

Electrochemical Reduction of *N*-Bromosuccinimide. Reaction Mechanism for Formation of the Succinimidyl Radical

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The electrochemical reduction of *N*-bromosuccinimide in acetonitrile at a platinum cathode generates the succinimidyl radical in an overall process for which the *n* value is 1. The succinimide anion, generated by two-electron reduction of *N*-bromosuccinimide, is an intermediate in this process, and its electron-transfer reaction with the *N*-bromo imide generates the radical. The intermediacy of the succinimide anion is demonstrated by trapping experiments in which the anion is captured by alkylating agents to give *N*-alkylsuccinimides. With increasing capture of the anion the *n* value for the electrochemical reaction approaches 2 as a limit. The reduction of *N*-bromosuccinimide by the succinimide anion, added as a quaternary ammonium succinimide, in a purely chemical system has also been studied. Rate constants for the pertinent reactions have been measured, and the reaction mechanisms have been discussed.

Recent work¹⁻⁸ on brominations with *N*-bromosuccinimide (SBr) has demonstrated that the Goldfinger mechanism,⁹ in which the intermediacy of bromine atoms is essential, can be suppressed by scavenging the bromine^{7,8} and hydrogen bromide⁸ produced. Under these conditions it becomes possible to observe chain reactions due to succinimidyl radicals, generated in both a ground state (Π) and a metastable excited state (Σ_N or Σ_O).

It occurred to us that the electrochemical reduction of SBr in an aprotic solvent provided reasonable prospects for generating the succinimidyl radical under conditions in which reactions with bromine and hydrogen bromide would be obviated. In exploratory experiments we found that SBr is reducible at $E_p = +0.03$ V vs. SCE at a platinum disk cathode in acetonitrile (AN) containing 0.25 M tetra-*n*-butylammonium fluoborate (TBAF). Bromine in AN containing 0.1 M lithium perchlorate is reducible at a platinum indicator electrode in two waves at +0.26 and +0.84 V vs. SCE,¹⁰ suggesting the possibility of rapid cathodic reduction of any bromine that might form during electrochemical reduction of SBr. It was our further expectation that hydrogen bromide would not build up in the cathode compartment of a divided cell in this aprotic system even though bromide ion was a reduction product.

In what follows, procedures for producing succinimidyl radicals (1) by electrochemical reduction of SBr and (2) by electron transfer to SBr from succinimide anion (S^-) in homogeneous solution will be detailed. The mechanisms and reaction rates of the reactions involved in both generating processes will be discussed.

Results and Discussion

Polarographic¹¹ and voltammetric¹² studies of SBr re-

duction in aqueous media have indicated a two-electron reduction process. Figure 1 illustrates a single-scan, cyclic voltammogram obtained with 8.3×10^{-3} M SBr in AN containing 0.25 M TBAF at a platinum disk electrode. The scan rate was 200 mV s⁻¹, and the scan started at 0.75 V, went to -1.9 V, reversed to +2.0 V, and finally returned to 0.75 V, all vs. SCE. The voltammogram shows two cathodic waves ($E_p = +0.03$ and -1.58 V vs. SCE) and one anodic wave ($E_p = +1.19$ V).

The first cathodic wave ($E_p = +0.03$ V) is due to SBr reduction, and the process is irreversible based upon the following criteria: (1) Even at temperatures as low as -25 °C and sweep rates as high as 1000 V s⁻¹ no oxidation wave for the anion radical (SBr^{-•}) is observable.¹³ This sets a lower limit of 10⁵ s⁻¹ for the rate of decomposition of SBr^{-•}. (2) The wave is extremely broad. The value $E_p - E_p/2$ is near 225 mV, whereas the corresponding value for a reversible process is 57 mV/*n*, where *n* is the number of electrons transferred. (3) The current function ($i_p/v^{1/2}C$, where *v* is the scan rate and *C* the concentration) decreased significantly for scan rates above 100 mV s⁻¹.

The assignment of the chemical process corresponding to the second reduction wave ($E_p = -1.58$ V) is more difficult. In a previous study¹⁴ we have shown that a cyclic voltammogram for succinimide (SH) under comparable conditions (10⁻² M) shows a cathodic wave near -1.5 V vs. SCE and anodic waves at -0.65 and +1.6 V, which were attributed to oxidation of adsorbed hydrogen atoms and to oxidation of S^- , respectively. Since SH is a major reduction product of SBr, one is tempted to attribute the reduction peak at $E_p = -1.58$ V in Figure 1 to succinimide reduction. However, the voltammogram for SBr shows anodic waves neither at -0.65 nor at +1.6 V. The anodic wave at -0.65 to -0.75 V is especially characteristic of SH cyclic voltammetry, and, as will be shown later, may even be used for the quantitative determination of SH. We conclude, therefore, that the peak is not due to succinimide reduction. For the moment we will assert that this peak is attributable to reduction of an SBr/ S^- complex, which then reacts slowly to give succinimide. The evidence for this conclusion will be provided later, although we would note at this point that a cyclic voltammogram of SBr at

(1) E. Hedaya, R. L. Hinman, V. Schomaker, S. Theodoropoulos, and L. M. Kyle, *J. Am. Chem. Soc.*, **89**, 4875 (1967).

(2) J. G. Traynham and Y.-S. Lee, *J. Am. Chem. Soc.*, **96**, 3590 (1974).

(3) J. C. Day, M. J. Lindstrom, and P. S. Skell, *J. Am. Chem. Soc.*, **96**, 5616 (1974).

(4) T. Koenig and R. A. Wielesek, *Tetrahedron Lett.*, 2007 (1975).

(5) J. C. Day, M. G. Katsaros, W. D. Kocher, A. E. Scott, and P. S. Skell, *J. Am. Chem. Soc.*, **100**, 1950 (1978).

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(7) P. S. Skell and J. C. Day, *Acc. Chem. Res.*, **11**, 381 (1978).

(8) F.-L. Lu, Y. M. A. Nagiub, M. Kitadani, and Y. L. Chow, *Can. J. Chem.*, **57**, 1967 (1979).

