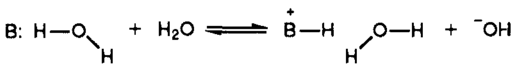
the base species as indicated in eq 13, then the relationship between ΔS° for eq 13 and $\Delta S_B{}^\ddagger$ for mechanism A becomes fairly clear.



$$\mathrm{B{:}\ H{-}O(H) + H_2O \rightleftharpoons \overset{+}{B}{-}H\ \ O{-}H(H) + {}^{-}OH} \qquad (13)$$

When ΔS° is quite negative, the differential structural effects upon the equilibrium protonation of B are well-modeled in the transition state for $\Delta S_B{}^\ddagger$ of mechanism A. However, as ΔS° becomes positive, all of the solvational changes that occur during the protonation equilibrium do not take place upon attaining the transition-state species in mechanism A. Since the positive (and less negative) ΔS° occur with the more highly hindered amine bases, it is not too surprising that these hindered bases do not follow $\Delta S_B{}^\ddagger$ described by the less hindered bases. We suggest that the levelling off in $\Delta S_B{}^\ddagger$ that occurs for positive ΔS° is due to steric hindrance to solvation of the developing ammonium ion with hindered amine bases. This can be seen in the reactivity that is found for nitrilotriacetate which is lower than for the other tertiary amine bases in Table III.

If one assumes that mechanism A is reasonably accurate in depicting a carbanionic transition state species, then considerable electronic delocalization must occur following the attainment of the rate-determining transition state species. Such electronic delocalization will have consequences in solvational reorganization for the enolate ion species. Such reorganization must precede the attainment of this transition state in the microscopic reverse of mechanism A, and consequently, $\Delta S_{BH}{}^\ddagger$ will not be as readily interpretable via a straightforward comparison of mechanism A and eq 13 as was possible for $\Delta S_B{}^\ddagger$. We note that the limiting value for $\Delta S_{BH}{}^\ddagger \approx -5$ cal deg^{-1} mol^{-1} is similar to the value observed[31] for the entropy of activation for the protonation by water of the conjugate bases of a number of carbon acids, but it is not clear whether this observation has any physical significance.

There seem to have been very few attempts to explore rate and equilibrium entropic effects in a systematic manner. Evans and Hamann[28] compared Pearson's limited data for deprotonation of nitroethane by amines[29] and several nucleophilic substitution reactions of the same amines and reported an entropic rate–equilibrium relationship similar to the linear region of Figure 7. Arnett and Reich[48] have also used a similar comparison in their studies of the alkylation of substituted pyridines, although in this case there is little variation in either $\Delta S^\ddagger$ or ΔS° for different substituents. Figure 7 seems to be the most extensive relationship of this type that is currently known, and we feel that this relationship is particularly impressive when one notes that it is found despite the apparent chaos in the Brønsted plot of Figure 3. While the generality of such relationships remains to be established, we feel that we have quantitatively established, for at least one reaction, that the usual qualitative interpretations of diverse phenomena in general-base catalysis in terms of solvation effects are indeed soundly based.

Acknowledgment. We appreciate the continued financial support of this work by the Natural Sciences and Engineering Research Council of Canada. We thank Charles Liang and Andrea Toth for the measurement of several rate constants.

---

[48] Arnett, E. M.; Reich, R. *J. Am. Chem. Soc.* **1980**, *102*, 5892.

Outer-Sphere and Inner-Sphere Processes in Organic Chemistry. Reaction of Trifluoromethyl Bromide with Electrochemically Generated Aromatic Anion Radicals and Sulfur Dioxide Anion Radicals

Claude P. Andrieux, Laurence Gelis, and Jean-Michel Saveant*

Contribution from the Laboratoire d'Electrochimie Moléculaire de l'Université de Paris 7, Unité de Recherche Associée au CNRS No. 438, 2, Place Jussieu Paris Cedex 05, France.

Received December 6, 1988. Revised Manuscript Received July 18, 1989

Abstract: The reduction of CF_3Br by electrochemically generated aromatic anion radicals gives rise to purely catalytic currents. An activation–driving force relationship characterizing outer-sphere electron donors can thus be established. Electrochemically generated sulfur dioxide anion radicals do not give rise to catalytic currents upon reaction with CF_3Br but rather produce trifluoromethyl sulfinate according to an overall two electron per molecule stoichiometry. The rate constant of the rate-determining step of the the reaction is at least 4 orders of magnitude larger than that of an aromatic anion radical of the same standard potential, unambiguously showing that $SO_2{}^{\bullet-}$ does not react as an outer-sphere electron donor. Among the various possible inner-sphere processes, bromine atom abstraction appears as the most likely.

The discovery of substitution reactions proceeding via radical-anion intermediates ($S_{RN}1$ reaction)[1] as well as the development of mechanistic studies in organic electrochemistry has triggered a growing interest for the role of single-electron transfer in organic processes. Besides its synthetic interest, the main features of the mechanism of the $S_{RN}1$ reaction at aliphatic and aromatic carbon centers are now reasonably well understood.[2] It is a chain process in which electrons play the role of a catalyst. Of different nature is the possible involvement of single-electron transfer in S_N2-substitution reactions. An essential question is

---

[1] (a) Kornblum, N.; Michel, R. E.; Kerber, R. C. *J. Am. Chem. Soc.* **1966**, *88*, 5662. (b) Russell, G. A.; Danen, W. C. *J. Am. Chem. Soc.* **1966**, *88*, 5663.

[2] (a) Russell, G. A. *Spec. Publ.–Chem. Soc.* **1970**, *24*, 271. (b) Kornblum, N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 734. (c) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. (d) Savéant, J.-M. *Acc. Chem. Res.* **1980**, *13*, 323. (e) Rossi, R. A.; Rossi, R. H. *Aromatic substitution by the SRN1 Mechanism*; ACS Monograph 178; The American Chemical Society: Washington, DC, 1983.

