

Electron Transfer Reactions in Organic Chemistry. X.* *N*-Bromosuccinimide as an Electron Transfer Oxidant; Standard Potential and Reorganization Energy

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N-Bromosuccinimide (SBr) reacts with easily oxidizable neutral organic compounds (D) to give radical cations, D^{•+}, according to (i). The kinetics of a number of such reactions in acetonitrile at 15.0°C have now been studied, D being selected with a standard potential in the range of 0.25–0.72 V vs. NHE.

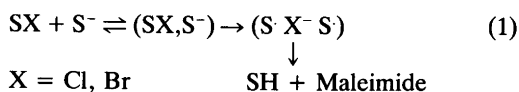


Ferrocene well exemplified the problems encountered in this type of study. Since SBr forms reactive complexes of different stoichiometry with bromide ion, the bromide ion liberated during the run gives rise to autocatalysis; moreover, bromide ion reacts with the ferricinium ion formed, causing a rather complex kinetic behaviour. Runs with added bromide confirmed its catalytic role upon (i) and the biphasic nature of the reaction. Fortunately, addition of a bromide ion scavenger, mercury(II) acetate, circumvented these obstacles and allowed for the determination of ET rate constants for a number of substrates. Using the Marcus treatment on the kinetic data obtained, $E^\circ(\text{SBr}/\text{SBr}^-)$ and $\lambda(\text{SBr}/\text{SBr}^-)$ were then calculated to be 0.17 ± 0.30 V and 72 ± 20 kcal mol⁻¹, respectively.

As a corollary, the reaction between SBr and 12-tungstocobalt(II)ate ion was predicted and found to exhibit kinetics with significant influence from the back ET reaction between SBr⁻ and 12-tungstocobalt(III)ate ion.

We have previously shown¹⁻³ that *N*-bromosuccinimide (SBr) and *N*-chlorosuccinimide (SCl) act as electron transfer (ET) oxidants toward succinimide anion (S⁻), in all likelihood via initial complex formation⁴ [eqn. (1)]. Upon ET within the complex, two succinimidyl radicals (S) are formed in a solvent cage and eventually give succinimide and maleimide via disproportionation. The

maleimide ends up as polymaleimide.²



Since S⁻ is an easily oxidizable species, $E^\circ(\text{S}/\text{S}^-)$ being estimated at 0.9–1.0 V vs. NHE* in acetonitrile, a few other substrates were tested as well.² Thus ferrocene ($E^\circ = 0.53$ V) was rapidly oxidized by SBr to ferricinium ion and

*Part IX, see Ref. 60.

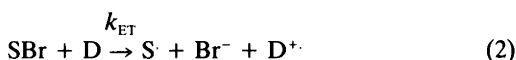
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*Normal hydrogen electrode; all potentials are given vs. NHE, unless otherwise stated.

N,N,N',N'-tetramethylphenylenediamine ($E^\circ = 0.25$ V) to its radical cation (Wurster's Blue). Similarly, Koshechko *et al.*⁵ reported the formation of radical cations from tri(*p*-tolyl)amine ($E^\circ = 1.0$ V), tris(4-methoxyphenyl)amine ($E^\circ = 0.72$ V) and 5,10-dihydro-5,10-dimethylphenazine ($E^\circ = 0.35$ V). Also, even a compound as difficult to oxidize as 2,4,6-trimethoxynitrosobenzene ($E^\circ = 1.20$ V) is converted to its radical cation by SBr.⁶

In order to define the properties of SBr as an ET oxidant, we now report a kinetic study of its reactions with a series of easily oxidizable compounds according to eqn. (2). Despite several complicating kinetic features, ET rate constants



could be determined and used in conjunction with the Marcus treatment⁷ to obtain $E^\circ(\text{SBr}/\text{SBr}^-)$ and the reorganization energy of the SBr/SBr^- self-exchange reaction.

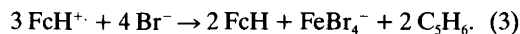
Results and Discussion

General considerations. Acetonitrile was chosen as solvent for the kinetic runs, since its dielectric constant (36) is high enough to ensure that the Marcus treatment can be applied without complications. The following substrates, covering an E° range of *ca.* 0.4 V, were studied: ferrocene (FcH), butylferrocene, chloromercuriferrocene, 1,1'-dimethylferrocene, 5,10-dihydro-5,10-dimethylphenazine, tris(4-methoxyphenyl)amine and *N,N,N',N'*-tetramethylphenylenediamine. The kinetics were followed by monitoring the rate of appearance of the radical cation spectrophotometrically at 15.0°C.

Preliminary experimentation showed that most substrates displayed several complicating features in their reaction with SBr. Not surprisingly, the reaction was biphasic, in that the bromide ion liberated during the reaction [eqn. (2)] slowly reacts with $\text{D}^{\cdot+}$.^{5,10,11} More unexpected was the appearance of an induction period during the initial phase, most likely due to a catalytic effect by bromide ion. Both these effects are typically present in the reaction between ferrocene and SBr, and are treated in detail in the next section.