(9) J. Adam, P. A. Gosselain, and P. Goldfinger, *Nature (London)*, **171**, 704 (1953); P. A. Gosselain, J. Adam, and P. Goldfinger, *Bull. Soc. Chim. Belg.*, **65**, 533 (1956).

(10) A. I. Popov and D. H. Geske, *J. Am. Chem. Soc.*, **80**, 5346 (1958).

(11) T. Nagai and T. Matsuda, *Nippon Kagaku Zasshi*, **88**, 66 (1967).

(12) T. Nagai and T. Matsuda, *Rev. Polarogr.*, **17**, 133 (1971).

(13) Private communication from Dr. Vernon D. Parker, The Norwegian Institute of Technology, Trondheim, Norway.

(14) W. M. Moore, M. Finkelstein, and S. D. Ross, *Tetrahedron*, **36**, 727 (1980).

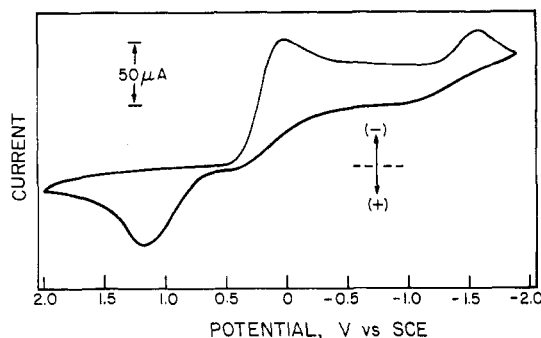
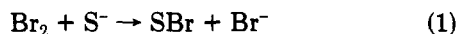


Figure 1. Cyclic voltammogram obtained for 8.3×10^{-3} M SBr in AN containing 0.25 M TBAF. A Pt disk working electrode was employed, the initial potential was 0.75 V vs. SCE, and the potential scan rate was 200 mV s^{-1} .

a slow scan rate, e.g., 10 mV s^{-1} , does show a small anodic wave at -0.65 to -0.75 V. Also, the reduction potential for the SBr/ S^- complex is strongly dependent on the SBr concentration. In one series of measurements the reduction peak potential was -1.15 V for 9.9×10^{-4} M SBr and became increasingly negative with increasing SBr concentration, reaching -1.85 V at 6.2×10^{-2} M SBr.

The large oxidation wave at $+1.19$ V results from the oxidation of the bromide ion liberated by reduction of *N*-bromosuccinimide. Bromide ion normally exhibits two oxidation waves on Pt. Thus 6.5×10^{-3} M tetrabutylammonium bromide (TBABr) in AN gave two peaks with $E_{p1} = +0.65$ V and $E_{p2} = +0.97$ V. However, in the presence of sufficient succinimide anion (S^-) only a single oxidation peak is observed. This was demonstrated by starting with 6.5×10^{-3} M TBABr, adding tetrabutylammonium succinimide (TBAS) in small (10^{-3} M) increments, and recording a cyclic voltammogram after each addition. The observed effect was that the magnitude of the first oxidation wave increased at the expense of the second one. The peak potential of the first wave also shifted in the anodic direction and was broadened by the addition of TBAS. With 6.4×10^{-3} M TBAS present a single broad oxidation peak, with $E_p = +1.19$ V and $i_p = 155 \mu\text{A}$ (compared with $i_p = 80 \mu\text{A}$ originally for the first oxidation peak for TBABr), was observed. In the SBr reduction, S^- and Br^- are generated simultaneously, and S^- is available to react with any Br_2 generated by Br^- oxidation according to eq 1. This reaction also accounts



for the absence in Figure 1 of an anodic peak at $+1.6$ V due to S^- oxidation, since reaction 1 simultaneously removes both Br_2 and S^- .

In a typical controlled-potential (-0.8 V vs. SCE) electrolysis of 0.068 M SBr in AN containing 0.25 M TBAF at a 1-cm^2 platinum foil cathode the major products found were succinimide ($72 \pm 3\%$, determined by VPC and IR) and bromide ion ($88 \pm 4\%$, determined by Volhard titration), and coulometry indicated an n value of unity. The apparent one-electron reduction of SBr, coupled with the observed products, suggests that a succinimidyl radical is formed by the electrochemical reaction shown in eq 2.



However, as will be shown in detail below, trapping experiments unequivocally demonstrate that the succinimide anion is an intermediate in the reduction of SBr. Equation 2, therefore, does not depict an adequate mechanism for the cathodic reduction of SBr.

Nevertheless, eq 2 may properly represent the initial electrode reaction. If so, it must be followed by two ad-

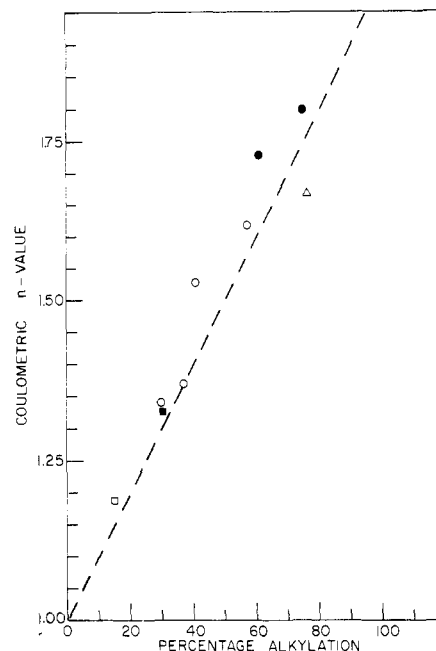
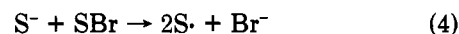


Figure 2. Plot of coulometric n value vs. percentage alkylation for SBr electrolyses containing 1-chlorobutane (\square), α -bromotoluene (Δ), *n*-butyl tosylate (\blacksquare), methyl tosylate (\bullet), and several runs with 1-bromobutane (\circ). The dotted line is theoretical for eq 7.

ditional steps. The succinimidyl radical formed in eq 2 must be rapidly converted to the succinimide anion by a second electron transfer (eq 3), and the anion formed in



(3) must react with SBr to generate the succinimidyl radical by the chemical electron-transfer reaction shown in (4). Thus, although three steps are involved, the for-



mation of the succinimidyl radical represents an overall, net, one-electron reaction.

