

## References and Notes

- (1) J. F. Bunnett in "Techniques of Chemistry", Vol. VI, "Investigations of Rates and Mechanisms of Reactions", Part I, E. S. Lewis, Ed., Wiley, New York, N.Y., 1974, p 143.
- (2) R. D. Gilliom, "Introduction to Physical Organic Chemistry", Addison-Wesley, Reading, Mass., 1970, p 92.
- (3) M. Zanger, C. A. VanderWerf, and W. E. McEwen, *J. Am. Chem. Soc.*, **81**, 3806 (1959).
- (4) W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **86**, 2378 (1964).
- (5) W. E. McEwen, G. Axelrad, M. Zanger, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **87**, 3948 (1965).
- (6) J. R. Corfield and S. Trippett, *Chem. Commun.*, 1267 (1970).
- (7) H. Hoffmann, *Justus Liebigs Ann. Chem.*, **634**, 1 (1960).
- (8) W. E. McEwen, A. W. Smalley, and C. E. Sullivan, *Phosphorus*, **1**, 259 (1972).
- (9) G. J. Reilly and W. E. McEwen, *Tetrahedron Lett.*, 1231 (1968).
- (10) D. W. Allen, *J. Chem. Soc. B*, 1490 (1970).
- (11) D. W. Allen, B. G. Hutley, and M. T. Mellor, *J. Chem. Soc., Perkin Trans. 2*, 63 (1972).
- (12) D. W. Allen and B. G. Hutley, *J. Chem. Soc., Perkin Trans. 2*, 67 (1972).
- (13) D. W. Allen, S. J. Grayson, I. Harness, B. G. Hutley, and I. W. Mowat, *J. Chem. Soc., Perkin Trans. 2*, 1912 (1973).
- (14) D. W. Allen, B. G. Hutley, and M. T. J. Mellor, *J. Chem. Soc., Perkin Trans. 2*, 1690 (1974).
- (15)  $\sigma$  values taken from A. J. Gordon and R. A. Ford, "The Chemist's Companion", Wiley, New York, N.Y., 1972, p 146.
- (16) L. Horner, H. Hoffmann, H. G. Wippel, and G. Hassel, *Chem. Ber.*, **91**, 52 (1958).
- (17) Y. I. Yeh, Ph.D. Dissertation, University of Massachusetts, Amherst, Mass., 1972, p 83.
- (18) S. Shore, Ph.D. Dissertation, University of Massachusetts, Amherst, Mass., 1973, p 45.
- (19) W. A. Henderson and S. A. Buckler, *J. Am. Chem. Soc.*, **82**, 5794 (1960).
- (20) G. B. Borowitz, D. Schuessler, W. McComas, L. I. Blaine, K. B. Field, P. Ward, P. Rahn, W. Glover, F. Roman, and I. J. Borowitz, *Phosphorus*, **2**, 91 (1972).
- (21) R. U. Pagilagan, Ph.D. Dissertation, University of Massachusetts, Amherst, Mass., 1965, p 91.
- (22) A. R. Bassindale, C. Eaborn, R. Taylor, A. R. Thompson, D. R. M. Walton, J. Cretney, and G. J. Wright, *J. Chem. Soc. B*, 1155 (1971).
- (23) R. Alexander, C. Eaborn, and T. G. Traylor, *J. Organomet. Chem.*, **21**, 65 (1970).
- (24) R. U. Pagilagan and W. E. McEwen, *Chem. Commun.*, 652 (1966).
- (25) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 3120 (1952).
- (26) Reference 15, p 109.
- (27) J. E. Fontaine and W. E. McEwen, *Phosphorus*, **1**, 57 (1971).
- (28) W. E. McEwen, V. L. Kyllingstad, D. N. Schulz, and Y. I. Yeh, *Phosphorus*, **1**, 145 (1971).
- (29) W. E. McEwen, W. I. Shiau, Y. I. Yeh, D. N. Schulz, R. U. Pagilagan, J. B. Levy, C. Symmes, Jr., G. O. Nelson, and I. Granoth, *J. Am. Chem. Soc.*, **97**, 1787 (1975).
- (30) W. E. McEwen, J. E. Fontaine, D. N. Schulz, and W. I. Shiau, *J. Org. Chem.*, **41**, 1684 (1976).
- (31) D. N. Schulz, Ph.D. Dissertation, University of Massachusetts, Amherst, Mass., 1971, p 81.
- (32) J. S. Wood, R. J. Wikholm, and W. E. McEwen, *Phosphorus Sulfur*, **3**, 163 (1977).
- (33) Although upfield shifts of the  $^{31}\text{P}$  NMR signals are observed in our *o*-anisylphosphonium salts, as against those of the corresponding *p*-anisyl salts, this cannot be taken as compelling evidence that the *o*-methoxy group shields a face of the tetrahedral phosphorus. The effects which we have observed are small, and, furthermore, Grim and Yankowsky have reported a reverse order of chemical shifts for other *o*- and *p*-anisylphosphonium salts: S. O. Grim and A. W. Yankowsky, *J. Org. Chem.*, **42**, 1263 (1977). As an example of our data, we have observed  $\delta\text{P}$  21.63 ppm (downfield with respect to 25%  $\text{H}_3\text{PO}_4$ ) for benzylbis-*p*-tolyl-*p*-anisylphosphonium chloride and  $\delta\text{P}$  20.08 for the corresponding *o*-anisyl salt. Grim and Yankowsky, on the other hand, have observed  $\delta\text{P}$  18.8 (downfield from 85%  $\text{H}_3\text{PO}_4$  in methanol solution) for methyltris-*p*-anisylphosphonium bromide and  $\delta\text{P}$  19.7 for the corresponding *o*-anisyl salt. Our *o*-anisylphosphonium have unusually large upfield chemical shifts (e.g.,  $\delta\text{P}$  -18.70 for *o*-anisylbis-*p*-tolylphosphine, upfield with respect to 25%  $\text{H}_3\text{PO}_4$ , as against  $\delta\text{P}$  -9.63 for the corresponding *p*-anisylphosphine), which reflects the known, but incompletely understood,  $\gamma$  effect: cf. S. O. Grim and A. W. Yankowsky, *Phosphorus Sulfur*, **3**, 191 (1977), and references cited therein.
- (35) I. M. Kolthoff, E. B. Sandell, E. J. Meehan, and S. Bruckenstein, "Quantitative Chemical Analysis", 4th ed., Macmillan, New York, N.Y., 1969, p 946.
- (36) P. D. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, **78**, 5610 (1956).
- (37) O. Neunhoeffer and L. Lamza, *Chem. Ber.*, **94**, 2514 (1961).
- (38) H. Schindlbauer and F. Mitterhoffer, *Z. Anal. Chem.*, **221**, 394 (1966).
- (39) Y. I. Yeh, Ph.D. Dissertation, University of Massachusetts, Amherst, Mass., 1972, p 24.
- (40) A. B. Janes, M.S. Thesis, University of Massachusetts, Amherst, Mass., 1977.
- (41) M. D. LaHue, R. J. Teck, G. Dombi, and H. D. Axelrod, *J. Chem. Educ.*, **50**, 867 (1973).

## A Study of Superoxide Reactivity. Reaction of Potassium Superoxide with Alkyl Halides and Tosylates

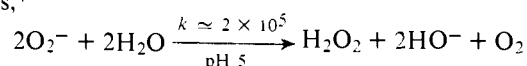
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**Abstract:** The reaction of superoxide with a representative series of alkyl halides and tosylates in  $\text{Me}_2\text{SO}$  and benzene has been shown to proceed by a pathway involving an initial  $\text{S}_{\text{N}}2$  displacement leading to alkylperoxy radicals which, in a subsequent one-electron reduction, are converted to peroxy anions. Processes involving the self-reaction of peroxy radicals play at most a very minor role in product determination. In most instances, the initially isolable principal product is the dialkyl peroxide which, in a subsequent, base-induced reaction(s), is converted into alkoxide. Product studies reveal that a number of factors can influence product ratios, including reactant ratios, the nature of the leaving groups, reaction time, reactant concentration, and workup conditions.

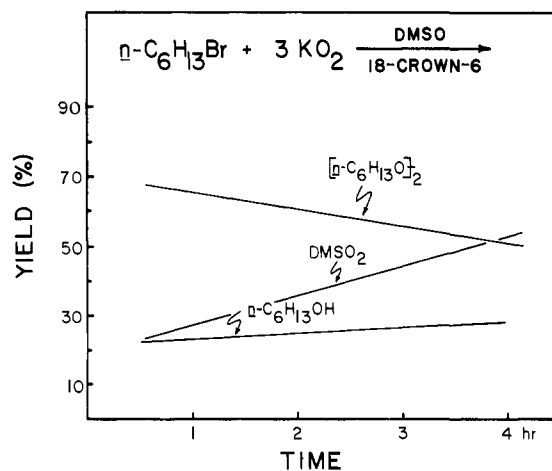
In recent years superoxide ( $\text{O}_2^-$ ), the one-electron reduction product of molecular oxygen, has become the subject of considerable chemical and biological interest and investigation.<sup>1</sup> Much of the current interest about superoxide centers around its production and reactions in biological systems and in particular its role in certain biological oxidations.<sup>2</sup> There are a number of early (pre-1975) reports describing the chemical reactivity of superoxide;<sup>3</sup> however, much of the basic chemistry of superoxide remains ill defined. The work reported here details one avenue of an investigation we have pursued, designed to explore, elucidate, and define the chemical reactivity of superoxide.

Superoxide disproportionates rapidly in aqueous solutions,<sup>4</sup>

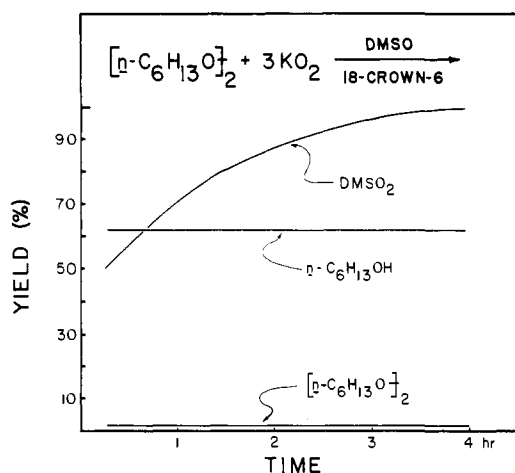


complicating the study and interpretation of the reactions of superoxide in protic media. By contrast, superoxide has extended stability in certain aprotic solvents, specifically dimethyl sulfoxide,  $\text{Me}_2\text{SO}$ . For this reason, the studies reported here have been carried out in either dimethyl sulfoxide or benzene. Such studies provide the indirect opportunity to assess the feasibility of superoxide's participation in such reactions when conducted under largely aqueous conditions.





**Figure 2.** Analysis of the products from the reaction of  $\text{KO}_2$  and *n*-hexyl bromide (3:1) in  $\text{Me}_2\text{SO}$ -18-crown-6 reveals the influence that reaction time has on product distribution (cf. Figure 1).