Kinetics of the reaction between ferrocene and

SBr. It has long¹² been known that FcH is oxidized to $\text{FcH}^{\cdot+}$ by SBr in acetic acid; with a 5.5-fold excess of SBr brominated decomposition products (tribromocyclopentene, 7% and acetoxydibromocyclopentene, 53%) were isolated.¹³ Later studies demonstrated that $\text{FcH}^{\cdot+}$ is very reactive toward nucleophiles, including bromide, in non-aqueous solvents,¹⁴⁻¹⁷ the stoichiometry of the overall decomposition process in the case of bromide ion being represented by eqn. (3).¹⁵ This



phenomenology [eqn. (2), followed by (3)] is reflected in the series of UV spectra shown in Fig. 1, where first the absorbance of $\text{FcH}^{\cdot+}$ builds up to a maximum at 617 nm (curves 1-4) and

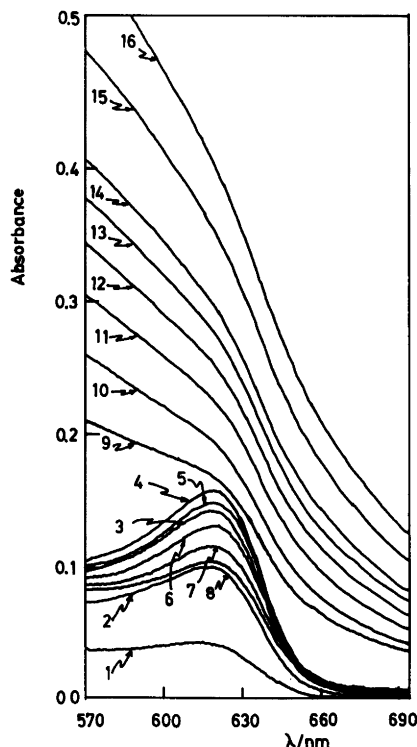
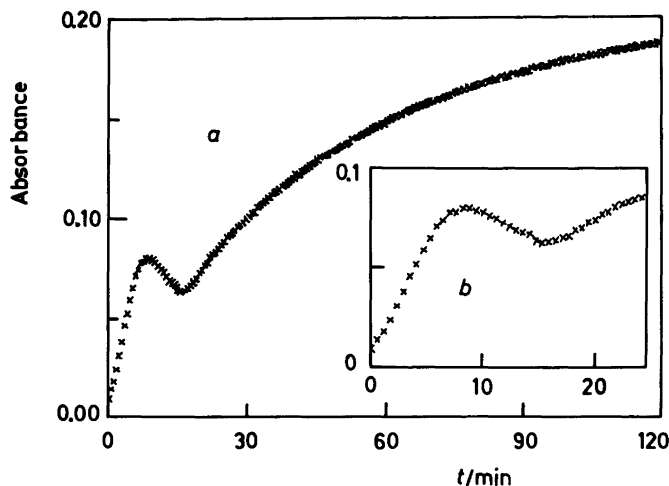


Fig. 1. Changes in the visible spectrum between 570 and 690 nm in a solution of FcH (18.8 mM) in acetonitrile at 15.0°C and SBr (initial concentration 0.63 mM) after 1.25 (1), 2.5 (2), 3.75 (3), 5.0 (4), 6.25 (5), 7.5 (6), 8.75 (7), 10.0 (8), 32 (9), 37 (10), 49 (11), 62 (12), 74 (13), 87 (14), 137 (15) and 260 (16) min.

Fig. 2a. Plot of absorbance at 628 nm vs. time for a solution of FcH (2.81 mM) and SBr (initial concentration 0.63 mM) in acetonitrile at 15.0°C. The insert (b) shows the first 25 min period on an extended time-scale.



then starts to decrease (curves 5–8). After this initial biphasic behaviour, the absorbance increases strongly (curves 9–16) but this time due

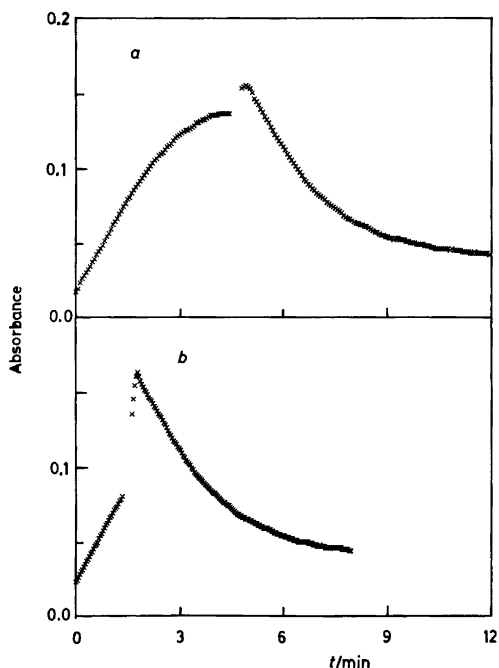


Fig. 3. Plot of absorbance at 620 nm vs. time for a solution of FcH (18.8 mM) and SBr (initially 0.63 mM) in acetonitrile at 15.0°C, with injection of tetrabutylammonium bromide solution (to make the solution 4 mM) at a) the absorbance maximum and b) at a point half-way up to the expected maximum absorbance.

to the much stronger absorption band of FeBr_4^- in the region of 500–700 nm.¹⁸ This process is demonstrated quantitatively in Fig. 2a where the absorbance at 620 nm was monitored at 15.0°C. Clearly, it is the initial biphasic reaction that is of interest in connection with the ET rate constant, while the later part of the curve reflects the final build-up of FeBr_4^- . The latter reaction showed excellent first-order behaviour with a rate constant of $1.5(2) \times 10^{-2} \text{ min}^{-1}$ (6 runs). Fig. 2b shows an enlargement of the initial part of the curve which displays a weak tendency to have an induction period.

