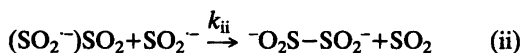
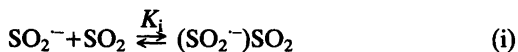


The Mechanisms of the Dimerization of Sulfur Dioxide Anion Radical in the Presence of Tetraalkylammonium Ions in DMF

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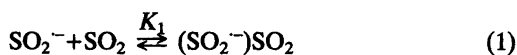
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In the presence of tetraethylammonium ion $\text{SO}_2^{\cdot -}$ undergoes reversible dimerization with an apparent rate constant of $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at 0°C and an apparent activation energy of -7 kcal/mol . Due to the reversibility of the anion radical–dimer equilibrium the reaction appears to be relatively slow at long measurement times. When the counter ion is tetrabutylammonium ion a different mechanism was observed consisting of the reversible association (i) followed by reaction (ii).



Reaction (ii) could either be an electron transfer or the displacement of SO_2 by $\text{SO}_2^{\cdot -}$. The latter pathway is deemed most likely on the basis of an apparent activation energy of the order of 5 kcal/mol since ΔH_i° is expected to be negative and the E_a for electron transfer to be small. K_1 was observed to be equal to 1640 M^{-1} at 293 K and k_{ii} was estimated to be equal to $1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at the same temperature. In the presence of Et_4N^+ , K_1 was observed to be equal to or less than about 200 M^{-1} . The data are discussed in context with other recent studies of the reactions of sulfur dioxide anion radical in DMF.

The electroreduction of SO_2 in nonaqueous media has been investigated intensively over the past fifteen years.^{1–13} In DMF containing Et_4N^+ ion, ESR and electrochemical measurements have shown that $\text{SO}_2^{\cdot -}$ exists along with the anion radical complex $(\text{SO}_2^{\cdot -})\text{SO}_2$ according to equilibrium (1).^{7,1–3}



However, the value of K_1 was found to depend strongly on the particular technique used in the study. Kastening and Gostisa-Mihelcic⁷ reported a value of 230 M^{-1} for K_1 based on a combination of polarographic and e.s.r. measurements. Gardner, Fouchard and Fawcett² determined K_1 to be 8400 M^{-1} by a.c. polarography, while the most recent study by Laman, Gardner and Fouchard using simultaneous electrochemical and e.s.r. measurements¹⁴ resulted in a value of 611 M^{-1} .¹ The latter study also resulted in an estimate of the forward rate constant for reaction (1) of $10^5 \text{ M}^{-1} \text{ s}^{-1}$.

Another interesting aspect of the reactions of $\text{SO}_2^{\cdot -}$ was reported by Gardner, Fouchard and Fawcett.³ They found that in the presence of either Et_4N^+ or Bu_4N^+ the reactions of $\text{SO}_2^{\cdot -}$ could be described by reaction (1) but in the presence of Li^+ only dimerization to dithionate ion (2) takes place.



The dependence of the reaction pathway upon both the supporting electrolyte cation and the solvent was interpreted in terms of the relative importance of ion pairing.

The previous studies all involved measurements at relatively long times and thus the details of the primary processes taking place are not evident. The competition between the reaction with substrate and dimerization of anion radicals is of interest with regard to some of our related

Table 1. The effect of substrate concentration on apparent rate constants for the dimerization of sulfur dioxide anion radical in DMF in the presence of tetraethylammonium ion.^a

[SO ₂]/mM	$v_{0.3}$	$10^{-6}k/M^{-1}s^{-1}$	$-E^p(100\text{ V s}^{-1})^b/\text{mV}$
0.095	35.5	9.22	1073
0.190	64.6	8.39	1073
0.285	90.7	7.85	1073
0.428	114.5	6.60	1073

^a Measurements by DCV at 291.9 K in solvent containing Et₄NBF₄ (0.1 M). ^b Peak potential vs. Ag/Ag⁺ in acetonitrile.

work.¹⁵⁻¹⁸ The study of the association of ion radicals to neutral molecules and the effect this has on kinetics and mechanism is pertinent to our recent work in other systems.¹⁹⁻²² Finally, we have been concerned with reversible dimerizations of ion radicals and the mechanisms of the reactions.^{23,24} Thus, because of interest in this general area of chemistry as well as the uncertainties remaining in the SO₂⁻ system, a re-investigation of the kinetics and mechanism of the dimerization of SO₂⁻ in DMF was undertaken.

