the thermodynamic transfer functions for the proton between water and ammonia ($\delta_m\Delta H^\circ = -96$ kJ mol^{-1}, $\delta_m\Delta S^\circ = -96$ J K^{-1} mol^{-1}).[40] The new compounds in Table III conform to this picture, with the exception of $Rh(NH_3)_5NO_3^{2+}$. Consequently the higher rates of solvation in liquid ammonia should be primarily attributed to the more favorable heat of solvation of the proton in liquid ammonia. Contrary to the conclusions drawn so far, this would suggest that the solvent dependence of the rate-determining step is only slight. A similar conclusion has been drawn by Goodall and Hardy[41] from a kinetic study of cobalt(III) ammine complexes in Me_2SO–water mixtures. The postulate of solvent independence of k_1 can be checked by calculating K^{CB} for aqueous solutions. For the compounds under study the calculated pK^{CB} values at 25 °C are then 18.3, 17.7, and 17.5 for (nitrato)pentaamminecobalt(III), bromopentaamminerhodium(III), and (nitrato)pentaamminerhodium(III), respectively. In view of the fact that for hexaammineruthenium(III) and tris(ethylenediamine)cobalt(III) aqueous pK^{CB} values of 14.9[26] and 13.1[41] (25 °C), respectively, have been reported, our calculated values are definitely too large. This means that the suggested assumption of medium independence of k_1 cannot be maintained.

Bromopentaamminerhodium(III) gave a small contribution of spontaneous ammoniation (k_s) to the overall rate. The activation parameters of k_s are $\Delta H^{\ddagger} = 59 \pm 2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -132 \pm 6$ J K^{-1} mol^{-1}. These values both are considerably lower than the ones found for spontaneous aquation (k_{aq}) (see Table III). The only cobalt(III) complex studied so far that showed spontaneous ammoniation is *trans*-dichlorobis(ethylenediamine)cobalt(III), with $\Delta H^{\ddagger} = 58$ kJ mol^{-1} and $\Delta S^{\ddagger} = -47$ J K^{-1} mol^{-1} for k_s.[6] The activation parameters for spontaneous aquation for this complex are[42] $\Delta H^{\ddagger} = 115$ kJ mol^{-1} and $\Delta S^{\ddagger} = 55$ J K^{-1} mol^{-1}, so in both cases almost the same differences between spontaneous ammoniation and aquation appear. The relatively low values for $\Delta H^{\ddagger}$ as well as $\Delta S^{\ddagger}$ in both cases may indicate a more pronounced degree of solvent assistance in liquid ammonia than in water.[6]

Acknowledgment. The authors thank the Netherlands Organisation for the Advancement of Pure Research (ZWO) for financial support via the Netherlands Foundation for Chemical Research (SON).

Registry No. $[Co(NH_3)_5NO_3](ClO_4)_2$, 15156-24-8; $[Rh(NH_3)_5NO_3](ClO_4)_2$, 75908-19-9; $[Rh(NH_3)_5Br](ClO_4)_2$, 14282-99-6.

Supplementary Material Available: Tables containing the observed and calculated rate constants as a function of complex concentration and ammonium perchlorate concentration at different temperatures (6 pages). Ordering information is given on any current masthead page.

---

[40] Jolly, W. L. *J. Phys. Chem.* **1954**, *58*, 250.

[41] Goodall, D. M.; Hardy, M. J. *J. Chem. Soc., Chem. Commun.* **1975**, 919.

[42] Pearson, R. G.; Boston, C. R.; Basolo, F. *J. Am. Chem. Soc.* **1953**, *75*, 3089.

Contribution from the Department of Chemistry,
University of California, Riverside, California 92521

Oxidation and Dismutation of Superoxide Ion Solutions to Molecular Oxygen. Singlet vs. Triplet State

EDWARD J. NANNI, JR., ROBERT R. BIRGE,* LYNN M. HUBBARD, MARK M. MORRISON, and DONALD T. SAWYER*

Received September 26, 1980

Photon counting and chemical trapping have been used to determine the yields of dimeric $^1\Delta_g$-state O_2 that result from oxidation and proton-induced dismutation of $O_2^-\cdot$. The results are consistent with theoretical predictions and indicate that those processes that involve adiabatic electron transfer or a triplet transition state favor formation of $^3\Sigma_g^-$-state O_2 (e.g., the $Fe^{III}(ClO_4)_3$–$O_2^-\cdot$ and the $HClO_4$–$O_2^-\cdot$ systems), and those that involve a singlet transition state favor formation of $^1\Delta_g$-state O_2 (e.g., the ferrocenium ion–$O_2^-\cdot$ system).