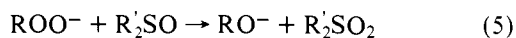


**Figure 3.** Plot showing the production of  $\text{Me}_2\text{SO}_2$  and 1-hexanol and the recovery of  $[\text{n-C}_6\text{H}_{13}\text{O}]_2$  resulting from the reaction of di-*n*-hexyl peroxide (3.33 mmol) with  $\text{KO}_2$  (10.0 mmol) in  $\text{Me}_2\text{SO}$  (20 mL) containing 18-crown-6 ether (1.00 mmol). Workup and analytical procedures were equivalent to those described in Figure 1.

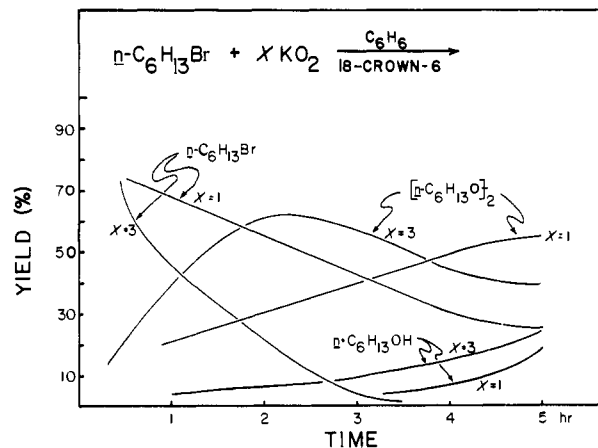
in Figure 3 than in Figure 2. This behavior is presumably a result of the increased solubility of  $\text{KO}_2$  in the former reaction mixture, a conclusion that is consistent with the data in Table I which indicate that the di-*n*-hexyl peroxide produced in the 1:3 reaction of *n*-hexyl bromide with  $\text{KO}_2$  is consumed much more rapidly when this reaction is carried out in the presence of an increased amount of 18-crown-6 ether.

Third, the generally high product balances observed in the reactions outlined above attest to the completeness of these product studies and sustain the accuracy of the analytical procedures used.

Finally, examination of these reaction mixtures for solvent-derived products revealed the presence of dimethyl sulfone. Peroxy anions are one of several likely intermediates formed during the reaction of  $\text{KO}_2$  with **1** (vide infra) and it is, of course, well known that peroxy anions will oxidize most sulfoxides to the corresponding sulfone, the observed reaction being<sup>12a</sup>



(Control experiments established that dissolution of potassium superoxide in  $\text{Me}_2\text{SO}$ -18-crown-6 yields no significant (<2%)  $\text{Me}_2\text{SO}_2$  after 5 h.) It follows from eq 5 that equal amounts of alcohol and sulfone are produced in this process. Indeed, Gibian has proposed that this process provides the principal



**Figure 4.** Influence of reaction time and reactant ratios on the product distribution produced by reaction of  $\text{KO}_2$  with *n*-hexyl bromide (3.33 mmol) in benzene (20 mL)-18-crown-6 at 25 °C. Individual reaction mixtures were quenched with an acidified solution of methanol prior to analysis. Di-*n*-hexyl peroxide and 1-hexanol yields were determined by LC. Unreacted *n*-hexyl bromide was determined by GLC. The stability of these substances under these workup and analytical conditions was demonstrated by control experiments. All yields are based on alkyl bromide.

**Table I.** Effect of the Quantity of 18-Crown-6 Ether on the 1:3 Reaction of *n*-Hexyl Bromide with  $\text{KO}_2$  in  $\text{Me}_2\text{SO}$ <sup>a</sup>

RBr, mM	$\text{KO}_2$ , mM	18-crown-6, mM	reaction time, h	yield, <sup>b</sup> %	
				ROOR	ROH
3.33	10.0	1.00	0.5	68	21
			1	63	22
			2	60	23
			3	57	26
3.33	10.0	3.33	0.5	50	29
			1	44	37
			2	<1	60
			3	<1	61
			4	<1	59
			4	<1	60

<sup>a</sup> Reaction volume, 20 mL of  $\text{Me}_2\text{SO}$ . <sup>b</sup> Yields were determined by LC and are based on alkyl halide.

pathway by which alcohol is produced in the reaction of  $\text{KO}_2$  with alkyl halide.<sup>12b</sup>

Figure 2 shows the yield of  $\text{Me}_2\text{SO}_2$  produced during the course of the reaction of 3 equiv of  $\text{KO}_2$  with *n*-hexyl bromide in  $\text{Me}_2\text{SO}$ . A comparison of these data with those shown in Figure 1 reveals that depending on the ratio of  $\text{KO}_2$  to *n*-hexyl bromide, the yield of 1-hexanol can greatly exceed the yield of  $\text{Me}_2\text{SO}_2$ . Thus, although a 1:1 ratio of these reactants produces an 18% yield of 1-hexanol, the corresponding yield of  $\text{Me}_2\text{SO}_2$  is only 4%. In light of eq 6, it follows that greater than 75% of the alcohol produced in the 1:1 reaction cannot arise via eq 5.

It is further apparent from Figures 1 and 2 that the yield of sulfone increases as the ratio of  $\text{KO}_2$  to *n*-hexyl bromide increases. In addition, the difference between the yield of 1-hexanol and  $\text{Me}_2\text{SO}_2$  decreases as the ratio of  $\text{KO}_2$  to *n*-hexyl bromide increases. Moreover, unlike the 1:1 reaction which was complete in  $\leq 15$  min, the yield of  $\text{Me}_2\text{SO}_2$  in the 3:1 and 5:1 reactions increases with extended reaction times. These facts suggest that the slower secondary reaction of  $\text{KO}_2$  with di-*n*-hexyl peroxide may also provide a pathway to  $\text{Me}_2\text{SO}_2$ . Figure 3 confirms this proposal.

**Reaction of *n*-hexyl bromide with  $\text{KO}_2$  in benzene** is illustrated graphically in Figure 4. Aside from the limited side reaction involving the formation of  $\text{Me}_2\text{SO}_2$  that accompanies the principal reaction in  $\text{Me}_2\text{SO}$ , the principal difference between the two

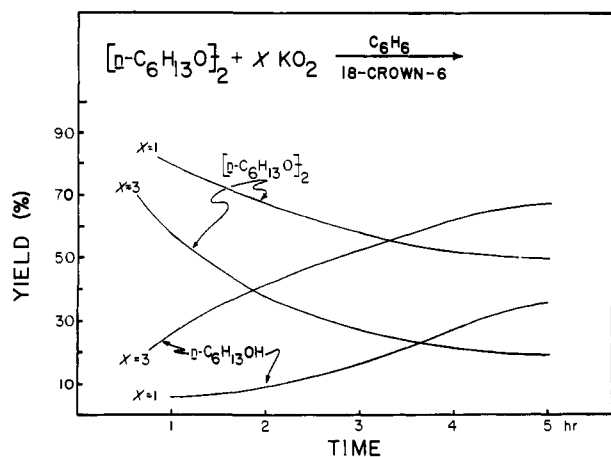


Figure 5. Data illustrating the influence of time and reactant ratios on product formation and reactant consumption during the reaction of  $\text{KO}_2$  with di-*n*-hexyl peroxide in benzene-18-crown-6 at 25 °C. Reaction workup and analyses were carried out as described in Figure 4.

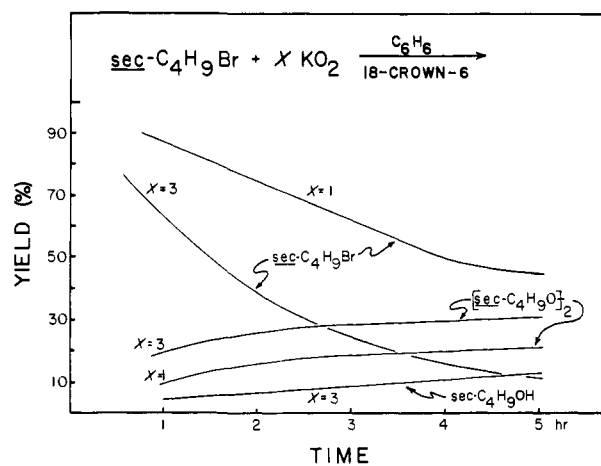
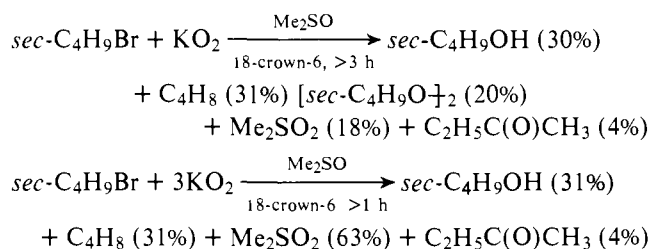


Figure 6. Reactant consumption and product formation during the course of the reaction of *sec*-butyl bromide (3.33 mmol) with  $\text{KO}_2$  in benzene-18-crown-6 at 25 °C. Di-*sec*-butyl peroxide, *sec*-butyl alcohol, and 2-butanone were analyzed by LC following the workup procedure outlined in Figure 4. The yield of recovered *sec*-butyl bromide was determined by GLC.

processes seems to be one of rates, the reaction in  $\text{Me}_2\text{SO}$  being appreciably faster than in benzene. This fact is presumably a consequence of, inter alia, the enhanced solubility of  $\text{KO}_2$  in  $\text{Me}_2\text{SO}$ -18-crown-6 relative to benzene-18-crown-6 mixtures.

**Reaction of *sec*-Butyl Bromide with  $\text{KO}_2$  in  $\text{Me}_2\text{SO}$  and Benzene.** The reaction of *sec*-butyl bromide with potassium superoxide in  $\text{Me}_2\text{SO}$ - and benzene-18-crown-6 is summarized below and in Figure 6. These results reveal a reactivity which, allowing for the difference in structure of the alkyl groups, parallels that observed for the corresponding reaction with *n*-hexyl bromide: the principal isolated products are



*sec*-butyl alcohol, di-*sec*-butyl peroxide, and butene(s). A further parallel is seen in the influence which reactant ratios

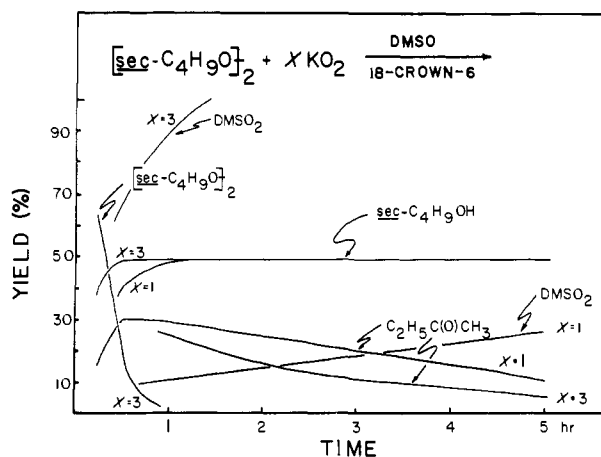


Figure 7. Data illustrating the influence of time and reactant ratio on the yield of products and consumption of peroxide during the reaction of di-*sec*-butyl peroxide with  $\text{KO}_2$  in  $\text{Me}_2\text{SO}$  containing 18-crown-6 ether. Analyses were carried out as follows: di-*sec*-butyl peroxide, *sec*-butyl alcohol, and 2-butanone were determined by LC after a workup that consisted of treating individual reaction mixtures with an acidified solution of aqueous methanol.  $\text{Me}_2\text{SO}_2$  was determined by GLC analysis prior to hydrolytic workup.

