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mmol) of CF_3OF. The concentrated reaction mixture showed ^{19}F NMR signals at ϕ 70 and 146. Chromatography revealed the presence of a complex mixture from which fluorenone (0.16 g, 48%) was isolated; melting point and mixture melting point with authentic sample were 80–83 °C. ^1H NMR and IR spectra were identical with those of an authentic sample.

VI. Diazepam (16),[26] **7-Chloro-1-methyl-2*H*-1,4-benzodiazepin-2-one**. A solution of **16** (0.5 g, 1.75 mmol) in 40 mL of acetone was allowed to react at −50 °C with 0.2 g (1.9 mmol) of CF_3OF. The concentrated reaction mixture gave 0.43 g of black crystals which after recrystallization from benzene–hexane gave **17** as tan crystals (0.3 g, 57%): mp 152–156 °C; ^1H NMR δ 6.9–7.6 (m, 8 H, aromatic), 4.6 (s, 2 H, NH_2), 3.4 (s, 2 H, CH_2), 1.6 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 134.0 (aromatic s), 244 (C=O), 49.0 (CH_2), 30 (CH_3); IR (KBr) 1640 and 1680 (C=O) cm^{-1}. Anal. Calcd for $C_{16}H_{15}N_2O_2Cl$: C, 63.6; H, 4.97; N, 9.27. Found: C, 63.5; H, 4.84; N, 9.50.

Acknowledgment. This research was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. Funds for the purchase of ^{19}F NMR accessories were obtained from the Research Corporation.

Registry No. 1, 530-48-3; **2**, 73037-93-1; **2** alcohol, 337-72-4; **3**, 73037-94-2; **4**, 379-83-9; **5**, 390-75-0; **6**, 73037-95-3; **6** alcohol, 337-53-1; **7**, 7151-64-6; **8**, 73037-96-4; **8** alcohol, 73037-97-5; **10**, 73037-98-6; **11**, 486-25-9; **12**, 50-48-6; **13**, 73037-99-7; **14**, 574-66-3; **15**, 10183-82-1; **16**, 439-14-5; **17**, 36020-94-7; **18**, 73048-41-6; CF_3OF, 373-91-1; benzanilide, 93-98-1.

Reactions of Superoxide with Peroxides

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Received September 17, 1979

The reactions of superoxide with *tert*-butyl hydroperoxide and 98% H_2O_2 have been studied in aprotic solvents. In benzene solvent, the proton-catalyzed disproportionation of superoxide followed by the base-catalyzed disproportionation of H_2O_2 appear to be the only reactions to occur. In acetonitrile, peroxy anions react with the solvent to form, ultimately, acetamide. Reactions of superoxide with diacyl peroxides are rather complex, but this reacting system produces intermediates capable of epoxidation of a number of olefins. Reactions of superoxide with acid chlorides and anhydrides in the presence of olefins also produce epoxides. Plausible mechanisms for these reactions are discussed.

The organic chemistry of superoxide ion, $O_2^{-}\cdot$ has been an area of intense interest in recent years. Examination of the biochemical[1,2] or the organic chemical[3,4] literature in this area, including a very recent excellent review,[5] shows that the reactions of superoxide with a large number of substrates proceed with the formation of a variety of peroxides, either as intermediates or as final products. Indeed, the initial experiments conducted in this work, aimed at elucidating the mechanism of nucleophilic attack by superoxide on a number of organic substrates, indicated that an understanding of the reactions between superoxide and various peroxidic species was crucial to the understanding of superoxide chemistry in general. The work reported here represents an attempt to elucidate the mechanisms of the direct reactions of superoxide with several peroxidic species.[6] For mechanistic reasons, the reactions of superoxide with protic peroxides will be discussed separately from the reactions with diacyl peroxides.

Results and Discussion

At the time of the initiation of this study, the most commonly written reaction in the literature[1-3,7] between superoxide and peroxides was the Haber–Weiss redox reaction (eq 1).

$$H_2O_2 + O_2^{-}\cdot \rightarrow O_2 + HO\cdot + HO^- \tag{1}$$

More recent studies,[8-13] including the present work, indicate that eq 1 is, at best, too slow to compete with more favorable processes. It now appears that the only reaction involving superoxide in the presence of protic peroxides in aprotic solvents is the proton-catalyzed disproportionation sequence (eq 2 and 3).

$$O_2^{-}\cdot + ROH \rightleftarrows HOO\cdot + RO^- \tag{2}$$

$$HOO\cdot + O_2^{-}\cdot \rightleftarrows O_2 + HOO^- \tag{3}$$

All of the data obtained in this work, which are summarized in Table I, can be explained by using only eq 2 and 3 plus subsequent reactions of RO^- or HOO^-, if any. R in eq 2 and 3 can be H, HO, *t*-BuO, or CH_3COO.

Addition of an excess of water to KO_2 suspended in 0.1 M 18-crown-6 ether in benzene causes an immediate re-

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[1] I. Fridovich, *Acc. Chem. Res.*, **5**, 321 (1972); *Adv. Enzymol.*, **41**, 35 (1974).

[2] A. M. Michelson, J. M. McCord, and I. Fridovich, Eds., "Superoxide and Superoxide Dismutases", Academic Press, New York, 1977.

[3] E. Lee-Ruff, *Chem. Soc. Rev.*, **6**, 195 (1977).

[4] W. C. Danen, J. Warner, and R. L. Arudi, *Am. Chem. Soc. Symp. Ser., No. 69*, 224-57 (1978).

[5] D. T. Sawyer and M. J. Gibian, *Tetrahedron*, **35**, 1471 (1979).

[6] J. P. Stanley, 177th National Meeting of the American Chemical Society, Honolulu, HI, April 1979, Abstract ORGN-66.

[7] J. W. Peters and C. S. Foote, *J. Am. Chem. Soc.*, **98**, 873 (1976).