Since nitrogen is more electronegative than bromine (3.0 vs. 2.8),¹⁵ reactions 5 and 6 represent a possible alternative



path for generation of S^- . In the present system (SBr in AN containing TBAF) cyclic voltammetry indicated a single wave at voltages more anodic than -1.0 V. Since electrons are transferred singly, the coalescence of the two electron transfers (2) and (3) or (5) and (6) into a single wave requires that the second electron transfer in each case occur more rapidly and at a less negative potential than the first.

The intermediacy of the succinimide anion in the electrochemical reduction of SBr was demonstrated with controlled-potential electrolyses performed with SBr in the presence of alkylating agents, added to intercept the succinimide anion. The results are summarized in Table I and Figure 2. The experimentally determined coulometric n value is 1 in the absence of an alkylating agent but increases and approaches 2 as a limit when an increasing amount of succinimide is alkylated, following the general eq 7.

$$n = 1 + \% \text{ alkylation}/100 \quad (7)$$

(15) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, New York, 1960, p 90.

Table I. Products and Coulometric Data for Controlled-Potential^a Reduction of 0.07 M SBr in AN Containing 0.25 M TBAF and Added Alkylating Agents

expt	alkylating agent (RX)	initial ratio of RX/SBr	<i>n</i> value	% products ^b			
				1	2	3	4
1	1-bromobutane	0.54	1.29	40	26		
2	1-bromobutane	1.29	1.34	44	30		
3	1-bromobutane	1.34	1.38	42	30		
4	1-bromobutane	2.74	1.38	37	37		
5	1-bromobutane	5.41	1.53	42	41		
6	1-bromobutane	13.8	1.62	28	57		
7	<i>n</i> -butyl tosylate	3.4	1.33	40	30		
8	1-chlorobutane	4.2	1.19	55	15		
9	methyl tosylate	3.9	1.73	33		61	
10	methyl tosylate	9.8	1.80	15		75	
11	α -bromotoluene	4.8	1.67	12			76
12	none		0.99	72			

^a The potential was -0.8 V vs. SCE. ^b 1 = succinimide; 2 = *N*-*n*-butylsuccinimide; 3 = *N*-methylsuccinimide; 4 = *N*-benzylsuccinimide.

Table II. Products on Reaction of Tetra-*n*-butylammonium Succinimide (TBAS) or Tetraethylammonium Succinimide (TEAS) with SBr in AN Containing an Added Alkylating Agent, RX

expt	succinimide salt (mmol)	SBr, mmol	RX	initial ratio of RX/SBr	products, ^a mmol			
					SBr	1	2	3
1	TBAS (0.98)	1.00	none		none	1.47		
2	TBAS (0.98)	1.00	methyl tosylate	3.9	1.05	0.025	0.85	
3	TEAS (0.95)	0.85	<i>n</i> -butyl tosylate	4.1	0.54	0.65		0.28
4	TBAS (0.98)	0.99	1-chlorobutane	4.8	none	1.45		0.023
5	TBAS (0.98)	1.00	1-bromobutane	1.8	none	1.17		0.42
6	TBAS (0.98)	1.00	1-bromobutane	13.9	0.64	0.30		0.79

^a 1 = succinimide; 2 = *N*-methylsuccinimide; 3 = *N*-*n*-butylsuccinimide.

As can be seen from Figure 2, the five different alkylating agents used all provided results in reasonable agreement with eq 7. Other alkylating agents that are electroinactive at the reduction potential used (-0.8 V vs. SCE) and can compete with SBr for reaction with S^- would be expected to do likewise. From the fact that the experimental *n* values in Figure 2 extrapolate to a value of 2 with increasing capture of the anion by the alkylating agent, it follows that none of the succinimidyl radicals generated by reaction 2 or bromine atoms produced by reaction 5 escape from the electrode and that they are all further reduced to anions. If a significant fraction of the radicals produced by (2) or (5) formed a final product, e.g., succinimide or hydrogen bromide by hydrogen atom abstraction, the limiting coulometric *n* value would approach some value lower than 2 with increasing amounts of anion alkylation.

Two corollaries follow from the foregoing. The addition of S^- to an AN solution of SBr should result in reduction of SBr, i.e., formation of bromide ion and the succinimidyl radical (reaction 4), and alkylating agents should compete effectively with SBr for the anion. Both of these expectations have been fulfilled.

The results of a series of experiments in which S^- , as a quaternary ammonium salt, was reacted with SBr in AN, with and without an alkylating agent present, are shown in Table II. The two succinimide salts, tetra-*n*-butylammonium succinimide (TBAS) and tetraethylammonium succinimide (TEAS), are conveniently prepared and used as determinate solutions in AN, as described in the Experimental Section. The two sets of experiments, those of Tables I and II, are not directly comparable. In the electrochemical experiments of Table I the initial SBr concentrations were 0.07 M, and the succinimide anion concentration was always initially zero. During the course of the electrolysis the succinimide anion was produced and reacted with either SBr or the alkylating agent.

All of the experiments of Table II were in a total solution volume of 10 mL, and the initial concentrations of both S^- and SBr were thus approximately 0.1 M and, therefore, higher than the reactant concentrations in the electrochemical experiments. Reaction was initiated by adding a determinate solution of the succinimide anion in AN to a determinate solution of SBr and the alkylating agent in AN, and the course of the reaction was followed by monitoring the increase in the IR absorbance due to the N-H stretching band for succinimide at 3280 cm^{-1} .

The product results given in Table II are those after at least 24 h, and the uncertainties in these results are discussed in the Experimental Section. In the electrochemical experiments (Table I) the reaction is continued until all the SBr is consumed. In the purely chemical experiments (Table II) SBr can persist as a final product, particularly if a significant fraction of the succinimide anion is captured by the alkylating agent.