Table I. Redox Catalysis of the Reduction of CF_3Br by Aromatic Anion Radical[a]

mediator	std potential (V vs SCE)	k_1 ($M^{-1}\ s^{-1}$)
9-fluorenone	−1.245	4.5×10^2
1,4-diacetylbenzene	−1.435	6.3×10^3
1,4-dicyanobenzene	−1.52	4.4×10^4
4-cyanopyridine	−1.75	6.5×10^6
1-cyanonaphthalene	−1.84	1.7×10^7

[a] In DMF + 0.1 M Bu_4NBF_4 at 25 °C.

then to know whether the reaction involves first a dissociative single-electron-transfer rate-determining step

$$D^- (D^{\bullet -}) + RX \rightarrow R^\bullet + X^- + D^\bullet\ (D)$$

followed, in a separate step, by the coupling of the R and D moieties or a single step in which electron transfer, bond breaking, and bond formation would be concerted. In the first case, the electron donor functions in an outer-sphere manner, and in the second, in an inner-sphere manner.[3] The dichotomy between these two mechanisms and appendent questions, such as how to distinguish one from the other, what are the factors that control their respective occurence, and the passage from one to the other, have attracted active attention.[3d,4,5] In this connection, the "kinetic advantage" strategy, initiated with a comparison between the electron-donor properties of iron(I) porphyrins and aromatic anion radicals,[4a] has been employed in several instances since then.[3d,4c–f] It consists of first constructing an activation–driving force relationship characterizing outer-sphere reagents by plotting the rate constant of their reaction with the electron acceptor against their standard potential (aromatic anion radicals in aprotic media are good candidates for establishing such an "ET" line). If the point representing the electron donor (nucleophile) under examination falls well above the ET line, it can be concluded that the reaction follows a mechanism different from an outer-sphere electron transfer from the electron donor to the substrate.

Although in the above-mentioned cases the alternative pathway has been shown to be, on stereochemical grounds, an S_N2 mechanism, other possibilities exist, particularly halogen atom transfer. This other variety of an inner-sphere process has been shown, on the basis of kinetic arguments, to occur for example in the reaction of alkyl halides with chromium(II) and cobalt(II) complexes.[6]

Comparison between the reactivity of alkyl and perfluoroalkyl compounds is a matter of fundamental interest. This is particularly the case for electron transfer to alkyl and perfluoroalkyl halides in the gas phase,[7a] in solid matrixes,[7b–d] and in polar liquids.[7e] In addition, the introduction of perfluoroalkyl groups in many types of organic molecules by means of electron transfer to perfluoroalkyl halides[8] is the object of active and continuing interest.

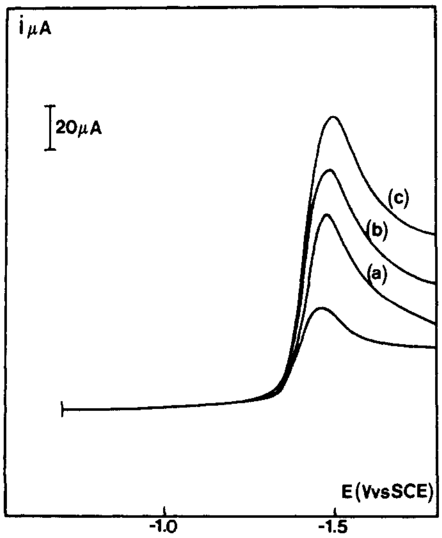


Figure 1. Redox catalysis of the reduction of CF_3Br by the anion radical of 1,4-diacetylbenzene (2 mM) at a GC electrode in DMF + 0.1 M NBu_4BF_4 at 25 °C. Scan rate: 0.5 V s^{-1}. CF_3Br concentrations (mM): 0, 2 (a), 4 (b), 40 (c).

We report in the following an investigation of the reaction of trifluoromethyl bromide with aromatic anion radicals and with the sulfur dioxide anion radical, both being generated electrochemically. The latter reaction yields trifluoromethanesulfinate ions that are of practical interest as precursors of trifluoromethanesulfonates (triflates). This is again, on the overall, a substitution reaction:

$$CF_3Br + SO_2 + 2e^- \rightarrow CF_3SO_2^- + Br^-$$

The question then arises whether the reaction proceeds by means of an outer-sphere electron transfer from the $SO_2^{\bullet -}$ anion radical to CF_3Br followed by coupling of the CF_3 and SO_2 moieties or in an inner-sphere manner. In the latter case, what is the reaction mechanism, S_N2, atom transfer, ...? The investigation of the reaction of CF_3Br with aromatic anion radicals is a necessary preliminary for knowing whether they can be considered to function as outer-sphere electron donors in this case.

Results

Cyclic voltammetric and preparative-scale electrolysis experiments were all carried out in *N*,*N*-dimethylformamide (DMF) containing 0.1 M NBu_4ClO_4 or NBu_4BF_4 at 25 °C.

Cyclic Voltammetry of the Reduction of CF_3Br by Aromatic Anion Radicals. They were generated in cyclic voltammetry from the parent aromatic compounds (Table I). In the absence of CF_3Br, these exhibit a one-electron reversible wave. It becomes irreversible and increases in height upon addition of increasing amounts of CF_3Br (Figure 1). In all cases, the peak current

---

(3) (a) The inner-sphere/outer-sphere terminology has been coined for reactions involving coordination complexes.[3b,c] It can, however, be extended to organic processes.[3d] (b) Taube, H. *Electron Transfer Reactions of Complex ions in Solution*; Academic Press: New York 1970. (c) Espenson, J. H. *Homogeneous Inorganic Reactions in Investigation of Rates and Mechanisms of Reactions, Techniques of Chemistry*, 4th ed.; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. VI, Part 1, pp 487–563. (d) Lexa, D.; Savéant, J.-M.; Su, K. B.; Wang, D. L. *J. Am. Chem. Soc.* **1988**, *110*, 7617. (e) A purely dissociative electron transfer, as found for example in the reduction of alkyl halides by aromatic anion radicals or inert electrodes, is not, strictly speaking, an outer-sphere process, even though the electron-donor functions in an outer-sphere manner. It indeed possesses an inner-sphere character from the point of view of the electron acceptor that undergoes a concerted electron-transfer–bond-breaking reaction.[3f] (f): Savéant, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 6788.