[8] J. Weinstein and B. H. J. Bielski, *J. Am. Chem. Soc.*, **101**, 58 (1979).

[9] J. M. McCord and E. D. Day, *FEBS Lett.*, **86**, 139 (1978).

[10] B. Halliwell, *FEBS Lett.*, **72**, 8 (1976).

[11] W. C. Danen and R. L. Arudi, *J. Am. Chem. Soc.*, **100**, 3944 (1978).

[12] D. T. Sawyer, M. J. Gibian, M. M. Morrison, and E. T. Seo, *J. Am. Chem. Soc.*, **100**, 627 (1978).

[13] M. J. Gibian and T. Ungermann, *J. Am. Chem. Soc.*, **101**, 1291 (1979).

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Table I. Reactions of Superoxide with Protic Peroxides

reaction	base, mmol	substrate, mmol	solvent^a	reaction time, min	products, mmol
1	KO_2, 2	large excess H_2O	benzene	<1	O_2, 1.0; H_2O_2, 1.0
2	KO_2, 2	H_2O,^{b} <3	benzene		O_2, 1.4; no H_2O_2
3	KO_2, 2	H_2O_2,^{c} 2	benzene	30	O_2, 2.2; no H_2O_2
4	KO_2, 2	H_2O_2,^{c} 3.8	benzene	45	O_2, 3.8; no H_2O_2
5	KOH, 1	H_2O_2,^{c} 3.2	benzene	45	O_2, 1.5; no H_2O_2
6	KOH, 1	H_2O_2,^{b} 2	benzene	30	O_2, 0.9; no H_2O_2
7	KO_2, 2	*t*-BuOOH, 2	benzene	20–40	O_2, 1.5; *t*-BuOO$^-$, 2
8	KO_2, 2	*t*-BuOOH, 4	benzene	20–40	O_2, 1.3; *t*-BuOO$^-$ (H), 4
9	KO_2, 1.8	*t*-BuOOH, 2	CH_3CN	20	O_2, 0.70; -00-,^{d} 0.95; CH_3CONH_2, 0.95; *t*-BuOH,^{e} 1.86
10	KOH, 1.2	*t*-BuOOH, 2	CH_3CN	20	-00-,^{c} 0.9; CH_3CONH_2,^{f} 0.5
11	KOH, 0.2	H_2O_2, 1	CH_3CN	15	O_2, 0.5; no -00-; CH_3CONH_2, 0.38
12	KO_2, 0.8	H_2O_2, 1	CH_3CN	15	O_2, 0.55; -00-,^{d} 0.2; CH_3CONH_2, 0.49
13	KO_2, 1	H_2O_2, 3.2	CH_3CN	15	O_2, 0.48; -00-,^{d} 0.32; CH_3CONH_2, 0.21
14	KO_2, 2	CH_3CO_3H, 2	benzene	15	O_2, 2.4; no -00-

[a] 10 mL of 0.1 M 18-crown-6 in indicated solvent. [b] Added slowly in 2-μL portions. [c] 98% H_2O_2 was used to prepare a "nonaqueous" solution in dry dioxane. [d] The exact nature of the peroxidic species is unknown, but was observed to react with KI in acetic acid faster than di-*tert*-butyl peroxide, but slower than H_2O_2 (see Experimental Section). [e] 0.1 mmol or less of acetone also formed. [f] Some *t*-BuOH and a trace of acetone detected.

action in which 1 mol of O_2 and 1 mol of H_2O_2 are produced per mole of $O_2^-\cdot$, as predicted from eq 2 and 3 (entry 1, Table I). If, however, the reaction is carried out by adding very small amounts of water over a period of time, the apparent stoichiometry of the reaction changes (as seen in entry 2, Table I), which indicates that the H_2O_2 presumably formed in the disproportionation reaction is unstable under these reaction conditions. That this is indeed the case can be seen from entries 3–6 in Table I. Equation 1 predicts the products for entry 4 in Table I to be 2 mmol of O_2 plus 1.8 mmol of H_2O_2; eqs 2 and 3 predict the products to be 1 mmol of O_2 plus 4.8 mmol of peroxide; both predictions are contrary to observation. Entries 5 and 6 in Table I clearly show that H_2O_2 is unstable to base in this nonaqueous solvent system. Furthermore, observation of the course of the reaction between superoxide and H_2O_2 shows that the reaction appears to take place in two stages. In the first, faster stage, about one-half of the O_2 is evolved and the yellow color of superoxide completely disappears. The second stage of the reaction displays a slower rate of O_2 evolution which is identical with the rate observed in the reaction of KOH with H_2O_2 (see Experimental Section). At about the midpoint of the second stage of the $O_2^-\cdot + H_2O_2$ reaction or of the KOH + H_2O_2 reaction, a transient yellow color was usually, but not always, observed.[14] The heterogeneous nature of this system makes these observed rate differences less meaningful than one would like. Immediately after these findings were made, Sawyer et al.[15] published the results of a related study in which H_2O_2 was reacted with tetra-*n*-propylammonium hydroxide in pyridine, and superoxide was observed as a transient intermediate. (A similar finding has been recently reported by other workers.[16]) Sawyer et al. explained their results as a base-catalyzed disproportionation of H_2O_2 via the following reaction (eq 4). The $O_2^-\cdot$ thus formed

$$HOO^- + H_2O_2 \rightarrow O_2^-\cdot + \cdot OH + H_2O \qquad (4)$$

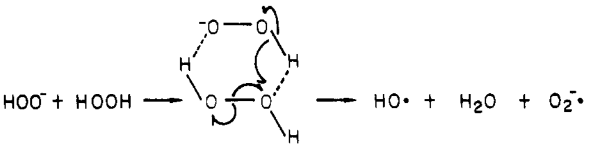
then reacts with water or H_2O_2 as in eq 2 and 3 or with HO· as in eq 5.[15]

$$HO\cdot + O_2^-\cdot \rightarrow HO^- + O_2 \qquad (5)$$

The previous authors did not speculate on the mechanism of eq 4 other than to note that the greatly increased rate in pyridine over that observed in water might be due to the enhanced nucleophilicity of HOO^- in aprotic solvents. A mechanism involving nucleophilic attack of H_2O_2 by HOO^- can be represented as in eq 6.