RESULTS

At voltage sweep rates of 200 mV/s or less, the cyclic voltammogram for the reduction of SO₂ in DMF containing Et₄NClO₄ takes the form expected for a reversible charge transfer followed by a slow homogeneous reaction of the anion radical (see Fig. 1 of Ref. 2). Nearly identical results are obtained when the supporting electrolyte is Et₄NBF₄. However, at higher voltage sweep rate (v) the peak current ratio is much less than unity indicating a very rapid follow-up reaction of SO₂⁻. Results for the measurement of $v_{0.3}$, the sweep rate necessary for the current derivative ratio to equal 0.300, are summarized in Table 1.* The peak potential measured at 100 V/s was constant at 1073±1 mV vs. an Ag/Ag⁺ reference electrode. The latter indicates that the association of SO₂⁻ with SO₂ is not favorable enough under the measurement conditions for a shift in reversible potential to be evident. The value of $v_{0.3}$ was observed to be concentration dependent and the rate constants given in column 3 of Table 1 are assuming a dimerization mechan-

Table 2. The effect of temperature on the apparent rate constant for the dimerization of sulfur dioxide anion radical in DMF in the presence of tetraethylammonium ion.^a $E_a = -7.1$ kcal/mol ($r=0.9993$).^b

T/K	$v_{0.3}/V\text{ s}^{-1}$	$10^{-6}k/M^{-1}\text{ s}^{-1}$
291.9	114.5	6.60
282.9	168	9.99
273.1	249	15.3
253.9	>500	>33.1

^a Measurements of DCV on solutions containing Et₄NBF₄ (0.1 M) and SO₂ (0.428 mM). ^b Linear regression correlation coefficient.

ism, eqn. (2), and were calculated from theoretical relationships previously reported.²⁵ A decreasing trend with increasing substrate concentration is found in the rate constants. This is not consistent with the interference of the dissocia-

Table 3. Evidence for the reversibility of the dimerization of sulfur dioxide in the presence of tetraethylammonium ion in DMF.^a

$v/V\text{ s}^{-1}$	R'_1 ^b
100.0	0.354
60.0	0.333
40.0	0.323
20.0	0.322
10.0	0.321
5.00	0.347
2.00	0.395
1.00	0.430

^a In solvent containing Et₄NBF₄ (0.1 M) and SO₂ (0.428 mM) at 304.6 K. ^b The ratio of first derivative peaks of the reverse and forward cyclic voltammetry scans.

* See Ref. 27 for a discussion of DCV mechanism analysis.

tion of the dimer, dithionate ion, which would be expected to cause the opposite trend in the rate constants. Although there is some deviation from second order kinetics, the effect is relatively small.

The data in Table 2 show the effect of temperature on the apparent rate constants. It was possible to measure $v_{0.3}$ at temperatures ranging from 292–273 K and the resulting rate constants gave an Arrhenius plot with an apparent activation energy of -7.1 kcal/mol and a linear regression correlation coefficient of 0.9993. The linearity of the Arrhenius plot suggests that the dissociation of the dimer is not seriously affecting the values of the observed rate constants. This has also been demonstrated to be the case in the reversible dimerization of 9-substituted anthracenes.^{23,24} At 253.9 K the reaction rate was observed to be so great that a reliable value of the rate constant could not be determined. Since the reaction continues to increase in rate with decreasing temperature at temperatures where the dissociation is surely not a problem, the apparent activation energy for the dimerization does indeed have a negative value.

