_D ($\sim 10^4 \text{ s}^{-1}$) suggests that both radicals may be loosely adsorbed on the surface of the catalyst: freely diffusing radicals would separate much faster than 10^4 s^{-1} . That τ_c (Table 1) is only a little larger than the Stokes-Einstein estimate (3.4 ps) implies that the rotational motion of $\text{CO}_2^{\bullet-}$ is not strongly constrained by adsorption.

Finally, we turn to the magnetic isotope effects in Fig. 2(a). The pronounced qualitative changes in the predicted magnetic field effects could form the basis of an experimental test of the reaction mechanism proposed by Pan *et al.*⁸ and of the model used here to interpret their data.

CONCLUSIONS

We have used radical pair spin dynamics simulations to interpret the effects of applied magnetic fields on the electrocatalytic reduction of CO_2 to HCO_2^- reported by Pan *et al.*⁸ Our main conclusions are: (1) The Δg mechanism favoured by Pan *et al.*⁸ cannot, on its own, account for the observed magnetic field effects. (2) The observed magneto-current is consistent with field-dependent spin relaxation in $\text{CO}_2^{\bullet-}$ combined with coherent singlet-triplet mixing driven by the isotropic hyperfine and Zeeman interactions in H^\bullet and $\text{CO}_2^{\bullet-}$. Our analysis puts strong constraints on the parameters of the model. (3) Isotopic substitution could be used to test both the proposed reaction mechanism,⁸ Fig. 1(a), and the model presented here.

SUPPLEMENTARY MATERIAL

See Supplementary Material for details of the spin dynamics calculations and additional simulations of magnetic field effects.

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analysed in this study.

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FIGURES

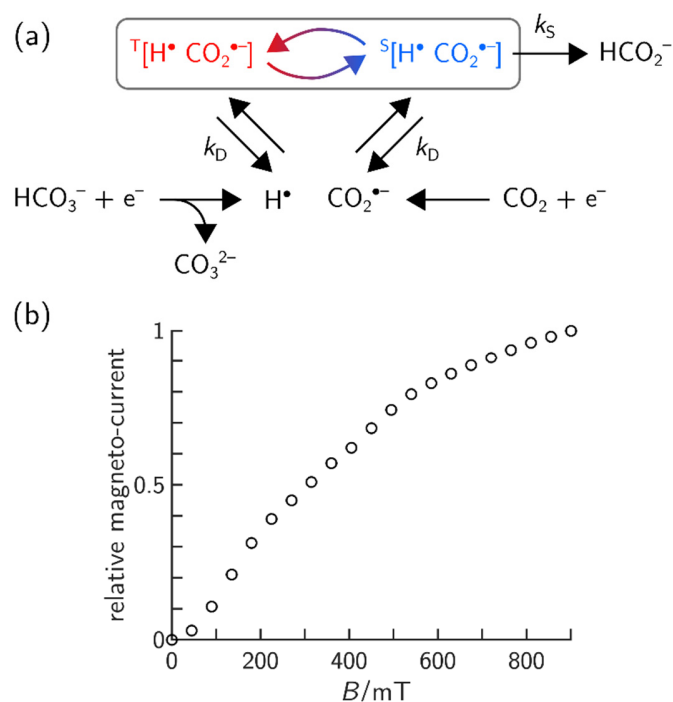


FIG. 1. (a) Proposed reaction scheme for the electrocatalytic reduction of carbon dioxide to formic acid.⁸ (b) Dependence of the magneto-current on the applied magnetic field constructed from the time-dependence of these two quantities depicted in Fig. 2(b) of Pan *et al.*⁸ The field-dependence shown here is that reported for a 0.3 M bicarbonate solution, rescaled to 1.0 at 0.9 T. The data recorded from 0.1 M and 0.2 M solutions have essentially identical shapes. Pan *et al.* have reported similar magnetic field effects for other chemical systems.^{39,40}

