character while Cr(III) exhibits some associative character, with Rh(III) being intermediate. At least they show that the degree of association between the complex and the entering aqua ligand in the transition state follows the order Co(III) < Rh(III) < Cr(III). Detailed comparisons of spontaneous and base-catalyzed substitution kinetics are under way and should provide mechanistic insights for the metal ions in question.

The triflato complexes are extremely versatile synthetic intermediates, and their general reactivity is summarized in Scheme I. When dissolved, the triflato ligand of the complexes was substituted for a molecule of the solvent, to produce the coordinated solvent species in quantitative yields. Other neutral ligands may be substituted by reactions of the triflato complexes in sulfolane, acetone, or triethyl phosphate with the appropriate ligand, since any solvent complexes initially formed are also comparatively labile for these solvents. These procedures have been extended to include the synthesis of binuclear species.[6,7,9] Finally, the synthesis of isotopically labeled complexes such as the $[M(NH_3)_5(^*OH_2)]^{3+}$ ions, in quantitative yields, without isotopic dilution of the residual solvent is a useful attribute.[10]

In summary, the triflato complexes have many desirable properties that make them the most versatile synthetic intermediates presently available for the more substitution-inert metal ions. These properties include (i) air stability, which allows ready handling in air and storage for months in a desiccator without noticeable decomposition, (ii) thermal and shock stability unlike the case of explosive perchlorato complexes[11] of similar lability, (iii) high to moderate solubility and comparatively rapid substitution kinetics in a wide variety of polar solvents, (iv) essentially quantitative syntheses from the readily available $[M(NH_3)_5Cl]Cl_n$ complexes, and (v) ready regeneration from other pentaammine complexes, by thermal reactions, either in the solid state (e.g., $[M(NH_3)_5(OH_2)](CF_3SO_3)_m$) or in neat CF_3SO_3H.

Registry No. $[Rh(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84254-57-9; $[Ir(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84254-59-1; $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84254-61-5; $[Ru(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84278-98-8; $[Pt(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_3$, 84254-63-7; $[Co(NH_2CH_3)_5(OSO_2CF_3)]^{2+}$, 84254-64-8; $[Rh(NH_2CH_3)_5(OSO_2CF_3)]^{2+}$, 84254-65-9; $[Cr(NH_2CH_3)_5(OSO_2CF_3)]^{2+}$, 84254-66-0; $[Cr(NH_3)_5Cl]Cl_2$, 13820-89-8; $[Rh(NH_3)_5Cl]Cl_2$, 13820-95-6; $[Ir(NH_3)_5Cl]Cl_2$, 15742-38-8; $[Ru(NH_3)_5Cl]Cl_2$, 18532-87-1; $[Pt(NH_3)_5Cl]Cl_3$, 16893-11-1.

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A Convenient Route to Superoxide Ion in Aqueous Solution

Sir:

The aqueous chemistry of the superoxide radical anion is of considerable chemical interest for several reasons, prominent among which is its role in biological processes.[1-4] Although it is stable in aprotic solvents, and readily prepared therein,[5-7] studies of O_2^- in aqueous media are hampered not only by its inherent instability but also by the specialized techniques required to date for its preparation.

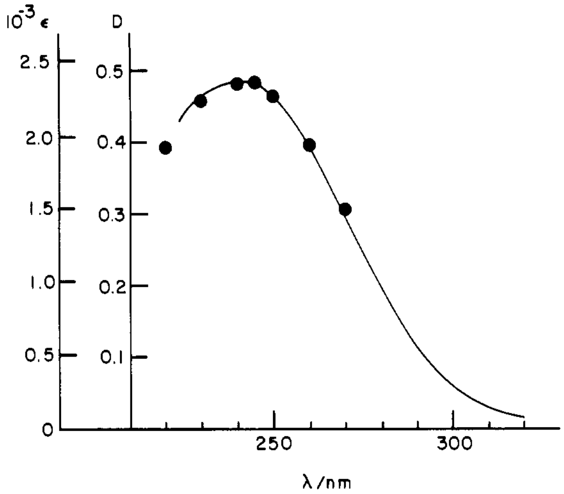

Figure 1. UV absorption spectrum of the long-lived metastable species produced by a 6-s photolysis of Ph_2CO (6.3 μM) in 5.0 M aqueous 2-propanol at pH 12.5 (the absorbance, D, was measured in a cell of 2.00-cm optical path). The scales of D and of the decadic molar absorptivity, $\epsilon/M^{-1}\ cm^{-1}$, were matched by using $[O_2^-] = 1.02 \times 10^{-4}$ M, calculated from the values of ϵ given[13b] for λ 230-270 nm; the latter are shown as solid points.