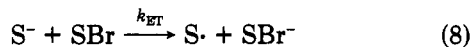
Despite some significant differences, there are major similarities in the two sets of results. In both cases succinimide and *N*-alkylated succinimide are the observed major products. In both cases the succinimide arises from an intermediate succinimidyl radical. Turning to the results of Table II, one observes that with a strong alkylating agent, methyl tosylate, all of the SBr is recovered unchanged, and the only observed reaction is alkylation of the succinimide anion. With a poor alkylating agent, 1-chlorobutane, only a trace of the anion is captured by the alkylating agent, and succinimide is formed in virtually the same yield as in the absence of the alkylating agent. With alkylating agents of intermediate strength, *n*-butyl tosylate and 1-bromobutane, there is a clear competition between SBr and the alkylating agent for reaction with the succinimide anion, and the product distribution shows a reasonable dependency on the initial alkylating agent/SBr ratio.

Thus, there is good evidence to conclude that reaction

Table III. Reaction of *n*-Butyl Bromide with Tetrabutylammonium Succinimide in Acetonitrile at 25 °C

[TBAS], mol L ⁻¹	[<i>n</i> -BuBr], mol L ⁻¹	10 ² <i>k</i> ₂ , L mol ⁻¹ s ⁻¹
0.029 92	0.020 93	1.18
0.021 25	0.029 95	1.22

of the succinimide anion with SBr (reaction 4) and with the alkylating agent leads to the observed products in both the electrochemical system and the purely chemical system. The feasibility of the heteronuclear electron-transfer process can be substantiated by using Marcus' theory for nonbonded¹⁶ electron transfer to estimate its rate constant according to (9),¹⁷ where $\kappa(RT/Nh) = 10^{11}$ and where ΔG^\ddagger is expressed in terms of ΔG° (the free energy of eq 8) and



$$k_{ET} = \kappa \frac{RT}{Nh} \exp\left(\frac{-\Delta G^\ddagger}{RT}\right) \quad (9)$$

λ [the bond and solvent reorganization energy in going from the initial species (at encounter distance) to the transition state for electron transfer] according to equation 10. With λ estimated to be 27.5 kcal/mol¹⁸ and ΔG°

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

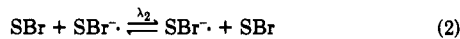
estimated to be 16.6 kcal/mol,¹⁹ ΔG^\ddagger is calculated to be ≥ 17.7 kcal/mol and $k_{ET} \leq 10^{-2}$ M⁻¹ s⁻¹.

It should be noted that the possible systematic errors

(16) The use of the term "nonbonded" instead of "outer sphere" is to be preferred for organic electron transfer processes. See J. S. Littler *Spec. Publ.—Chem. Soc.*, No. 24, 383 (1970).

(17) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer", The Ronald Press Co., New York, 1966, p 74. For detailed discussion on carrying out Marcus calculations see, L. Ebersson, *Adv. Phys. Org. Chem.*, 18, in press.

(18) The term λ can be estimated from the mean value of the λ 's of the two self-exchange reactions to which any heteronuclear electron transfer reaction in principle can be related, in this case eq 1 and 2. For



the first reaction, λ_1 was chosen to be 15 kcal mol⁻¹, a value similar to those for aromatic nitriles and nitro compounds [T. Layloff, T. Miller, R. N. Adams, H. Föh, A. Horsfield, and W. Proctor, *Nature (London)*, 205, 382 (1965); B. A. Kowert, L. Marcoux, and A. J. Bard, *J. Am. Chem. Soc.*, 94, 5538 (1972)]. For the latter process the value of λ_2 employed was 40 kcal mol⁻¹, a value similar to that of bromobenzene, [C. P. Andrieux, C. Blocman, J.-M. Dumas-Bouchiat, and J.-M. Dumas-Bouchiat, and J.-M. Saveant, *J. Am. Chem. Soc.* 101, 3431 (1979)].

(19) ΔG° can be estimated from the standard potentials of the two redox couples, SBr/SBr \cdot^- and S \cdot^- /S \cdot^- . For the former we simply have used $E_p = -0.1$ V vs. SCE (0.14 V vs. NHE). E° for S \cdot^- /S \cdot^- was calculated from thermodynamic data by using the method employed earlier for RCOO \cdot^- /RCOO \cdot^- couples [L. Ebersson, *Acta Chem. Scand.*, 17, 2004 (1963)]. This gives $E^\circ \geq 1.36$ V vs. NHE in aqueous solution. The following data were employed: ΔH_f° [SH] \cdot^- = -109.7 kcal mol⁻¹ and heat of solution of SH is half that of disuccinimide, S-S, ΔH_f° [S-S] \cdot^- = -169.6 kcal mol⁻¹ [D. J. Coleman and H. A. Skinner, *Trans. Faraday Soc.*, 62, 2057 (1966)]; the enthalpy of cleavage of the N-N bond in S-S ≥ 50 kcal mol⁻¹ [E. Hedaya, R. L. Hinman, V. Schomaker, S. Theodoropoulos, and L. M. Kyle, *J. Am. Chem. Soc.*, 89, 4875 (1967)]; the heat of ionization of SH in water = 6.6 kcal mol⁻¹ [M. J. Blais, O. Enea, and G. Berthon, *Thermochim. Acta*, 20, 335 (1977)]. Since $S^\circ(S^-)$ and $S^\circ(S\cdot^-)$ are not known, their difference had to be approximated as $S^\circ(RCOO\cdot^-) - S^\circ(RCOO^-) \approx 25$ cal deg⁻¹ mol⁻¹ [L. Ebersson, *Acta Chem. Scand.*, 17, 2004 (1963)]. To convert the value for E° in aqueous solution to one valid in acetonitrile, one can simply use an estimated value for the free energy of transfer of S \cdot^- (by far the dominant term) from water to acetonitrile. Since S \cdot^- is a strongly hydrated ion similar to acetate ion, it is reasonable to use the same value for the free energy of transfer, namely, 13.5 kcal mol⁻¹ [L. Ebersson and K. Nyberg, *Acta Chem. Scand., Ser. B*, B32, 235 (1978)]. This brings down $E^\circ(S\cdot^-/S^-)$ to ≥ 0.86 V in acetonitrile, and ΔE° for reaction 7 comes out as $\leq (0.14 - 0.86) = -0.72$ V, i.e., $\Delta G^\circ \geq 16.6$ kcal mol⁻¹.