(4) (a) Lexa, D.; Mispelter, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1981**, *103*, 6806. (b) Ebert, E.; Mazaleyrat, J. P.; Nadjo, L.; Savéant, J.-M.; Welvart, Z. *Nouv. J. Chim.* **1985**, *9*, 75. (c) Lund, T.; Lund, H. *Acta Chem. Scand., Ser. B* **1986**, *40*, 470. (d) Bordwell, F. G.; Wilson, C. A. *J. Am. Chem. Soc.* **1987**, *109*, 5470. (e) Bordwell, F. G.; Harrelson, J. A. *J. Am. Chem. Soc.* **1987**, *119*, 8112. (f) Bordwell, F. G.; Harrelson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 1052.

(5) (a) See also: References 5b–d, and references cited therein. (b) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978. (c) Eberson, L. *Electron Transfer in Organic Chemistry*; Springer-Verlag: Berlin, 1987. (d) Ashby, E. C. *Acc. Chem. Res.* **1988**, *21*, 414.

(6) See: Reference 5b, pp 139–142, and references cited therein.

(7) (a) Compton, R. N.; Reinhard, P. W.; Cooper, C. D. *J. Chem. Phys.* **1978**, *68*, 4360. (b) Hasegawa, A.; Williams, F.; *Chem. Phys. Lett.* **1977**, *46*, 66. (c) Hasegawa, A.; Shiotani, M.; Williams, F. *Faraday Discuss. Chem. Soc.* **1977**, *157*. (d) Symons, M. C. R. *Pure Appl. Chem.* **1981**, *53*, 223. (e) Andrieux, C. P.; Gélis, L.; Medebielle, M.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* In press.

(8) See: Reference 7e, and references cited herein.

(9) (a) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J.-M.; Savéant, J.-M. *J. Am. Chem. Soc.* **1979**, *101*, 3431. (b) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J.-M.; M'Halla, F.; Savéant, J.-M. *J. Am. Chem. Soc.* **1980**, *102*, 3806. (c) Andrieux, C. P.; Dumas-Bouchiat, J.-M.; Savéant, J.-M. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *113*, 19. (d) Andrieux, C. P.; Savéant, J.-M.; Zann, D. *Nouv. J. Chim.* **1984**, *8*, 107. (e) Savéant, J.-M.; Su, K. B. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *171*, 341. (f) Andrieux, C. P.; Savéant, J.-M. *Electrochemical reaction in Investigation of Rates and Mechanisms of Reactions, Techniques of Chemistry*, 4th ed.; Bernasconi, Ed.; Wiley: New York, 1986; Vol. VI, Part 2, pp 305–390.

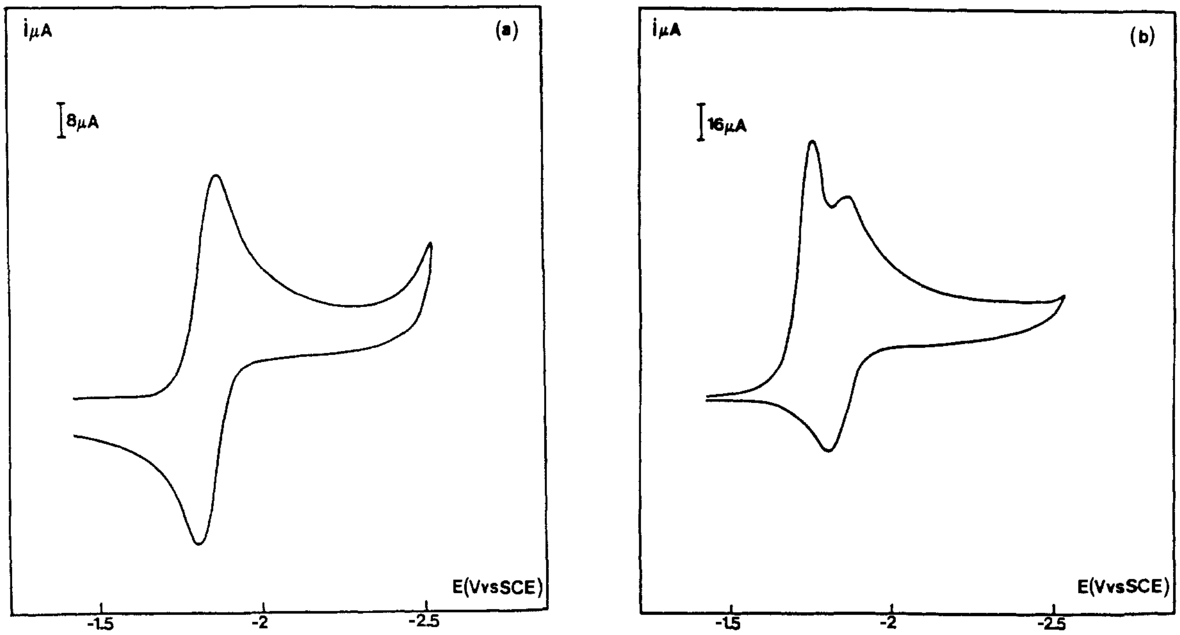


Figure 2. Reduction of the anion radical of 1-cyanonaphthalene at a GC electrode in DMF + 0.1 NBu_4BF_4 at 25 °C: an example of "total catalysis". Cyclic voltammetry of 1-cyanonaphthalene (2 mM) in the absence (a) and presence (b) of CF_3Br (2 mM). Scan rate: 0.1 V s^{-1}.

continues to increase without saturation as the CF_3Br concentration is made larger. For the two most negative mediators, a "total catalysis" situation is met (Figure 2) as shown by the characteristic appearance of an irreversible prewave in front of the mediator wave. These observations unambiguously show that we deal with pure catalysis of the reduction of CF_3Br by the aromatic anion radicals

$$P + e^- \rightleftharpoons Q \text{ (mediator couple)}$$

$$Q + CF_3Br \rightarrow P + CF_3^\bullet + Br^- \qquad (1)$$

with no coupling between the mediator and the CF_3 moiety unlike what happens in the case of alkyl halides.[10] Although reaction 1 is the rate-determining step of the overall process, the reaction does not stop at this stage. As shown in detail elsewhere,[7c] $CF_3^\bullet$ competitively abstracts an H atom from the solvent (SH) and is further reduced by electron transfer from another Q molecule:

$$CF_3^\bullet + SH \rightarrow CF_3H + S^\bullet \qquad (2)$$

$$CF_3^\bullet + Q \rightarrow P + CF_3^- (\rightarrow CF_3H) \qquad (3)$$

If reaction 2 predominates, the electron stoichiometry is one aromatic anion radical per CF_3Br, since the DMF radical is reduced at more negative potentials.[7c,9d] The opposite case involves a two aromatic anion radical per CF_3Br stoichiometry. In the case where "total catalysis" is reached, i.e., for 1-cyanonaphthalene and 4-cyanopyridine, the electron stoichiometry, n, can be obtained from the ratio of the peak current of the prewave, i_p, and that of the mediator wave in the absence of CF_3Br, i_p^0:

$$n = 0.733 \frac{i_p}{i_p^0} \frac{[\text{mediator}]}{[CF_3Br]}$$

$n = 1.5$ and 1.2 in the first and second cases, respectively. The value of the rate constant, k_1, can then be derived from the potential distance between the prepeak and the mediator peak for $n = 2$ and for $n = 1$.[9] In the latter case, the value of k_1 is twice that in the former.[9] k_1 can thus be obtained approximatively by linear interpolation between these two values, leading to the figures listed in Table I. It has been found previously that reduction of CF_3I by 1,4-diacetylbenzene and 3-fluorenone gives rises to pure catalysis, then leading to an electron stoichiometry of 1.[7c] This means that $CF_3^\bullet$ is not reduced at the corresponding standard potentials but rather abstracts an hydrogen atom from the solvent. Thus, in the case of CF_3Br also, the electron stoichiometry is 1 for these two mediators. The standard procedures can thus be used for deriving the rate constant k_1 from the peak current increase data.[9] For the intermediary mediator, 1-4 dicyanobenzene, we also used $n = 1$ for determining k_1. The values of k_1 for the five mediators are summarized in Table I.

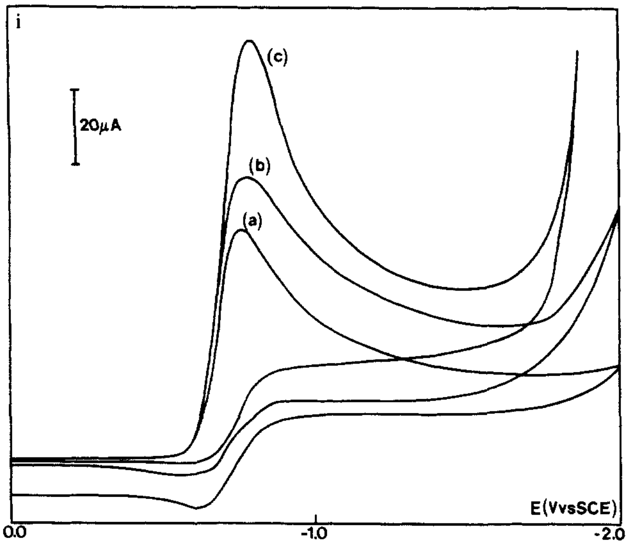


Figure 3. (a) Cyclic voltammetry of SO_2 (2 mM) in DMF + 0.1 M NBu_4BF_4 in the absence (a) and presence of 2 mM (b) and 10 mM (c) SO_2.

Cyclic Voltammetry of the Reduction of CF_3Br by Sulfur Dioxide Anion Radicals. Figure 3a shows the variations of the cyclic voltammogram of SO_2 in DMF (+0.1 M NBu_4BF_4) upon addition of increasing amounts of CF_3Br. In the absence of CF_3Br, SO_2 exhibits a partially reversible one-electron wave that becomes irreversible and increases in height upon addition of CF_3Br, eventually reaching a two electron per molecule height. As shown in the next section, the reaction leads to the formation of $CF_3SO_2^-$, which is indeed consistent with the two electron per molecule stoichiometry observed here:

$$CF_3Br + SO_2 + 2e^- \rightarrow CF_3SO_2^- + Br^-$$

---

[10] Andrieux, C. P.; Gallardo, I.; Savéant, J.-M.; Su, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 638.

Table II. Kinetics of the Reaction of SO_2^- with CF_3Br^a and Variations of the Current Ratio $i_p/i_p^{0\,b}$ with the CF_3Br Concentration

$[CF_3Br]$ (mM)	i_p/i_p^0	k_1 ($M^{-1}\ s^{-1}$)
2	1.32	1.8×10^3
4	1.46	1.2×10^3
10	1.75	2.4×10^3
150	2.20	

[a] In DMF + 0.1 M NBu_4BF_4 at 25 °C. SO_2 concentration: 2 mM. [b] i_p and i_p^0: peak currents of the SO_2 cyclic voltammetric wave in the presence and absence of CF_3Br, respectively. Scan rate: 0.2 V s^{-1}.

The variation of the i_p/i_p^0 ratio (from a one electron to a two electron per molecule stoichiometry) with the CF_3Br concentration (Table II) is compatible with a DISP1 kinetics[11]

$$SO_2 + e^- \rightleftharpoons SO_2^{\bullet -}$$

$$SO_2^{\bullet -} + CF_3Br \xrightarrow{k_1} CF_3^{\bullet} + SO_2\ (+Br^- \rightleftharpoons SO_2Br^-) \quad (4)$$

or

$$SO_2^{\bullet -} + CF_3Br \rightarrow CF_3^{\bullet} + SO_2Br^-\ (\rightleftharpoons SO_2 + Br^-) \quad (5)$$

$$SO_2^{\bullet -} + CF_3^{\bullet} \rightarrow CF_3SO_2^-$$

involving as homogeneous rate laws for the disappearance of $SO_2^{\bullet -}$ and regeneration of SO_2