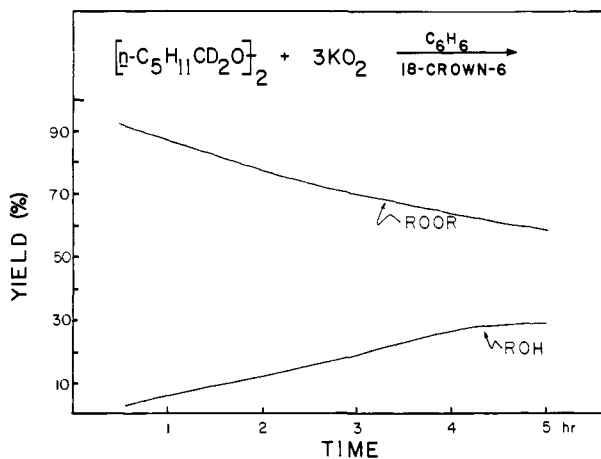


Figure 8. Reaction of di-*n*-hexyl-1,1,1',1'- $d_4$  peroxide with  $\text{KO}_2$  in benzene-18-crown-6 illustrating the influence which deuterium substitution at the  $\alpha$  carbon has on reaction rate (cf. Figure 5).

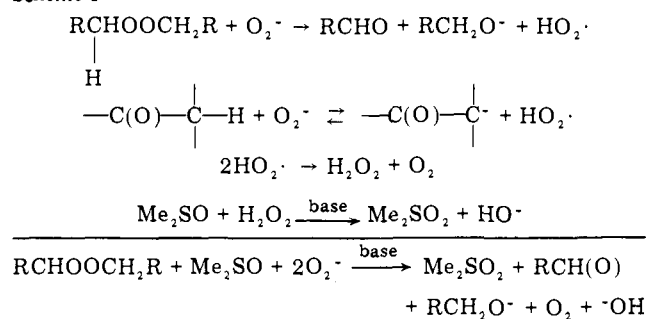
have on product ratios: the yield of olefin is insensitive to the reactant ratios while that of *sec*-butyl alcohol increases and that of di-*sec*-butyl peroxide diminishes as the ratio of  $\text{KO}_2$  to *sec*-butyl bromide increases.

Figure 8 illustrates the reaction of di-*sec*-butyl peroxide with  $\text{KO}_2$  in  $\text{Me}_2\text{SO}$ . Again, the observed behavior is reminiscent of that exhibited by di-*n*-hexyl peroxide in its reaction with  $\text{KO}_2$  (cf. Figures 3 and 5).

A similar reactivity is observed for the reaction of  $[\text{sec-C}_4\text{H}_9\text{O}]_2$  with  $\text{KO}_2$  in benzene-18-crown-6, although, as before, the reaction in benzene is significantly slower than the corresponding reaction in  $\text{Me}_2\text{SO}$ . It follows that the direct reaction of  $\text{KO}_2$  with the initial product, di-*sec*-butyl peroxide, provides one plausible pathway for the production of *sec*-butyl alcohol produced during the course of the reaction of *sec*-butyl bromide with  $\text{KO}_2$ .

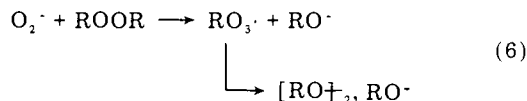
The most outstanding difference between the reaction of  $\text{KO}_2$  with *n*-hexyl bromide and *sec*-butyl bromide appears to be the increased yields of olefin (and corresponding decreased yields of alcohol and peroxide) produced in the reactions of the latter. This difference is in qualitative accord with the proposition that the response of the product-determining step to the structure of the organic moiety is that expected for competing substitution and elimination reactions (vide infra). In contrast

Scheme I

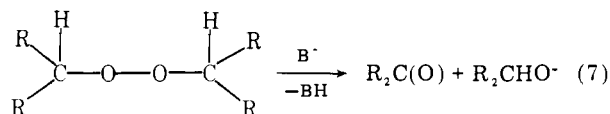


to *n*-hexyl bromide, the 1:1 reaction of *sec*-butyl bromide with  $\text{KO}_2$  produces a moderate yield of  $\text{Me}_2\text{SO}_2$  while the 1:3 reaction results in a substantial yield of this material. This difference, too, can be rationalized in terms of the effect which the structure of the organic moiety is expected to have on competing processes (vide infra).

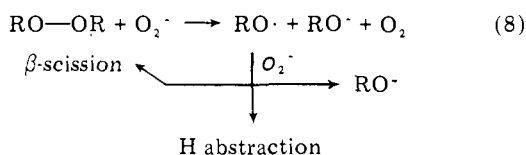
**Reaction of Dialkyl Peroxides with  $\text{KO}_2$  in  $\text{Me}_2\text{SO}$  and Benzene.**<sup>16</sup> It is apparent from the results presented here and elsewhere<sup>20b</sup> that dialkyl peroxides are intimately involved in the reaction of primary and secondary halides and tosylates (vide infra) with potassium superoxide in both  $\text{Me}_2\text{SO}$  and benzene. Given the nature of superoxide, its reaction with dialkyl peroxide might, a priori, take place by any of three pathways: (1) nucleophilic displacement on peroxide oxygen<sup>13</sup>



(2) base-catalyzed decomposition of those peroxides bearing protons on the  $\alpha$  carbon,<sup>14</sup>



and (3) electron transfer, similar to that observed in the facile reaction of organolithium and Grignard reagents with alkyl peroxides.<sup>15</sup>



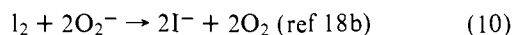
The reaction of *n*-hexyl and *sec*-butyl peroxide with  $\text{KO}_2$  in  $\text{Me}_2\text{SO}$  and benzene is summarized in Figures 3, 5, 7, and 8 and shows that reaction in  $\text{Me}_2\text{SO}$  is much more rapid than in benzene. The reaction of *sec*-butyl peroxide with  $\text{KO}_2$  in  $\text{Me}_2\text{SO}$  produces both *sec*-butyl alcohol and 2-butanone, suggesting that base-catalyzed cleavage is perhaps dominant. The former product is obtained in 50% yield but the yield of ketone passes through a maximum, presumably because of further base-catalyzed condensations. Indeed, 2-butanone is unstable in the presence of  $\text{KO}_2$  in benzene-18-crown-6, and a 0.15 M solution is completely consumed in 8 h by 1 equiv of  $\text{KO}_2$ . The presence of carbonyl compounds also provides an explanation for the formation of  $\text{Me}_2\text{SO}_2$  observed in the reaction of di-*n*-hexyl and di-*sec*-butyl peroxide (cf. Figures 3 and 7; Scheme I).

Finally, only the elimination mechanism can account for both the failure of di-*tert*-butyl peroxide to undergo any apparent reaction with  $\text{KO}_2$  in  $\text{Me}_2\text{SO}$  even after 24 h and the substantial isotope effect observed in the reaction of  $\text{KO}_2$  with

di-*n*-hexyl-1,1,1',1'-*d*<sub>4</sub> peroxide (Figure 8). However, the fact that alcohol is produced in greater than 50% yield in the reaction of excess  $\text{KO}_2$  with certain alkyl halides and dialkyl peroxides (cf. Figures 2, 3, and 5) necessarily requires an additional pathway(s) leading to alcohol. Indeed, in a separate experiment when di-*n*-hexyl peroxide was allowed to react with powdered  $\text{KOH}$  in benzene-18-crown-6, analysis after 8 h revealed no unreacted di-*n*-hexyl peroxide and a 60% yield of 1-hexanol. Thus, even in the reaction of dialkyl peroxides with hydroxide ion, an alternative pathway(s) to base-induced decomposition (presumably involving nucleophilic displacement on oxygen) exists.

**Effect of Halide. Reaction of  $\text{KO}_2$  with *n*-Hexyl Iodide.** The oxidation of halide ion by peroxides is well known.<sup>13</sup> Since peroxides are products in the reaction of alkyl halides with  $\text{KO}_2$ , we have investigated the possible ancillary role of halide in these reactions.

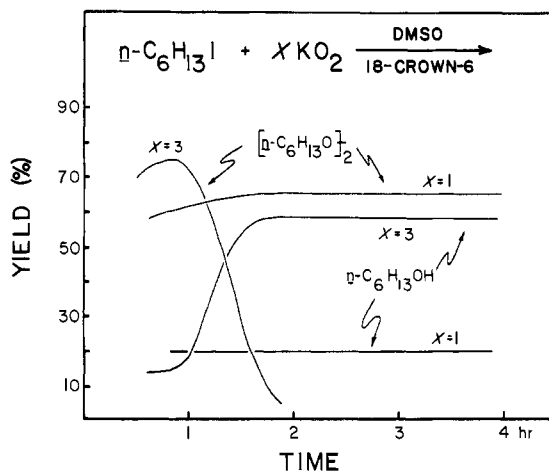
Potassium bromide shows no apparent reactivity toward di-*n*-hexyl peroxide in  $\text{Me}_2\text{SO}$  after several hours. Nor does added potassium bromide have any discernible influence on the yield of di-*n*-hexyl peroxide produced by the reaction of  $\text{KO}_2$  with *n*-hexyl bromide. In contrast, iodide ion reacts readily with di-*n*-hexyl peroxide in  $\text{Me}_2\text{SO}$ , according to eq 10.<sup>17</sup>



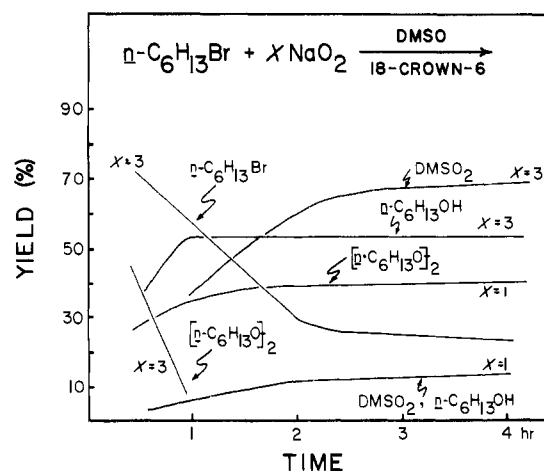
This fact permits a reasonable explanation of the difference between the product distributions observed in the 1:3 reaction of *n*-hexyl bromide (Figure 2) and iodide (Figure 9) with  $\text{KO}_2$  in  $\text{Me}_2\text{SO}$ . Comparison of these data reveals that the reaction of  $\text{KO}_2$  with *n*-hexyl iodide produces a substantially greater yield of 1-hexanol than the corresponding reaction with *n*-hexyl bromide, presumably as a consequence of eq 9 and 10.