Several recent investigations describe the formation of singlet oxygen $O_2(^1\Delta_g)$) by oxidation of superoxide ion ($O_2^-\cdot$) with ferrocenium ion[1] and diacyl peroxides[2] and by dismutation of superoxide with proton sources.[3–5] To further test the reaction chemistry of $O_2^-\cdot$, we have undertaken a study to determine by photon counting and chemical quenching the yield of dimeric[6] $^1\Delta_g$-state O_2 from the oxidation and dismutation of $O_2^-\cdot$ in aprotic media.

Reaction by electron transfer to a cation radical from an anion radical such as $O_2^-\cdot$ is likely to result in excited-state product molecules which may emit characteristic fluorescence.[7–10] Mayeda and Bard have shown that in the reaction of ferrocenium ion with $O_2^-\cdot$ singlet oxygen is a product.[1] This was detected by the chemical quencher 1,3-diphenylisobenzofuran (DPBF), which has the largest rate constant, 8×10^8 M^{-1} s^{-1}, for quenching $O_2(^1\Delta_g)$.[11] However, luminescence was not observed.

Under suitable conditions we have been able to measure the chemiluminescence due to the $O_2(^1\Delta_g)$ that results from the oxidation of $O_2^-\cdot$. Consistent with theoretical calculations, the formation of $O_2(^1\Delta_g)$ is dependent upon substrates which favor singlet transition states in the electron-transfer process. Systems involving either adiabatic electron transfer or a triplet transition produce directly the $^3\Sigma_g^-$ state of O_2. To verify that

---

[1] Mayeda, E. A.; Bard, A. J. *J. Am. Chem. Soc.* **1973**, *95*, 6223.

[2] Danen, W. C.; Arudi, R. L. *J. Am. Chem. Soc.* **1978**, *100*, 3944.

[3] Mayeda, E. A.; Bard, A. J. *J. Am. Chem. Soc.* **1974**, *96*, 4023.

[4] Goda, K.; Chu, J.; Kimura, T.; Schaap, A. P. *Biochem. Biophys. Res. Commun.* **1973**, *52*, 1300.

[5] Khan, A. U. *Science (Washington, D.C.)* **1970**, *168*, 476.

[6] Bader, L. W.; Ogryzko, E. A. *Discuss. Faraday Soc.* **1964**, *37*, 46.

[7] Hercules, D. M. *Acc. Chem. Res.* **1969**, *2*, 301.

[8] Weissberger, A., Rossiter, B., Eds. "Physical Methods of Organic Chemistry", 4th ed.; Academic Press: New York, 1971; Part IIA.

[9] Bard, A. J.; Santhanam, S. V.; Cruser, S. A.; Faulkner, L. R. *Fluorescence* **1967**, Chapter 14.

[10] Kuwana, T. *Electroanal. Chem.* **1966**, *1*, Chapter 3.

[11] Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 7244.

0020-1669/81/1320-0737$01.00/0 © 1981 American Chemical Society

Table I. Photon Yields from the Oxidation and Dismutation of $O_2^{-}\cdot$ in Dimethylformamide