$$\frac{d[SO_2^{\bullet -}]}{dt} = -2k_1[SO_2^{\bullet -}][CF_3Br]$$

$$\frac{d([SO_2] + [SO_2Br^-])}{dt} = k_1[SO_2^{\bullet -}][CF_3Br]$$

to be combined with the diffusion law for simulating the cyclic voltammetric current response. SO_2Br^- is considered together with SO_2 in the above equation because, as discussed later, SO_2 is partially complexed by the Br^- ions in DMF. $CF_3^{\bullet}$ is certainly an unstable species a priori able to react rapidly in various ways: coupling with $SO_2^{\bullet -}$ (reaction 2), H atom abstraction from the solvent,[7e] reduction by outer-sphere electron-transfer reagents,[7e] possibly $SO_2^{\bullet -}$ in the present case.[12] The rapidity of the reactions undergone by $CF_3^{\bullet}$ justifies the steady-state assumption made in the derivation of the above rate laws. As discussed later, reaction 5 predominates over H atom abstraction from the solvent and over electron transfer from $SO_2^{\bullet -}$. The formal kinetics are obviously the same whatever the intimate nature of the reaction of CF_3Br with $SO_2^{\bullet -}$, outer-sphere electron transfer from $SO_2^{\bullet -}$ (reaction 4) or Br atom abstraction by $SO_2^{\bullet -}$ (reaction 5).[13] The distinction between these two mechanisms, the main issue of the present study, therefore requires other means to be achieved. The formal kinetics are also the same for two other conceivable mechanisms, namely an S_N2 reaction (at carbon)

$$SO_2^{\bullet -} + CF_3Br \rightarrow CF_3SO_2^{\bullet} + Br^- \quad (6)$$

$$CF_3SO_2^{\bullet} + SO_2^{\bullet -} \rightarrow CF_3SO_2^- + SO_2$$

or for an X-philic reaction (Br^+ abstraction, S_N2 at Br)[14]

$$SO_2^{\bullet -} + CF_3Br \rightarrow CF_3^- + {}^{\bullet}SO_2Br \quad (7)$$

$${}^{\bullet}SO_2Br + SO_2^{\bullet -} \rightarrow SO_2 + SO_2Br^-\ (\rightleftharpoons SO_2 + Br^-)$$

again requiring further evidence to be distinguished from the other possible mechanisms.

Unlike previously investigated cases,[11] the substrate (here CF_3Br) is not in large excess over the electrochemically active species (here SO_2) so that pseudo-first-order conditions are not fulfilled. For second-order conditions, a working curve relating i_p/i_p^0 to $(RT/F)(k_1[SO_2]/v)$ can be simulated for each value of the $[CF_3Br]/[SO_2]$ ratio that allows the determination of k_1 for each CF_3Br concentration and scan rate. As seen in Table II the values of k_1 thus determined are satisfactorily constant, leading to an average value of $(1.8 \pm 0.6) \times 10^3\ M^{-1}\ s^{-1}$.

The above analysis neglects the fact that the $SO_2^{\bullet -}$ anion radical generated from SO_2 undergoes, in the absence of CF_3Br, other reactions that might also take place in the presence of CF_3Br concurrently with the reaction of $SO_2^{\bullet -}$ with CF_3Br. That such reactions occur is revealed by the fact that the $SO_2/SO_2^{\bullet -}$ wave, in the absence of CF_3Br, is not completely reversible in slow-scan cyclic voltammetry (Figure 3a). Although actively investigated, the reduction mechanism of SO_2 in aprotic solvents such as DMF[15] has so far not been the object of a general agreement in the case where the supporting electrolyte is a quaternary ammonium salt,[15] as it is in the present study. What appears as ascertained, especially from ESR studies,[15a,d,f,g] is the rapid formation of a complex between the $SO_2^{\bullet -}$ radical and one molecule of SO_2. The ensuing fate of this complex is more debatable. It has been hypothesized[15e] that through coupling with a bare $SO_2^{\bullet -}$ radical it would ultimately yield a dithionite like compound, in the case of alkali cations[16] with however regeneration of one SO_2 molecule in the present case. However, a second anodic wave was found at more positive potentials than the first anodic wave, corresponding to the oxidation of $SO_2^{\bullet -}$, and seemed to correspond to the oxidation of SO_3^{2-} rather than to that of dithionite. SO_3^{2-} thus obtained has been assumed to result from the disproportionation of $SO_2^{\bullet -}$ radicals:[15c]

$$2SO_2^{\bullet -} \rightleftharpoons SO_3^{2-} + SO$$

It could also, more likely, be the result of the reduction of the primary $SO_2(SO_2^{\bullet -})$ adduct at the electrode or in the solution (by $SO_2^{\bullet -}$ itself). A more recent study[15f] provides evidence that the primary reduction product of SO_2 in DMF is an $S_3O_6^{2-}$ adduct that could correpond to the S–S coupling of $SO_2(SO_2^{\bullet -})$ adduct without concomitant expulsion of an SO_2 molecule. All the reactions following the reduction of $SO_2^{\bullet -}$ and its primary association with SO_2 are, in any case, reversible since slow-scan cyclic voltammetry shows a partial reversibility that tends to increase as the scan rate decreases. Addition of CF_3Br suppresses this reversibility, showing that the reaction of $SO_2^{\bullet -}$ with CF_3Br is more rapid than these reactions. It remains that, in the presence of CF_3Br, $SO_2^{\bullet -}$ may be partially converted into the adduct it gives with SO_2. The neglect of this possibility would lead to an underestimation of the rate constant of the reaction of $SO_2^{\bullet -}$ with CF_3Br by a factor at maximum equal to $K_{SO_2}[SO_2]$, i.e., in our case ($[SO_2]$, = 2 mM, NBu_4^+ as supporting cation, $K_{SO_2} = 1635$ M^{-1} [15e]) by a factor of 3.

---

(11) (a) Mastragostino, M.; Nadjo, L.; Savéant, J.-M. *Electrochim. Acta.* **1968**, *13*, 721. (b) Amatore, C.; Gareil, M.; Savéant, J.-M. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *147*, 1.

(12) In fact, as discussed in the case where the electron donor is an aromatic anion radical, H atom abstraction predominates over electron transfer as soon as the standard potential of the electron donor is positive to −1.5 V vs SCE. This is a fortiori the case with $SO_2^{\bullet -}$ since its standard potential (−0.8 V vs SCE) is well above this value.