$$HOO^- + HOOH \rightarrow HO^- + HOOOH \rightarrow HO\cdot + HOO\cdot \rightleftarrows H^+ + O_2^-\cdot \qquad (6)$$

Another mechanism can be envisioned which involves the formation of a cyclic hydrogen-bonded intermediate (eq 7), which might be unlikely to form in protic media because of hydrogen bonding to solvent.



(7)

Although there is no direct evidence to favor either mechanism, the author favors eq 7 somewhat because it appears to explain the failure of *t*-BuOOH to undergo a similar reaction (vide infra).

The reactions of superoxide with *t*-BuOOH in benzene, entries 7 and 8 in Table I, can be explained by eq 2 and 3 (R = *t*-BuO), followed by the decomposition of the hydrogen peroxy anion formed as in eq 3 to O_2 and H_2O via eq 4 and 5. *t*-BuOO$^-$ is stable in benzene solution. As recently reported by other workers,[13] *t*-BuOO$^-$ reacts with acetonitrile to form a perimidic ester[17] which presumably decomposes to produce acetamide, *tert*-butyl alcohol, and acetone (entries 9 and 10 in Table I). Hydrogen peroxide undergoes a similar nitrile-addition reaction (entries 11–13, Table I) as expected from earlier work.[17] These findings of acetonitrile solvent participation in the superoxide/*t*-BuOOH reaction resolve a previous report[7,18] that was once interpreted as evidence for the Haber–Weiss reaction.

The reaction of superoxide with peracetic acid in benzene (entry 14, Table I) can be explained by the acid-catalyzed disproportionation of superoxide, followed by the base-catalyzed disproportionation of both the peracetic acid and of the H_2O_2 formed in the former reaction. The base-induced decomposition of peracids is well known,[19]

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[14] Addition of water to this "yellow stage" of the reaction produced immediate O_2 evolution and a color change to white, characteristic of $O_2^-\cdot$ disproportionation.

[15] J. L. Roberts, M. M. Morrison, and D. T. Sawyer, *J. Am. Chem. Soc.*, **100**, 329 (1978).

[16] M. A. Symonyan and R. M. Nalbandyan, *Biochim. Biophys. Acta.*, **583**, 279 (1979).

[17] K. B. Wiberg, *J. Am. Chem. Soc.*, **75**, 396 (1963); G. B. Payne, P. H. Deming, and P. H. Williams, *J. Org. Chem.*, **26**, 659 (1961).

[18] M. J. Gibian and T. Ungermann, *J. Org. Chem.*, **41**, 2300 (1976).

and it is worth noting that the previously established mechanism for this reaction involves nucleophilic attack of a peracid anion on the carbonyl carbon (90%) and on the peroxide oxygen (10%) of a peracid molecule. The latter process is analogous to eq 6.

Thus, the data obtained in this work indicate that superoxide reacts with protic peroxides primarily as a base.[12] In view of the rather strong effective basicity of superoxide,[12,20] it is perhaps not surprising that other potential reactions (i.e., the Haber–Weiss reaction) cannot compete effectively. Much of the misinterpretation of these reactions by earlier workers can be explained as a failure to understand the subsequent reactions of various peroxy anions in these systems.

Diacyl Peroxides. On the basis of the known or suspected chemistry of superoxide, one might expect, a priori, reaction with diacyl peroxides to occur by either electron transfer (eq 8), similar to the Haber–Weiss reaction, or by

$$\mathrm{RC(O)OOC(O)R + O_2^{-}\cdot \rightarrow RC(O)O\cdot + RC(O)O^{-} + O_2} \quad (8)$$

nucleophilic displacement on the carbonyl carbon (eq 9).

$$\mathrm{RC(O)OOC(O)R + O_2^{-}\cdot \rightarrow RC(O)OO\cdot + RC(O)OO^{-}} \quad (9)$$

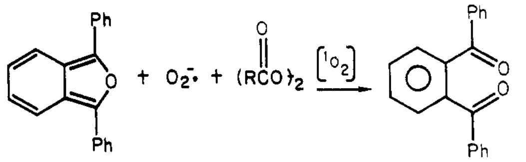
Each of these reactions would be expected to be followed by reduction of the acyloxy or acylperoxy radicals analogous to eq 3 and 5. Nucleophilic attack by superoxide on carbonyl groups has considerable precedent in the literature, having been observed for esters,[21,22] acid chlorides,[23,24] and anhydrides.[24] Indeed, for carbonyl compounds containing better leaving groups than alkoxy ions, eq 9 is predicted to be quite facile.[22]

At the beginning of this work, it was felt that distinguishing between eq 8, followed by superoxide reduction of the acyloxy radical, and eq 9, followed by a similar reduction of the acylperoxy radical, should be straightforward. The former process requires 2 mmol of $O_2^{-}\cdot$ per mmol of diacyl peroxide to produce 2 mmol of O_2 with no peroxidic material remaining, while the latter process requires the same reactant stoichiometry but produces only 1 mmol of O_2 and 2 mmol of peracid. In practice, the reactions were found to be more complicated than either of these predictions. Reaction of 2 mmol of $O_2^{-}\cdot$ with 1 mmol of lauroyl peroxide for 20 min produced 1.2–1.5 mmol of O_2, a trace of CO_2 (<0.1 mmol), and 0.3 mmol of peroxidic material; the nature of the latter was not accurately determined, but appeared from the rate of reaction with KI to be a mixture of starting lauroyl peroxide and the corresponding peracid (see Experimental Section). Reaction of 2 mmol of $O_2^{-}\cdot$ with 2 mmol of lauroyl peroxide produced the same amount of O_2 as the previous reaction, but 1.12 mmol of peroxidic material remained after 20 min. No CO_2 or undecane could be detected from the latter reaction. Reaction of 2 mmol of $O_2^{-}\cdot$ with 2 mmol of benzoyl peroxide produced 1.3 mmol of O_2.