	photon yield, counts		cor photon yield, counts[b]		ratio of cor photon yields
reactants (5 mL of each)	filter 2-73	filter[a] 2-64	filter 2-73	filter[a] 2-62	2-73/2-64
5.00 mM NaOCl + 6.35 M H_2O_2[c]	$(9.12 \pm 1.82) \times 10^3$	$(2.32 \pm 0.46) \times 10^3$			3.93
1.00 mM $[FeCp_2]BF_4$ + 1.00 mM $O_2^{-}\cdot$	$(1.62 \pm 0.32) \times 10^5$	$(3.51 \pm 0.70) \times 10^4$	$(1.62 \pm 0.32) \times 10^5$	$(3.49 \pm 0.70) \times 10^4$	4.63
1.00 mM $[Mn(bpyO_2)_3](ClO_4)_3$ + 1.00 mM $O_2^{-}\cdot$	$(2.26 \pm 0.45) \times 10^4$	$(7.65 \pm 1.53) \times 10^3$	$(2.18 \pm 0.43) \times 10^4$	$(7.49 \pm 1.50) \times 10^3$	2.91
1.00 mM $[Mn(phen)_2O)_2](ClO_4)_4$ + 1.00 mM $O_2^{-}\cdot$	$(3.21 \pm 0.64) \times 10^3$	$(6.30 \pm 1.26) \times 10^2$	$(2.36 \pm 0.47) \times 10^3$	$(4.68 \pm 0.93) \times 10^2$	5.05
1.00 mM $Fe(ClO_4)_3$ + 1.30 mM $O_2^{-}\cdot$	$(1.30 \pm 0.26) \times 10^3$	$(5.00 \pm 1.00) \times 10^2$	$(4.51 \pm 0.90) \times 10^2$	$(3.38 \pm 0.68) \times 10^2$	1.33
1.00 mM $HClO_4$ + 0.97 mM $O_2^{-}\cdot$	$(8.56 \pm 1.71) \times 10^2$	$(2.48 \pm 0.50) \times 10^2$	6.0 ± 1.7	$(8.63 \pm 1.72) \times 10$	0.07
1.00 mM $[FeCp_2]BF_4$ + 1.00 mM $DTBQ^{-}\cdot$	$(8.50 \pm 1.70) \times 10^2$	$(1.62 \pm 0.32) \times 10^2$			

[a] Counts normalized to filter 2-73 by multiplying the observed number by 0.511 (filter 2-64 transmits nearly twice as much light in the spectral range where both filters transmit). [b] Counts corrected for background luminescence from excited species other than $O_2{}^*$; the observed counts for the $[FeCp_2]BF$–$DTBQ^{-}\cdot$ system have been subtracted from the counts for the $O_2^{-}\cdot$ systems in DMF. [c] Water used as the solvent rather than DMF.

$O_2(^1\Delta_g)$ is a product in the $O_2^{-}\cdot$ oxidation, we employed the quencher DPBF.

The substrates which have been used to oxidize and to dismutate $O_2^{-}\cdot$ include ferrocenium tetrafluoroborate ($[FeCp_2]BF_4$), ferric perchlorate, tris(*N,N'*-dioxobipyridyl)manganese(III) perchlorate ($[Mn^{III}(bpyO_2)_3](ClO_4)_3$), di-$\mu$-oxo-bis[phenanthrolinato)manganese(IV)] perchlorate ($[Mn^{IV}(phen)_2O]_2(ClO_4)_4$), and perchloric acid.

Experimental Section

Chemicals and Reagents. Burdick and Jackson "distilled in glass" dimethylformamide (DMF) was obtained in quart bottles to minimize contamination by water. The water content as specified by the manufacturer was 0.016%. Tetraethylammonium perchlorate (TEAP) and ferric perchlorate from G. Frederick Smith were dried in vacuo. TEAP was used as the supporting electrolyte (0.1 M) in the electrochemical experiments. 1,3-Diphenylisobenzofuran (DPBF) from K & K Laboratories was used without further purification; its IR spectrum (Nujol mull) did not exhibit a carbonyl absorption at 1650 cm^{-1}. High-purity argon and oxygen were obtained from the Chemetron Corp. All solutions were degassed with argon prior to analysis. Perchloric acid, hydrogen peroxide, and sodium hypochlorite were obtained from Mallinkrodt, Inc. Ferrocence from Aldrich Chemical Co. was purified by sublimation. Ferrocenium tetrafluoroborate ($[FeCp_2]BF_4$) was prepared by the method of Hendrickson, Sohn, and Gray.[12] Tris(*N,N'*-dioxobipyridyl)manganese(III) perchlorate ($[Mn^{III}(bpyO_2)_3]ClO_4)_3$) was prepared by the method of Nyholm and Turco.[13] Di-μ-oxo-bis[bis(phenanthrolinato)manganese(IV)] perchlorate ($[Mn^{IV}(phen)_2O]_2(ClO_4)_4$) was prepared by the method of Goodwin and Sylva.[14] Known concentrations of $O_2^{-}\cdot$ were generated electrochemically by reduction of O_2-saturated solutions at −1.2 V vs. SCE. Upon completion of the electrolysis, the $O_2^{-}\cdot$ solution was degassed with argon to remove any residual oxygen. The concentration of $O_2^{-}\cdot$ was monitored by cyclic voltammetry with the anodic current measured at −0.7 V vs. SCE. The current in relation to $O_2^{-}\cdot$ concentration was standardized by controlled-potential coulometric analysis.