**Influence of the Nature of the Crown Ether.** Reaction of superoxide with alkyl halides and tosylates has been observed by a number of investigators.<sup>18-20</sup> Despite certain basic similarities, these studies are characterized by unusual inconsistencies in the reported product studies. Merritt and Johnson have suggested that these variations reflect the influence of the reaction conditions on the fate of the initially formed alkylperoxy radicals.<sup>21</sup> Such an explanation is unlikely (vide infra). We have shown that factors such as the nature of the workup conditions, the ratio of  $\text{KO}_2$  to substrate, ratio of  $\text{KO}_2$  to crown ether, nature of the halide, and reaction time can all influence product ratios; however, it remained to be determined what, if any, effect the nature of the macrocyclic ether has on the course of the reaction of  $\text{KO}_2$  with alkyl halides. In an effort to determine if such an influence exists, we have examined the reaction of *n*-hexyl bromide with  $\text{KO}_2$  in  $\text{Me}_2\text{SO}$  in the presence of different crown ethers. A comparison of these results is seen in Table II. They reveal that, in our hands, similar product distributions are observed with several 18-crown-6 ethers of differing grades suggesting that the nature of the crown ether does not substantially influence the course of this reaction.

**Reaction of *n*-Hexyl Bromide with  $\text{NaO}_2$  in  $\text{Me}_2\text{SO}$ .** Based on a consideration of stability constants,  $K$  (determined in water), for the polyether-cation complex of dicyclohexyl-18-crown-6, with sodium and potassium ions,<sup>22</sup> and the estimated size of the cavity (2.6-3.2 Å) 18-crown-6<sup>23</sup> (ionic radii:  $\text{Na}^+ = 1.93$  Å,  $\text{K}^+ = 2.66$  Å;  $K_{\text{Na}^+(\text{H}_2\text{O})} = 1.7 \text{ M}^{-1}$ ,  $K_{\text{K}^+(\text{H}_2\text{O})} = 2.2 \text{ M}^{-1}$ ),  $\text{NaO}_2$  might be expected to be less reactive than  $\text{KO}_2$  because of its reduced solubility. Figure 10 shows that this is the case: even after 5 h, a substantial quantity of unreacted *n*-hexyl bromide remains in the 1:1 reaction of  $\text{NaO}_2$  with **1**, whereas the equivalent reaction with  $\text{KO}_2$  results in complete consumption of **1** in  $\leq 15$  min. It is interesting to note that in



**Figure 9.** Reaction of  $\text{KO}_2$  with *n*-hexyl iodide (1:1 and 3:1) in  $\text{Me}_2\text{SO}$ -18-crown-6 exhibits a different profile than the corresponding reaction with *n*-hexyl bromide (cf. Figures 1 and 2).



**Figure 10.** Plot showing the production of di-*n*-hexyl peroxide, 1-hexanol, and  $\text{Me}_2\text{SO}_2$  as well as consumption of *n*-hexyl bromide during the course of the reaction of  $\text{NaO}_2$  with **I** (1:1 and 3:1) in  $\text{Me}_2\text{SO}$ . Workup and analytical procedures were equivalent to those described in Figure 1.

**Table II.** Influence of Different 18-Crown-6 Ethers on the Reaction of  $\text{KO}_2$  with *n*-Hexyl Bromide in  $\text{Me}_2\text{SO}^a$

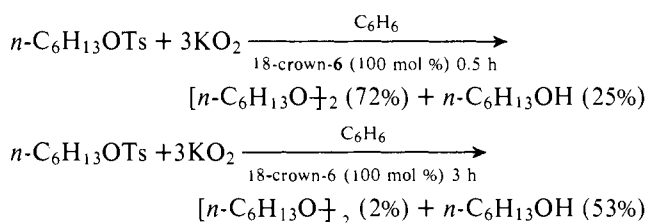
RBr, mM	$\text{KO}_2$ , mM	crown ether, mM	time, h	products, %	
				ROH	ROOR
3.00	3.00	dicyclohexyl-18-crown-6 <sup>b</sup> (0.30)	0.5	10	60
			1	13	63
			2	12	66
			3	12	68
			4	12	65
3.00	3.00	dicyclohexyl-18-crown-6 <sup>c</sup> (0.30)	5	15	65
			0.5	6	54
			1	10	65
			2	12	68
			3	14	68
3.00	3.00	18-crown-6 <sup>c</sup> (0.30)	4	12	70
			5	15	71
			0.5	11	74
			1	10	67
			2	14	70
			3	15	68
			4	15	72
			5	14	68

<sup>a</sup> Solution volume, 20 mL of  $\text{Me}_2\text{SO}$ . <sup>b</sup> Purchased from Fluka Chemical Co., "puriss" grade, and used without further purification. <sup>c</sup> Purchased from Aldrich Chemical Co., "technical" grade, and used without further purification.

contrast to the 3:1 reaction of  $\text{KO}_2$  with **1** in which the yield of 1-hexanol increases gradually over a period of ca. 24 h to a maximum value of ~60%, the equivalent reaction employing  $\text{NaO}_2$  is over  $\leq 2$  h. A reasonable explanation of this result would seem to be that  $\text{NaO}_2$  is more basic under these conditions than is  $\text{KO}_2$ ; hence, the base-induced destruction of peroxide (Scheme I) occurs more rapidly.

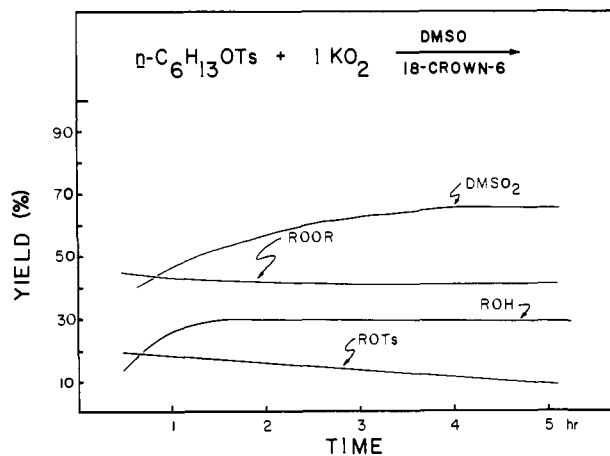
**Reaction of *n*-Hexyl and *sec*-Hexyl Tosylate with  $\text{KO}_2$  in  $\text{Me}_2\text{SO}$  and Benzene.** Different leaving groups can influence the course of a substitution reaction in different ways and in so doing frequently provide additional insight into the mechanism of the reaction. With this purpose in mind, we undertook an investigation of the reaction of  $\text{KO}_2$  with *n*-hexyl and *sec*-hexyl tosylate in  $\text{Me}_2\text{SO}$  and benzene. The results of this study are summarized below and in Figures 11–13. These data reveal a reactivity which in several ways parallels that observed for the corresponding bromides: the 1:1 reaction of  $\text{KO}_2$  with *n*-hexyl tosylate in  $\text{Me}_2\text{SO}$  produces a reaction mixture consisting of two major components, di-*n*-hexyl peroxide and 1-hexanol, and two minor ( $\leq 5\%$ ) components,  $\text{Me}_2\text{SO}_2$  and hexene(s). Also, reactant ratios appear to influence product

yields in a manner reminiscent of the effect caused by similar changes in the analogous reaction with *n*-hexyl bromide, viz., increasing the ratio of  $\text{KO}_2$  to tosylate diminishes the yield of di-*n*-hexyl peroxide but increases the yield of alcohol and  $\text{Me}_2\text{SO}_2$ . Likewise, there are parallels between the reaction of  $\text{KO}_2$  with *sec*-butyl bromide and *sec*-hexyl tosylate: both reactions produce equivalent products, the yields of which exhibit a parallel dependence on reactant ratios. The results summarized below show that in benzene-18-crown-6, reactions of  $\text{KO}_2$  with *n*-hexyl and *sec*-hexyl tosylate, like the corresponding reactions with *n*-hexyl and *sec*-butyl bromide, display gross similarities (product yields, influence of reactant ratios on product distributions, etc.) to the same reaction performed in  $\text{Me}_2\text{SO}$ , the principal difference being one of reaction rate: reactions carried out in  $\text{Me}_2\text{SO}$  are significantly more rapid than the corresponding reactions in benzene. However, this difference in rate can be diminished by increasing the amount of 18-crown-6, thus,

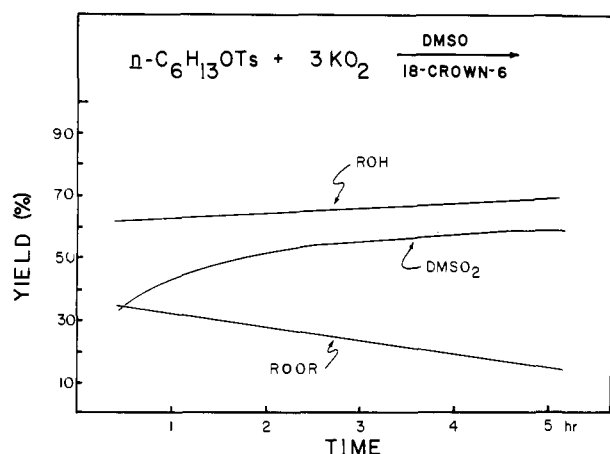


A closer comparison of the reaction of  $\text{KO}_2$  with alkyl halides and tosylates reveals two noteworthy differences. First, it is apparent that the reaction of  $\text{KO}_2$  with *n*-hexyl and *sec*-hexyl tosylate in benzene to produce di-*n*-hexyl peroxide is substantially slower than the corresponding reaction with *n*-hexyl and *sec*-butyl bromides. Second, the reaction of  $\text{KO}_2$  with *n*-hexyl and *sec*-hexyl tosylate in  $\text{Me}_2\text{SO}$  produces lower yields of the corresponding dialkyl peroxide but higher yields of the respective alcohol than is observed in the analogous reaction with *n*-hexyl and *sec*-butyl bromides. Although inverted from the reactivity order generally observed for displacements on alkyl bromides and tosylates in protic solvents, the first difference, i.e., an observed reactivity order of  $\text{Br} > \text{OTs}$ , is not unreasonable in this instance in view of the demonstrated and frequently dramatically different reactivities observed between displacement reactions in a protic solvent vs. the same reaction in an aprotic solvent. In DMF, for example, the leaving group tendencies for  $\text{S}_{\text{N}}2$  reactions at saturated carbons are  $\text{I} > \text{Br} > \text{OTs} > \text{Cl} > +\text{SMe}_2$ .<sup>24</sup>

Similar considerations provide a rational explanation of the



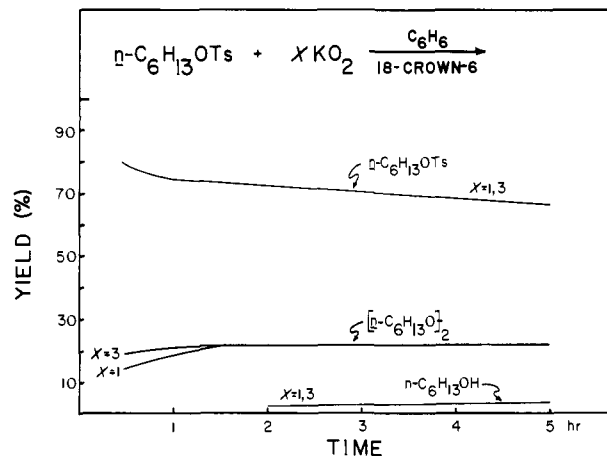
**Figure 11.** Analysis of the products and recovered tosylate resulting from the reaction of *n*-hexyl tosylate with 1 equiv of  $\text{KO}_2$  in  $\text{Me}_2\text{SO}$ -18-crown-6.  $\text{Me}_2\text{SO}_2$  was determined by GLC prior to workup. The analysis of di-*n*-hexyl peroxide, 1-hexanol, and recovered *n*-hexyl tosylate was performed by LC following individual reaction workup as described in Figure 1.



