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

VERNON D. PARKER

Laboratory for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim,
N-7034 Trondheim-NTH, Norway

In the presence of tetraethylammonium ion $SO_2^{\cdot-}$ undergoes reversible dimerization with an apparent rate constant of $1.5\times10^7$ $M^{-1}$ $s^{-1}$ 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).

$$SO_2^{\cdot-}+SO_2 \overset{K_i}{\rightleftarrows} (SO_2^{\cdot-})SO_2 \qquad \text{(i)}$$

$$(SO_2^{\cdot-})SO_2+SO_2^{\cdot-} \xrightarrow{k_{ii}} {}^{-}O_2S-SO_2^{-}+SO_2 \qquad \text{(ii)}$$

Reaction (ii) could either be an electron transfer or the displacement of $SO_2$ by $SO_2^{\cdot-}$. The latter pathway is deemed most likely on the basis of an apparent activation energy of the order of 5 kcal/mol since $\Delta H_i^\circ$ is expected to be negative and the $E_a$ for electron transfer to be small. $K_i$ was observed to be equal to 1640 $M^{-1}$ at 293 K and $k_{ii}$ was estimated to be equal to $1.7\times10^7$ $M^{-1}$ $s^{-1}$ at the same temperature. In the presence of $Et_4N^+$, $K_i$ 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 $SO_2^{\cdot-}$ exists along with the anion radical complex $(SO_2^{\cdot-})SO_2$ according to equilibrium (1).[7,1-3]

$$SO_2^{\cdot-}+SO_2 \overset{K_1}{\rightleftarrows} (SO_2^{\cdot-})SO_2 \qquad (1)$$

However, the value of $K_1$ was found to depend strongly on the particular technique used in the study. Kastening and Gostisa-Mihelcic [7] reported a value of 230 $M^{-1}$ for $K_1$ based on a combination of polarographic and e.s.r. measurements. Gardner, Fouchard and Fawcett [2] 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. measurements [14] 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 $10^5$ $M^{-1}s^{-1}$.

Another interesting aspect of the reactions of $SO_2^{\cdot-}$ was reported by Gardner, Fouchard and Fawcett.[3] They found that in the presence of either $Et_4N^+$ or $Bu_4N^+$ the reactions of $SO_2^{\cdot-}$ could be described by reaction (1) but in the presence of $Li^+$ only dimerization to dithionate ion (2) takes place.

$$2\,SO_2^{\cdot-} \xrightarrow{k_2} S_2O_4^{2-} \qquad (2)$$

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

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*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 | $\nu_{0.3}$ | $10^{-6}k/M^{-1}s^{-1}$ | $-E^p(100\ V\ s^{-1})^b$/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 $Et_4NBF_4$ (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 $SO_2^{\cdot-}$ system, a re-investigation of the kinetics and mechanism of the dimerization of $SO_2^{\cdot-}$ in DMF was undertaken.

## RESULTS

At voltage sweep rates of 200 mV/s or less, the cyclic voltammogram for the reduction of $SO_2$ in DMF containing $Et_4NClO_4$ 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 $Et_4NBF_4$. However, at higher voltage sweep rate ($\nu$) the peak current ratio is much less than unity indicating a very rapid follow-up reaction of $SO_2^{\cdot-}$. Results for the measurement of $\nu_{0.3}$, 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 $SO_2^{\cdot-}$ with $SO_2$ is not favorable enough under the measurement conditions for a shift in reversible potential to be evident. The value of $\nu_{0.3}$ was observed to be concentration dependent and the rate constants given in column 3 of Table 1 are assuming a dimerization mechanism, 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 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 | $\nu_{0.3}$/V $s^{-1}$ | $10^{-6}k/M^{-1}\ s^{-1}$ |
|---|---|---|
| 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 $Et_4NBF_4$ (0.1 M) and $SO_2$ (0.428 mM). [b] Linear regression correlation coefficient.

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

| $\nu$/V $s^{-1}$ | $R'_I$ [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 $Et_4NBF_4$ (0.1 M) and $SO_2$ (0.428 mM) at 304.6 K. [b] The ratio of first derivative peaks of the reverse and forward cyclic voltammetry scans.

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* 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, $R'_{\mathrm{I}}$, 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 $R'_{\mathrm{I}}$ 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 ($\Delta E_{\mathrm{rev}}$) by eqn. (3).

$$\Delta E_{\mathrm{rev}} = RT/F \ln(1+K_1[\mathrm{SO_2}]) \tag{3}$$

This equation has been derived earlier [2] 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 $E_{\mathrm{rev}}$ 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 $E_{\mathrm{rev}}$ 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 ±5.4 % of the mean value. Assuming either higher or lower values of $\Delta E_{\mathrm{rev}}$ 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]

| $10^4[\mathrm{SO_2}]$/M | $-E_p{}^b$/mV | $\Delta E_{\mathrm{rev}}{}^c$/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±5.4 % |

[a] Measurements by derivative cyclic voltammetry at 293 K. [b] The peak potential, refered 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 | $v_{0.3}$/V $s^{-1}$ | $v_{0.3}/[SO_2]^2$ | $10^{-10}k^b/M^{-2}s^{-1}$ |
|---|---|---|---|
| 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 $Bu_4NBF_4$ (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 $SO_2^{\cdot-}$ in DMF in the presence of $Bu_4N^+$ ion was also observed to be markedly different than when the counter ion was $Et_4N^+$. The data are summarized in Table 5 for two independent series of experiments. The third column gives $v_{0.3}$ divided by the square of the substrate concentration. According to the principles of DCV mechanism analysis [27] 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.

