Electrochemical Studies of the Reactivity of Superoxide Ion with Several Alkyl Halides in Dimethyl Sulfoxide

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Stable solutions of tetraethylammonium superoxide can be prepared in aprotic solvents by electrochemical generation. This has provided a basis for a chronopotentiometric study of the kinetics for the nucleophilic displacement by superoxide of halide from alkyl halides to give peroxide radicals. The reaction is first order in superoxide and occurs with 1:1 stoichiometry. The pseudo-first-order rate constants at 28° for a series of butyl chlorides in dimethyl sulfoxide follow: n-butyl chloride, $3.2 \times 10^{-1} \sec^{-1}$; sec-butyl chloride, $0.6 \times 10^{-1} \sec^{-1}$; and t-butyl chloride, $0.4 \times 10^{-1} \sec^{-1}$. The rates of reaction for the butyl bromides and iodides are too rapid for quantitative evaluation of their rate constants.

The reactions of the superoxide ion with organic compounds have not been studied extensively. Although both the sodium and potassium salts are commercially available, their low solubility in organic solvents has limited investigations of their reactions.[1] Russell and coworkers have suggested that superoxide is an intermediate in the oxidation of hydrocarbons in basic dimethyl sulfoxide.[2]

The studies that have been made of superoxide reactions have employed the solid salts in suspensions. Schmidt and Bipp[3] have treated potassium superoxide as an ether suspension with benzoyl chloride to give dibenzoyl peroxide, and with triphenylmethyl chloride to yield ditriphenylmethyl peroxide. These workers did not observe a reaction with simple aliphatic alkyl halides.

Le Berre and Berguer, who have studied the organic reactions of superoxides in detail, made similar observations.[4] They investigated the reactions of suspensions of potassium and sodium superoxides in tetrahydrofuran and benzene with various organic materials. Their results indicate that the superoxide does not act as a radical, but either as a mild reductant or as a very weak nucleophile. In terms of nucleophilicity, the solid superoxides react with triphenylmethyl chloride, but not with other alkyl halides under these conditions. After nucleophilic attack, the resulting peroxide radical reactions were postulated to depend upon substrate and reaction conditions.

The electrochemical behavior of oxygen and the superoxide ion in nonaqueous solvents has been studied extensively.[5-9] The results establish that the tetraalkylammonium superoxides are soluble and stable in a variety of aprotic organic solvents.[8,9] The present paper summarizes the results of a preliminary investigation of the reactions of tetraethylammonium superoxide in dimethyl sulfoxide with alkyl halides. The study illustrates the use of electrochemistry to study reactions of organic species not readily accessible by more conventional techniques. The results indicate that superoxide, under these conditions, behaves as a nucleophile rather than as a radical. Its nucleophilicity is stronger than previously reported.

Experimental Section

Materials.—Baker Analyzed reagent grade dimethyl sulfoxide (DMSO) was used without further purification. Acetonitrile, Mallinckrodt, was purified by a modification of Mann's procedure.[10] The alkyl halides, t-butyl hydroperoxide, and lithium chloride were obtained from Matheson Coleman and Bell and were used without purification. Tetraethylammonium perchlorate (TEAP), Distillation Products, was recrystallized three times from water and dried at 100°. Tetrabutylammonium bromide, Distillation Products, was recrystallized from ethyl acetate.

Equipment.—All electrochemical measurements were made using a solid-state potentiostat–amperostat[11] with a Sargent Model SR strip chart recorder and a Moseley Model 7030-A X–Y recorder. Standard two-compartment electrochemical cells with a three-electrode configuration were used. For controlled potential electrolysis experiments a large gold foil served as the working electrode. The chronopotentiometric and cyclic voltammetric studies utilized a gold billet sealed in a polyethylene tube (gold inlay electrode) as the working electrode. The area of this electrode was determined by reduction of ferricyanide ion in water. An aqueous Ag|AgCl reference electrode was used which has been previously described;[7] its potential was 0.000 V vs. sce. The reference electrode was isolated from the bulk of the solution by a fine frit and a large platinum gauze served as the isolated auxiliary electrode. A Sargent thermonitor was used to regulate the temperature of the water bath at 28.0 ± 0.5° for the kinetic studies. An Aerograph A90-P3 gas chromatograph was used to detect t-butyl hydroperoxide with two columns, 6% didecylphthalate on firebrick and 10% XE-60 on Chromosorb P. Columns of Teflon tubing (5 ft) (Penntube Plastics Corp.) were used and the injection port of the chromatograph was lined with Teflon to prevent decomposition of hydroperoxides.