(13) (a) A reviewer suggested that the $CF_3^{\bullet}$ could couple with SO_2 itself rather than with the $SO_2^{\bullet -}$ molecule.

$$CF_3^{\bullet} + SO_2 \rightarrow CF_3SO_2^{\bullet}$$

$$CF_3SO_2^{\bullet} + SO_2^{\bullet -} \rightarrow CF_3SO_2^- + SO_2$$

This would also lead to the same formal kinetics provided, as seems quite likely, that the steady-state assumption applies to $CF_3SO_2^{\bullet}$. It actually seems very improbable that $CF_3^{\bullet}$, which possesses an acid character,[13b] would couple with SO_2, another Lewis acid. (b) $CF_3^{\bullet}$ generated by direct or indirect electrochemical means readily reacts with various soft nucleophiles in the framework of an electron-transfer-induced S_RN1 substitution reaction.[13c] (c) Medebielle, M.; Pinson, J.; Savéant, J.-M. Manuscript in preparation.

(14) Zefirov, N. S.; Makhon'Kov, D. I. *Chem. Rev.* **1982**, *82*, 615.

(15) (a) Kastening, B.; Gostisa-Michelsic, B. *J. Electroanal. Chem.* **1979**, *100*, 801. (b) Gardner, C. L.; Fouchard, D. T.; Fawcett, W. R. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *128*, 2337. (c) *Ibid.* 2345. (d) Laman, F. C.; Gardner, C. L.; Fouchard, D. T. *J. Phys. Chem.* **1982**, *86*, 3130. (e) Parker, V. D. *Acta Chem. Scand., Ser. A* **1983**, *37*, 423. (f) Knittel, D. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *195*, 345. (g) Wille, H. J.; Kastening, B.; Knittel, D. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *214*, 221.

(16) (a) In the case of lithium salts, dimerization involving ion-paired anion radicals and yielding dithionites appears as the main reaction pathway.[15b,d]

We also attempt to investigate the reaction of electrochemically generated superoxide anion radicals with CF_3Br. No modification of the reversible wave of dioxygen[17] was found upon addition of CF_3Br to saturation (0.33 M), even at scan rates as low as 0.05 V s^{-1}, thus showing that the bimolecular rate constant of the reaction of $O_2^{\bullet-}$ with CF_3Br is smaller than 0.6 M^{-1} s^{-1}.

Preparative-Scale Reduction of SO_2 in the Presence of CF_3Br. Preliminary communications or patents have reported the formation of trifluoromethyl sulfinate salts from the reaction of SO_2 with CF_3Br under reducing conditions.[18] The following results were obtained by electrolysis at a glassy-carbon electrode at the potential of the SO_2 wave of mixtures of SO_2 and CF_3Br in DMF with 0.1 M NBu_4ClO_4 as supporting electrolyte with 0.1 M with a nonsoluble anode (platinum) separated from the cathodic compartment by a glass frit. In a typical experiment, the solution contained 0.08 M CF_3Br. After exhaustion of SO_2, which required the consumption of two electrons per molecule, the solution was analyzed by ^{19}F NMR spectroscopy and gas chromatography. Two ^{19}F NMR peaks were found at −87 (ppm/$CFCl_3$) and −81, corresponding to two products in a 3/1 ratio. These peaks are those of $CF_3SO_2^-$[18b] and CF_3SO_2H.[19b] No trace of the sulfone $CF_3SO_2CF_3$,[19a] expected to give a peak at −74,[19c,d] was found. Faradaic yields for the conversion of SO_2 into $CF_3SO_2^-$ and CF_3SO_2H were typically 60%.[19e] Likewise, no trace of CF_3H was found by chromatographic analysis of the gas over the electrolyzed solutions.

Discussion

As revealed by the results of the preparative-scale electrolyses, the only product deriving from CF_3Br in its reaction with the $SO_2^{\bullet-}$ radical is the $CF_3SO_2^-$ ion (which is further converted partially into the conjugated acid). The reaction may proceed according to four different mechanisms: outer-sphere electron transfer from $SO_2^{\bullet-}$ (designated by ET in the following, rate-determining step (rds): reaction 4), Br atom abstraction leading directly to SO_2Br in the rate-determining step (reaction 5), S_N2 leading to $CF_3SO_2^\bullet$ in the rate-determining step (reaction 6) and Br^+ abstraction leading to $^\bullet SO_2Br$ in the rds (reaction 7).

Comparison of the reactivity of $SO_2^{\bullet-}$ toward CF_3Br with that of the aromatic anion radicals allows one to decide whether or not the reaction proceeds according to the ET mechanism. Let us first note in this connection that the aromatic anion radicals unambiguously play the role of outer-sphere electron donors in their reaction with CF_3Br. Pure catalytic currents are indeed obtained in the reduction of the corresponding aromatic molecules in the presence of CF_3Br without formation of a bond between the aromatic moiety and CF_3, unlike what happens with alkyl halides.[20] No S_N2 pathway is thus involved. Transient $Br^\bullet$ or Br^+ abstraction is also quite unlikely. Thus, the plot of the rate constant of the reaction, k_1, versus the standard potential of the aromatic anion radicals (Figure 4) provides an activation–driving force relationship characteristic of the reaction of outer-sphere electron donors with CF_3Br.[21] As seen in Figure 4, the point representing the rate constant obtained with $SO_2^{\bullet-}$ in the same diagram falls well above, by at least 4 orders of magnitude, the outer-sphere line. The rate constant of the reaction of CF_3Br outer-sphere electron donors is the result of the self-exchange characteristics of both CF_3Br and the electron donor. Aromatic anion radicals, of the type used in the present study, have a small self-exchange intrinsic barrier of ca 0.16 eV, which is about constant from one aromatic anion radical to the other,[22] whereas CF_3Br has a much larger self-exchange intrinsic barrier, on the order of 0.9 eV.[7e] This is the reason why the aromatic anion radicals give rise to a single outer-sphere line (Figure 4) that is essentially representative of the intrinsic electron properties of CF_3Br itself. The self-exchange intrinsic barrier the $SO_2/SO_2^{\bullet-}$ couple in DMF is not known with certainty. However, it should not be smaller than that of the aromatic anion radicals since both the solvent and internal (change is bond lengths and angles) reorganization factors have no reason to be smaller and are most probably larger (the charge is more concentrated in $SO_2^{\bullet-}$ than in the aromatic anion radicals and the nuclei framework likely to be less rigid). It follows that the fact that the rate constant obtained with $SO_2^{\bullet-}$ is much larger than with an aromatic anion radical of same standard potential cannot be attributed to a variation of the self-exchange intrinsic barrier when passing from the first electron donor to the second. If such a variation exists, it should actually lead to the opposite effect. It is interesting to note in this connection that the $O_2/O_2^{\bullet-}$ couple, which has about the same standard potential (−0.87 V vs SCE[17]) as the $SO_2/SO_2^{\bullet-}$ couple and should have closer self-exchange kinetics than aromatic anion radicals, does not give rise to any detectable reaction even