Table IV. Competition Experiments: *n*-Butyl Bromide and the Succinimide Anion Reacting with *N*-Bromosuccinimide in AN at 25 °C

[reactants], mol L ⁻¹			[products], mol L ⁻¹		10 ² <i>k</i> _{ET} , L mol ⁻¹ s ⁻¹
<i>n</i> -BuBr _i	SBr _i	TBAS _i	SH _f	SBU _f	
0.180	0.100	0.098	0.117	0.042	3.0
0.297	0.160	0.150	0.184	0.045	4.6
0.460	0.100	0.098	0.107	0.047	2.8
0.594	0.199	0.150	0.224	0.032	12.5
0.791	0.200	0.150	0.222	0.038	13.9
1.39	0.100	0.098	0.030	0.079	3.2

in ΔE° for eq 8 should work in the direction of making it larger. The N-N bond dissociation energy of disuccinimide (S-S) is probably greater than 50 kcal mol⁻¹, and the E° value for the SBr/SBr \cdot^- couple should be less than 0.14 V vs. NHE, since this value presumably is influenced by a rapid chemical follow-up reaction. Therefore, the estimated k_{ET} represents an upper limit, and it might in fact be smaller by 5-6 powers of ten.

Our attention next turned to experiments designed to determine the rate of reaction between SBr and S \cdot^- (eq 4). The results of Table II indicated that the rates of reaction of SBr with S \cdot^- and with 1-bromobutane (*n*-BuBr) are comparable in magnitude, and this suggested the possibility of obtaining the rate constant for reaction 4 from competition experiments. It was our expectation that both reactions would be simple, bimolecular processes. Given this assumption, it may be shown that eq 11 holds, where

$$k_{ET} \approx \frac{k_2[SH]_f[BuBr]_i}{2[SBU]_f[SBr]_i} \quad (11)$$

k_{ET} is the rate of reaction 4, k_2 is the rate of reaction of S \cdot^- with *n*-BuBr, SBU is *N*-*n*-butylsuccinimide, and the subscripts i and f refer to initial concentrations and to concentrations at infinite time, respectively.

As anticipated the reaction between S \cdot^- and BuBr in AN at 25 °C proved to be a well-behaved S_N2 process. The results of two determinations, shown in Table III, provided an average value for k_2 of 1.20×10^{-2} L mol⁻¹ s⁻¹.

The results of a series of competition experiments to determine k_{ET} are shown in Table IV. The average value, obtained from the six measurements, is 6.7×10^{-2} L mol⁻¹ s⁻¹. This value is consistent with the results in Table II and in reasonable agreement with the calculated value of k_{ET} . Nevertheless, the result is unsatisfactory. The spread in the observed values of k_{ET} is much too large, suggesting that the assumption that the electron transfer reaction is second-order may be invalid. More important, when we monitored the rate of appearance of succinimide in one of these experiments by measuring the increase in the IR absorbance due to the N-H stretching band for SH at 3280 cm⁻¹, we found that the SH concentrations increased very slowly, much more slowly than the concentrations of SBU increased during our measurements of the rate of reaction of *n*-BuBr and S \cdot^- , and this despite the fact that our values for k_{ET} are larger than the value for k_2 !

This apparent inconsistency was resolved when it was observed that SBr and S \cdot^- form a complex, probably of the charge-transfer type, and that this complex is very strongly favored at equilibrium. Evidence for such a complex is provided by both infrared spectroscopy and cyclic voltammetry. Both SBr and SH in AN have carbonyl absorption frequencies at 1725-1730 cm⁻¹, but the carbonyl absorption frequency (1575 cm⁻¹) for TBAS is significantly different. In an AN solution which was initially 0.050 M in SBr and 0.054 M in TBAS, the TBAS band at 1575 cm⁻¹ has essentially disappeared immediately after mixing, and

Table V. Rates of Decomposition of the Complex Formed from *N*-Bromosuccinimide and Succinimide Anion in Acetonitrile at 25 °C

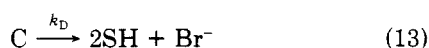
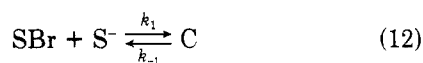
[SBr] _i , mol L ⁻¹	[S ⁻] _i , mol L ⁻¹	10 ⁵ k _D , s ⁻¹	analytical method
0.0349	0.0397	3.3	IR
0.0499	0.0545	5.4	IR
0.0950 ^a	0.0970	8.0	cyclic voltammetry
0.110 ^a	0.117	5.0	IR and cyclic voltammetry
0.350	0.350	4.1	IR

^a Also contained 0.25 M TBAF, as a supporting electrolyte.

the intensity of absorption at 1725–1730 cm⁻¹, due to SBr and/or SH, is very much reduced. Additionally, a new, very strong band appears at 1650 cm⁻¹. As the reaction proceeds, absorption at 1725 cm⁻¹ increases in intensity. After 2 h the intensity of the band at 1650 cm⁻¹ is very much reduced. After 2.5 h it has essentially disappeared, and no further changes were observed after 5.5 h. We attribute the band at 1650 cm⁻¹ to the complex and its disappearance, accompanied by enhancement of the absorption at 1725 cm⁻¹, to conversion of complex to succinimide.

Supporting evidence is provided by cyclic voltammetry, scanning between +0.75 and -2.2 V vs. SCE. In a solution, mixed at zero time so that it contained 0.111 M SBr, 0.118 M TBAS, and 0.25 M TBAF in AN at 25 °C, cyclic voltammetry after 1 min showed a single reduction wave (*E*_p = -1.93 V), no reduction wave characteristic of SBr at *E*_p = +0.03 V, and no oxidation wave characteristic of SH at -0.75 V. After 31 min the reduction peak had shifted to -1.88 V, and a small but clearly detectable oxidation peak appeared in the neighborhood of -0.75 V. With time the cathodic peak kept shifting to more anodic values: to -1.88 V after 31 min, to -1.79 V after 124 min, and to -1.75 V after 304 min.²⁰ The anodic wave remained at -0.75 V but kept continuously increasing in size. We attribute these observed changes to an initial complete conversion of reactants to complex, followed by the slow transformation of complex to succinimide.