In order to elucidate the role of bromide ion in the second phase of the reaction (breakdown of FcH^+), external bromide ion (as the tetrabutylammonium salt), was added to the kinetics solution, either before the reaction was started or at the point where the maximum concentration of FcH^+ is reached. As shown in Fig. 3, curve a, injection of bromide solution in *ca.* 6-fold excess over $[\text{SBr}]_0$ produces a small instantaneous jump in absorbance, followed by the decay of FcH^+ . This behaviour turned out to be a reflection of a catalytic effect of bromide ion on the initial reaction between FcH and SBr, as clearly demonstrated in an experiment where the bromide solution was injected halfway up to the absorption maximum (Fig. 3, curve b).

Returning to the decay of FcH^+ , this part of the absorbance/time curve followed first-order kinetics, the observed rate constants being summarized in Table 1. There is practically no de-

Table 1. Observed first-order rate constants (k_2) for the disappearance of FcH^+ in reactions between FcH (18.8 mM) and SBr (0.63 mM) in acetonitrile at 15°C.

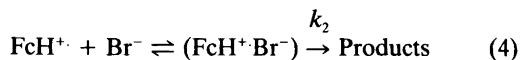
Reaction mode ^a	$[\text{Bu}_4\text{NBr}]/\text{mM}$	k_2/min^{-1}
A	1.02	0.53
A	2.02	0.49
A	3.95	0.31
A	7.7	0.39
B	3.95	0.50
B	7.7	0.48
B	17.7	0.56
C	2.02	0.51
C	3.95	0.48
	Mean value:	0.47(7)
D	4.2	0.78
D	8.2	0.81
D	18.7	0.54
	Mean value:	0.71(1)

^aA: Bromide ion present from the start of the reaction. B: Bromide ion added at time of maximum absorbance of FcH^+ . C: Bromide ion added half-way up to the maximum absorbance of FcH^+ . D: Run with presynthesized $\text{FcH}^+\text{PF}_6^-$.

pendence of k_2 upon $[\text{Br}^-]_0$, the average rate constant being $0.47(7) \text{ min}^{-1}$ over a concentration range of added bromide ion between 1.0 and ca. 18 mM. Presynthesized $\text{FcH}^+\text{PF}_6^-$ behaved similarly, although the average rate constants came

out as slightly larger, $0.7(1) \text{ min}^{-1}$. This difference is expected in view of the approximation inherent in the calculation of k_2 from the second part only of a biphasic process. FcH^+ is still being generated during the descending phase and therefore a lower rate constant is obtained.

Thus, the following picture of the initial stage of the FcH^+ decomposition reaction appears to be valid: FcH^+ and bromide ion form a 1:1 complex (for which there is ample precedence in the literature¹⁹), which undergoes the first step of the breakdown process [eqn. (4)] as an intramolecular reaction. The equilibrium position for complex formation is situated well to the right which explains the independence of k_2 of added bromide ion.



In order to study the catalytic effect of bromide ion on the initial reaction between SBr and FcH , it became necessary to compute the rate constants from the complete kinetic expression for the biphasic scheme. Since both steps are run under pseudo-first-order or first-order conditions, the expression for two consecutive first-order reactions [eqn. (5)] derived by Espensen²⁰ [eqn. (6)] was employed. Here D_1 and D_∞ are equal to



$$D_1 = D_\infty + \frac{(\epsilon_B - \epsilon_A)k_1 + (\epsilon_A - \epsilon_C)k_2}{k_2 - k_1} [\text{A}]^0 \exp(-k_1 t) + \frac{(\epsilon_C - \epsilon_B)k_1}{k_2 - k_1} [\text{A}]^0 \exp(-k_2 t) \quad (6)$$

Table 2. Calculation of parameters of eqn. (6) from five identical runs $[\text{FcH}] = 18.8 \text{ M}$, $[\text{SBr}]_0 = 0.63 \text{ mM}$ and $[\text{Br}^-]_0 = 2.5 \text{ mM}$.

Run no.	D_∞	$\epsilon_B/\text{M}^{-1} \text{ cm}^{-1}$	k_1/min^{-1}	k_2/min^{-1}
1	0.046	335	5.09	0.53
2	0.048	360	4.97	0.58
3	0.042	338	5.23	0.50
4	0.041	333	5.45	0.47
5	0.045	325	5.69	0.52
Mean value:	0.044	338	5.3	0.52

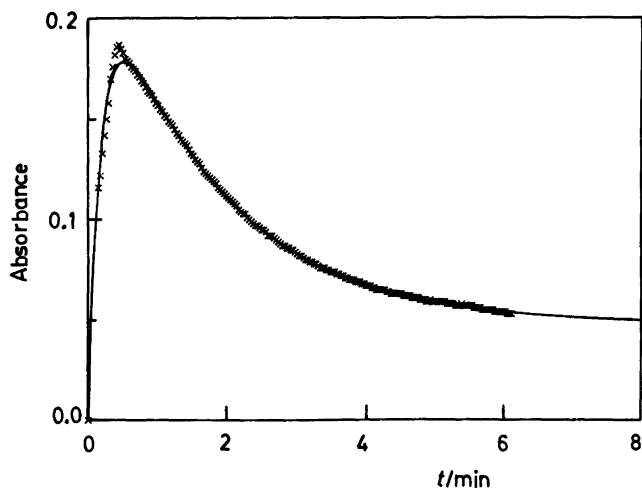


Fig. 4. Plot of absorbance at 620 nm vs. time for a solution of FcH (18.8 mM) and SBr (initially 0.63 mM) in acetonitrile with Bu_4NBr (2.50 mM) added (run 2 of Table 2). The solid curve represents the best fit of the data points to eqn. (6).