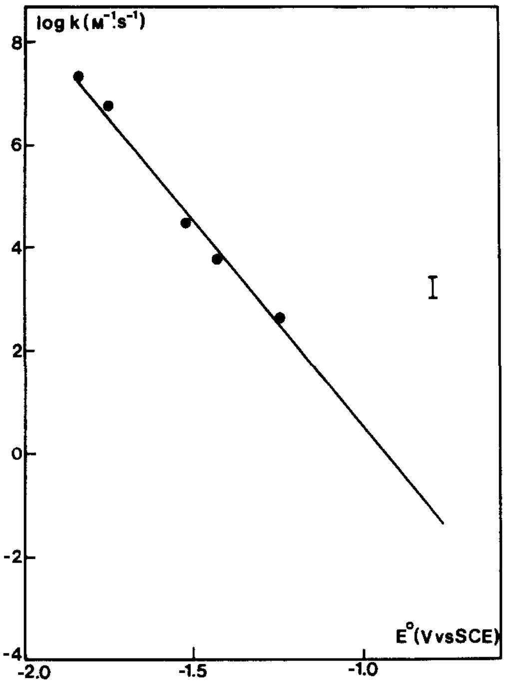


Figure 4. Rate constants of the reaction of CF_3Br with aromatic anion radicals (●, from left to right 1-naphthonitrile, 4-cyanopyridine, terephthalonitrile, 1,4-diacetylbenzene, 9-fluorenone) and with $SO_2^{\bullet-}$ (I) as a function of their standard potentials in DMF + 0.1 M NBu_4BF_4 at 25 °C.

---

[17] Stallings, M. O.; Sawyer, D. T. *J. Chem. Soc., Chem. Commun.* **1979**, 340.

[18] (a) I.e., by zinc in dimethylformamide[18b–d] or by electrochemical reduction in the same solvent with[18f] or without[18e] a soluble anode or from its reaction with sodium dithionite.[18g,h] (b) Wakselman, C.; Tordeux, M. *Bull. Soc. Chim. Fr.* **1986**, *6*, 1868. (c) Wakselman, C.; Tordeux, M. French Pat. 2564829; *Chem. Abstr.* **1986**, *105*, 171845v. (d) Wakselman, C.; Tordeux, M. *J. Chem. Soc., Chem. Commun.* **1987**, 1701. (e) Andrieux, C.; Gélis, L.; Jaccaud, M.; Leroux, F.; Savéant, J.-M. French. Pat. 88.09336. (f) Folest, J.-C.; Nedelec, J.-Y.; Perichon, J. *Synth. Commun.* **1988**, *18*, 1491. (g) Tordeux, M.; Langlois, B.; Wakselman, B. French Pat. 2593808; *Chem. Abstr.* **1988**, *108*, 166975v. (h) Tordeux, M.; Langlois, B.; Wakselman, C. *J. Org. Chem.* **1989**, *54*, 2452.

[19] (a) The sulfone is obtained quantitatively in the reaction of alkyl halides with electrogenerated sulfur dioxide anion radicals.[15g] (b) Harzdorf, C.; Meussdoerffer, J.-N.; Niederprum, H.; Wechsberg, M. *Liebigs Ann. Chem.* **1973**, 33. (c) Oberhammer, H.; Knerr, G. D.; Shreeve, J. M. *J. Mol. Struct.* **1982**, *82*, 143. (d) Harmon, R. J. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2675. (e) A part of the $CF_3SO_2^-$ anions are presumably reoxidized at the anode after diffusion through the glass frit.

[20] See: Reference 10, and references cited therein.

[21] Although not central to the present discussion,[21b] it is interesting to note that the cleavage of the F_3C–Br bond, occuring upon electron transfer from an outer-sphere electron donor, is most probably concerted with the electron-transfer step itself in polar solvents such as DMF.[7e] This conclusion was based on an analysis of the kinetics of CF_3Br electrochemical reduction and is also consistent with that of its reduction by aromatic anion radicals.[7e] This is the reason why the $CF_3Br^{\bullet-}$ anion radical that would be the first intermediate in a stepwise process does not appear in the representation of the mechanism of the ET reactions given above. (b) The kinetic advantage approach employed to distinguish between the ET pathway and the other possible mechanisms would also be valid in the case where bond breaking and electron transfer would occur stepwisely rather than concertedly.

[22] Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317.

at low scan rate, showing that $O_2^{\bullet-}$ reacts at least 2000 times slower with CF_3Br than $SO_2^{\bullet-}$.

We are thus led to conclude that $SO_2^{\bullet-}$ does not react with CF_3Br along an ET mechanism. Among the three other possibilities, the S_N2 and the bromonium transfer mechanisms are unlikely for several reasons. One is that $CF_3^\bullet$ appears as an intermediate in the reaction as indicated by the fact that it is trapped by aniline when it is added to the solution in reactions where SO_2 is reduced by zinc in DMF in the presence of CF_3Br.[18d] This falls in line with the fact that an S_N2 pathway is quite unlikely for electronic distribution reasons. It is also remarkable that bromides that are good electrophiles in S_N2 reactions, such as methyl, *n*-propyl, and even allyl bromide, react much more slowly than CF_3Br with $SO_2^{\bullet-}$.[15g,19a] As regards to the Br^+ abstraction pathway, there is obviously much less driving force for generating $BrSO_2^\bullet$ than $BrSO_2^-$, the primary intermediate in the Br atom transfer pathway (see below).