The rate of reaction of SBr with S⁻ in AN at 25 °C can be followed either by infrared spectroscopy (increase in absorbance due to the N-H stretching band for succinimide at 3280 cm⁻¹) or by cyclic voltammetry (increase in the wave height for SH oxidation at -0.75 V), and we have used both analytical techniques. In treating the data we have taken as the proper mechanism for the reaction of SBr and S⁻ the equilibrium shown in eq 12 followed by eq 13, where C represents the complex formed from SBr and S⁻.



We assume that $k_1 \gg k_{-1}$ and also that $k_1 \gg k_D$. Given these assumptions

$$[\text{C}]_t = [\text{S}^-]_i - [\text{SH}]_t/2, \text{ when } [\text{SBr}]_i > [\text{S}^-]_i \quad (14)$$

and

$$[\text{C}]_t = [\text{SBr}]_i - [\text{SH}]_t/2, \text{ when } [\text{S}^-]_i > [\text{SBr}]_i \quad (15)$$

(20) The peak potential for succinimide reduction in AN is strongly concentration dependent. At 10⁻² M *E*_p is -1.5 V but rapidly becomes more cathodic with increasing SH concentration, reaching values of -1.62 V at a SH concentration of 1.3 × 10⁻² M and -1.74 V at a SH concentration of 10.1 × 10⁻² M.

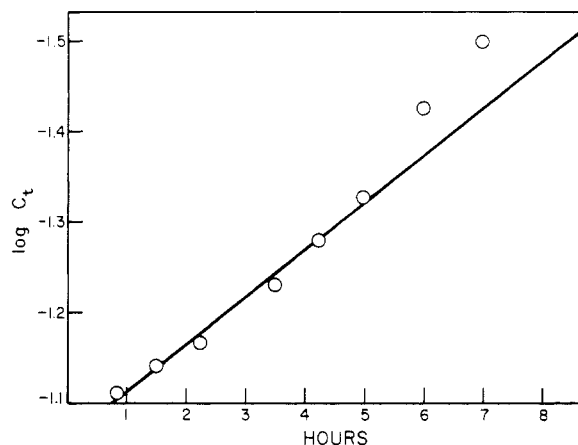


Figure 3. Plot of the logarithm of complex concentration, log *C*_{*t*}, vs. time for the reaction of SBr and the succinimide anion in AN at 25 °C.

Table VI. Rates of Formation (*k*₁) and Decomposition (*k*_d) of the Complex Formed from *N*-Bromosuccinimide and Succinimide Anion in Acetonitrile at 23 ± 0.3 °C

run	<i>k</i> ₁ , s ⁻¹	10 ⁴ <i>k</i> _d , s ⁻¹
1	not followed	5.8
2	0.037	6.2
3	0.032	5.7

where the subscript *t* indicates the concentration at time *t*. The rate equation is given by eq 16, and a plot of log

$$\frac{-d[\text{C}]}{dt} = \frac{2d[\text{SH}]}{dt} = k_D[\text{C}] \quad (16)$$

[*C*]_{*t*} vs. *t* should be linear with a slope equal to -0.4343*k*_D. The values obtained for *k*_D are summarized in Table V. The average value for *k*_D is 5.2 × 10⁻⁵ s⁻¹. The average deviation from this average rate is 1.2 × 10⁻⁵, and the maximum deviation is 2.8 × 10⁻⁵. On consideration of the many assumptions involved, this level of constancy is as high as can be reasonably expected. Figure 3 shows the first-order plot for the reaction with [SBr]_i = 0.0950 M and [S⁻]_i = 0.0970 M. In this case the reaction was followed by cyclic voltammetry to 66.8% of completion. The points shown in Figure 3 are reasonably linear through 50% reaction (the 5-h point), but beyond this point the reaction rate appears to increase appreciably. The other values of *k*_D in Table V are based on reactions followed to only 30–35% of completion, but in every case the plot of log [*C*]_{*t*} vs. *t* was nicely linear.

The complex described above is most probably of the charge-transfer type, and there should, therefore, be a useful charge-transfer band to permit measurement of the relevant reaction rates. Indeed, when 0.1 M solutions of SBr and tetra-*n*-butylammonium succinimide, both in AN, were mixed, one could observe the rapid development of a shoulder at 360 nm, and by monitoring log ϵ at this wavelength, it is possible to obtain values for the rate constants involved.

The actual measurements were made under pseudo-first-order conditions by mixing 0.050 mL of 0.1 M SBr with 3.00 mL of 0.1 M S⁻, both in AN at 23 ± 0.3 °C. The temperature of the cell was not controlled. One could observe two reactions, a very fast one followed by a slow one, with both first order under the conditions of these experiments. The data could be fitted with precision, and the rate constants obtained are given in Table VI. The results described previously suggest strongly that *k*₁ in Table VI corresponds to formation of the charge-transfer complex and *k*_d in Table VI to its decomposition. The

average value for k_d in Table VI is $5.9 \times 10^{-4} \text{ s}^{-1}$, and the relationship between k_d and k_D needs to be explored.

From our previous treatment eq 17 holds, and the

$$d[C]/dt = -k_D[C] \quad (17)$$

equilibrium constant for complex formation is given by eq 18. Combining the above two gives eq 19. Under con-

$$K_{\text{eq}} = \frac{[C]}{[\text{SBr}][\text{S}^-]} \quad (18)$$

$$d[C]/dt = -k_D K_{\text{eq}} [\text{S}^-][\text{SBr}] \quad (19)$$

ditions of the measurements in Table VI $[\text{S}^-]$ is a constant and eq 19 may be rewritten as eq 20, where $k_d = k_D K_{\text{eq}} [\text{S}^-]$.

$$d[C]/dt = -k_d[\text{SBr}] \quad (20)$$

Since $\text{S}^- \approx 0.1 \text{ M}$ it follows that $K_{\text{eq}} \approx 100$ and that the two sets of measurements are self-consistent.