the absorbance at time = t and infinity, respectively, ϵ_A , ϵ_B and ϵ_C are the extinction coefficients of A, B and C and $[\text{A}]_0$ the initial concentration of A ($\equiv \text{SBr}$). Then D_∞ , ϵ_B (extinction coefficient of FcH^+), k_1 and k_2 are treated as adjustable parameters and calculated by adapting the experimental points to eqn. (6) by a nonlinear regression method.²¹ The reproducibility of this method is shown in Table 2, where results from five identical runs are given (see also Fig. 4 for a demonstration of the fit of the data to the kinetic model).

Using this method, k_1 and k_2 were determined for a series of bromide ion concentrations. The

resulting data are plotted in Fig. 5. As noted above, k_2 is essentially independent of $[\text{Br}^-]_0$, whereas k_1 increases strongly with increasing $[\text{Br}^-]_0$ according to a relationship that is curved upward. How can one then explain this catalytic effect by bromide ion upon what is assumed to be a simple, non-bonded ET process?

Although there are other reasonable possibilities, we think this effect is due to complexation between SBr and Br^- , a phenomenon that was early found²² to influence the reactivity of SBr toward allylic substrates in a profound manner. In a paper to be published elsewhere,²³ we separately studied SBr/ Br^- complexes and found them ca-

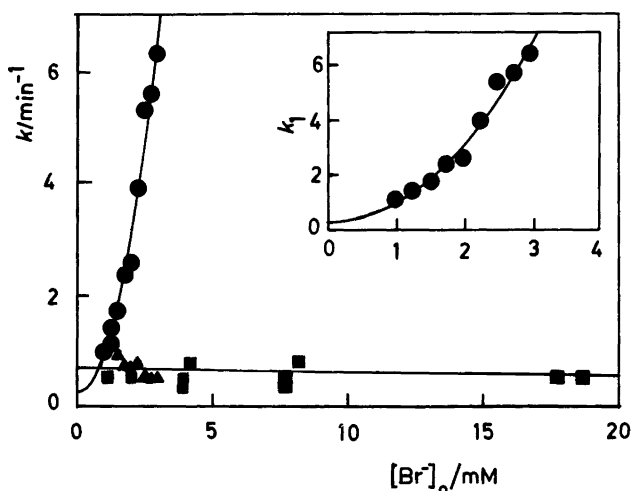
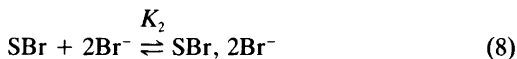
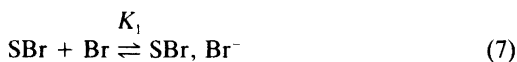


Fig. 5. Plot of k_1 (●) and k_2 (▲ for values calculated from eqn. (6) and ■ for values from Table 1) vs. $[\text{Br}^-]_0$. The curve represents the best fit of the k_1 data points to eqn. (9), giving $k_1^\circ = 0.3 \pm 0.7 \text{ min}^{-1}$. The line is the regression line for all k_2 data points (slope -0.01). The insert shows the k_1 data on an enlarged $[\text{Br}^-]_0$ scale.

pable of rather special reactivity in themselves, but this reaction (in effect an ET process within the complex to give ultimately SH, polymaleimide and tribromide ion) proceeds on a much slower time-scale, its half-life being of the order of 20 h at 50 °C. In the FcH reaction, it is then postulated that SBr forms ET-reactive complexes with one or two bromide ions in fast equilibria [eqns. (7) and (8)]. This leads to the expression (9) for k_1 , where k_1° , k_1' and k_1'' are the rate constants for reaction between FcH and SBr, (SBr, Br⁻) and (SBr, 2Br⁻), respectively. Clearly it is k_1° that is of interest here.

Unfortunately, attempts to extract a meaningful k_1° value by fitting the data of Fig. 5 to eqn. (9) were not successful due to the large errors in this parameter. A value of $0.3 \pm 0.7 \text{ min}^{-1}$ is obtained, but obviously this is of no use for the purpose at hand.



$$k_1 = k_1^\circ + k_1' K_1 [\text{Br}^-]_0 + k_1'' K_2 [\text{Br}^-]_0^2 \quad (9)$$

The assumption of the existence of several types of reactive complexes between SBr and bromide ion is one possible explanation of the bromide ion dependence of k_1 . Another possibility would be to include a rapidly equilibrating

FcH/Br⁻ complex, analogies of which have been proposed in other similar cases ("cyclopentadiene ring slippage"²⁴), together with the 1:1 SBr, Br⁻ complex only. This kinetic scheme would give identical kinetic behaviour.