**Figure 12.** Plot showing the influence of time and reactant ratio (cf. Figure 13) on distribution of products produced by the reaction of *n*-hexyl tosylate (3.33 mmol) with  $\text{KO}_2$  (10.0 mmol) in  $\text{Me}_2\text{SO}$ -18-crown-6 (20 mL, 1.00 mmol) at 25 °C. Analytical procedures are those described in Figure 13.

second difference. Thus, in view of the fact that the carbon-oxygen bond forming step is the same for both *n*-hexyl bromide and tosylate (vide infra), it follows that any difference in peroxide and alcohol yields observed in the reaction of  $\text{KO}_2$  with these two substrates is a reflection of differences between the subsequent reaction sequences that lead from alkylperoxy radicals to these products. Of the three such pathways available (vide infra) only one (viz., that involving nucleophilic displacement by alkylperoxy anion on an alkyl halide or tosylate) can be expected to exhibit the significant leaving group influence and order observed in these reactions. Moreover, if, as required by this argument, tosylate is a poorer leaving group than bromide, it follows as a consequence of eq 5 (all other factors being equal), that the 1:1 reaction of *n*-hexyl tosylate with  $\text{KO}_2$  in  $\text{Me}_2\text{SO}$  should result in a significant increase in the yield of  $\text{Me}_2\text{SO}_2$  relative to that observed for the corresponding reaction with *n*-hexyl bromide. Indeed, a comparison of Figures 1 and 11 sustains this expectation.

**Oxygen Evolution Studies.** The reaction of alkyl halides and tosylates with  $\text{KO}_2$  is characterized by the evolution of molecular oxygen. The rate of evolution, consonant with the rate of reaction, is rapid in  $\text{Me}_2\text{SO}$  and much slower in benzene. A summary of our brief study of this behavior is seen in Table III. It is apparent that all the alkyl halides and tosylates ex-



**Figure 13.** Analysis of the consumption of *n*-hexyl tosylate (3.33 mmol) and the production of di-*n*-hexyl peroxide and 1-hexanol during the reaction of *n*-hexyl tosylate with  $\text{KO}_2$  (1:1 and 1:3) in benzene-18-crown-6 at 25 °C. Individual reactions were worked up by treatment with an acidified solution of aqueous methanol; analyses were performed by LC.

**Table III.** Oxygen Evolution from the Reaction of Alkyl Halides, Tosylates, and Related Substrates with Potassium Superoxide in  $\text{Me}_2\text{SO}$ -18-Crown-6<sup>a</sup>

substrate (3.33 mM)	$\text{O}_2$ , % <sup>b</sup>	substrate (3.33 mM)	$\text{O}_2$ , % <sup>b</sup>
<i>n</i> - $\text{C}_8\text{H}_{17}\text{Br}$	46	<i>n</i> - $\text{C}_6\text{H}_{13}\text{OTs}$	31
<i>n</i> - $\text{C}_6\text{H}_{13}\text{Br}$	42	<i>sec</i> - $\text{C}_8\text{H}_{17}\text{OTs}$	3.5
<i>sec</i> - $\text{C}_4\text{H}_9\text{Br}$	44	<i>sec</i> - $\text{C}_6\text{H}_{13}\text{OTs}$	3.5
<i>n</i> - $\text{C}_8\text{H}_{17}\text{I}$	43	$[\text{n-C}_6\text{H}_{13}\text{O}]_2$	5.0
<i>n</i> - $\text{C}_8\text{H}_{17}\text{OTs}$	30		

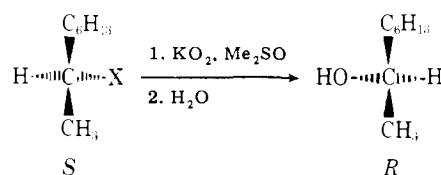
<sup>a</sup> All reactions were carried out in  $\text{Me}_2\text{SO}$  (20 mL) containing 10 mol % 18-crown-6 (1.0 mM) and 10.0 mM of  $\text{KO}_2$ . <sup>b</sup> Oxygen evolution was metered with a gas buret; yields are based on substrate, i.e., %  $\text{O}_2$  = mM  $\text{O}_2$ /mM (substrate)  $\times 10^2$ .

amined produce less than 50% yield of dioxygen. Indeed, 50% would appear to be the upper limiting value for the yield of molecular oxygen. Such a conclusion is certainly consistent with the stoichiometry of the reaction



A dramatic reduction in oxygen evolution is observed in the reaction of  $\text{KO}_2$  with secondary tosylates. The reason for this puzzling observation remains unclear.

**Stereochemistry of Carbon-Oxygen Bond Formation and the Relative Reactivity of Superoxide toward Alkyl Halides and Tosylates.** The mild conditions and good yields associated with the reaction of superoxide with alkyl halides and tosylates afforded an opportunity to examine the stereochemistry of carbon-oxygen bond formation. Optically active (+)-(*S*)-2-octanol ( $\alpha_{\text{D}}^{20} + 7.97^\circ$ , optical purity 99.4%) was converted to tosylate and thence to (-)-(*R*)-2-bromooctane ( $\alpha_{\text{D}}^{20} - 41.56^\circ$ , optical purity 95.4%). Reaction of this tosylate with  $\text{KO}_2$  in  $\text{Me}_2\text{SO}$  yields (-)-(*R*)-2-octanol ( $\alpha_{\text{D}}^{20} - 7.71^\circ$ ), corresponding to an optical purity and overall stereochemistry of 97% *inversion* of configuration. Similar reaction with (-)-(*R*)-2-bromooctane affords (+)-(*S*)-2-octanol in 90% optical purity (95% net *inversion* of configuration). A similar result (94% net



**Table IV.** Reaction of Potassium Superoxide with Various Organic Halides and Tosylates in Me<sub>2</sub>SO<sup>a</sup>

substrate	rel reactivity <sup>a</sup>	substrate	rel reactivity <sup>a</sup>
1-C <sub>8</sub> H <sub>17</sub> I	4.5	1-C <sub>8</sub> H <sub>17</sub>	0.089
2-C <sub>8</sub> H <sub>17</sub> I	3.3	2-C <sub>8</sub> H <sub>17</sub> Cl	0.020
1-C <sub>8</sub> H <sub>17</sub> Br	1.00 <sup>a</sup>	1-C <sub>8</sub> H <sub>17</sub> OTs	0.52 (0.55) <sup>b</sup>
2-C <sub>8</sub> H <sub>17</sub> Br	0.98	2-C <sub>8</sub> H <sub>17</sub> OTs	0.63 (0.27) <sup>b</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> Br	0.90	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	2.9

<sup>a</sup> Reactivities were determined relative to 1-bromooctane (1.00) in Me<sub>2</sub>SO by the standard competitive technique of allowing a mixture of a designated standard (1-bromooctane) and one additional substrate to react with a limited amount of potassium superoxide and determining the amount of unreacted starting substrate. <sup>b</sup> Determined in benzene.

inversion) has been observed by Johnson and Nidy for the reaction of KO<sub>2</sub> with (–)-(R)-2-bromooctane in benzene–18-crown-6.<sup>19</sup>

The data presented thus far suggest that the reaction of superoxide with *n*-hexyl bromide and tosylate in Me<sub>2</sub>SO is rapid. In an effort to gain further insight into the reactivity of superoxide we carried out a series of experiments designed to determine the relative reactivity of KO<sub>2</sub> toward various organic halides and tosylates. A portion of the results of this study has been previously published<sup>18</sup> and is summarized in Table IV. Several points concerning these data deserve brief comment. First, it is apparent that the observed substrate reactivity is benzyl > primary > secondary > aryl and iodide > bromide > tosylate > chloride. Second, substitution is predominant with primary halides; however, substantial elimination occurs with secondary systems. Elimination is the predominant process observed from the reaction with the tertiary halide 2-bromo-2-methylpentane, but adamantyl bromide is quantitatively recovered after treatment with KO<sub>2</sub>–18-crown-6 in Me<sub>2</sub>SO and benzene for 24 h. These observations are in qualitative accord with the proposition that the response of the reaction of KO<sub>2</sub> with alkyl halides and tosylates in Me<sub>2</sub>SO to changes in the nature of the leaving group and structure of the organic group bonded to it are those expected for an S<sub>N</sub>2 reaction.<sup>25</sup>

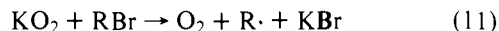
It is noteworthy that the spread in reactivities is substantially smaller than that commonly observed for S<sub>N</sub>2 reactions in protic solvents.<sup>25</sup> A similar leveling effect has been observed by others studying nucleophilic displacement in aprotic solvents.<sup>24,26</sup> Finally, although the differences in reactivity of KO<sub>2</sub> toward primary and secondary substrates is small, the nucleophilicity of superoxide is substantially greater than that of other nucleophiles under comparable conditions. For example, we previously reported data which indicated that the reaction of KO<sub>2</sub> with 1-bromooctane in Me<sub>2</sub>SO–18-crown-6 occurs  $\geq 10^3$  times faster than KI reacts with the same substrate under equivalent conditions.<sup>18</sup> A similar conclusion has been presented by Danen and Warner, who recently determined the absolute rate constants for the reaction of KO<sub>2</sub> with several alkyl bromides.<sup>27</sup> Their relative rate (2.3) for the reaction of KO<sub>2</sub> with 1-bromobutane vs. 2-bromobutane in Me<sub>2</sub>SO (determined in the absence of 18-crown-6) is in substantial agreement, considering the differences in reaction conditions, with the relative reactivity reported in Table IV for 1- vs. 2-bromooctane.