To demonstrate that the SBr/S^- complex is an intermediate in the electrochemical reaction as well as in the purely chemical reaction, we continuously recorded the current as a function of time for an electrolysis in AN at 25°C in which the initial concentrations were 0.201 M SBr and 0.25 M TBAF . Simultaneously, aliquots were withdrawn at appropriate time intervals and analyzed for SH by IR. The amounts of charge passed were used to calculate the amounts of SBr consumed for each of the times at which an aliquot had been withdrawn for SH analysis. More than 80% of the total charge was passed in the first hour, and a plot of $[\text{SBr}]_t$ vs. time for this time period was reasonably linear with a slope of $-5.1 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$. A plot of $[\text{SH}]_t$ vs. time was also linear over the first 3 h of reaction with a slope equal to $4.4 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$. Thus $-d[\text{SBr}]/dt > d[\text{SH}]/dt$ by more than an order of magnitude, and when 90% of the total charge has passed, less than 10% SH has been produced.

Experimental Section

Chemicals. *N*-Bromosuccinimide was reagent grade material from Aldrich Chemical Co. It was recrystallized from water-acetone and dried over P_2O_5 in vacuo before use. Its purity was assayed by an iodimetric procedure;²¹ active bromine was 44.90% corresponding to an SBr purity of 100%. TBAF, prepared as previously described,²² was the supporting electrolyte for the electrochemical studies. Purified N_2 (Airco, Inc.) was employed to remove O_2 and maintain an inert atmosphere. The N_2 was passed through a column of 8-mesh Drierite to remove residual water and was saturated with AN before passage into the electrochemical cell.

The acetonitrile was first dried over mixed 3- and 4-Å molecular sieves for several days, distilled from P_2O_5 , collecting a middle portion, and finally distilled from CaH_2 , again collecting a middle portion. The purity, determined by VPC on a $6 \text{ ft} \times 1/8 \text{ in.}$ column packed with 100–120 Porapak Q, was 99.7%. An IR spectrum indicated the AN was free from interference in the region $4000\text{--}3000 \text{ cm}^{-1}$.

N-*n*-Butylsuccinimide was prepared by treating succinic acid with *n*-butylamine according to the method of Hoey and Lester;²³ bp $132\text{--}135^\circ \text{C}$ (25 mm). The same method was used to prepare *N*-methylsuccinimide from succinic acid and 40% aqueous methylamine; mp $66\text{--}68^\circ \text{C}$ (from acetone-hexane). *N*-Benzylsuccinimide was prepared from the reaction of sodium succinimide and benzyl chloride in refluxing methanol; mp $100\text{--}103^\circ \text{C}$ (from ethanol-water).

Tetra-*n*-butylammonium succinimide (TBAS) was prepared by treating a solution of tetra-*n*-butylammonium bromide (6.47 g, 0.02 mol) in 60 mL of methanol with silver oxide (4.0 g, 0.0173

mol). After the mixture was stirred for 1 h, a test of the supernatant liquid for bromide ion was negative. The mixture was filtered through Celite, and succinimide (2.0 g, 0.02 mol) was added to the filtrate. The filtrate was taken to dryness at water pump pressure. The crystalline salt, without further purification, was made up to 100 mL with freshly distilled AN. A 2.0-mL portion of this solution was diluted with water and titrated with 0.05 M (aqueous) HCl. From the single break in the pH titration curve, TBAS in AN was determined to be 0.196 M. Tetraethylammonium succinimide (TEAS) was prepared in a similar fashion from tetraethylammonium iodide (5.16 g, 0.02 mol) and succinimide (2.0 g, 0.02 mol) and dissolved in 100 mL of AN. TEAS in AN was determined to be 0.189 M by titration.²⁴

Apparatus and Instrumentation. Electrochemical experiments were performed by using a Princeton Applied Research Corp. (PARC) Model 170 electrochemistry system, a PARC cell top (K0066), a PARC cell bottom (K0060), and a PARC purge tube (9330). Cyclic voltammetry and controlled-potential experiments were run at 25°C with the aid of a PARC jacketed cell bottom (K0064) and a Lauda Model C-3 circulator. A tube (12 mm diameter \times 125 mm length) with a fritted glass tip (porosity "D") from Ace Glass (7209-08) was the anode compartment. A 50-mil Pt wire was inserted through a red rubber septum, and the septum was fitted over the end of the tube. The air-tight seal prevented any significant mixing of anolyte and catholyte solutions. A 2.3-mm-diameter Pt disk sealed in soft glass was employed for voltammetry. Controlled-potential electrolyses were performed with a Pt foil electrode (1 cm^2). Pt electrodes were treated with chromic acid, rinsed with water, and dried before use. The Pt disk microelectrode was polished between scans with γ alumina (Gamal from Fisher Scientific Co.). A saturated calomel electrode (SCE) was the reference electrode. The SCE was placed into a cracked-glass salt bridge tube which contained aqueous KCl; the tip of this salt bridge was placed into another salt bridge which was fitted with an asbestos fiber tip and contained 0.25 M TBAF in AN. The tip of the reference electrode compartment was positioned to within 2–3 mm of the working electrode. The working electrode, auxiliary electrode compartment, reference electrode salt bridge tube, and nitrogen purge tube were fitted through holes provided in the plastic cell top and made contact with the catholyte in the cell bottom.

Gas chromatograms were obtained on either a Varian Model 2720 or Hewlett-Packard Model 5840 gas chromatograph. Both instruments were equipped with thermal-conductivity detection and employed $6 \text{ ft} \times 0.25 \text{ in.}$ (Varian) and $6 \text{ ft} \times 1/8 \text{ in.}$ (Hewlett-Packard) stainless-steel columns packed with 10% poly(*m*-phenyl ether) on 80/100 HP Chromosorb W. Analyses for succinimide and *N*-alkylsuccinimides were run isothermally at column temperatures of 180°C (Varian) and 190°C (Hewlett-Packard) with helium as the carrier gas.

A Waters Associates liquid chromatograph, consisting of the Model 660 solvent programmer, Model 6000A solvent delivery system, and Model 440 absorbance detector, was employed with a $2 \text{ ft} \times 1/8 \text{ in.}$ column packed with Corasil for HPLC experiments.