Results and Discussion

Previous investigations[9] have shown that solutions of superoxide in DMSO (0.1 F TEAP), formed by the electrochemical reduction of oxygen, decay less than 3%/hour. Such stability indicates that this solvent is suitable for studies of the reactivity of superoxide.

Figure 1 illustrates cyclic voltammograms obtained for a solution of DMSO (0.1 F TEAP) saturated with oxygen, both in the absence and presence of sec-butyl chloride. (With cyclic voltammetry the peak current is proportional to the concentration of the electroactive species.) In the absence of the alkyl halide, the ratio of

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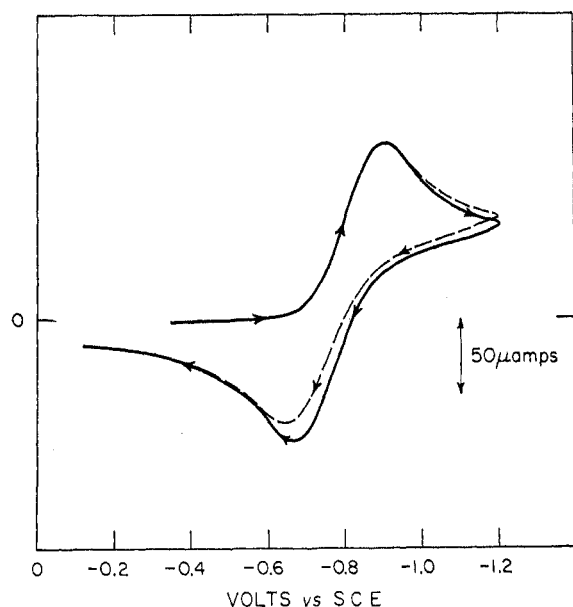(11) A. D. Goolsby and D. T. Sawyer, *ibid.*, **39**, 411 (1967).

Figure 1.—Cyclic voltammetry of oxygen in DMSO (0.1 *F* TEAP) at a gold billet electrode; sweep rate, 0.1 V sec⁻¹; – – –, voltammogram taken in the presence of 0.10 *F* sec-butyl chloride.

Figure 2.—Chronopotentiogram of oxygen in DMSO (0.1 *F* TEAP), in the presence of 0.10 *F* sec-butyl chloride at a gold billet electrode; *i*, 40 μA.

the anodic peak current to the cathodic peak current is 1; *i.e.*, the superoxide formed during the cathodic sweep does not react but can all be reoxidized when the potential sweep is reversed. In the presence of sec-butyl chloride the anodic peak current is reduced in height, which indicates that some of the superoxide has been consumed by reaction with the alkyl chloride. By comparing the ratio of i_p (anodic)/i_p (cathodic) for the oxygen redox system in the presence of a variety of alkyl halides, the primary halides are found to react faster than secondary species which react faster than tertiary halides; furthermore, iodides react faster than bromides. These results imply that the reaction of superoxide with alkyl halides is a nucleophilic displacement reaction. Although cyclic voltammetry can be used to determine the kinetics of reactions, it does not appear to offer any advantages over chronopotentiometry for this system.

In chronopotentiometry the transition time, τ, is proportional to the concentration of electroactive species

$$\tau^{1/2} = \frac{\pi^{1/2} nFD^{1/2} AC}{2i}$$ (1)

where n is the number of electrons transferred, F the faraday constant, A the electrode area, C the concentration of electroactive species, and i the current. The use of chronopotentiometry permits the concentration of superoxide to be monitored in the reaction with alkyl halides. The diffusion coefficient, D, for superoxide in this media has been reported previously.[9]