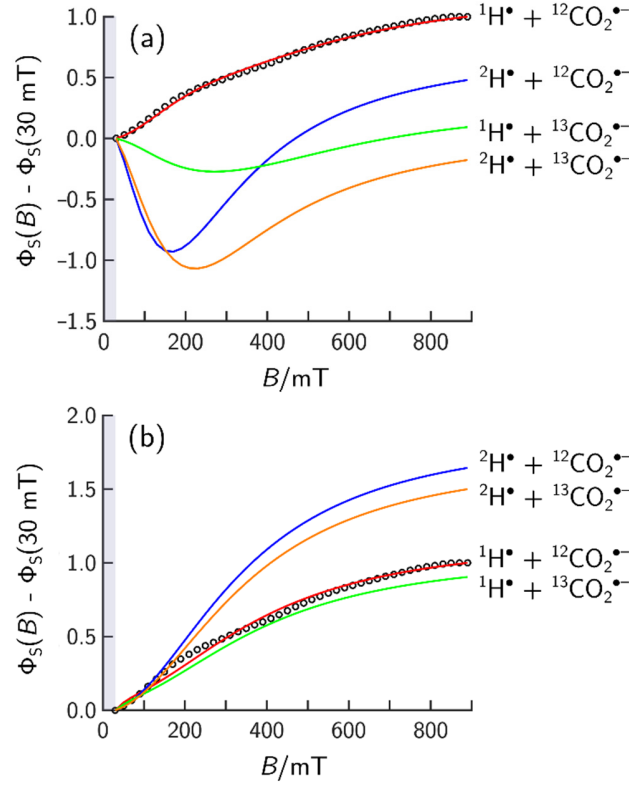


FIG. 2. Calculated magnetic field effects on the $\text{H}^\bullet + \text{CO}_2^{\bullet-}$ reaction with spin-relaxation arising from the g -tensor anisotropy mechanism, Eq. (4). (a) $k_s = 10^7 \text{ s}^{-1}$, $k_D = 10^4 \text{ s}^{-1}$, $\tau_c = 8.9 \text{ ps}$. (b) $k_s = 10^{11} \text{ s}^{-1}$, $k_D = 10^9 \text{ s}^{-1}$, $\tau_c = 1.0 \text{ } \mu\text{s}$. The graphs show the difference between the reaction yield at field B and that at 30 mT, scaled to 1.0 at 900 mT for $^1\text{H}^\bullet + ^{12}\text{CO}_2^{\bullet-}$. In each panel, the same scaling factor was used for the four isotopologues. The open circles show the measured magneto-current.⁸ The corresponding plots showing the low field effects ($B < 30 \text{ mT}$) can be found in the Supplementary Material. Although giving a satisfactory fit to the experimental magneto-current, the parameters required for (b) are unlikely to be realistic (see Discussion section).

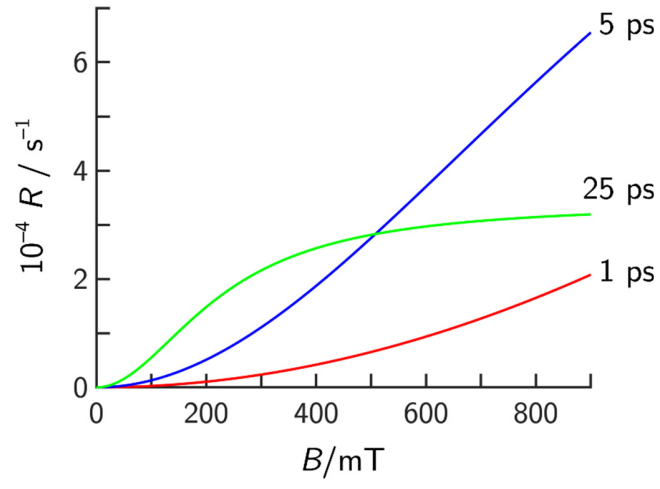


FIG. 3. Calculated spin-lattice relaxation rate, Eq. (11), of $CO_2^{\bullet-}$ (g -tensor anisotropy mechanism) plotted as a function of the magnetic field strength, for $\tau_c = 1, 5$ and 25 ps.

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