The only remaining possibility is the Br atom transfer mechanism in which the primarily formed $CF_3^\bullet$ radical would couple with an $SO_2^{\bullet-}$ radical.[13a] As compared to the ET pathway, the Br atom transfer pathway possesses an additional driving force equal to (RT/F) ln K, where K is the equilibrium constant of the reaction $SO_2 + Br^- \rightleftharpoons SO_2Br^-$. K is equal to 160, 21, and 0.22 M^{-1} in CH_3CN, $(CH_3)_2SO$, and H_2O, respectively.[23] The additional amount of driving force can thus be estimated to be of the order of 0.1 eV. Although there is thus a definite driving force advantage of the Br atom transfer over the ET pathway, this cannot fully explain why the $SO_2^{\bullet-}$ radical reacts so much faster than an outer-sphere reagent of the same standard potential. One has, however, to consider that the bonding interactions that stabilize the transition state occur within a solvent cage and are thus much stronger than in the case where the intervening species are separated by the solvent. No data are available for the association of SO_2 and Br^- in the gas phase. This is, however, expected to be much stronger than in a polar solvent since the presence of solvent stabilizes Br^- by its acidic properties and SO_2 by its basic properties.

Atom transfer is formally equivalent to one variety of inner-sphere electron transfer.[3b,c,24] In the present case, the reaction

$$CF_3Br + SO_2^{\bullet-} \rightarrow CF_3^\bullet + BrSO_2^-$$

may be viewed as involving either the homolytic fission of the C–Br bond concertedly with the homolytic coupling of $Br^\bullet$ and $SO_2^{\bullet-}$ (atom transfer) or the electron transfer from $SO_2^{\bullet-}$ concerted with the cleavage of the C–Br bond and association of the resulting SO_2 and Br^- moieties (inner-sphere electron transfer). The actual mechanism probably lies in between these two extremes, with partial development of a negative charge on the Br atom in the transition state.

Experimental Section

Chemicals. DMF was from commmerical origin and was distilled under reduced pressure before use. The supporting electrolytes NBu_4Cl_4 and NBu_4BF_4 (Fluka) were used as received. In both cyclic voltammetry and preparative-scale electrolysis, a stream of CF_3Br (Atochem) was first passed through the solution and then maintained over the solution during the whole experiment. It was diluted with nitrogen by means of a mass-flow regulator (Alphagas). The concentration of CF_3Br in the solution was adjusted on the basis of its solubility, i.e., 40 g in 1 kg of DMF at 20 °C as determined by weighting. For example, 2 mM CF_3Br corresponds to a 90 cm^3/min N_2 and a 0.676 cm^3/min CF_3Br flow.

Cyclic Voltammetry. A thermostated cell (25 °C) was used with a platinum wire as the counter electrode and an aqueous SCE as reference electrode. The working electrode was a 0.03-cm^2 glassy-carbon (Tokai Corp.) disk. It was carefully polished with a 1-μm diamond paste and ultrasonically rinsed in ethanol before each run.

Preparative-Scale Electrolysis. The experiments were carried out in a cylindrical glassy-carbon (Carbone Lorraine V 25) crucible serving as working electrode with 100 cm^3 of solution in the cathodic compartment. The counter electrode was a platinum wire separated from the anodic compartment by a glass frit (porosity 4). The same procedure as in cyclic voltammetry was used for setting the concentration of CF_3Br. The electrolyzed solution was analyzed by ^{19}F NMR spectroscopy on a 250-MHz (Brucker) instrument. The chemical shifts are reported in parts per million relative to fluorotrichloromethane as internal standard. The gas over the solution was analyzed by gas chromatography (with the catharometer detector (IG 11 Delsi instrument with a 2.5-m neutral alumina column treated with 3% tetramethylsilane containing 2% 112 Alcatel oil)).

Conclusion

In summary, the electrochemical reduction of SO_2 in DMF in the presence of CF_3Br leads to the complete conversion of the latter in $CF_3SO_2^-$ with a two electron per molecule (of SO_2 and CF_3Br) stoichiometry. Comparison of the rate constant of the reaction of $SO_2^{\bullet-}$ with CF_3Br with the outer-sphere electron-transfer activation–driving force plot derived from the rate constants of the reaction with aromatic radicals allows the determination of the reaction mechanism. Although $CF_3^\bullet$ is the primary intermediate in both cases, $SO_2^{\bullet-}$ does not merely react as an outer-sphere electron donor but rather abstracts the bromine atom. In this inner-sphere process, bonding interactions stabilize the transition state, thus leading to a much larger rate constant than that of an outer-sphere electron donor of same standard potential. This is another example of a substitution reaction where the electron donor (nucleophile), although a member of a reversible redox couple, does not react in an outer-sphere manner. An S_N2 pathway is not involved either, but rather an atom-transfer mechanism is involved.

Acknowledgment. Discussions with Claude Wakselman (CNRS, Thiais, France) on the matter of the present note were pleasant and helpful. The work received partial financial support from ATOCHEM Co. We are indebted to K. B. Su (Laboratoire d'Electrochimie Moléculaire) for the computation of the second-order DISP1 working curves used for analyzing the kinetics of the reaction of CF_3Br with $SO_2^{\bullet-}$.

Registry No. CF_3Br, 75-63-8; SO_2, 7446-09-5; $CF_3SO_2^-$, 48022-83-9; CF_3SO_2H, 34642-42-7; $SO_2^{\bullet-}$, 12143-17-8; 9-fluorenone, 486-25-9; 1,4-diacetylbenzene, 1009-61-6; 1,4-dicyanobenzene, 623-26-7; 4-cyanopyridine, 100-48-1; 1-cyanonaphthalene, 86-53-3; 9-fluorenone radical anion, 3101-67-5; 1,4-diacetylbenzene radical anion, 40475-62-5; 1,4-dicyanobenzene radical anion, 34536-47-5; 4-cyanopyridine radical anion, 34536-53-3; 1-cyanonaphthalene radical anion, 34478-12-1.

---

(23) Salama, S. B.; Nasif, S. *J. Chem. Soc., Trans. Dalton* **1975**, 151.

(24) The S_N2 and Br^+ transfer pathways are formally other varieties of inner-sphere electron-transfer processes. In the former, electron transfer is concerted with the cleavage of the C–Br bond into $C^\bullet$ and Br^- and with the coupling of $^\bullet CF_3$ with SO_2. In the latter, it is concerted with the cleavage of the C–Br bond into C^- and $Br^\bullet$ and with the coupling between $Br^\bullet$ and SO_2.