To determine the stoichiometry of the superoxide–alkyl halide reaction a solution of superoxide was prepared by reducing oxygen at −1.10 V *vs.* sce; the solution was then degassed with prepurified nitrogen, *t*-butyl bromide was added in small amounts, the solution was stirred briefly, and a chronopotentiogram was recorded to measure the superoxide concentration. (*t*-Butyl bromide was chosen because it appears to react instantaneously with superoxide as determined by cyclic voltammetry.) A plot of moles of superoxide
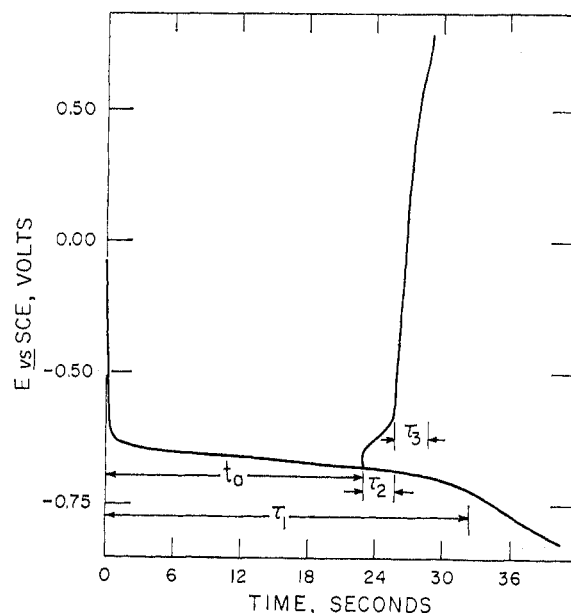
consumed (calculated from the chronopotentiometric data) *vs.* moles of *t*-butyl bromide added yielded a straight line with a slope of one. This indicates that the superoxide and alkyl halide react with a 1:1 stoichiometry. Similar experiments in acetonitrile (0.1 *F* TEAP) indicate that both *n*-butyl bromide and *t*-butyl bromide consume about 3.5 mol of superoxide/mol of added alkyl bromide.

Figure 2 shows a typical chronopotentiogram of oxygen in DMSO (0.1 *F* TEAP) in the presence of sec-butyl chloride. For a chemically reversible, diffusion-controlled redox system, the ratio of the reverse transition time, τ_2, to the time, t_a, in which reduction has occurred, is equal to 1/3, provided $t_a \leq \tau_1$, the transition time for the reduction. In the absence of the alkyl halide, the ratio is 1/3 for oxygen in this solution. The ratio τ_2/t_a is reduced, however, in the presence of the halide. Hence, the extent of the decrease in this ratio is a measure of the rate of reaction with superoxide.

In Figure 2, τ_3 characterizes the amount of chloride ion formed in the reaction of superoxide with sec-butyl chloride. The anodic behavior of halide ions at a gold electrode in acetonitrile has been studied previously.[12] Chronopotentiograms of DMSO (0.1 *F* TEAP) solutions of lithium chloride and tetrabutylammonium bromide exhibit $E_{1/4}$ values which are approximately the same, respectively, as the $E_{0.22}$ values observed in reverse chronopotentiograms of oxygen in the presence of an alkyl chloride and an alkyl bromide. Furthermore, the ratio of $(\tau_2 + \tau_3)/t_a$ is equal to 1/3. This indicates that the only reaction of superoxide is one in which free halide is formed.

Testa and Reinmuth have described a method for obtaining kinetic parameters for homogeneous reactions between a substrate and a material generated chronopotentiometrically.[13] Their method involves measurement of the ratio of τ_2/t_a for various values of t_a and i. Using this ratio in an analytical function, values of kt_a

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can be determined. Then, a plot of kt_a vs. t_a yields a straight line with a slope equal to k.