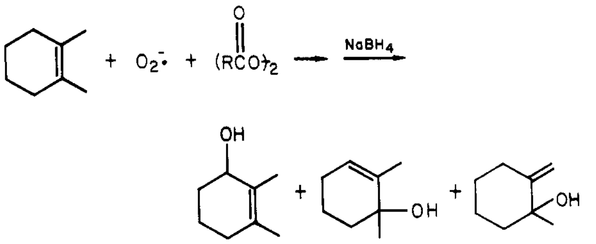
The reproducibility of product yields in these dialkyl peroxide reactions was considerably poorer than that for the other reactions studied in this work, and it would appear that several processes may be occurring simultaneously. Any adventitious protic material, in addition to causing the disproportionation of superoxide, could lead to peracid decomposition[19] upon protonation of the peracid anion formed in eq 9.

Although it is difficult to explain all of the data presented above by a single simple mechanism, the data do seem to rule out the Haber–Weiss type peroxide reduction of eq 8. Neither the peroxide yields nor the gas evolution observed is consistent with this mechanism.

The possibility that singlet oxygen is produced in some of these superoxide/peroxide reactions was investigated briefly. 9,10-Diphenylanthracene was added to reactions of superoxide with H_2O_2, *t*-BuOOH, and lauroyl peroxide, but in no case was either the yield or rate of oxygen evolution altered by the addition of the singlet-oxygen trap. These results do not, of course, prove that no singlet oxygen is formed in any of these reactions, especially since it is known[25] that superoxide quenches singlet oxygen at near-diffusion-controlled rates. However, as this work was in progress, Danen and Arudi[11] published results of a study which seemed to indicate singlet-oxygen production in the reaction of superoxide with lauroyl and benzoyl peroxides. These workers reacted superoxide with lauroyl and benzoyl peroxides in the presence of 1,3-diphenylisobenzofuran and found *o*-dibenzoylbenzene which they interpreted as evidence for singlet oxygen production (eq 10). Acknowledging that the furan is a somewhat ambiguous singlet-oxygen trap, these workers also conducted this reaction in the presence of 1,2-dimethylcyclohexene and obtained, after treatment with $NaBH_4$, the products given in eq 11.



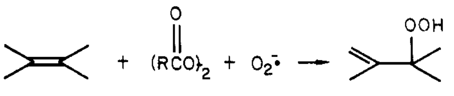
(10)



(11)

The ratio of the products obtained suggested a singlet oxygen "ene" reaction to produce the hydroperoxides corresponding to the above alcohols.[11]

Reactions of Superoxide in the Presence of Olefins. In an attempt to reproduce some of Danen's[11] results and to study the reaction in more detail, we added a benzene solution of lauroyl peroxide to a mixture of superoxide, tetramethylethylene (TME), and 18-crown-6 ether in benzene. According to Danen's results, this reaction would have been expected to yield the allyl hydroperoxide seen below, a singlet oxygen "ene" reaction. Instead, only one



product derived from the olefin was found, the epoxide,

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[19] E. Koubek, M. L. Haggett, C. J. Battaglia, K. M. Ibne-Rase, H. Y. Pyun, and J. O. Edwards, *J. Am. Chem. Soc.*, **85**, 2263 (1963); E. Koubek and J. E. Welsch, *J. Org. Chem.*, **33**, 445 (1968).

[20] As futher evidence[12] of the effective basicity of superoxide, it was found that methanol, ethanol, diethyl malonate, and cyclopentadiene cause the (apparently) instantaneous disproportionation of $O_2^{-}\cdot$, isopropyl alcohol requires several minutes for complete reaction, and *tert*-butyl alcohol reacts at appreciable rates only at relatively high concentration. Alkyl hydroperoxides and hydrogen peroxide, being more acidic than any of the above, would be expected to react quite fast with superoxide.

[21] J. San Filippo, L. J. Romano, C-I. Chern, and J. S. Valentine, *J. Org. Chem.*, 41, 586 (1976).

[22] M. J. Gibian, D. T. Sawyer, T. Ungermann, R. Tangpoonpholvivat, and M. M. Morrison, *J. Am. Chem. Soc.*, **101**, 640 (1979).

[23] R. A. Johnson, *Tetrahedron Lett.*, 331 (1976).

[24] A. LeBerre and Y. Berguer, *Bull. Soc. Chim. Fr.*, 2363 (1966).

[25] H. J. Guiraud and C. S. Foote, *J. Am. Chem. Soc.*, **98**, 1984 (1976).