## Discussion

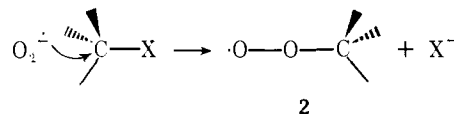
The experimental data presented in this paper indicate that the reaction of potassium superoxide with alkyl halides and tosylates proceeds by a similar pathway, but at substantially different rates, in Me<sub>2</sub>SO- and benzene–18-crown-6, by a mechanism which requires, in at least two instances, essentially

complete inversion of configuration at the carbon originally bonded to halogen.

It has been calculated that direct electron transfer from superoxide to an alkyl bromide (eq 11) is thermodynamically disallowed.<sup>21</sup>



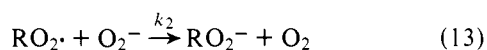
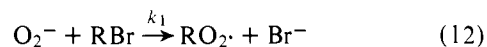
A more accurate consideration of the thermodynamics for this reaction reveals its distinct plausibility.<sup>28</sup> We have argued, however, that the high stereoselectivity observed in this reaction is inconsistent with the intermediacy of free alkyl radicals.<sup>18</sup> Furthermore, the structure of the alkyl group bonded to the halogen, the nature of the leaving group, and the polarity of the solvent all exert an influence on the course of the carbon–oxygen bond forming step which is consistent with a mechanism that involves an S<sub>N</sub>2 displacement at carbon. It follows that the initial reaction of superoxide with an alkyl halide produces an alkylperoxy radical, **2**. Three fundamentally



different types of mechanistic schemes can be envisioned for the subsequent conversion of this intermediate to product. In one, self-reaction leads to a tetroxide, homolysis of which results in the production of geminate alkoxy radicals and oxygen, followed either by geminate coupling to yield the dialkyl peroxide or diffusion from the cage to produce free alkoxy radical.<sup>29</sup>

A second would involve the self-reaction of secondary and primary peroxy radicals by way of a tetroxide intermediate proceeding through a cyclic transition state in which one of the  $\alpha$ -hydrogen atoms is transferred to give the observed products: ketone (aldehyde), alcohol, and oxygen.<sup>30,31</sup> Merritt and Johnson<sup>21</sup> have concluded that a concerted mechanism of this nature is largely responsible for the formation of alcohol and ketone (aldehyde) products produced in the reaction of alkyl halides with KO<sub>2</sub>. It is clear, however, from the data presented here that such a reaction need not be invoked to explain the formation of alcohol and ketone (aldehyde). Indeed, our results demonstrate that these products probably arise from the direct reaction of superoxide with the initially formed alkyl peroxide (Scheme I).

A third pathway consists of the one-electron reduction of alkylperoxy radicals to peroxy anions, which in a subsequent step combine with alkyl bromide to produce dialkyl peroxide. It is possible to demonstrate that this process is the only one occurring to any significant extent during the reaction of KO<sub>2</sub> with alkyl halides. This conclusion rests on the reasonable assumption that the rate of reduction of alkylperoxy radicals by superoxide is approximately equal to or greater than the rate of reduction of HO<sub>2</sub>· by O<sub>2</sub><sup>–</sup>, i.e.,  $k_2 \gtrsim 8.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>32</sup> The three reactions of interest are given in the equations



A consideration of the rate laws governing these reactions leads to the expression

$$\text{rate}_2 = \frac{k_2}{2k_3} \frac{[\text{O}_2^-]}{[\text{RO}_2\cdot]} \text{rate}_3$$

relating the relative rates of one-electron reduction (eq 13) and the bimolecular or self-reaction of two peroxy radicals (eq 14).



For all the reactions studied in this work the initial concentration of alkyl halide [RX] was ca. 0.2 M. Assuming a steady-state concentration of  $[\text{RO}_2^\cdot] \approx 1 \times 10^{-6} \text{ M}$ <sup>33</sup> and the literature values for  $k_1 = 1.5 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ <sup>27</sup> and  $k_3 = 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>30</sup> it follows that  $\text{rate}_2 \approx 10^3$  ( $\text{rate}_3$ ). Thus, we conclude that the bimolecular coupling of peroxy radicals plays a negligible role in the reaction of  $\text{KO}_2$  with alkyl halides. The elimination of this alternative mechanism leaves eq 13 as the only plausible description of the fate of the intermediate peroxy radicals. It should be recalled that this same conclusion was also reached from a consideration of the differences observed between the reactivity of alkyl bromides and tosylates with  $\text{KO}_2$  as discussed above.

Finally, the nature of the principal side reaction observed during the reaction of superoxide with alkyl halides and tosylates deserves brief comment. Dehydrohalogenation is, of course, a well-known side reaction that occurs in varying degree in displacement reactions involving alkyl halides. In light of the earlier discussion concerning the substantially increased basicity of bases in  $\text{Me}_2\text{SO}$ , it is not unreasonable to suspect that superoxide is sufficiently basic in  $\text{Me}_2\text{SO}$  to affect dehydrohalogenation of an alkyl halide or tosylate. More intriguing is the possibility that this reaction possesses for the convenient,



deliberate, and metered preparation of hydroperoxy radicals,  $\text{HO}_2^\cdot$ .

In conclusion, it is worthwhile to make explicit two general points concerning the reaction of potassium superoxide with alkyl halides and tosylates. First, while it is clear from the work reported in this paper that reaction of most alkyl halides does not proceed through an electron-transfer process involving free alkyl radicals, it is not clear that the reaction of all classes of alkyl halides will follow a related mechanism. In particular, electron-transfer reactions are notoriously sensitive to changes in the structure of the alkyl moiety and halide center, the recognized order of facility of such reactions being benzyl, allyl, tertiary > secondary > primary, and  $1 > \text{Br} > \text{Cl}$ .<sup>32</sup> Second, accepting the limitations on the generality of this reaction, the treatment of alkyl halides and tosylates with potassium superoxide provides a convenient method of generating free alkylperoxy radicals under mild conditions by a procedure that does not require autoxidation techniques. As such, the reaction merits further development as a probe for the study of this important class of free radicals.

## Experimental Section

**General.** Melting points were obtained using a Thomas-Hoover capillary melting point apparatus and are uncorrected. All boiling points are uncorrected. <sup>1</sup>H NMR spectra were determined on Varian T-60 or Jeol MH-100 spectrometers. Chemical shifts are reported in parts per million relative to internal tetramethylsilane. Coupling constants are in hertz. Infrared spectra were recorded in sodium chloride cells on a Perkin-Elmer Model 727B grating spectrometer. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU-7 mass spectrometer. Analytical GLC analyses were performed on Hewlett-Packard Model 5750 or Varian Model 1400 instruments equipped with flame ionization detectors and a Hewlett-Packard Model 3380A electronic integrator. Response factors were obtained with authentic samples. Analytical LC analyses were carried out on a Waters Model 6000A instrument equipped with UV and refractive index indicator. Response factors were determined with authentic samples. Unless otherwise indicated, all reagents were stored, weighed, and handled under a nitrogen atmosphere in a Vacuum Atmosphere glovebox. A static nitrogen atmosphere was employed in all reactions. Optical rotations were recorded as neat liquids in a 1-mm cell using a Perkin-Elmer Model 141 spectropolarimeter.

*n*-Hexyl iodide and bromide, *sec*-hexyl bromide, *sec*-butyl bromide, and 1-adamantyl bromide as well as the halides listed in Table IV were

purchased from commercial sources and used without further purification. Dimethyl sulfone and di-*tert*-butyl peroxide were also obtained from commercial distributors. Potassium superoxide was purchased from MSA (Evans City, Pa.). This material was ground to a fine powder in a mortar and pestle following preliminary dispersion in a Waring blender.

Dimethyl sulfoxide ( $\text{Me}_2\text{SO}$ ) was dried by distillation at reduced pressure (96 °C, 25 Torr) from calcium hydride and stored over activated molecular sieves (4 Å). Benzene was distilled under nitrogen from benzophenone-sodium.

**18-Crown-6 Ether.** Unless otherwise noted, 18-crown-6 ether was prepared as described by Gokel, Cram, Liotta, and Harris,<sup>34</sup> purified by two successive applications of the purification procedure described therein, and stored over  $\text{P}_2\text{O}_5$  under nitrogen, mp 39.5–41.0 °C (lit.<sup>34</sup> mp 36.5–38.0 °C).

**Di-*n*-hexyl peroxide,** prepared by the reaction of *n*-hexyl methanesulfonate and hydrogen peroxide,<sup>35</sup> had bp 59 °C (0.2 Torr) [lit.<sup>35</sup> bp 58 °C (0.5 Torr)]. *n*-Hexyl hydroperoxide was prepared in 42% yield as described by Williams and Mosher;<sup>36</sup> it had bp 42–43 °C (2.0 Torr) [lit.<sup>36</sup> bp 42–43 °C (2.0 Torr)].

**Di-*sec*-butyl peroxide,** prepared following the procedure of Welch, Homer, and Mosher,<sup>35</sup> had bp 52 °C (20 Torr) [lit.<sup>35</sup> bp 59 °C (50 Torr)].

***sec*-Butyl hydroperoxide** was prepared by the reaction of *sec*-butyl methanesulfonate and hydrogen peroxide as reported by Williams and Mosher,<sup>37</sup> bp 49 °C (1.0 Torr) [lit.<sup>37</sup> bp 41–42 °C (11.0 Torr)].

***n*-Hexyl, *sec*-hexyl, and *n*-octyl tosylates** were prepared from the corresponding alcohol by a recognized procedure.<sup>38</sup>

**(-)-(*R*)-2-Octyl bromide,**  $\alpha_{\text{D}}^{20} -41.56^\circ$ , 95.4% optically pure, was prepared from optically active (+)-(*S*)-2-octanol (Aldrich) according to the preferred literature procedure.<sup>39</sup>

**Preparation of  $\text{CH}_3(\text{CH}_2)_4\text{CD}_2\text{OH}$  and  $[\text{CH}_3(\text{CH}_2)_2\text{CD}_2\text{O}]_2$ .** Hexanol-*l,l*-*d*<sub>2</sub> was prepared in 87% yield from ethyl caproate (62.58 g, 0.434 mol) by treatment with lithium aluminum deuteride by a procedure analogous to that described by Max and Deatherage<sup>40</sup> for the preparation of octanol-*l,l*-*d*<sub>2</sub>. Hexanol-*l,l*-*d*<sub>2</sub> was converted into the corresponding peroxide by the procedure outlined above.

**Procedures for Reactions.** Similar procedures were used to carry out the reactions examined. Representative procedures for each reaction follow.