The reversibility of the dimerization reaction is demonstrated by the data in Table 3. At 304.6 K the ratio of the derivative peaks of the cyclic voltammogram, R'_1 , decreases as v is decreased from 100 V/s and reaches a minimum value of about 0.321 in the region near 10 V/s. Further decreases in v are then accompanied by increasing R'_1 values. Similar behaviour has been shown

to be due to the dissociation of the dimer dianion in a related case.²³

When Bu_4NBF_4 was the supporting electrolyte, quite a different situation was encountered. The peak potential measured by derivative cyclic voltammetry (DCV) at 100 V/s was observed to depend strongly on the substrate concentration. The data in Table 4 show this effect. If the shift in the peak potential with increasing substrate concentration is caused by the association equilibrium (1), the equilibrium constant (K_1) is related to the shift in reversible potential (ΔE_{rev}) by eqn. (3).

$$\Delta E_{\text{rev}} = RT/F \ln(1 + K_1[\text{SO}_2]) \quad (3)$$

This equation has been derived earlier² using an analysis similar to that employed by Peover and Davies for the determination of ion pair equilibrium constants.²⁶ When the substrate is involved in the equilibrium as in (1) a special problem is encountered since the direct determination of E_{rev} under conditions where it is not affected by the association reaction is not possible if K_1 is large. The values of K_1 listed in the last column of Table 4 were obtained assuming E_{rev} was 4.0 mV less negative than that measured at a substrate concentration of 0.000211 M. The standard deviation in the calculated K_1 values was observed to be only $\pm 5.4\%$ of the mean value. Assuming either higher or lower values of ΔE_{rev} resulted in a larger standard deviation and hence a poorer fit of the data to eqn. (3).

Table 4. The equilibrium constant for the association of sulfur dioxide anion radical with substrate in DMF in the presence of tetrabutylammonium ion.^a

$10^4[\text{SO}_2]/\text{M}$	$-E_p^b/\text{mV}$	$\Delta E_{\text{rev}}^c/\text{mV}$	K^d/M^{-1}
2.11	522.7(0.9)	4.0	1631
3.16	522.3(1.6)	4.4	1513
4.21	518.8(0.5)	7.9	1749
5.26	518.0(0.6)	8.7	1568
6.32	516.1(1.1)	10.6	1655
7.37	514.2(0.8)	12.5	1743
8.42	513.8(1.6)	12.9	1588
			$1635 \pm 5.4\%$

^a Measurements by derivative cyclic voltammetry at 293 K. ^b The peak potential, referred to a bias potential of -600 mV vs. Ag/Ag^+ in acetonitrile, measured by DCV at 100 V s^{-1} . The numbers in parentheses refer to the standard deviations in five replicate measurements. ^c The values giving the best fit to eqn. (3). ^d Calculated according to eqn. (3).

Table 5. The effect of substrate concentration on the rate of dimerization of sulfur dioxide anion radical in DMF in the presence of tetrabutylammonium ion.^a

[SO ₂]/mM	$\nu_{0.3}/V\ s^{-1}$	$\nu_{0.3}/[SO_2]^2$	$10^{-10}k^b/M^{-2}s^{-1}$
0.421	35.0	197.5	1.72
0.526	47.2	170.6	1.49
0.632	75.2	188.3	1.64
0.737	107.9	198.7	1.73
0.842	121.0	170.7	1.49
		185.2(13.8)	1.61(0.12)
0.211	7.45	167.3	1.46
0.316	18.6	186.1	1.63
0.421	39.1	220.6	1.93
0.526	49.6	179.3	1.57
		188.3(22.8)	1.65(0.20)

^a Measurements by DCV in solvent containing Bu₄NBF₄ (0.1 M) at 293.0 K. ^b Calculated from theoretical data reported in Ref. 25.

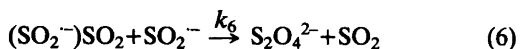
The effect of substrate concentration on the rate of reaction of SO₂⁻ in DMF in the presence of Bu₄N⁺ ion was also observed to be markedly different than when the counter ion was Et₄N⁺. The data are summarized in Table 5 for two independent series of experiments. The third column gives $\nu_{0.3}$ divided by the square of the substrate concentration. According to the principles of DCV mechanism analysis²⁷ the overall reaction order, $R_{A/B}$, is given by eqn. (4) where z is the number necessary for the term in parentheses to be constant.

$$R_{A/B} = 1 + z \quad (\nu_{0.3}/C_A^z = \text{constant}) \quad (4)$$

The data fit relationship (4) with $z=2$ indicating that $R_{A/B}$ is 3. This result is consistent with rate law (5) where R_B , the reaction order in primary intermediate, or SO₂⁻ in this case is 2, and R_A the reaction order in substrate is 1.

$$\text{Rate} = k_{\text{app}}[SO_2^-]^2[SO_2] \quad (5)$$

This rate law is that expected for the association of SO₂⁻ with SO₂ followed by rate determining reaction between the complex and anion radical (6) in which case $k_{\text{app}}=k_6K_1$.