Table II. Epoxide Yields from Reactions of Superoxide with Various Substrates in the Presence of Olefins[a,b]

	olefin					
substrate	TME, 1 mL	cyclohexene, 1 mL	styrene, 1 mL	styrene, 1 mL/ cyclohexene, 0.2[c]	1-octene, 1 mL	1,2-dimethyl-cyclohexene, 1mL
AcOAc	0.74	0.20	0.16	0.08/trace	0.04	0.65
$(PhCO)_2O$	0.46	0.14	0.14	0.19/0.01		
$(PhCO_2)_2$	0.40	0.28	0.08	0.06/0.10	0.09	0.13
LPO[d]	0.73	0.10	trace	trace/trace		

[a] Yields of epoxide in millimoles from reaction of 2 mmol of KO_2 with 2 mmol of substrate in 10 mL of 0.1 M 18-crown-6 ether in benzene plus the indicated amount of olefin. [b] In addition to the above yields, reactions of the following compounds produced the indicated amounts of epoxide (mmol) from TME; succinic anhydride, 0.17; phthalic anhydride, 0.28; and acetyl chloride, 0.44. [c] Reaction of 0.2 mmol of CH_3CO_3H with this mixture produced 0.19 mmol of cyclohexene oxide and only a trace of styrene oxide. [d] Lauroyl peroxide.

tetramethylethylene oxide. This product was identified by peak matching on two different GC columns with authentic samples, both before and after neutralization of the reaction mixtures. None of the expected hydroperoxide nor any other product corresponding to the predicted retention time for a polar-substituted TME was observed. Proton NMR of a reaction mixture using benzoyl peroxide instead of lauroyl peroxide showed, in addition to signals from solvent, substituted benzene, and 18-crown-6, only two singlets, one from TME (1.7 ppm) and one from the epoxide (1.3 ppm). No olefinic protons were detected.[26,27] The epoxide was found to be stable under these reaction conditions for over 1 h.

The scope of this olefin epoxidation reaction has been studied by examining different olefins as well as different acyl substrates, and the results of these studies are summarized in Table II. It can be seen from the data in Table II that the epoxidation reaction is rather general giving epoxides from several substrates and various olefins. Anhydrides appear to be about equally as good as epoxidation substrates as diacyl peroxides, although the yields of epoxide from, say, TME, vary widely with the different substrates. It is clear from the table that, in general, for reactions with a given substrate, more highly substituted olefins give higher yields of epoxides than do simpler olefins.

Competition experiments with a mixture of styrene and cyclohexene were designed to elucidate the nature of the epoxidizing agent. When this mixture of 5:1 (v/v) styrene/cyclohexene, shown in Table II, was reacted with a limiting amount of peracetic acid, virtually all of the reaction occurred with cyclohexene, as was expected from previous work.[29] It can be seen from the data in Table II that these superoxide/substrate epoxidations are considerably less selective than peracetic acid, indicating that at least some of the epoxidation is effected by some other species.

Table III. Yield of Epoxide from $O_2^-\cdot$/AcOAc/TME Reaction under Various Conditions[a]

$O_2^-\cdot$, mmol	AcOAc, mmol	TME, mmol	18-crown-6, mmol	tetramethylethylene oxide, mmol
2.0	2.0	8.4	0.95	0.70
2.7	1.3	8.4	0.95	0.75
2.0	4.0	8.4	0.95	0.65
4.0	2.0	8.4	0.95	1.37
3.0	3.0 add slow	8.4	0.95	0.70
3.0	3.2	8.4	0.95	0.93
2.0	2.0	1.7	0.95	0.42
2.3	2.6	25.3	0.95	0.68
1.8	2.1	8.4	2.8	0.85
2.4	2.1	8.4	0.2	0.42
2.0	2.0	8.4	0.95 (336)	0.30
2.0	2.0	8.4 add after	0.95	0.20
+2.0				+0.55

[a] All in 10 mL of benzene.

The reaction of superoxide with acetic anhydride in the presence of TME was studied in detail under a variety of conditions in an effort to better understand the mechanism of this reaction. These data are summarized in Table III. From the first six entries in the table, covering a range of $O_2^-\cdot$ to AcOAc ratios of 1:2 to 2:1, it can be seen that the ratio of epoxide formed to initial $O_2^-\cdot$ is approximately constant (0.31 ± 0.06), whereas the ratio of epoxide formed to initial AcOAc varies from 0.16 (3rd entry) to 0.69 (4th entry). Reactions conducted with less than 0.5 mol of AcOAc per mole of $O_2^-\cdot$ did not consume all of the superoxide. The normal experimental procedure for these reactions involved addition of the acetic anhydride to a stirred mixture of the olefin, superoxide, and 18-crown-6 in benzene. Addition of the anhydride slowly in small portions instead of all at once had no effect on the epoxide yield. Changing the concentration of the olefin greatly had only a rather small effect on epoxide yield. Changing the concentration of crown ether by a factor of 10 produced only a small change in the epoxide yield. (The actual concentration of superoxide in solution is proportional to the concentration of crown ether, not the total amount of KO_2 in the flask.) This change in crown concentration, and thus $O_2^-\cdot$ concentration, affects the rate of the reaction but not, as appreciably, the yield of epoxide. This relationship between rate and yield of epoxide is further complicated by the fact that using Aliquot 336 (a long-chain tetraalkylammonium salt) as a phase-transfer catalyst in place of crown ether results in a significantly faster reaction and a somewhat lower yield of epoxide.

The fact that at least some of the epoxidizing agent in these systems has only a limited lifetime was demonstrated when it was found that addition of the TME immediately upon completion of the $O_2^-\cdot$/AcOAc reaction (instead of having the TME present in solution initially) results in a significantly lower yield of epoxide. Subquent addition of a fresh charge of superoxide resulted in the formation of more epoxide.

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[26] The apparent discrepancy between the results obtained in this work and those of previous workers[11] may be due to different experimental conditions, i.e., the workup procedure employed by Danen and Arudi, which was not employed in this work, or the higher 18-crown-6 concentration (and thus $O_2^-\cdot$ concentration in solution) used in this work.

[27] It was found, as predicted from earlier work,[28] that peracetic acid converts 1,3-diphenylisobenzofuran almost quantitatively to *o*-dibenzoylbenzene.

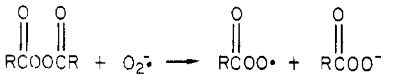
[28] R. F. Boyer, C. G. Lindstrom, B. Darbe, and M. Hylarides, *Tetrahedron Lett.*, 4111 (1975).