**Reaction of Potassium Superoxide with *n*-Hexyl Bromide (1) in  $\text{Me}_2\text{SO}$ .** In a typical experiment 0.711 g (10.0 mmol) of  $\text{KO}_2$  was placed in a 100-mL flask equipped with a Teflon-coated magnetic stirrer bar. The vessel was capped with a rubber septum and 17 mL of  $\text{Me}_2\text{SO}$  added by syringe before adding 3.0 mL of a 0.33 M solution of 18-crown-6 in  $\text{Me}_2\text{SO}$  followed by 0.550 g (3.33 mmol) of *n*-hexyl bromide. The resulting mixture was stirred for 1 h, then treated with 20 mL of 95% methanol containing ~1 mL of 9 M  $\text{H}_2\text{SO}_4$ . Known amounts of *n*-decane and bromobenzene were added as internal standards along with methylene chloride (7.5 mL), added to provide a homogeneous mixture. This mixture was analyzed by LC for di-*n*-hexyl peroxide, 1-hexanol, 1-hexanal, and 1-hexene on a  $10 \times 0.25$  in. column of  $\mu$ -Bondapak-C<sub>18</sub> (Waters Associates) using respectively 95/5, 70/30, 60/40, and 65/35 methanol-water as eluent.

To determine the yield of unreacted *n*-hexyl bromide, a separate reaction was carried out and worked up by addition of ca. 1 mL of 9 M  $\text{H}_2\text{SO}_4$  followed by the addition of methylene chloride and a known amount of *n*-decane as internal standard. The resulting reaction mixture was transferred to a separatory funnel and a solution (20 mL) of saturated brine added before the contents of the flask was extracted with four 10-mL portions of petroleum ether (bp 30–60 °C). The combined ether extracts were dried ( $\text{MgSO}_4$ ) and analyzed by GLC on a 10 ft  $\times$  0.125 in. column of 3% SE-30 on 80/100 Chromosorb Q.

To determine the yield of dimethyl sulfone, the above reaction was repeated adding, in addition to the reagents already described, a known amount of di-*n*-propyl sulfone as an internal standard. The resulting mixture was stirred vigorously at room temperature. Aliquots (0.20 mL) were removed by syringe at selected intervals and analyzed by GLC on a 3 ft  $\times$  0.25 in. column of 20% Carbowax 20M on Chromosorb W.

Oxygen evolution studies were performed in a flame-dried, 50-mL flask equipped with a Teflon-coated stirrer bar and a side arm connected by a length of flexible Tygon tubing to a mercury-filled gas buret. Reagents were added in the amounts described above and the flask was then stoppered with a rubber septum. With vigorous stirring,

Table V

substrate	LC Conditions for Reactions in Benzene internal standard	column	solvent
di- <i>n</i> -hexyl peroxide	di- <i>n</i> -butyl ether	$\mu$ -Porasil	C <sub>6</sub> H <sub>6</sub>
di- <i>sec</i> -hexyl peroxide	di- <i>n</i> -butyl ether	$\mu$ -Porasil	C <sub>6</sub> H <sub>6</sub>
1-hexanol	2-butanol	Corasil 11	C <sub>6</sub> H <sub>6</sub>
2-hexanol	<i>tert</i> -butyl alcohol	Corasil 11	C <sub>6</sub> H <sub>6</sub>
hexanal	di- <i>n</i> -butyl ether	$\mu$ -Porasil	C <sub>6</sub> H <sub>6</sub>
2-hexanone	di- <i>n</i> -butyl ether	$\mu$ -Porasil	C <sub>6</sub> H <sub>6</sub>
<i>n</i> -hexyl tosylate	benzotrile	$\mu$ -Porasil	CHCl <sub>3</sub>
<i>sec</i> -hexyl tosylate	benzotrile	$\mu$ -Porasil	CHCl <sub>3</sub>
<i>sec</i> -butyl tosylate	di- <i>n</i> -butyl ether	$\mu$ -Porasil	C <sub>6</sub> H <sub>6</sub>
2-butanol	1-hexanol	Corasil 11	C <sub>6</sub> H <sub>6</sub>
2-butanone	1-hexanol	$\mu$ -Porasil	CHCl <sub>3</sub>

substrate	GLC Conditions for Reactions in Benzene internal standard	column
<i>sec</i> -butyl bromide	<i>n</i> -octane	0.125 in. $\times$ 10 ft 10% Carbowax on 80/100 Chromosorb Q
<i>n</i> -hexyl bromide	<i>n</i> -decane	0.125 in. $\times$ 10 ft 3% SE-30
butenes	<i>n</i> -heptane	0.125 in. $\times$ 10 ft 10% Carbowax
hexenes	cyclopentane	0.125 in. $\times$ 10 ft 3% SE-30
1-bromoadamantane	<i>n</i> -tridecane	0.125 in. $\times$ 6 ft UCW 98

*n*-hexyl bromide (0.550 g, 3.33 mmol) was added by syringe. The resulting evolution of oxygen was monitored by the volume of mercury displaced. All readings were corrected for barometric pressure. This value was converted to millimoles of oxygen using the perfect gas equation.

**Reaction of Potassium Superoxide with *n*-Hexyl and *sec*-Hexyl Tosylate in Me<sub>2</sub>SO.** Procedures similar to those described for the reaction of KO<sub>2</sub> with *n*-hexyl bromide were employed in the reaction of KO<sub>2</sub> with *n*-hexyl and *sec*-hexyl tosylates in Me<sub>2</sub>SO. Analysis for recovered tosylate was performed by LC on  $\mu$ -Bondapak C<sub>18</sub> using 70/30 methanol-water and bromobenzene as internal standard.

**Reaction of Potassium Superoxide with Di-*n*-hexyl Peroxide in Me<sub>2</sub>SO.** In a procedure similar to that described above, Me<sub>2</sub>SO (19 mL) and 0.90 mL of a 0.33 M solution of 18-crown-6 in Me<sub>2</sub>SO was added to 0.213 g (3.00 mmol) of powdered KO<sub>2</sub> contained in a 100-mL flask equipped with a Teflon-coated stirrer bar and capped with a rubber septum. Di-*n*-hexyl peroxide (0.605 g, 3.00 mmol) was added by syringe and the resulting reaction mixture stirred for a selected period of time. Workup and analysis procedures were equivalent to those described above.

**Reaction of Potassium Superoxide with *n*-Hexyl Iodide in Me<sub>2</sub>SO.** In a typical experiment, *n*-hexyl iodide (0.706 g, 3.33 mmol) and KO<sub>2</sub> (0.711 g, 10.0 mmol) were allowed to react as described above. Analytical conditions (LC and GLC) were equivalent to those already outlined.

**Reaction of Potassium Superoxide with 2-Bromobutane in Me<sub>2</sub>SO.** In a typical experiment, 0.711 g (10.0 mmol) of powdered potassium superoxide was placed in a flame-dried, 100-mL round-bottom flask equipped with a Teflon-coated magnetic stirrer bar. The flask was capped with a rubber septum and flushed with nitrogen before adding Me<sub>2</sub>SO (17 mL) by syringe. With stirring, a solution of 18-crown-6 in Me<sub>2</sub>SO (3.0 mL, 0.33 M) followed by 0.456 g (3.33 mmol) of 2-bromobutane were added by syringe. The resulting mixture was stirred for 1 h, then treated with 20 mL of 95% methanol containing  $\sim$ 1 mL of 9 M H<sub>2</sub>SO<sub>4</sub>. A known amount of 1-butanol and bromobenzene were added as internal standards along with methylene chloride (7.5 mL), added to provide a homogeneous mixture. This mixture was analyzed by LC for di-*sec*-butyl peroxide, 2-butanol, and 2-butanone on a 10  $\times$  0.25 in.  $\mu$ -Bondapak-C<sub>18</sub> column (Waters Associates) using respectively 75, 30, and 30% methanol-water solutions as eluent.

The yield of unreacted 2-bromobutane was obtained by repeating the above reaction followed by a workup consisting of the addition of 1 mL of 9 M H<sub>2</sub>SO<sub>4</sub> followed by 7.5 mL of methylene chloride. A known amount of *n*-octane was added as internal standard, and the reaction mixture transferred to a separatory funnel. Saturated brine solution (20 mL) was added to the separatory funnel and the mixture extracted with four 10-mL portions of petroleum ether (bp 30-60 °C). The combined ether extracts were dried (MgSO<sub>4</sub>) and analyzed by GLC on a 10 ft  $\times$  0.125 in. column of 3% SE-30 on 80/100 chromosorb Q.

The yield of butene(s) was determined as follows. Powdered potassium superoxide (0.711 g, 10.0 mmol) was placed in a flame-dried 100-mL flask equipped with a Teflon-coated magnetic stirrer bar. The flask was capped with a rubber septum and 17 mL of Me<sub>2</sub>SO added by syringe followed by 3.0 mL of a 0.33 M solution of 18-crown-6 in Me<sub>2</sub>SO. The flask was then placed under a positive pressure of nitrogen and the rubber septum replaced with a fresh septum which was then securely wired down. To the flask was then added by syringe 0.456 g (3.33 mmol) of 2-bromobutane and the reaction mixture stirred for 1 h as a sealed system. Methylene chloride (5.0 mL) was added by syringe followed by a known amount of *n*-heptane as internal standard. The reaction was immediately analyzed by GLC using a 10 ft  $\times$  0.125 in., 10% Carbowax on 80/100 GCQ.

The yields of Me<sub>2</sub>SO<sub>2</sub> and oxygen evolution were obtained by procedures equivalent to those described for similar determinations carried out for the reaction of KO<sub>2</sub> with *n*-hexyl bromide in Me<sub>2</sub>SO.

**Reaction of Potassium Superoxide with Di-*sec*-butyl Peroxide in Me<sub>2</sub>SO.** The reaction of KO<sub>2</sub> with (*sec*-C<sub>4</sub>H<sub>9</sub>O)<sub>2</sub> in Me<sub>2</sub>SO and subsequent analyses were carried out by procedures equivalent to those described for the reaction of 2-bromobutane with KO<sub>2</sub> in Me<sub>2</sub>SO.

**Reaction of Potassium Superoxide and 2-Butanone in Me<sub>2</sub>SO.** In a typical experiment, 0.711 g (10.0 mmol) of powdered potassium superoxide was placed in a flame-dried 100-mL round-bottom flask equipped with a Teflon-coated magnetic stirrer bar and capped with a rubber septum. To the flask were then added by syringe 17.0 mL of Me<sub>2</sub>SO, 3.0 mL of a 0.33 M solution of 18-crown-6 in Me<sub>2</sub>SO, and 0.239 g (3.33 mmol) of 2-butanone. The resulting mixture was stirred for 1 h, then treated with 20 mL of 95% methanol containing 1 mL of 9 M H<sub>2</sub>SO<sub>4</sub>. A known amount of 1-butanol was added as internal standard along with methylene chloride (7.5 mL), added to provide a homogeneous mixture. This mixture was analyzed by LC for recovered 2-butanone using a 10  $\times$  0.25 in.  $\mu$ -Bondapak-C<sub>18</sub> column employing 30% methanol-water as eluent.