Theoretical data are available for the DCV analysis of this mechanism.²⁵ The rate constants listed in the last column of Table 5 were calculated assuming mechanism (1)+(6) and rate law (5). The apparent rate constants for the two independent sets of experiments were nearly identical at $1.61(\pm 0.12)$ and $1.65(\pm 0.20) \times 10^{10} M^{-2}s^{-1}$.

The effect of temperature on the reaction rate of SO₂⁻ in DMF in the presence of Bu₄N⁺ is illustrated by the data in Table 6. There was some scatter in the data and the correlation coefficient for the Arrhenius plot was only 0.96. The apparent activation energy was 5.5 kcal/mol.

According to mechanism (1)+(6) the linear sweep voltammetry (LSV) peak potential is predicted to shift by 39.4 mV per decade change in substrate concentration at 298 K. This value can be derived from eqn. (7) where a is the reaction order in substrate and b that in primary intermediate.²⁸

$$d \log E^p / d \log C_A = RT/F(a+b-1)/(b+1) \quad (7)$$

The LSV data shown in Table 7 were obtained to further test the compatibility of rate law (5) with the data. At 292 K the theoretical value of the slope is -38.6 mV. The value observed was -51.6 mV/decade. However, we must keep in mind that the reversible potential also changes

Table 6. The effect of temperature on the apparent third order rate constants for the dimerization of sulfur dioxide anion radical in DMF in the presence of Bu₄N⁺.^a $E_a=5.5$ kcal/mol.

T/K	$v_{0.3}/V\ s^{-1}$	$10^{-10}k/M^{-2}s^{-1}$
292.6	53.8	2.66
273.1	44.5	2.35
252.7	40.0	2.29
242.7	36.0	2.14

^a Measurements by DCV on solutions containing SO₂ (0.421 mM) and Bu₄NBF₄ (0.1 M).

with substrate concentration and this must be corrected for. The corrections in the third column reflect the reversible potential changes in this concentration range. After correction a slope of -33.9 mV/decade was obtained. Deleting the data at the highest concentration improved the linearity of the analysis and a slope of -37.2 mV/decade with a correlation coefficient of 0.9993 was found. We can safely conclude that the LSV data are consistent with rate law (5).

DISCUSSION

The cause of some of the inconsistencies in previously reported values of K_1 in DMF in the presence of Et₄N⁺ is now obvious. The highest value $8,400\ M^{-1}$, was calculated from polarographic half-wave potentials assuming the dimerization reaction (2) is so slow that the cyclic voltammogram is essentially reversible at only

200 mV/s.² The apparent reversibility of the electrode process has been shown in this work to be due to the reversibility of reaction (2) and under the conditions of the polarographic work² the reversible reaction can be described by (8).



However, eqn. (8) only holds when the time scale of the experiment is long compared to the rate of dissociation of dithionite ion. The influence of the time scale of the experiment is shown clearly by the data in Table 3. The high value of the apparent ΔE_{rev} which led to the assumption of the high K_1 value² was simply due to the fact that the potential for reaction (8) is concentration dependent and the reversible potential shift is a reflection of that. In order to derive the equilibrium constant for (9) it would be advisable to work on a time scale where other reactions are not interfering. Further work is necessary along these lines.