Enzymatic reactions[8] aside, existing methods for the generation of significant concentrations of O_2^- in aqueous or other protic media are limited. Known photochemical methods not only produce O_2^- continuously at a low concentration but also involve highly light-absorbing substances in solution.[9-12] Of the methods described in the literature, only radiolysis (pulse and stopped-flow)[13] and the vacuum-UV photolysis of water[14] produce aqueous O_2^- solutions of appreciable concentration. Reading about the photodissociation of water in aqueous

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(9) Organic compounds such as flavins,[10] chemically and photochemically reduced dyes,[11] and certain aromatic compounds[11b,12] undergo one-electron transfer to O_2 (Lee-Ruff, E. *Chem. Soc. Rev.* **1977**, *6*, 195). These reactions have mostly been used for the production of continuous low concentrations of O_2^- in the presence of the desired substrate. These systems are less than ideal for the preparation of O_2^-, however, owing to the high light absorption of the dyes and to possible reactions of O_2^- with the precursors themselves.

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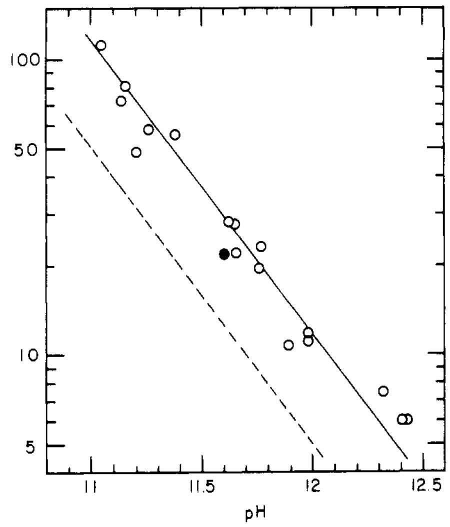

Figure 2. Rate constant–pH profile for the decay of the metastable O_2^- prepared with use of a ketone photosensitizer (6.3 μM benzophenone or 8.2–41.0 mM acetone) in aqueous alcohol (1 M methanol or 1–5 M 2-propanol) after photolysis. The solid point at pH 11.6 is for 12 M ethanol,[14b] and the dashed line for aqueous solution[13b] at ~24 °C. Kinetic measurements were made at λ 245–252 nm.

ethanol,[14] we reasoned that it should be possible to develop a convenient and inexpensive alternative. We describe here the conditions necessary for doing so and the evidence that O_2^- is formed.

The n–π* triplet state of a ketone (benzophenone, acetophenone, or acetone) is quenched by reaction with a primary or secondary alcohol (methanol, ethanol, and 2-propanol were used). The chemical reactions used in air- or O_2-saturated solutions to generate O_2^- are given in eq 1–4, where acetone and 2-propanol are used for illustrative purposes.

$$(CH_3)_2CO \xrightarrow{h\nu} (CH_3)_2\dot{C}\text{–}\dot{O}^3 \tag{1}$$

$$(CH_3)_2\dot{C}\text{–}\dot{O}^3 + (CH_3)_2CHOH \rightarrow 2\cdot C(CH_3)_2OH \tag{2}$$

$$O_2 + \cdot C(CH_3)_2OH \rightarrow \cdot OOC(CH_3)_2OH \tag{3}$$

$$\cdot OOC(CH_3)_2OH + OH^- \rightarrow (CH_3)_2CO + H_2O + O_2^- \tag{4}$$

The species formed has an absorption spectrum, independent of the alcohol or ketone used, which matches (Figure 1) that reported for O_2^-. This species slowly decays, exhibiting kinetics second order with respect to $[O_2^-]$. The rate constant and its pH dependence (Figure 2) match those reported for the disproportionation of O_2^- prepared pulse radiolytically.[15] The half-time for decay of 100 μM O_2^- rises from 90 s (pH 11.0) to 41 min (pH 12.5) and increases inversely with $[O_2^-]$. The final UV spectrum is essentially the same as it was prior to photolysis, that of the ketone photosensitizer. If desired, the entire process may be repeated on the same solution.