In a limited study, involving two bromide ion concentrations, we checked the influence of [Br⁻] upon k_1 for a substrate of entirely different structure, namely tris(4-methoxyphenyl)amine. The effect is similar, a reaction order of 1.2 in bromide ion being obtained.

In order to circumvent the problem of bromide ion catalysis we eventually resorted to an entirely different approach, namely to add a bromide ion scavenger to the reaction, as has been utilized in other studies of SBr reactivity.²⁵ As such, mercury(II) acetate or chloride can be used. The dramatic effect of adding mercury(II) acetate to the SBr/FcH reaction is seen in Fig. 6, the biphasic behaviour being replaced by a straight first-order process upon addition of 0.02 M Hg(II) acetate.

Table 3 gives rate constants for FcH/SBr reactions with added bromide ion scavengers at different [SBr]₀. Good first-order kinetics were noted in all cases, and in separate experiments it was established that possibly competing mercuriation of ferrocene, feasible at least in the case of mercury(II) acetate,²⁶ was more than 20 times slower and thus could not perturb the reaction under study. It is therefore reasonable to assume that the rate constants thus determined are entirely due to the ET reaction between SBr and FcH.

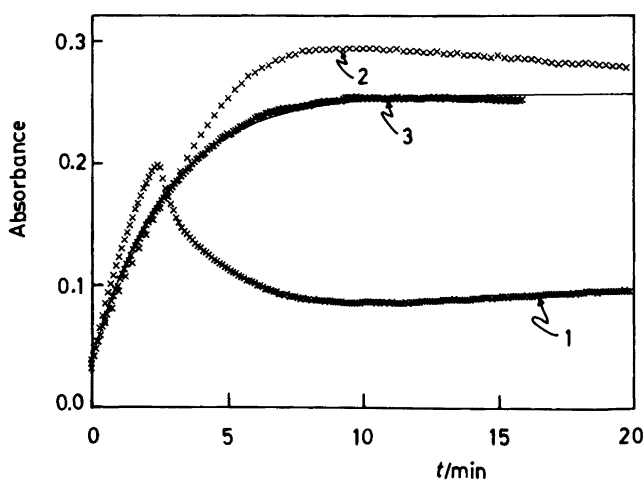


Fig. 6. Plots of absorbance at 620 nm vs. time for solutions of FcH (18.8 mM) and SBr (initially 0.63 mM) in acetonitrile at 15.0 °C. 1) No Hg(II) acetate added, 2) 12.5 mM in Hg(II) acetate and 3) 21 mM in Hg(II) acetate.

Table 3. Observed first-order rate constants for the reaction between SBr and FcH in the presence of HgX_2 as bromide ion scavenger. $[\text{FcH}] = 18.8 \text{ mM}$; $[\text{HgX}_2] = 20 \text{ mM}$.

X in HgX_2	$[\text{SBr}]_0/\text{mM}$	k_1/min^{-1}
AcO	0.152	0.39
AcO	0.315	0.36
AcO	0.63	0.37
Cl	0.63	0.41

^aMean value from three runs.

Kinetics of the reaction between SBr and other substrates. The Hg(II) scavenger method was then used to determine ET rate constants between SBr and the substrates listed above, except for the two most easily oxidizable ones, 5,10-dihydro-5,10-dimethylphenazine and *N,N,N',N'*-tetramethylphenylenediamine. These are rapidly oxidized by Hg(II) acetate or chloride in themselves, and thus the method could not be used. Instead, these rate constants were evaluated from early parts of the kinetic runs, where the effect of the bromide ion generated [eqn. (3)] is relatively small.

Rate constants were determined under pseudo-first-order conditions from absorbance/time readings monitoring the growth of the concentration of the radical cations. The identity of the UV/VIS spectra of the radical cation solutions thus obtained was verified by comparison with literature data.

Table 4 gives second-order rate constants at 15.0°C for the reactions studied, together with the corresponding ΔG^* values (calculated *via* the Eyring equation, $k = 10^{11} \exp(-\Delta G^*/RT)$). As expected, the rate constants increase with decreasing $E^\circ(\text{D}^+/\text{D})$, and it now remains to extract the parameters of interest for the ET oxidizing properties of SBr.

According to the Marcus theory,⁷⁻⁹ the relationship between ΔG^* and $\Delta G^{o'}$ for a non-bonded ET step, *i.e.*, one in which there is some, but maximally 1 kcal mol^{-1} of electronic interaction between the reactants (assumed to be structureless spheres of charge Z_1 and Z_2 and radii r_1 and r_2 , respectively) in the transition state, is given by eqn. (10). Here λ is the reorganization energy, the increase in energy of the system needed to reach the transition state from the initially formed collision complex through bond

$$\Delta G^* = \frac{\lambda}{4} \left(1 + \frac{\Delta G^{o'}}{\lambda} \right)^2 \quad (10)$$

(compression, expansion, bending, torsional change, etc.) and solvent reorganization. $\Delta G^{o'}$ is the standard free energy change, corrected by a term for describing the change in the electrostatic situation when the electron is transferred in the transition state. In this particular case this term is calculated to be $-2.3 \text{ kcal mol}^{-1}$, Z_1Z_2 changing from 0 to -1 upon ET, and assuming that r_1 and r_2 are each equal to 2 \AA and with the dielectric constant of the solvent equal to 36. Thus $\Delta G^{o'}$ becomes equal to $\{23.06[E^\circ(\text{D}^+/\text{D}) - E^\circ(\text{SBr}/$

Table 4. Second-order rate constants for the reaction between SBr and electron donors (D) in acetonitrile at 15.0°C .