Reversible potential shifts were calculated assuming each of the previously reported K_1 values and are compared to that observed in this work in Table 8. The peak potential measured by DCV at 100 V/s was observed to be independent of substrate concentration ranging from 0.095 to 0.428 mM within the limits of experimental error which was estimated to be about ± 1 mV. The two higher values, 8400 and $611\ M^{-1}$, are clearly ruled out under the conditions of the measure-

Table 7. The effect of substrate concentration on the linear sweep voltammetry peak potential during the dimerization of sulfur dioxide anion radical in DMF containing Bu₄N⁺.^a

[SO ₂]/mM	$-E_p$	Correction ^b	$-E_p(\text{corr})/\text{mV}$
0.211	380.4(0.5)	4.0	384.4
0.422	366.4(0.2)	7.5	373.9
0.844	348.8(0.1)	13.2	362.0
1.266	341.0(0.1)	17.9	358.9
$(dE_p/d \log [SO_2])/$ (mV/decade)	-51.6		-33.9^c

^a Measurements at 200 mV/s in solvent containing Bu₄NBF₄ (0.1 M) at 292 K. ^b The shift in the reversible potential calculated from the equilibrium constant for: $SO_2^- + SO_2 \rightleftharpoons (SO_2^-)SO_2$. ^c Omitting the data at the highest concentration results in a value of -37.2 mV/decade with a correlation coefficient of 0.9993.

Table 8. Calculated reversible potential shifts ($\Delta E_{\text{rev}}/\text{mV}$) from equilibrium constants reported in the literature for the association of SO_2^- with SO_2 in DMF containing Et_4N^+ .

$[\text{SO}_2]/\text{mM}$	Ref. 2 $K=8400 \text{ M}^{-1}$	Ref. 1 $K=611 \text{ M}^{-1}$	Ref. 7 $K=230 \text{ M}^{-1}$	This work Observed ^a
0.095	8.5	0.72	0.27	± 1
0.190	14.8	1.42	0.54	± 1
0.285	19.8	2.10	0.81	± 1
0.428	25.9	3.10	1.28	± 1

^a From measurements by DCV at 100 V s^{-1} .

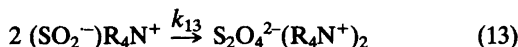
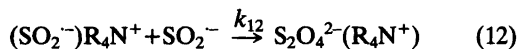
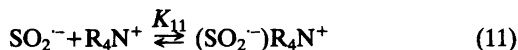
ments used. The value reported by Kastening and Gostisa-Mihelcic ⁷ appears to be just a little bit higher than is compatible with the peak potential shift data. It is likely that the value is 200 M^{-1} or less. The very large equilibrium constant for reaction (9) would have to be taken into account in the analysis of all of the previous data in order to come up with a reasonable estimate of K_1 .

On the other hand, K_1 is sufficiently large in DMF in the presence of Bu_4N^+ to completely change the situation. A value of 1635 M^{-1} was estimated from the shift in peak potential measured at 100 V/s (Table 4). The equilibrium constant expression for reaction (1) can be rearranged to (10),

$$[(\text{SO}_2^-)\text{SO}_2]/[\text{SO}_2^-] = K_1[\text{SO}_2] \quad (10)$$

which gives the relative concentrations of complexed to uncomplexed anion radical at a given substrate concentration. Since the concentrations employed in the experiments ranged from 2.11 to $8.42 \times 10^{-4} \text{ M}$, there was always an appreciable fraction of uncomplexed SO_2^- in the reaction layer. Thus, the magnitude of K_1 in the presence of Bu_4N^+ cannot be responsible for the exclusion of dimerization reaction (2). This can also be deduced from considering the first entries in Tables 2 and 5. At the same $[\text{SO}_2]$ and temperature, $v_{0.3}$ was observed to be nearly 3 times as great in the presence of Et_4N^+ than in the presence of Bu_4N^+ which means that the lifetime of SO_2^- under these conditions is about 3 times as great in the presence of Bu_4N^+ . The reaction order data indicate that dimerization is the predominant reaction in the presence of Et_4N^+ (Table 1) and that the third order mechanism (1)+(6) is the nearly exclusive pathway in the presence of Bu_4N^+ (Table 5). It appears that the

electrolyte effect is best described by the influence of Et_4N^+ on reaction (2) and on the magnitude of equilibrium constant K_9 as well as on the magnitude of K_1 . A plausible explanation of these observations is that ion pairing is much more pronounced in the case of Et_4N^+ as the counter ion than when Bu_4N^+ is the supporting electrolyte cation. This suggests that the dimerization reaction can be described by a mechanism involving equilibrium (11) and coupling reactions (12) and (13), the latter depending upon the magnitude of K_{11} .