A Perkin-Elmer 281B infrared spectrophotometer was employed to record IR spectra.

Procedures. Electrolyte solutions for electrochemical experiments were freshly prepared. The anolyte and catholyte solutions were each 0.25 M TBAF in AN; the anolyte also contained 0.8 M *N,N*-dimethylformamide. The electrolyte volume was 5.0 mL in the anode and cathode compartments. The catholyte was purged with dry N_2 to remove O_2 and then blanketed with N_2 during an experiment. A blank electrolysis was performed with the Pt sheet electrode until the current decayed essentially to zero. SBr was carefully weighed (0.06–0.065 g, 0.34–0.37 mmol) and dissolved in the cathode solution. For electrochemical experiments carried out with an alkylating agent present, these were generally added to the catholyte before the background electrolysis. The Pt disk microelectrode replaced the Pt sheet electrode and an IR-compensated voltammetric scan of SBr was performed at 0.20 V/s. The Pt sheet electrode was cleaned with chromic acid, rinsed with water, dried, and placed back in the system.

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Controlled-potential electrolysis was commenced at -0.8 V vs. SCE and continued until the current decayed to background level. Solution agitation was provided by magnetic stirring. Electrolysis duration was typically 2-3 h. After an electrolysis the anolyte and catholyte solutions were transferred to separate 5.0-mL volumetric flasks for analysis.

To carry out the series of chemical reactions, we dissolved SBr (0.178 g, 0.001 mol) and the desired amount of alkylating agent in 4.0 mL of AN in a 50-mL round-bottomed flask. The reaction was initiated when 5.0 mL (0.001 mol) of the appropriate tetraalkylammonium succinimide salt was added. Reactions were allowed to proceed for at least 24 h before analysis.

Identification and Determination of Products. The procedure employed to identify and determine succinimide and alkylated succinimides from VPC traces has been described.¹⁴ Tri-*n*-butylamine and *n*-butyl bromide, which derived from the reaction of bromide ion with TBAF in the injection port, were also present in the VPC traces, but these decomposition products were not determined. Analysis of anolyte and catholyte solutions demonstrated that 2-3% of the total product yield was found in the anolyte. One particular SBr electrolysis mixture (Table I, expt 5) was analyzed by HPLC and linear-sweep voltammetry in addition to gas chromatography. The Corasil column used for HPLC was activated prior to use by heating overnight at 110 °C with a N₂ purge. The mobile phase was 99% CH₂Cl₂-1% CH₃CN for determination of *N*-*n*-butylsuccinimide and 97% CH₂Cl₂-3% CH₃CN for succinimide. The mobile phase flow rate was 1.0 mL/min for all runs. Component peaks were detected by UV absorbance at 254 nm; quantitative analyses were achieved by comparison of sample peak areas with those of authentic standards. Succinimide in the catholyte was determined by HPLC, VPC, and voltammetry; agreement among these three analytical methods was within 10%. *N*-*n*-Butylsuccinimide was determined

by both HPLC and VPC, and the values obtained differed by less than 8%. A linear sweep voltammetric method for determination of bromide ion, utilizing the oxidation peak at +0.65 V vs. SCE, showed that the yield of bromide ion was 90%; this yield was based upon the initial SBr present plus the amount of *N*-*n*-butylsuccinimide formed during the electrolysis. With a separate electrolysis mixture (Table I, expt 12), the Volhard titration method was employed to determine that, based upon the number of moles of SBr, the bromide yield was 88%.

Analysis of the chemical reaction mixtures (Table II) required that SBr be determined as well as succinimide and *N*-alkylsuccinimides. The analytical scheme included determination of succinimide by standard additions by using the IR absorbance at 3280 cm⁻¹ (N-H stretch). Spectra of reaction mixtures were obtained differentially in 0.2-mm cells with AN as a reference. Gas chromatography was used to determine *N*-alkylsuccinimides and the total of SBr and succinimide in chemical reactions. SBr decomposed to succinimide in the injection port, and thus a single peak was present for SBr and succinimide. However, since succinimide had been determined independently by IR, SBr could be estimated by difference. Uncertainty in the data for SBr, determined in this fashion, is probably ±10%. Bromide ion concentration following reaction of SBr with TBAS (Table II, expt 1) was determined by the Volhard titration method, and the yield was 97% based upon the number of moles of SBr.

Registry No. *N*-Bromosuccinimide, 128-08-5; succinimide, 123-56-8; *N*-butylsuccinimide, 3470-96-0; *N*-methylsuccinimide, 1121-07-9; *N*-benzylsuccinimide, 2142-06-5; 1-bromobutane, 109-65-9; butyl tosylate, 778-28-9; 1-chlorobutane, 109-69-3; methyl tosylate, 80-48-8; α -bromotoluene, 100-39-0; tetrabutylammonium succinimide, 74830-30-1; tetraethylammonium succinimide, 74830-35-6; succinimide anion, 28627-67-0; succinimidyl radical, 24344-83-0.

Hydroxymethyl Derivatives of 18-Crown-6 and [2.2.2]Cryptand: Versatile Intermediates for the Synthesis of Lipophilic and Polymer-Bonded Macrocyclic Ligands

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The synthesis of (hydroxymethyl)-18-crown-6 and of (hydroxymethyl)[2.2.2]cryptand is described. These systems allow facile binding of lipophilic chains and/or of polymeric matrices. In this way efficient chemically stable phase-transfer catalysts are obtained. Polymer-bound systems are easily recyclable without loss of catalytic activity. Use of these systems for the removal of lanthanide shift reagents from organic solutions is reported.

Use of multidentate macrocyclic and macrobicyclic polyethers is often limited by the difficulties of recovery at the end of reaction and, for cryptands, by the relatively complex multistep syntheses. The introduction of long alkyl chains, to make the polyether insoluble in water and soluble in nonpolar organic media, partially alleviates these problems.^{1,2} An increased possibility of recycling is ob-

tained by anchoring the polyether to a polymer support.³

An important use of polyether ligands is anion activation in nucleophilic reactions, particularly significant in the case of cryptates. It occurs both in nonpolar, homogeneous

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