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### Base-Induced Generation of Superoxide Ion and Hydroxyl Radical from Hydrogen Peroxide

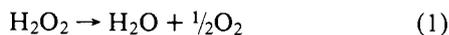
Sir:

Substantial yields of superoxide ion,  $O_2^{\cdot-}$ , are obtained when tetraalkylammonium hydroxide is added to hydrogen peroxide in pyridine. Superoxide ion has been identified by its ESR spectrum at 77 K, which is identical with the previously reported spectra,<sup>1</sup> and by cyclic voltammetry (see Figure 1a).<sup>2</sup>

Table I summarizes the results for a series of reactions in which varying amounts of tetra-*n*-propylammonium hydroxide (TPAOH) have been added to hydrogen peroxide in pyridine. The initial yield approaches 0.5 mol of  $O_2^{\cdot-}$ /mol of  $H_2O_2$ . The superoxide ion subsequently disappears over a period of 1–2 h and oxygen is evolved.

To measure both the concentration of  $O_2^{\cdot-}$  and the amount of evolved  $O_2$  from the base-induced decomposition of  $H_2O_2$ , several reactions have been carried out in a sealed cell (with negligible headspace) that contained 50 mL of 0.1 M tetra-*n*-propylammonium perchlorate (TPAP) in pyridine (initially bubbled with argon to remove dissolved oxygen). In a typical reaction, 0.08 mmol of  $H_2O_2$  (8  $\mu$ L of 30% aqueous  $H_2O_2$ ) is combined with 0.03 mmol of TPAOH (25  $\mu$ L of 25% aqueous TPAOH). (The concentration of water in the final reaction mixture is  $\sim$ 0.05 M.) The formation of superoxide ion is complete in  $<$ 30 s with a yield of 0.011 mmol of  $O_2^{\cdot-}$  (0.22 mM) and  $\sim$ 0.02 mmol of  $O_2$  (0.4 mM). Other possible products have not been identified. Figure 1b illustrates the cyclic voltammetry of the mixture of  $O_2^{\cdot-}$  and  $O_2$ . (The peak above the axis is due to  $O_2$  and the peak below the axis represents  $O_2^{\cdot-}$ .)

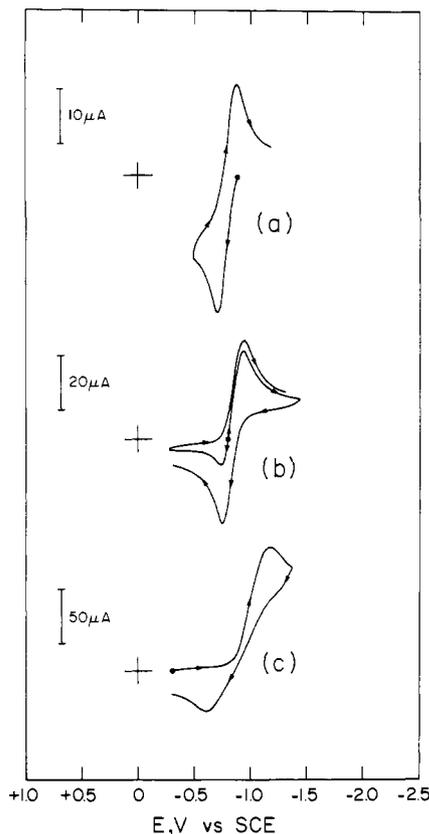
When 50-fold larger concentrations of  $H_2O_2$  and TPAOH are combined,  $O_2^{\cdot-}$  is not obtained,<sup>3</sup> but a stoichiometric amount of  $O_2$  is produced, based on the reaction



We also have carried out the reaction of  $H_2O_2$  and TPAOH in the presence of the spin trap, phenyl-*N-tert*-butylnitron (PBN). The ESR spectrum in acetonitrile at room temperature for a reaction mixture of 3 M pyridine, 1 M PBN, 0.01 M  $H_2O_2$ , 0.005 M TPAOH, and 0.25 M  $H_2O$  exhibits three doublets of approximately equal intensity with splittings of  $15.2 \pm 0.2$  and  $2.8 \pm 0.2$  G. This is consistent with the previously reported ESR spectrum<sup>4</sup> of the PBN adduct with  $\cdot OH$ ,<sup>1</sup> but the possibility that the spectrum corresponds to the PBN adduct with  $HO_2\cdot$  cannot be excluded. (The approximately equal relative intensities of the three doublets and the fact that the solution is basic argue in favor of the  $\cdot OH$  adduct.)

Efforts have been made to identify the reaction products that result from the combination of  $\cdot OH$  and pyridine, but without success. The reaction mixtures are pale yellow and exhibit a weak absorption band with a  $\lambda_{max}$  at 313 nm.