D	$E^\circ(\text{D}^+/\text{D})/\text{V}$	$\lambda(\text{D}^+/\text{D})/\text{kcal/mol}^{-1}$	$k_{\text{ET}}/\text{M}^{-1} \text{ s}^{-1}$	$\Delta G^*/\text{kcal mol}^{-1}$ Exp.	Calc. ^a
Ferrocene (FcH)	0.529 ^b	23.2 ^c	0.33	15.1	15.3
Butylferrocene	0.504 ^b	22.8 ^c	0.98	14.5	14.7
Chloromercuriferrocene	0.533 ^b	23.3 ^c	0.76	14.7	15.1
1,1'-Dimethylferrocene	0.445 ^b	22.8 ^c	2.67	13.9	14.0
5,10-Dihydro-5,10-dimethylphenazine	0.32 ^d	22 ^e	6×10^1	12.2	12.7
<i>N,N,N',N'</i> -Tetramethylphenylenediamine	0.25 ^f	10.8 ^g	6×10^2	10.9	10.1
Tris(4-methoxyphenyl)amine	0.72 ^h	12.1 ⁱ	2.6×10^{-2}	16.6	16.3

^aUsing $E^\circ(\text{SBr}/\text{SBr}^-) = 0.17 \text{ V}$ and $\lambda(\text{SBr}/\text{SBr}^-) = 72 \text{ kcal mol}^{-1}$. ^bRef. 8. ^cIn isopropyl alcohol/water (1:1);²⁷ for ferrocene and its derivatives, the reorganization energy changes little with solvent.²⁸ ^dRef. 29. ^eRef. 30. ^fRef. 31. ^gRef. 32. ^hRef. 33. ⁱRef. 34.

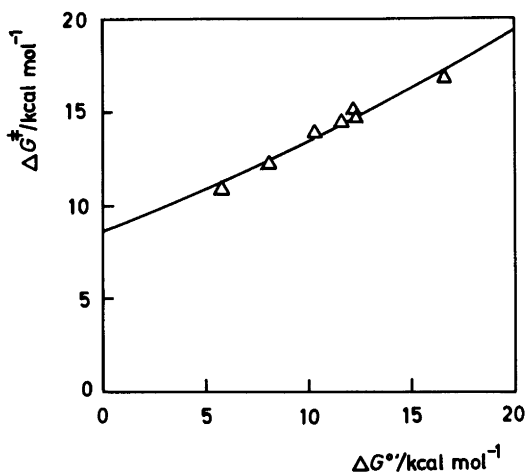


Fig. 7. Plot of ΔG^\ddagger vs. ΔG° . The curve represents the best fit of the data points (Table 4) to eqn. (10).

$\text{SBr}^-] - 2.3\} \text{ kcal mol}^{-1}$. Fitting the data of Table 4 to eqn. (10) (see Fig. 7) eventually gives:

$$E^\circ(\text{SBr}/\text{SBr}^-) = 0.17 \pm 0.30 \text{ V}$$

$$\lambda = 46(19) \text{ kcal mol}^{-1}.$$

In the $\log k/\Delta G^\circ$ space, these values are represented by the parabolically shaped curve shown as the full line in Fig. 8, and with those representing the outer λ parameter limits given above also drawn (broken lines).

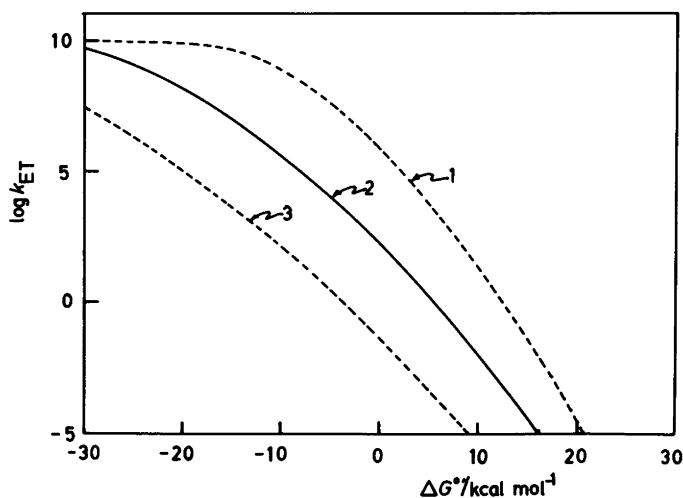
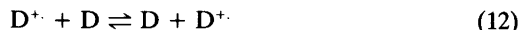
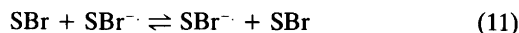


Fig. 8. Plot of $\log k_{\text{ET}}$ vs. ΔG° for values of $\lambda = 27$ (curve 1), 46 (curve 2) and 65 (curve 3) kcal mol^{-1} .