The conditions are not critical and can be adjusted within broad limits to suit the subsequent use planned for the O_2^- solution. Irradiations were carried out in carefully cleaned quartz spectrophotometer cells or beakers. Solutions were made up in distilled water further purified by a Millipore Q filtering system or by triple distillation. Reagent or spectrophotometric grade chemicals and solvents were used. Following earlier work[13] the solutions contained ~15 μM Na_2edta. The pH, adjusted with solid or aqueous KOH, was measured before and/or after the irradiation. The temperature was held at 25.0 ± 0.5 °C. The various UV sources employed each gave reproducible $[O_2^-]$ provided the cell was carefully repositioned. Prolonged photolysis lowered the yield of O_2^-, possibly because of the reaction of O_2^- with alcohol radicals in oxygen-depleted solutions.[14b]

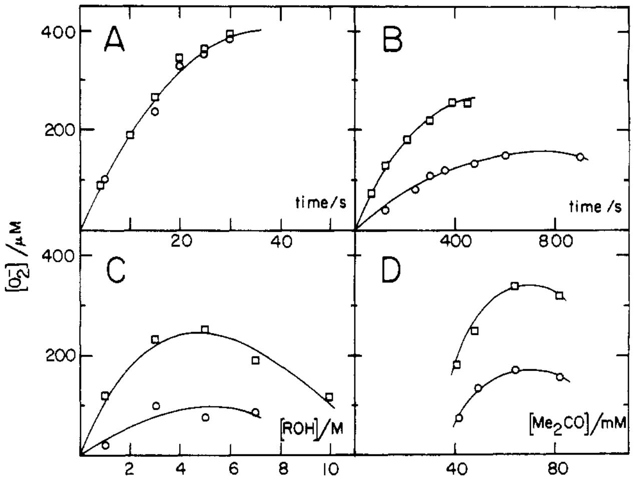

Figure 3. Yields of O_2^- under different reaction conditions: (A) benzophenone (6.3 μM, circles) or acetone (41 mM, squares) in oxygen-saturated 5.0 M 2-propanol after photolysis using a mercury arc lamp; (B) acetone (41 mM) in oxygen-saturated 2-propanol (1 M, circles; 5 M, squares) after photolysis using a xenon plasma lamp; (C) acetone (41 mM) in oxygen-saturated 5.0 M 2-propanol after 60-s (circles) or 450-s (squares) photolysis using a xenon plasma lamp; (D) acetone in oxygen-saturated 5.0 M 2-propanol after 60-s (circles) or 210-s (squares) photolysis using a xenon plasma lamp.

The yields of O_2^- formed under a few of the conditions examined are shown in Figure 3. Concentrations of 100–400 μM O_2^- were routinely obtained by using xenon flash lamps or steady irradiation with common laboratory xenon plasma or mercury arc lamps. Even sunlight proved effective: 85 μM O_2^- was generated in a cylindrical quartz spectrophotometer cell (2-cm optical path, 6-cm^3 volume) held for ca. 5 min in direct sunlight when the cell was partially surrounded by shiny aluminum foil to act as a reflector.

We limited our experiments to the pH range 11.0–12.5, where the lifetime of O_2^- is sufficiently long to permit easy handling and workup and where buffers would not be needed to control the pH. Of course, the O_2^- solution produced can be added to buffers at lower pH if desired, although the lifetime of O_2^- is correspondingly decreased. Similarly, although this point was not examined at length, photolysis in less basic solutions should be able to produce O_2^- and HO_2 in the presence of photoinactive substrates with which they might react.

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Registry No. O_2^-, 11062-77-4; Ph_2CO, 119-61-9; acetone, 67-64-1; methanol, 67-56-1; 2-propanol, 67-63-0; ethanol, 64-17-5; disodium ethylenediaminetetraacetate, 139-33-3.

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(15) The initial concentration of O_2^-, needed for the second-order kinetic analysis, was calculated by using the reported values[13b] of ε. Alternatively the kinetic equation can be recast so as to eliminate $[O_2^-]_0$:

$$D_t = D_\infty + (D_0 - D_\infty)/[1 + (k/\epsilon)(D_0 - D_\infty)t]$$

This equation yielded equally good fits, by using a nonlinear least-squares program, with values of k/ϵ at each wavelength within 5% of those obtained by the method described.