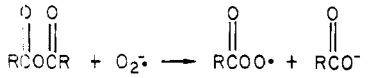
[29] D. Swern in "Organic Peroxides", Vol. II, D. Swern, Ed., Wiley Interscience, New York, 1971, Chapter V.

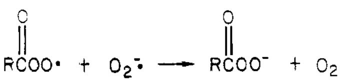
No direct reaction occurs between TME and superoxide. The reaction between superoxide and acetic anhydride in the absence of olefin is rather complex. The acetic anhydride is converted, partially, into acetyl peroxide which itself can react with superoxide, as expected from previous work.[23] Acetyl peroxide was determined by titration and observation of CH_4 and CO_2 as thermal decomposition products. Oxygen is evolved (0.25–0.4 mol/mol of $O_2^-\cdot$), and about the same amount of CO_2 is formed along with traces of CO, CH_4, and C_2H_6. The formation of the latter products suggests decarboxylation of the $CH_3CO_2\cdot$ radical. The yield of CO_2 appeared to be independent of the presence or absence of olefin, but the yield of oxygen generally decreased upon addition of olefin. Reaction of acetyl chloride produced 0.15 mol of CO_2 per mol of $O_2^-\cdot$, but less than 0.1 mol of CO_2 per mol of $O_2^-\cdot$ was observed with the remaining substrates in Table II.

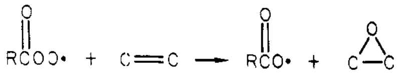
The reaction between $O_2^-\cdot$ and benzoyl peroxide, in the absence of olefin, gives about $^2/_3$ mol of O_2 per mol of $O_2^-\cdot$. In the presence of TME the O_2 yield decreases, and in addition to the epoxide shown in Table II, acetone is also formed. The ratio of epoxide to acetone increased from 0.25 to 1 when the benzoyl peroxide:superoxide ratio was changed from 0.5 to 2. Benzoyl peroxide and benzoic anhydride are the only substrates studied in this work which produced significant yields of acetone; the yield of acetone from reactions with benzoic anhydride was generally about one-half the yield of epoxide. Acetone production suggests the possible formation of tetramethyldioxetane.

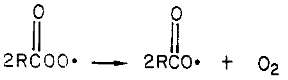
A plausible, but by no means unique, sequence of reactions which explains most of the observations made in this work is presented below. As discussed above, eq 9 and 12 have considerable precedence in the literature,[21–24] as does the sequence represented by eq 12, 13, and 17.[30]

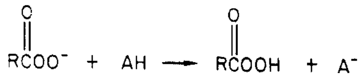

$$\mathrm{R\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}R + O_2^{-}\cdot \longrightarrow R\overset{\overset{O}{\|}}{C}OO\cdot + R\overset{\overset{O}{\|}}{C}OO^-} \qquad (9)$$

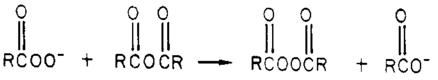

$$\mathrm{R\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}R + O_2^{-}\cdot \longrightarrow R\overset{\overset{O}{\|}}{C}OO\cdot + R\overset{\overset{O}{\|}}{C}O^-} \qquad (12)$$

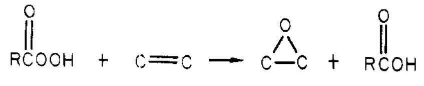

$$\mathrm{R\overset{\overset{O}{\|}}{C}OO\cdot + O_2^{-}\cdot \longrightarrow R\overset{\overset{O}{\|}}{C}OO^- + O_2} \qquad (13)$$

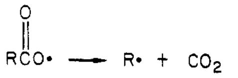

$$\mathrm{R\overset{\overset{O}{\|}}{C}OO\cdot + C{=}C \longrightarrow R\overset{\overset{O}{\|}}{C}O\cdot + \overset{O}{\overset{/\backslash}{C{-}C}}} \qquad (14)$$


$$\mathrm{2R\overset{\overset{O}{\|}}{C}OO\cdot \longrightarrow 2R\overset{\overset{O}{\|}}{C}O\cdot + O_2} \qquad (15)$$


$$\mathrm{R\overset{\overset{O}{\|}}{C}OO^- + AH \longrightarrow R\overset{\overset{O}{\|}}{C}OOH + A^-} \qquad (16)$$


$$\mathrm{R\overset{\overset{O}{\|}}{C}OO^- + R\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}R \longrightarrow R\overset{\overset{O}{\|}}{C}OO\overset{\overset{O}{\|}}{C}R + R\overset{\overset{O}{\|}}{C}O^-} \qquad (17)$$


$$\mathrm{R\overset{\overset{O}{\|}}{C}OOH + C{=}C \longrightarrow \overset{O}{\overset{/\backslash}{C{-}C}} + R\overset{\overset{O}{\|}}{C}OH} \qquad (18)$$


$$\mathrm{R\overset{\overset{O}{\|}}{C}O\cdot \longrightarrow R\cdot + CO_2} \qquad (19)$$

Equations 15 and 19 are well-known in the free-radical literature,[31] as are the epoxidation reactions, eq 14[32] and 18.[29] AH in eq 16 is any adventitious protic material present in the reaction mixture or formed by, for example, hydrogen abstraction by an acyloxy radical. Small amounts of protic material could lead to significant amounts of epoxide via repetition of eq 16 and 18. In addition to the reactions above, some base-catalyzed disproportionation of peracids[19] may occur in these systems.

The evidence for eq 12, 13, and 17 is the finding, in accord with previous work,[23] of acetyl peroxide from reaction of superoxide and acetic anhydride in the absence of olefin. Equation 14 is indicated as well as eq 18 because these epoxidations appear to have a selectivity for different olefins which is different from peracid epoxidation and because some of the epoxidizing agent in these systems appears to have a rather short lifetime. (Peracid decomposition could account for this latter finding, however.) High concentrations of either free peracid or the peroxyacyl radical seem unlikely in this highly basic media containing superoxide, however, which probably explains the fairly low yields of epoxide.