The addition of base to hydrogen peroxide in acetonitrile yields  $O_2$ , but there is no evidence of  $O_2^{\cdot-}$  (see Figure 1c). The maximum yield of oxygen is obtained when the ratio of base to hydrogen peroxide is low (e.g., 0.1 mol of  $OH^-$ /mol of



**Figure 1.** Cyclic voltammograms of the reaction products from the combination of  $H_2O_2$  and TPAOH. All solutions contain 0.1 M TPAP; scan rate, 0.1 V/s at a platinum electrode (area, 0.23 cm<sup>2</sup>): (a) 2 mM  $H_2O_2$  + 7.5 mM TPAOH in pyridine (argon bubbled to remove  $O_2$ ); (b) 1.6 mM  $H_2O_2$  + 0.62 mM TPAOH in pyridine, sealed cell; (c) 2 mM  $H_2O_2$  + 0.24 mM TPAOH in acetonitrile, sealed cell.

**Table I.** Concentrations<sup>a</sup> of  $O_2^{\cdot-}$  That Result from the Reaction of 2 mM Hydrogen Peroxide<sup>b</sup> with Varying Concentrations of TPAOH<sup>c</sup> in 0.1 M TPAP-Pyridine (Saturated with Argon)

[TPAOH], mM	[ $O_2^{\cdot-}$ ], mM	Yield, mmol of $O_2^{\cdot-}$ /mmol of $H_2O_2$
0	0	0
0.25	0.08	0.04
0.50	0.23	0.12
1.0	0.58	0.29
2.0	0.89	0.44
4.0	1.08	0.54

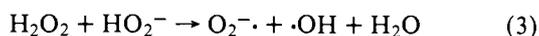
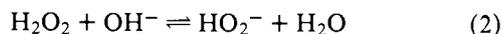
<sup>a</sup> Extrapolated to the time of mixing.  $O_2^{\cdot-}$  concentrations were determined by cyclic voltammetry with 0.1 M TPAP as the supporting electrolyte.<sup>2</sup> <sup>b</sup> Added as 30% aqueous  $H_2O_2$ . <sup>c</sup> Added as 25% aqueous TPAOH.

$H_2O_2$ ). At higher concentrations of  $OH^-$ , a secondary reaction slowly consumes the  $O_2$  that is produced; this is presumed to be the base-catalyzed reaction of  $O_2$  with acetonitrile. When 3 M pyridine is present in the  $H_2O_2$ -acetonitrile solution, addition of base results in the transient formation of  $O_2^{\cdot-}$  (detected by cyclic voltammetry), but it disappears in 2–5 min.

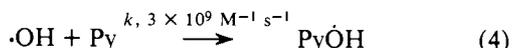
The addition of base to  $H_2O_2$  in water results in the slow base-catalyzed disproportionation of  $H_2O_2$  to water and oxygen.<sup>5</sup> A reaction that contains 0.1 M PBN, 0.02 M  $H_2O_2$ , 0.01 M TPAOH, and 0.1 mM  $Na_2EDTA$  in water, when allowed to stand overnight, exhibits a weak three-line ESR spectrum.<sup>6</sup>

Based on the present results and other evidence that  $O_2^{\cdot-}$  can be produced by reaction of base with hydrogen peroxide,

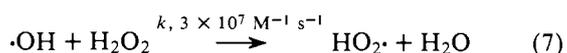
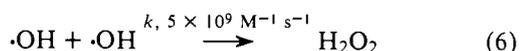
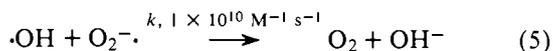
e.g., by decomposition of the perhydrate of potassium peroxide,  $K_2O_2 \cdot 2H_2O_2$ ,<sup>7</sup> a self-consistent reaction scheme is proposed:



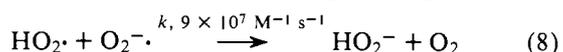
The initial neutralization step is followed by an anion induced disproportionation step. Pulse radiolysis data indicate that the reaction of  $\cdot OH$  with pyridine is rapid:<sup>8</sup>



Hence, pyridine should trap and react with  $\cdot OH$ <sup>9</sup> before it can participate in several well-characterized subsequent reactions:<sup>10</sup>

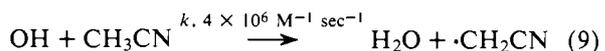


In pyridine the net result of reactions 2, 3, and 4 is the production of 0.5 mol of  $O_2^{\cdot-}$ /mol of added base. When the ratio of base to  $H_2O_2$  is low, oxygen can be produced by reaction of a small but finite concentration of  $HO_2^{\cdot}$  with  $O_2^{\cdot-}$ :



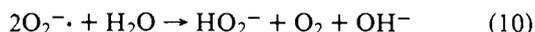
The  $HO_2^{\cdot}$  is produced by reaction of  $O_2^{\cdot-}$  with  $H_2O_2$  or water.<sup>11</sup>

The reaction of  $\cdot OH$  with acetonitrile is much slower<sup>12</sup> than with pyridine:



Hence, reaction 5 becomes competitive with reaction 9. Consideration of the relative rates that can be calculated for these reactions (assuming that the aqueous rate constants are the same in the acetonitrile solvent) indicates that only some 10–20% of the  $O_2^{\cdot-}$  that is formed by reaction 3 would be converted to  $O_2$ . Apparently the radical product (or products) of reaction 9 converts the remaining  $O_2^{\cdot-}$  to  $O_2$  to give the observed yield of 0.5 mol of  $O_2$ /mol of  $H_2O_2$  without consumption of  $OH^-$ . Reactions 2, 3, and 5 appear to represent a viable mechanism for the base-catalyzed decomposition of  $H_2O_2$  to oxygen and water (as expressed by reaction 1).