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

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 $SO_2^{\cdot-}$ in this case is 2, and $R_A$ the reaction order in substrate is 1.

$$\text{Rate} = k_{app}[SO_2^{\cdot-}]^2[SO_2] \tag{5}$$

This rate law is that expected for the association of $SO_2^{\cdot-}$ with $SO_2$ followed by rate determining reaction between the complex and anion radical (6) in which case $k_{app}=k_6K_1$.

$$(SO_2^{\cdot-})SO_2+SO_2^{\cdot-} \xrightarrow{k_6} S_2O_4^{2-}+SO_2 \tag{6}$$

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(±0.12) and 1.65(±0.20)$\times 10^{10}$ $M^{-2}s^{-1}$.

The effect of temperature on the reaction rate of $SO_2^{\cdot-}$ in DMF in the presence of $Bu_4N^+$ 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]

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

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 $Bu_4N^+$.[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 $SO_2$ (0.421 mM) and $Bu_4NBF_4$ (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 $Et_4N^+$ 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 work [2] the reversible reaction can be described by (8).

$$2\ SO_2+2\ e^- \rightleftharpoons S_2O_4^{2-} \qquad (8)$$

However, eqn. (8) only holds when the time scale of the experiment is long compared to the rate of dissociation of dithionate 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 $\Delta E_{rev}$ which led to the assumption of the high $K_1$ value [2] 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.

$$2\ SO_2^{\cdot-} \overset{K_9}{\rightleftharpoons} S_2O_4^{2-} \qquad (9)$$

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 $Bu_4N^+$.[a]

| $[SO_2]$/mM | $-E_p$ | Correction [b] | $-E_p$(corr)/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 $Bu_4NBF_4$ (0.1 M) at 292 K. [b] The shift in the reversible potential calculated from the equilibrium constant for: $SO_2^{\cdot-}+SO_2 \rightleftharpoons (SO_2^{\cdot-})SO_2$. [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 ($\Delta E_{\mathrm{rev}}$/mV) from equilibrium constants reported in the literature for the association of $\mathrm{SO_2^{\cdot-}}$ with $\mathrm{SO_2}$ in DMF containing $\mathrm{Et_4N^+}$.

| $[\mathrm{SO_2}]$/mM | Ref. 2<br>$K=8400\ \mathrm{M^{-1}}$ | Ref. 1<br>$K=611\ \mathrm{M^{-1}}$ | Ref. 7<br>$K=230\ \mathrm{M^{-1}}$ | This work<br>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 $\mathrm{s^{-1}}$.

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 $\mathrm{M^{-1}}$ 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 $\mathrm{Bu_4N^+}$ to completely change the situation. A value of 1635 $\mathrm{M^{-1}}$ 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),

$$[(\mathrm{SO_2^{\cdot-}})\mathrm{SO_2}]/[\mathrm{SO_2^{\cdot-}}] = K_1[\mathrm{SO_2}] \tag{10}$$

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 $8.42\times10^{-4}$ M, there was always an appreciable fraction of uncomplexed $\mathrm{SO_2^{\cdot-}}$ in the reaction layer. Thus, the magnitude of $K_1$ in the presence of $\mathrm{Bu_4N^+}$ 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 $[\mathrm{SO_2}]$ and temperature, $\nu_{0.3}$ was observed to be nearly 3 times as great in the presence of $\mathrm{Et_4N^+}$ than in the presence of $\mathrm{Bu_4N^+}$ which means that the lifetime of $\mathrm{SO_2^{\cdot-}}$ under these conditions is about 3 times as great in the presence of $\mathrm{Bu_4N^+}$. The reaction order data indicate that dimerization is the predominant reaction in the presence of $\mathrm{Et_4N^+}$ (Table 1) and that the third order mechanism (1)+(6) is the nearly exclusive pathway in the presence of $\mathrm{Bu_4N^+}$ (Table 5). It appears that the electrolyte effect is best described by the influence of $\mathrm{Et_4N^+}$ 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 $\mathrm{Et_4N^+}$ as the counter ion than when $\mathrm{Bu_4N^+}$ 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 $K_{11}$.

$$\mathrm{SO_2^{\cdot-}}+\mathrm{R_4N^+} \overset{K_{11}}{\rightleftharpoons} (\mathrm{SO_2^{\cdot-}})\mathrm{R_4N^+} \tag{11}$$

$$(\mathrm{SO_2^{\cdot-}})\mathrm{R_4N^+}+\mathrm{SO_2^{\cdot-}} \xrightarrow{k_{12}} \mathrm{S_2O_4^{2-}}(\mathrm{R_4N^+}) \tag{12}$$

$$2\,(\mathrm{SO_2^{\cdot-}})\mathrm{R_4N^+} \xrightarrow{k_{13}} \mathrm{S_2O_4^{2-}}(\mathrm{R_4N^+})_2 \tag{13}$$