In the Marcus theory, the λ value of any redox step can be obtained as the mean value of the λ values [denoted $\lambda(0)$] of the corresponding self-exchange reactions. In the case at hand, these are given by eqns. (11) and (12), the $\lambda(\text{D}^+/\text{D})$ values being listed in Table 4. From an average $\lambda(\text{D}^+/\text{D})$

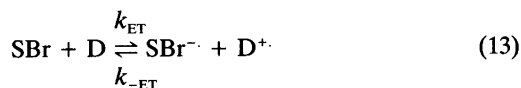


$= 20 \text{ kcal mol}^{-1}$, one obtains a value of $\lambda(\text{SBr}/\text{SBr}^-)$ at 72 kcal mol^{-1} . It should be noted that ideally one should keep all $\lambda(\text{D}^+/\text{D})$ identical in order to use eqn. (10) for the determination of $E^\circ(\text{SBr}/\text{SBr}^-)$ and $\lambda(\text{SBr}/\text{SBr}^-)$. In this case the spread of (D^+/D) values is, however, small compared to $\lambda(\text{SBr}/\text{SBr}^-)$ and errors due to this approximation are therefore also small. This is seen from the last column of Table 4, where the ΔG^\ddagger calculated from eqn. (10) and the E°/λ parameters of SBr and the actual E°/λ of D are given. The differences are less than 8% in all cases.

We now must inquire whether the reorganization energy of the SBr/SBr^- couple, 72 kcal mol^{-1} , is a reasonable one. As $\lambda(0)$ values go,³⁵ it is a rather large one, on par with those of simple alkyl halides,³⁶ $70\text{--}80 \text{ kcal mol}^{-1}$. For the latter, the large $\lambda(0)$ has been explained in terms of dissociative ET, *i.e.*, the C-X bond is lengthened to the point of breaking in the transition state. For the SBr system, the radical anion is stable enough

for ESR investigation at 77 K,^{37,38} so we are not dealing with dissociative ET in this case. Since SBr^- is a σ^* radical, it is quite likely that the N-Br bond is appreciably lengthened in going from SBr to SBr^- ; moreover, it has been suggested that SBr^- is non-planar, the N-Br bond deviating by 20–26° from the CONCO plane.³⁰ Both these geometrical changes would combine to cause a large bond reorganization energy and thus a large $\lambda(\text{SBr}/\text{SBr}^-)$ is to be expected.

Possible difficulties with the suggested ET mechanism. Eqn. (2) should actually be represented by two reactions, namely eqns. (13) and (14), since SBr^- is known to have a finite lifetime.^{37,38} Unfortunately, no good experimental value for k_{diss} is known, but electrochemical studies by V. D. Parker³⁹ put it at $>10^5 \text{ s}^{-1}$. Applica-



tion of the steady state approximation to $[\text{SBr}^-]$ gives eqn. (15), relating k_{obs} to k_{ET} , $k_{-\text{ET}}$ and k_{diss} . Only if $k_{\text{diss}} \gg k_{-\text{ET}} [\text{D}^+]$ will k_{obs} be identical to

$$k_{\text{obs}} = \frac{k_{\text{ET}} k_{\text{diss}}}{k_{-\text{ET}} [\text{D}^+] + k_{\text{diss}}} \quad (15)$$

k_{ET} , and we must therefore show that there are good reasons to assume that this condition is fulfilled.

Let us translate the condition above to the requirement that $k_{\text{diss}} > 10 \times k_{-\text{ET}}$ and take $k_{\text{diss}} = 10^5 \text{ s}^{-1}$ as the lower limit. Since $[\text{D}^+]$ is maximally of the order of 1 mM during the kinetic runs, this means that $k_{-\text{ET}}$ should be $<10^7 \text{ M}^{-1} \text{ s}^{-1}$. Inspection of the $\log k/\Delta G^\circ$ curve (full line of Fig. 8) shows that this corresponds to the requirement that $|\Delta G^\circ| < 15 \text{ kcal mol}^{-1}$. Given that the limit set above represents a conservatively estimated minimum value, one can safely conclude that the substrates studied are within the range where k_{obs} is a direct measure of k_{ET} .

Kinetics of the reaction between SBr and 12-tungstocobalt(II)ate ion. As a corollary of the above reasoning, it should be possible to find a more difficultly oxidizable substrate where the effect of the back ET step would be detectable.

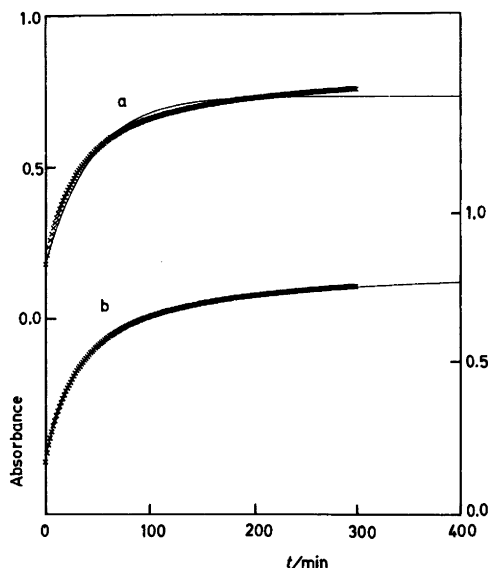


Fig. 9. Kinetic trace of a run between SBr (9.4 mM) and Co(II)W (0.63 mM) in acetonitrile at 25°C. The full curve at trace a represents the best fit of the data points to a first-order model, whereas at trace b it represents the best fit to the kinetic model of eqns. (13) and (14), using a previously reported method of computation.⁴⁰

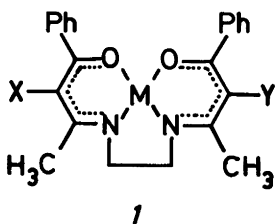
12-Tungstocobalt(II)ate ion, $\text{Co(II)W}_{12}\text{O}_{40}^{6-}$ [abbreviated Co(II)W], earlier shown to be a good model compound for ET behaviour vs. organic substrates,⁴⁰ turned out to be such a species. With $E^\circ = 0.7 \text{ V}$ in acetonitrile (as the tetrabutylammonium salt), ΔG° is calculated to be ca. 19 kcal mol^{-1} , and thus influence from $k_{-\text{ET}}$ upon k_{obs} is expected.