**Reaction of Potassium Superoxide and 1-Bromoadamantane in Me<sub>2</sub>SO.** Into a flame-dried 50-mL round-bottom flask equipped with a Teflon-coated magnetic stirrer bar was placed 0.711 g (10.0 mmol) of powdered potassium superoxide. The flask was capped with a rubber septum and flushed with nitrogen. Then 17.0 mL of Me<sub>2</sub>SO and 3.0 mL of a 0.33 M solution of 18-crown-6 in Me<sub>2</sub>SO were added by syringe, followed by 0.7197 g (3.33 mmol) of 1-bromoadamantane. The resulting mixture was stirred for 24 h, then poured into a 125-mL Erlenmeyer flask containing 20 mL of water. The reaction flask was rinsed with 30 mL of benzene and the rinsings added to the Erlenmeyer flask along with a known amount of *n*-tridecane as an internal standard and 10 mL of a solution of saturated brine. The benzene layer was separated, dried over MgSO<sub>4</sub>, and analyzed by GLC on a 6 ft  $\times$  0.125 in. UCW-98 on 80/100 Chromosorb W column.

**Reaction of Potassium Superoxide with Dimethyl Sulfone in Me<sub>2</sub>SO.** Into a flame-dried, 50-mL flask equipped with a Teflon-coated

magnetic stirrer bar was placed 0.213 g (3.00 mmol) of powdered potassium superoxide. The flask was capped with a rubber septum and 19.0 mL of Me<sub>2</sub>SO added by syringe before 0.9 mL of a 0.33 M solution of 18-crown-6 in Me<sub>2</sub>SO was added followed by 0.0941 g (1.00 mmol) of Me<sub>2</sub>SO<sub>2</sub> and a known amount of di-*n*-propyl sulfone as internal standard. The resulting mixture was stirred and 0.20-mL aliquots removed at 1-h intervals and immediately analyzed without workup for recovered Me<sub>2</sub>SO<sub>2</sub> by GLC on a 3 ft × 0.25 in. 20% Carbowax on Chromosorb W column.

**Reactions in Benzene.** The same general procedures employed for reactions carried out in Me<sub>2</sub>SO were also used for reactions carried out in benzene. All reactions were run in 20 mL of benzene containing 10 mol % 18-crown-6 ether, based on superoxide. Reactions were worked up by adding ~1 mL of 9 M H<sub>2</sub>SO<sub>4</sub> followed by the appropriate internal standards. Analysis for various products was carried out under the conditions in Table V.

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## References and Notes

- (1) A. M. Michelson, J. M. McCord, and I. Fridovich, "Superoxide and Superoxide Dismutases", Academic Press, New York, N.Y., 1977.
- (2) Cf. E. W. Kellogg, III, and I. Fridovich, *J. Biol. Chem.*, **252**, 6721 (1977); B. Halliwell, *Eur. J. Biochem.*, **55**, 355 (1975); G. A. Hamilton, R. Daniel Libby, and C. R. Hartzell, *Biochem. Biophys. Res. Commun.*, **55**, 333 (1973); J. F. Allen, *ibid.*, **66**, 36 (1975).
- (3) For a review of pertinent early literature, see (a) E. Lee-Ruff, *Chem. Soc. Rev.*, **2**, 195 (1977); (b) J. A. Fee and J. S. Valentine in "Superoxide and Superoxide Dismutases", A. M. Michelson, J. M. McCord, and I. Fridovich, Ed., Academic Press, New York, N.Y., 1977, p. 19.
- (4) J. Chevalet, F. Rouelle, L. Gierst, and J. P. Lambert, *J. Electroanal. Chem.*, **39**, 201 (1972); J. Divisek and B. Kastening, *ibid.*, **65**, 603 (1975); B. Kastening and G. Kazemifard, *Ber. Bunsenges. Phys. Chem.*, **74**, 551 (1970); see also ref 3b.
- (5) G. Czapski and L. M. Dorfman, *J. Phys. Chem.*, **68**, 1169 (1964); J. L. Weeks and J. Rabani, *ibid.*, **70**, 2100 (1966); D. Behar et al., *ibid.*, **74**, 3209 (1970).
- (6) D. Dolman and R. Stewart, *Can. J. Chem.*, **45**, 911 (1967); R. Stewart and J. P. O'Donnell, *ibid.*, **42**, 1681 (1964); K. Bowden, A. Buckley, and R. Stewart, *J. Am. Chem. Soc.*, **88**, 947 (1966).
- (7) D. L. Maricle and W. G. Hodgson, *Anal. Chem.*, **37**, 1562 (1965).
- (8) J. San Filippo, Jr., C.-I. Chern, and J. S. Valentine, *J. Org. Chem.*, **41**, 1077 (1976).
- (9) C.-I. Chern and J. San Filippo, Jr., *J. Org. Chem.*, **42**, 178 (1977).
- (10) J. San Filippo, Jr., L. J. Romano, C.-I. Chern, and J. S. Valentine, *J. Org. Chem.*, **41**, 392 (1976); for a discussion of the chemical properties of superoxide, see ref 3b.
- (11) J. S. Valentine and A. B. Curtis, *J. Am. Chem. Soc.*, **97**, 224 (1975).
- (12) (a) J. A. Howard in "Free Radicals", J. K. Kochi, Ed., Wiley, New York, N.Y., 1972, p. 38. (b) M. J. Gibian and T. Ungermaun, *J. Org. Chem.*, **41**, 2500 (1976); this paper contains a number of experimental and conceptual errors (see text for discussion).
- (13) R. Curci and J. O. Edwards in "Organic Peroxides", Vol. 1, D. Swern, Ed., Wiley, New York, N.Y., 1970, Chapter IV.
- (14) O. L. Mageli and C. S. Sheppard in ref 13, Chapter 1.
- (15) W. A. Nugent, F. Bertini, and J. K. Kochi, *J. Am. Chem. Soc.*, **96**, 4945 (1974).
- (16) For a discussion of the reaction of superoxide with *tert*-butyl hydroperoxide, see J. W. Peters and C. S. Foote, *J. Am. Chem. Soc.*, **98**, 873 (1976).
- (17) The apparent differences in reactivity between iodide and bromide in this instance are consistent with the relative rates of reaction of iodide and bromide with hydrogen peroxide in neutral aqueous solution at 25 °C ( $k_I/k_{Br} = 3.0 \times 10^4$ ).<sup>13</sup>
- (18) (a) J. San Filippo, Jr., C.-I. Chern, and J. S. Valentine, *J. Org. Chem.*, **40**, 1678 (1975); (b) S. Kim, R. DiCosomo, and J. San Filippo, *Anal. Chem.*, submitted.
- (19) R. Johnson and J. Nidy, *J. Org. Chem.*, **40**, 1679 (1975).
- (20) (a) E. J. Corey, K. C. Nicolaou, M. Shibusaki, and C. S. Shiner, *Tetrahedron Lett.*, 8183 (1975); (b) R. Dietz, E. J. Forno, B. E. Lacombe, and M. E. Power, *J. Chem. Soc. B*, 816 (1970); V. M. Schmidt and H. Bipp, *Z. Anorg. Allg. Chem.*, **303**, 190 (1960).
- (21) M. V. Merritt and R. A. Johnson, *J. Am. Chem. Soc.*, **99**, 3713 (1977).
- (22) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972).
- (23) C. J. Pedersen, *J. Am. Chem. Soc.*, **92**, 356 (1970).
- (24) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).
- (25) A. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill, New York, N.Y., 1962, pp 13-31.
- (26) C. L. Liotta, E. E. Grisdale, and H. P. Hopkins, Jr., *Tetrahedron Lett.*, 4205 (1975).
- (27) W. C. Danen and R. J. Warner, *Tetrahedron Lett.*, 989 (1977).
- (28) This conclusion derives from a consideration of the following thermochemical data ("Handbook of Chemistry and Physics", 43rd ed., Chemical Rubber Publishing Co., Cleveland, Ohio; I. Prigogine and R. Defay, "Chemical Thermodynamics", Wiley, New York, N.Y., 1962, p 102):
 

	$KO_2 + CH_3Br \rightarrow O_2 + CH_3 + KBr$				
$\Delta G^\circ$ (kcal/mol)	-56	-5.9	0	21	-90

$$\Delta G^\circ_{\text{reaction}} \sim -7 \text{ kcal/mol}$$

This calculation neglects the free energy of solution of the species involved. Clearly, this is a valid assumption for the neutral species CH<sub>3</sub>Br, O<sub>2</sub>, and CH<sub>3</sub>. An examination of the free energy of dissolution in water for a variety of potassium salts of monovalent anions similar in size to O<sub>2</sub><sup>-</sup> reveals that they are substantially similar (ca. -85 ± 3 kcal/mol) and, in general, somewhat less than the corresponding value for potassium bromide. It seems reasonable to conclude that the difference between the free energy of solution for KO<sub>2</sub> and KBr is likely to be small in magnitude and such that it will reinforce the above conclusion.

- (29) D. Lindsay et al., *Can. J. Chem.*, **51**, 870 (1973), and references cited therein.
- (30) K. U. Ingold, *Acc. Chem. Res.*, **2**, 1 (1969).
- (31) J. A. Howard in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 1.
- (32) "Specific Rates of Reaction of Transients from Water in Aqueous Solution", *Natl. Stand. Ref. Data. Ser., Natl. Bur. Stand.*, **No. 43** (1973); "Reactivity of the Hydroxyl Radical and Related Species in Aqueous Solution", *ibid.*, **No. 46** (1973).
- (33) Steady-state treatment of the processes outlined in eq 12-14 leads to the expression

$$[RO_2] = \frac{-k_2[O_2^-] + \sqrt{k_2^2[O_2^-]^2 + 8k_3k_1[O_2^-][RBr]}}{4k_3}$$

- Assuming  $[RBr] \approx 0.1 \text{ M}$ ,  $[O_2^-] \approx 0.01 \text{ M}$ , and  $k_2 = 8.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , the steady-state value of  $[RO_2] \approx 1 \times 10^{-6} \text{ M}^{-1}$  leads to the relationship  $\text{rate}_2 \approx 10^3 \text{ rate}_3$ . Examination of this steady-state solution reveals that the relative difference between  $\text{rate}_2$  and  $\text{rate}_3$  is (1) only increased with higher values of  $k_2$  and (2) relatively insensitive to the values of  $[RBr]$  and  $[O_2^-]$ .
- (34) G. W. Gokel, D. J. Cram, C. L. Liotta, H. P. Harris, and F. L. Cook, *J. Org. Chem.*, **39**, 2445 (1974).
  - (35) F. Welch, H. R. Williams, and H. S. Mosher, *J. Am. Chem. Soc.*, **77**, 551 (1955).
  - (36) H. R. Williams and H. S. Mosher, *J. Am. Chem. Soc.*, **76**, 2984 (1954).
  - (37) H. R. Williams and H. S. Mosher, *J. Am. Chem. Soc.*, **76**, 2987 (1954).
  - (38) A. Streitwieser, Jr., T. D. Walsh, and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, **87**, 3682 (1965).
  - (39) J. San Filippo, Jr., and L. J. Romano, *J. Org. Chem.*, **40**, 1514 (1975).
  - (40) R. A. Max and F. E. Deatherage, *J. Am. Oil Chem. Soc.*, 110 (1951).