In fact, this is essentially the same interpretation that Gardner, Fouchard and Fawcett [3] presented for the dimerization reaction in the presence of $\mathrm{Li^+}$. However, they assumed that ion pairing was insignificant in the presence of $\mathrm{Et_4N^+}$. 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 $\Delta H^{\circ}_{11}$ and $E_{\mathrm{a}}$ 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 $10^5\ \mathrm{M^{-1}s^{-1}}$.[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 $1.63\times10^{10}$ $M^{-2}s^{-1}$ 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 $10^7$ $M^{-1}s^{-1}$ for $k_6$. Since rate law (5) requires that (1) is at equilibrium, we can estimate the value of $k_1$ from eqn. (14),

$$k_1[SO_2^{\cdot-}][SO_2]>10\,k_6[(SO_2^{\cdot-})SO_2][SO_2^{\cdot-}] \quad (14)$$

which results in a value of the order $k_1>10^8$ $M^{-1}s^{-1}$ 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 $SO_2^{\cdot-}$ 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 $\Delta H^\circ_1$. 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 $SO_2^{\cdot-}$. The relatively large activation energy, *i.e.* for a reaction with a rate constant of $10^7$ $M^{-1}s^{-1}$, 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).

$$(SO_2^{\cdot-})SO_2+SO_2^{\cdot-} \overset{K_{15}}{\rightleftarrows} (SO_2^{\cdot-})SO_2^{\cdot-}+SO_2 \quad (15)$$

$$(SO_2^{\cdot-})SO_2^{\cdot-} \xrightarrow{k_{16}} S_2O_4^{2-} \quad (16)$$

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

$$\text{Rate} = k_{16}K_1K_{15}[SO_2^{\cdot-}]^2 \quad (17)$$

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 $SO_2^{\cdot-}$ 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]

## REFERENCES

1. Laman, F. C., Gardner, C. L. and Fouchard, D. T. *J. Phys. Chem. 86* (1982) 3130.
2. Gardner, C. L., Fouchard, D. T. and Fawcett, W. R. *J. Electrochem. Soc. 128* (1981) 2337.
3. Gardner, C. L., Fouchard, D. T. and Fawcett, W. R. *J. Electrochem. Soc. 128* (1981) 2345.
4. Geronov, V., Moshtev, R. V. and Puresheva, B. *J. Electroanal. Chem. 108* (1980) 335.
5. Shembel, E. M., Litvinova, V. I., Maksyuta, I. M. and Ksezhek, O. S. *Sov. Electrochem. 15* (1980) 1534.
6. Shembel, E. M., Litvinova, V. I., Maksyuta, I. M. and Ksezhek, O. S. *Sov. Electrochem. 15* (1980) 1435.
7. Kastening, B. and Gostisa-Mihelcic, B. *J. Electroanal. Chem. 100* (1979) 801.

8. Magno, R. P., Mazzoccin, G. A. and Bontempelli, G. *J. Electroanal. Chem. 57* (1974) 89.
9. Martin, R. P. and Sawyer, D. T. *Inorg. Chem. 11* (1972) 2644.
10. Bonnaterre, R. and Cauquis, G. *J. Electroanal. Chem. 32* (1971) 215.
11. Rinker, R. G. and Lynn, S. *Ind. Eng. Chem. Prod. Res. Dev. 8* (1969) 338.
12. Rinker, R. G. and Lynn, S. *J. Phys. Chem. 72* (1968) 4706.
13. Dinse, K. P. and Möbius, K. *Z. Naturforsch. A 23* (1968) 695.
14. Goldberg, I. B. and Bard, A. J. *J. Phys. Chem. 75* (1971) 3281.
15. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 149.
16. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 279.
17. Margaretha, P. and Parker. V. D. *Acta Chem. Scand. B 36* (1982) 260.
18. Parker, V. D. Adv. *Phys. Org. Chem. 19* (1983) 131.
19. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 147.
20. Lerflaten, O. and Parker, V. D. *Acta Chem. Scand. B 36* (1982) 193.
21. Parker, V. D. *Acta Chem. Scand. B 37* (1983). *In press.*
22. Lerflaten, O. and Parker, V. D. *Acta Chem. Scand. B 37* (1983). *In press.*
23. Hammerich, O. and Parker, V. D. *Acta Chem. Scand. B 35* (1981) 341.
24. Hammerich, O. and Parker, V. D. *Acta Chem. Scand. B 37* (1983). *In press.*
25. Ahlberg, E. and Parker, V. D. *Acta Chem. Scand. B 35* (1981) 117.
26. Peover, M. E. and Davies, J. D. *J. Electroanal. Chem. 6* (1963) 46.
27. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 233.
28. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 259.
29. Ahlberg, E. and Parker, V. D. *Acta Chem. Scand. B 34* (1980) 97.
30. Ahlberg, E. and Parker, V. D. *J. Electroanal. Chem. 121* (1981) 73.

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