DMSO (0.1 F TEAP) solutions of n-butyl, sec-butyl, and t-butyl chloride have been prepared with each 0.10 F in alkyl halide. A series of reverse chronopotentiograms have been recorded for each solution at 28.0 ± 0.5° for various values of t_a. The current density also has been varied over a minimum range of five for each solution; in the case of t-butyl chloride, the range of current density has been ten. In all cases, the ratio of τ_2/t_a is a function only of t_a and is independent of current density. This independence of current density indicates that the reaction is first order in the electroactive species; i.e., superoxide.[13] The pseudo-first-order rate constants, k, for the reaction

$$RCl + O_2^- \longrightarrow RO_2\cdot + Cl^- \qquad (2)$$
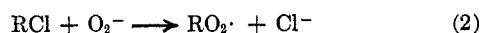
are, for n-butyl chloride, 3.2×10^{-1} sec^{-1}; sec-butyl chloride, 0.6×10^{-1} sec^{-1}; and t-butyl chloride, 0.4×10^{-1} sec^{-1}. The rate of the reactions with any of the butyl bromides or butyl iodides is too rapid to measure by this method; i.e., $\tau_2 = 0$.

Attempts have been made to detect hydroperoxide as an eventual product of the reaction to substantiate the belief that the initial product of the reaction is a peroxide radical. The latter would abstract a hydrogen atom from the solvent or the electrolyte to form a hydroperoxide. Large-scale electrolyses have been performed in which solutions of DMSO (0.1 F TEAP)–t-butyl bromide are kept saturated with oxygen while several hundred coulombs are allowed to pass through the solution. Samples then have been injected into a gas chromatograph and a material exhibiting the same retention time as that of an authentic sample of t-butyl hydroperoxide has been detected with two different

columns. On this basis, some hydroperoxide is concluded to be formed from the superoxide–alkyl halide reaction. t-Butyl hydroperoxide also has been detected by gas chromatography in acetonitrile and acetone in similar experiments.

Summary and Conclusions

The data indicate that tetraethylammonium superoxide reacts with alkyl halide by a nucleophilic displacement of the halide to give peroxide radicals as the initial product. The reaction is first order with respect to superoxide, and occurs with 1:1 stoichiometry. Furthermore, n-butyl chloride reacts faster than sec-butyl chloride, which is faster than t-butyl chloride; alkyl chlorides react slower than bromides and iodides.

The results differ from those reported by Schmidt and Bipp[3] and by Le Berre and Berguer[4] who did not observe reactions for suspensions of potassium and sodium superoxide with alkyl halides. This difference probably is related to the fact that alkali and alkaline earth salts have a large effect on the reactivity of superoxide with water[5] and on its electrochemistry.[6] The greater reactivity of the tetraethylammonium salt implies that it may be of synthetic utility. A preparative procedure for the synthesis of tetramethylammonium superoxide is available.[14]

Registry No.—Superoxide ion, 12185-08-9; n-butyl chloride, 109-69-3; sec-butyl chloride, 78-86-4; t-butyl chloride, 507-20-0.

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Stable Carbonium Ions. XCIV.[1] Diprotonated Ketocarboxylic Acids and Keto Esters and Their Cleavage to Protonated Ketooxocarbonium Ions in Fluorosulfuric Acid–Antimony Pentafluoride Solution

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Protonation of a series of keto acids has been studied in FSO$_3$H–SbF$_5$–SO$_2$ solution. O-Diprotonation was observed at low temperature. Two isomeric species were found for protonated acetylvaleric acid and 3- and 4-benzoylbenzoic acids. At higher temperatures acetylbutyric, acetylvaleric, and 2-acetylbenzoic acids underwent dehydration to give the corresponding ketooxocarbonium ions. No cleavage reaction was observed for protonated levulinic acid and 3-acetyl-, 4-acetyl-, 3-benzoyl-, and 4-benzoylbenzoic acids even when solutions were heated up to +50°. Protonated pyruvic acid underwent dehydration and decarbonylation to give the methyloxocarbonium ion. Methyl and ethyl acetoacetates in FSO$_3$H–SbF$_5$–SO$_2$ solution are diprotonated. t-Butyl acetoacetate cleaves without observation of the protonated ester to diprotonated acetoacetic acid and the trimethylcarbonium ion.

Our recent investigations of protonated ketones,[3] carboxylic acids,[4] and dicarboxylic acids[5] lead us now to study the protonation of a series of aliphatic and aromatic keto acids in the super acid system, FSO$_3$H–SbF$_5$–

SO$_2$. No nuclear magnetic resonance study of protonated keto acids has been reported in the literature, although a number of investigations of protonated carboxylic acids are known.[6–10]

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