This mechanism is, of course, largely speculative and fails to account qualitatively for some findings (acetone production from aromatic, but not aliphatic substrates) and quantitatively for other findings. For example, eq 14, competing with eq 13 and 15, predicts a diminished oxygen yield upon addition of an olefin, as is observed, but would also predict an increase in CO_2 yield (via eq 19) upon addition of olefin, contrary to observation. Also, from the above mechanism, one would expect reactive esters[22] (e.g., phenyl acetate) to react with superoxide in the presence of olefins to also give epoxides, but no epoxide was detected when this reaction was conducted.

It is clear that much more work needs to be done before all the details of the reactions of superoxide with peroxides are understood.

Experimental Section

Materials. Potassium superoxide was obtained from Ventron, ground to a fine powder in a N_2-filled drybag, and stored in a desiccator prior to use. Benzene was Aldrich reagent grade and was stored over molecular sieves before use. Hydrogen peroxide, 98%, was from FMC (several years old) and was diluted with dry dioxane to obtain a "nonaqueous" solution of H_2O_2. All other peroxides were obtained from Lucidol and used without futher purification. Crown ethers were obtained from Parish Chemicals. All other organic compounds were from Aldrich.

General Procedure. Most of the reactions described in this work were carried out in a 25-mL conical flask with a side arm to which was attached a septum. The flask was attached at the main joint to a gas buret. The usual procedure for these reactions was as follows: 2 mmol (0.142 g) of the powdered potassium superoxide was added to a dry, N_2-purged, reaction flask containing a magnetic stirring bar, and 10 mL of benzene solvent containing the crown ether was added immediately. The flask was then attached to the gas buret system and stirred vigorously at ambient temperature. The substrate to be reacted was then added by syringe through the septum, and gas evolution was monitored as a function of time. Samples of the mixture were withdrawn by syringe for GC analyses and for peroxide titrations. For the latter, the sample was neutralized with dilute HCl and titrated by the iodometric method of Mair and Graupner.[33] In the author's hands, this procedure was found capable of quantitatively distinguishing very easily reduced peroxides (H_2O_2, ROOH, RCO_3H) from very difficultly reduced peroxides (*t*-

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(30) See ref 3 and 4 and references cited therein.

(31) C. Walling, "Free Radicals in Solution", McGraw-Hill, New York, 1966.

(32) L. Reich and S. S. Stivala, "Autoxidation of Hydrocarbons and Polyolefins", Marcel Dekker, New York, 1969, pp 122–124.

(33) R. D. Mair and A. J. Graupner, *Anal. Chem.*, **36**, 194 (1964).

BuOO-*t*-Bu). However, intermediate peroxides (diacyl peroxides and peresters) could only be qualitatively differentiated from either of the other two types. For reactions where appropriate, the aqueous and organic layers were separated and titrated for peroxide separately. When the reaction was judged complete, usually by cessation of gas evolution and/or complete disappearance of the yellow superoxide color, water or dilute HCl was injected into the mixture and any additional gas evolution noted. For reactions which seemed likely to produce gas other than oxygen, gas samples from the gas buret were withdrawn by syringe and analyzed by gas chromatography. It was found that suspensions of superoxide in benzene/crown ether prepared in this way were quite stable over the time periods studied in this work; less than 10% of the original superoxide had disappeared after 24 h. Because of the relative volumes of the apparatus, gas solubility, etc., gas evolution measurements are believed to be accurate to no better than 10–15%. Some specific experimental procedures are described below as typical examples.

Reaction of Superoxide with H_2O_2. To a stirred suspension of 1.96 mmol of KO_2 in 10 mL of 0.1 M 18-crown-6 ether in benzene was added 2.02 mmol of "98%" H_2O_2 in 1 mL of dioxane over a 10-min period. At the end of this time, gas evolution slowed and the mixture was white. Over the next 45 min, the rate of O_2 evolution increased, and the mixture turned yellow and then faded back to white as gas evolution ceased completely. Total O_2 yield was 2.21 mmol and titration showed that no peroxidic material remained.

Reaction of Superoxide with *t*-BuOOH. A solution containing 4.0 mmol of *t*-BuOOH in benzene was added over 20 min to a mixture of 2.07 mmol of KO_2 in benzene containing 18-crown-6. After 20 min of stirring, the mixture was white, 1.31 mmol of O_2 had been evolved, and titration showed 3.96 mmol of total peroxidic material.

Reaction of Superoxide with Benzoyl Peroxide in the Presence of Cyclohexene. A mixture containing 2.0 mmol of KO_2, 1 mL of cyclohexene, and 6 mL of 0.1 M 18-crown-6 ether in benzene was stirred vigorously, and then 2.0 mmol of benzoyl peroxide in 3 mL of 0.1 M 18-crown-6 ether in benzene was added by syringe. Gas evolution began immediately and was complete within 20 min, whereupon 1.3 mmol of O_2 had been evolved. Gas chromatographic analysis of the final solution showed the presence of 0.28 mmol of cyclohexene oxide.

Reaction of Superoxide and Acetic Anhydride with Tetramethylethylene. Acetic anhydride (2.0 mmol) was injected into a mixture containing 4.0 mmol of KO_2, 9 mL of 0.1 M 18-crown-6 in benzene, and 1 mL of tetramethylethylene. Gas evolution began immediately; after 15 min, 0.75 mmol of O_2 had been evolved, and GC analysis showed the formation of 0.98 mmol of tetramethylethylene oxide. After 1 h, 1 mmol of O_2 and 1.15 mmol of epoxide were observed and after 2 h the reaction was apparently complete with the evolution of 1.25 mmol of O_2 and the formation of 1.37 mmol of epoxide. A trace of acetone was also detected by GC.