Fig. 9a shows a kinetic run between SBr (0.0094 M) and Co(II)W (0.63 mM) at 25.0°C, monitored at the emerging absorbance maximum of Co(III)W at 390 nm. The curve drawn represents the best fit to a first-order reaction [rate constant $0.023(1) \text{ min}^{-1}$] but clearly this is not a good choice of kinetic model. If we instead fit the data to the kinetic model of eqns. (13) and (14), using a previously developed method of computation,⁴⁰ the fit becomes almost perfect (Fig. 9b). A full account of this reaction will be reported later.

Connection with earlier work. The results obtained above demonstrate that SBr is a relatively weak ET oxidant, its oxidizing power being

equivalent to, say, Cu(II)aq ($E^\circ = 0.17$ V). Since SBr^- is a very unstable species, the relatively low E° and large $\lambda(0)$ are "compensated for" by the driving force inherent in the cleavage of the N-Br bond, so that even medium difficultly oxidizable compounds, like 2,4,6-trimethoxynitrosobenzene⁶ ($E^\circ = 1.2$ V) and tris(*p*-tolyl)amine⁵ ($E^\circ = 1.0$ V) undergo ET to SBr. Compounds of higher E° , like tetraalkylstannanes⁴¹ and tetraalkylplumbanes⁴² (both with E° around 1.5 V⁴²) clearly undergo radical chain reactions with SBr, so that an E° of ca. 1.2 V represents the upper limit for ET reductive capability vs. SBr.

A search of the immense literature on SBr reactions revealed many potential candidates for ET processes, using the criterion defined above. Apart from the fact that the early chemistry of ferrocene¹² had produced the first unambiguous case of ET, it was clear already around the end of the 1950s that SBr might act as an ET reagent toward neutral organic donors,⁴⁴ e.g., amines⁴⁵ and carbanions.⁴⁶ Later, substrates as diverse as Meisenheimer complexes,⁴⁷ porphins⁴⁸ and cytochrome *c*⁴⁹ were added to the list of probable ET



processes, and, perhaps most interestingly, inorganic reagents* and complexes.⁵¹⁻⁵⁶

Of the latter, a particularly interesting observation^{51,52} is the oxidative substitution of Cu(II) and Ni(II) complexes of type *I*, X=Y=H by SBr^{\cdot} ⁵¹ and SCl^{\cdot} ,⁵² where both bromo and succinimido substitution occurred at the methine carbons (formation of *I*, X=Y=Br, *I*, X=Br, Y=S, *I*, X=Y=S). It is an interesting possibility that these reactions might proceed *via* reactive Cu(III) or Ni(III) species, by analogy with the indisputable $\text{Co(II)W} \rightarrow \text{Co(III)W}$ oxidation reported above. Finally, the easy substitution of hydrogen by succinimido by SBr in vanadocene⁵⁷ (E° ca. -0.3 V⁵⁸) is noteworthy, pointing to a

*Even silver metal is oxidized by SBr.⁵⁰

possible role for SBr as an oxidant toward organometallics (for a review on this topic, see Ref. 59).

Experimental

Materials. Substrates, except tris(4-methoxyphenyl)amine⁶⁰ and 5,10-dihydro-5,10-dimethylphenazine,⁶¹ were of commercial origin and distilled or recrystallized before use. *N*-Bromosuccinimide was recrystallized from dichloromethane. Ferricinium hexafluorophosphate was prepared by sulfuric acid oxidation of ferrocene.⁶² Acetonitrile was of HPLC quality (Baker).

The tetrabutylammonium salt of Co(II)W was prepared by reducing $\text{K}_3\text{Co(III)W}_{12}\text{O}_{40} \cdot 11 \text{H}_2\text{O}$ (1.0 mmol) in 20 ml of water by adding sodium dithionite (1.0 mmol). Then tetrabutylammonium hydrogen sulfate (6.0 mmol, dissolved in 30 ml of water and neutralized by sodium hydroxide) was added and the mixture stirred for a few min. The Co(II)W salt was then quantitatively extracted⁶³ into dichloromethane (150 ml). After washing with 20 ml of water, the dichloromethane solution was filtered and evaporated to dryness. The blue solid was dissolved in acetonitrile (100.0 ml) and this solution was used as stock solution (stored at 0°C).

Methods. UV spectra were recorded on a Cary 219 spectrophotometer. Absorbance/time measurements, generally 200 per kinetic run, were performed by an Ultrospec UV/VIS spectrophotometer (from LKB, Sweden), interfaced to an HP-85 microcomputer. Calculations of rate constants were done on an HP-9835 table-top computer, using the NONLIN program developed by Hewlett-Packard Co.

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