In fact, this is essentially the same interpretation that Gardner, Fouchard and Fawcett ³ presented for the dimerization reaction in the presence of Li^+ . However, they assumed that ion pairing was insignificant in the presence of Et_4N^+ . The pre-equilibrium mechanism (11)–(13) also accounts for the apparent negative activation energy (Table 2). The apparent activation energy for this mechanism is the sum of ΔH_{11}^\ddagger and E_a for the coupling reactions (12) or (13) depending upon which is important under the conditions of the measurements.

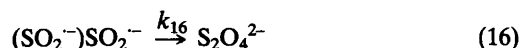
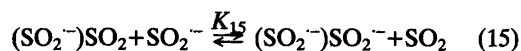
One of the features of the previous work that was of special interest to the author was that the forward rate constant for reaction (1) was proposed to be equal to only $10^5 \text{ M}^{-1}\text{s}^{-1}$.¹ This value appeared to be quite low for a reaction which only involves the formation of a non-bonded association complex. However, in this work we

see that forward reaction (1) is fast enough so that (1) is in equilibrium in spite of the occurrence of a very rapid further reaction (6). The apparent rate constant for mechanism (1)+(6) is equal to k_6K_1 and was found to be $1.63 \times 10^{10} \text{ M}^{-2}\text{s}^{-1}$ at 293 K (Table 5). Since K_1 was estimated to be equal to 1635 at the same temperature (Table 4) this results in a value of $10^7 \text{ M}^{-1}\text{s}^{-1}$ for k_6 . Since rate law (5) requires that (1) is at equilibrium, we can estimate the value of k_1 from eqn. (14),

$$k_1[\text{SO}_2^-][\text{SO}_2] > 10 k_6[(\text{SO}_2^-)\text{SO}_2][\text{SO}_2^-] \quad (14)$$

which results in a value of the order $k_1 > 10^8 \text{ M}^{-1}\text{s}^{-1}$ assuming that average ratio of the concentrations of SO_2 and the anion radical complex is about 1 in the reaction layer. Thus, it is quite probable that forward reaction (1) is diffusion controlled.

Reaction (6) is an intriguing one. At first glance one might assume that it is a simple electron transfer with SO_2^- donating an electron to the complex. This could indeed be the case. However, the apparent activation energy for the process was observed to be of the order of 5.5 kcal/mol (Table 6). Since reaction (1) is a simple association which would be expected to be exothermic, an overall activation energy of 5.5 kcal/mol implies that E_a for reaction (6) may be somewhat greater after accounting for ΔH_1° . If reaction (6) only involves the transfer of an electron, the activation energy would be expected to be considerably smaller. On this basis it would appear to be more likely that (6) is not an electron transfer reaction but rather a displacement of SO_2 from the complex by SO_2^- . The relatively large activation energy, i.e. for a reaction with a rate constant of $10^7 \text{ M}^{-1}\text{s}^{-1}$, could then be due to the charge repulsion in the transition state leading to the formation of dithionate ion. Still another possibility is that the reaction does involve electron transfer but that (6) is a two-step process. The first step could be electron transfer (15) which is then followed by the formation of dithionate ion (16).



This sequence would also account for the activation energy but would give rise to rate law (17) and overall second order kinetics.

$$\text{Rate} = k_{16}K_{15}[\text{SO}_2^-]^2 \quad (17)$$

Mechanism (15)+(16) can be ruled out on this basis. Thus, the most likely mechanism appears to be the displacement reaction.

In conclusion, it should be emphasized that the reaction pathway followed by SO_2^- in DMF depends very much upon the reaction conditions. A change from Et_4N^+ to Bu_4N^+ as counter ion brought about a change in mechanism. It is quite likely that other factors such as the presence and concentration of proton donors could cause equally dramatic changes.

EXPERIMENTAL

The instrumentation, electrodes, cells and data handling procedures were those described earlier.²⁹ Reagent grade DMF containing the supporting electrolyte (Bu_4NBF_4) were passed through a column containing neutral alumina before use. Anhydrous SO_2 from Matheson was used as received. A stock solution of SO_2 in DMF was added to the electrolyte solution after oxygen had been removed by purging with nitrogen. Derivative cyclic voltammetry experiments were carried out as previously described.³⁰

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