Registry No. KO_2, 12030-88-5; H_2O_2, 7722-84-1; *t*-BuOOH, 75-91-2; $(PhCO_2)_2$, 110-22-5; AcOAc, 108-24-7; H_2O, 7732-18-5; CH_3CO_3H, 79-21-0; $(PhCO)_2O$, 93-97-0; LPO, 2388-12-7; cyclohexene, 110-83-8; TME, 563-79-1; styrene, 100-42-5; 1-octene, 111-66-0; 1,2-dimethylcyclohexene, 1674-10-8; TME epoxide, 5076-20-0; cyclohexene epoxide, 286-20-4; styrene epoxide, 96-09-3; 1-octene epoxide, 2984-50-1; 1,2-dimethylcyclohexene epoxide, 17612-36-1; KOH, 1310-58-3; O_2, 7782-44-7; CH_3CONH_2, 60-35-5; *t*-BuOH, 75-65-0.

Hydrogenation with Anthranilic Acid Anchored, Polymer-Bound Nickel Catalysts

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Received July 23, 1979

A Ni^{II} polymer-bound catalyst was prepared by anchoring anthranilic acid to chloromethylated, highly crosslinked polystyrene beads and then equilibrating with $NiCl_2{\cdot}6H_2O$. By treating this catalyst with sodium borohydride, a second catalyst was prepared. Both nickel catalysts are active in the hydrogenation of alkenes and dienes and in the reduction of nitrobenzene. The structures of the catalysts were probed by XPS studies.

The literature of hydrogenation with homogeneous nickel complexes, in contrast to that of second row group 8 metal complexes, is relatively limited and reflects the modest hydrogenation activity of all first-row transition-metal complexes. The nickel complexes receiving attention may be grouped into rather general categories: Ni^{II} complexes activated with an alkylaluminum (Ziegler),[1] Ni^{II} complexes,[2] borohydride-activated species,[3] $Ni_2(CN)_6{}^{4-}$,[4] and the nickel phthalocyanines.[5] Alkenes, dienes, alkynes,

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(1) Only references more recent than 1971 are given. Futamura, S. U.S. Public Patent Application B 575 851, 1976. Butter, S. A.; Murray, J. G. U.S. Patent 3 959 239, 1976. Sharifkanova, G. N.; Noskova, N. F.; Sokol'skii, D. V. *Ah. Prikl. Khim.*, **1977**, *50*(6), 1340. Poloso, A.; Murray, J. G. U.S. Patent 4 028 485, 1977. Sokol'skii, D. V.; Noskova, N. F.; Marusich, N. I.; Petrova, T. A. *Kinet. Katal.* **1976**, *17*(5), 1325. Fel'dblyum, V. S.; Kohovalova, T. V.; Leshcheva, A. I. *Ibid.* **1977**, *18*(20), 387. Gosselain, P. A.; Hardy, J. C.; Simoens, G.; Slegers, J.; Verbelen, R. *Bull. Soc. Chim. Belg.* **1972**, *81* (1), 29–43. Giezynski, R.; Pasynkiewicz, S. *Przem. Chem.* **1973**, *52*(11), 746–50. Born, M.; Lassau, C.; Trinh, D. C.; Dang, V. Q. German Offen. 2 310 468, 1973. Durand, D.; Hillion, G.; Lassau, C.; Sanjus, L. German Offen. 2 421 934, 1974. Eachus, S. W.; Dence, C. W. *Holzforschung* **1975**, *29*(2), 41–8.

(2) Only references more recent than 1971 are given. Maruyama, K.; Kuroki, T.; Mizoroki, T.; Ozaki, A. *Bull. Chem. Soc. Jap.* **1971**, *44*, 2002. Musser, M. T. U.S. Patent 3 631 210; *Chem. Abstr.* **1972**, *76*, 72116. Kanai, H. *J. Chem. Soc., Chem. Commun.* **1972**, 203. Noskova, N. F.; Marusich, N. I.; Grechko, M. P.; Sokol'skii, D. V. *Kinet. Katal.* **1977**, *18*, 1436. Frolov, V. M.; Parenago, O. P.; Dolgoplosk, B. A. *Probl. Kinet. Katal.* **1973**, *15*, 125. Lisichkin, G. V.; Denisov, F. S.; Yuffa, A. Y. *Katal. Konversiya Uglevodorodov* **1975**, *no. 2*, 170. Itatani, H.; Bailar, J. C., Jr. *Ind. Eng. Chem., Prod. Res. Dev.* **1972**, *11*, 146. Kaufman, J. A.; Gupta, D. V.; Szathowski, S. T.; Weiss, A. H. *Chem. Eng. World* **1974**, *9*, 55.

(3) Only references more recent than 1971 are given. Brown, C. A.; Ahuja, V. K. *J. Chem. Soc., Chem. Commun.* **1973**, *15*, 553. Strohmeier, W.; Steigerwald, H. *Z. Naturforsch., B* **1976**, *31*(8), 1149. Abley, P.; McQuillin, F. J. *J. Catal.* **1972**, *24*, 536. Hinze, A. G.; Frost, D. J. *Ibid.* **1972**, *24*, 541.

(4) References are listed from 1970. Bingham, D.; Burnett, M. G. *J. Chem. Soc. A* **1971**, 1782. Hashimoto, I.; Tsuruta, N.; Ryang, M.; Tsutsumi, S. *J. Org. Chem.* **1970**, *35*, 3748. Bingham, D.; Burnett, M. G. *Ibid.* **1970**, 2165.

(5) Kropf, H.; Witt, F. D. *Z. Phys. Chem.* **1971**, *76*(5), 331.

0022-3263/80/1945-1418$01.00/0