The same processes that dominate the base-induced decomposition of  $H_2O_2$  in acetonitrile probably also occur in aqueous solutions of  $H_2O_2$ . However, a second pathway for  $O_2^{\cdot-}$  decomposition, in addition to reaction 5, is likely in aqueous solutions (via reaction 8).



In the presence of a large excess of the spin trap, PBN, a substantial fraction of the  $\cdot OH$  is trapped (as is the case with pyridine solvent) and  $O_2$  evolution by means of reaction 5 is blocked.



The primary step represented by reaction 3 is presumed to be much faster in pyridine and acetonitrile than in water because of the general enhancement of the nucleophilic reactivity of  $HO_2^-$  in aprotic solvents.

The base-induced decomposition of  $H_2O_2$  offers several potentially useful applications. (a) It provides a convenient method to produce  $O_2^{\cdot-}$  in pyridine. The only other products

apparently are inert. (b) It also provides a means to generate  $\cdot OH$ , which, in solvents like  $CH_3CN$  and  $H_2O$ , has sufficient long lifetimes to react with substrates whose reaction rates are competitive with reaction 5. (c) It may give a means to react  $\cdot OH$  and a substrate without interfering side reactions or parallel processes. A possible approach is the use of the substrate as the solvent for the  $H_2O_2 + HO_2^-$  reaction.

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## References and Notes

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- (2) M. E. Peover and B. S. White, *Electrochim. Acta*, **11**, 1061 (1966).
- (3) The water concentration for this reaction mixture is  $\sim 2.4$  M. Previous experience has established that water promotes the disproportionation of  $O_2^{\cdot-}$  to  $O_2$  and  $HO_2^-$ .
- (4) J. R. Harbour, V. Chow, and J. R. Bolton, *Can. J. Chem.*, **52**, 3549 (1974); F. P. Sargent and E. M. Gardy, *ibid.*, **54**, 275 (1976).
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- (6) The triplet splitting is  $\sim 15$  G. The modulation amplitude (320 G) that was required to obtain a signal precludes observation of splittings of the order of 2–3 G. Therefore, this spectrum cannot be assigned with certainty to PBN $\cdot OH$ .
- (7) I. A. Kazarnovskii, *Dokl. Akad. Nauk. SSSR*, **221**, 353 (1975) (p 200 in English translation).
- (8) L. M. Dorfman and G. E. Adams, "Reactivity of the Hydroxyl Radical in Aqueous solutions", NSRDS-NBS 46 (SD Catalog No. C13.48:46), U.S. Government Printing Office, Washington, D.C., June 1973, p 20.
- (9) Products of the presumed reaction between  $\cdot OH$  and pyridine have not been identified. The mixture of reaction products exhibits no ESR spectrum except that for  $O_2^{\cdot-}$ . With the exception of  $O_2$  and  $O_2^{\cdot-}$ , the product solution does not contain species that are electroactive in the range from +1 V to  $-1$  V vs. SCE. Only a very weak absorption ( $\lambda_{max}$  313 nm) is observed before the pyridine cutoff. The initial step of the reaction is presumed to be addition of  $\cdot OH$  to pyridine. Reaction products which have been considered, but whose presence has not been confirmed or excluded, include pyridine *N*-oxide, 2-pyridone (2-hydroxypyridine), bipyridine, and *N*-(2-pyridyl)pyridinium ion.
- (10) The rate constants are from pulse radiolysis studies in aqueous solutions, ref 8; reaction 5, p 39; reaction 6, p 38; reaction 7, p 35.
- (11) B. H. J. Bielski and A. O. Allen, *J. Phys. Chem.*, **81**, 1048 (1977).
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## Relationship between Charge Delocalization and Stability of Some Oxocarbenium Ions

Sir:

Recently there has been increasing interest in the relationship between the delocalization of charge by substituents on organic ions and the thermodynamic stability of those ions.<sup>1–3</sup> Two generalizations are frequently made. One is that for a homologous series of compounds or ions extraneous effects will cancel and the <sup>13</sup>C chemical shift will mirror the changes in charge density on carbon.<sup>4,5</sup> The other is that the more charge is delocalized, the more stable the ion.<sup>3</sup> To date, two exceptions to the above generalizations have been recognized.<sup>1,2</sup> We wish to draw attention to three additional systems for which the above relationships cannot both be true.

Data for the three additional exceptional systems are given in Tables I and II. It is obvious that these data are inconsistent with at least one of the above generalizations. Consider first the ketones. Comparing the heats of protonation, protonated acetone is the most stable while protonated benzophenone is the