Instrumentation. The cyclic voltammetric experiments were accomplished either with a three-electrode potentiostat–amperostat constructed with operational amplifiers[15] or with a Princeton Applied Research Model 173/175/179 potentiostat–galvanostat and universal programmer. The voltammograms were recorded with a Houston Instruments Omnigraph 2000 X-Y recorder. Either a Princeton Applied Research Model 175 potentiostat–galvanostat or a Wenking Model 61RH potentiostat was utilized for the controlled-potential electrolysis experiments.

The working electrode for the cyclic voltammetric experiments was a Beckman platinum-inlay electrode (No. 39273) which had surface area of 0.23 cm^2. The auxiliary electrode was a platinum flag electrode which was isolated from the bulk solution by a medium-porosity frit which contained solvent and a granule of activated alumina to neutralize and adsorb oxidation products. The reference electrode was a Ag/AgCl (aqueous tetramethylammonium chloride) cracked glass-bead electrode which was adjusted to 0.00 V vs. SCE.[16] The reference electrode was located inside a Luggin capillary in the cell assembly. A cylindrical platinum-mesh electrode was used as the working electrode for the controlled-potential electrolysis experiments.

The UV–visible spectra was recorded with either a Cary 17D or Cary 219 spectrophotometer. IR spectra were recorded with a Perkin-Elmer Model 283 spectrophotometer. A Princeton Applied Research Model 1140A/B quantum photometer equipped with a 1P28 photomultiplier tube in combination with a Houston Instruments Omnigraph 100 Series recorder was used to count photons.

In the chemiluminescence experiments, the optical cell was a 25 × 200 mm Pyrex test tube which was positioned adjacent to the photomultiplier. Two Hamilton gastight syringes were placed on an aluminum apparatus that allowed equal volumes of the reactant solutions to be delivered simultaneously to the optical cell. Corning filters 2-73 and 2-64 were used to resolve the emitted radiation and were placed between the optical cell and the photomultiplier. All luminescence experiments were carried out in a photographic darkroom to minimize stray light.

Results

$^1O_2$ Photon Yield. The chemiluminescence of dimeric $O_2(^1\Delta_g)$ has a band at 633.4 nm and a more intense one at 703.2 nm.[17,18] In addition, $O_2(^1\Sigma_g{}^+)$ emits at 762.0 nm, and dimeric $O_2(^1\Delta_g)$ has a much weaker emission at 786.0 nm.[19] These bands are for aqueous media and may not represent the emission spectrum for $O_2(^1\Delta_g)$ in DMF.

Under suitable conditions the photoemission of dimeric $O_2(^1\Delta_g)$ can be observed by photon-counting techniques. Because of the low concentrations of reactants in these experiments, a monochromator or an interference filter cannot be employed to resolve light emission. Consequently, two Corning dielectric filters, 2-73 and 2-64, have been used to resolve the emitted light. Filter 2-73 transmits from 570 (0.5% *T*) to 900 nm (36.6% *T*) with maxima at 622 (40.0% *T*), 638 (42.9% *T*), and 756 nm (44.7% *T*) and minima at 626 (39.7% *T*) and at 660 nm (38.3% *T*). Filter 2-64 transmits from 650 (2.1% *T*) to 900 nm (85.2% *T*) with a broad maximum from 740 to 770 nm (81.4% *T*). With the assumption that solvent-induced shifts are minimal, filter 2-73 should transmit the emission for both major bands of $O_2(^1\Delta_g)$ whereas filter 2-64 should transmit emission only from the 703.2-nm band. Employing these filters, experiments have been carried out by syringing a solution of electrogenerated $O_2^{-}\cdot$ (5.0 mL, ~2.0 mM) and a solution of substrate (5.0 mL, ~2.0 mM) into a

---

(12) Hendrickson, D. N.; Sohn, Y. S.; Gray, H. B. *Inorg. Chem.* **1971**, *10*, 1559.

(13) Nyholm, R. S.; Turco, A. *J. Chem. Soc.* **1962**, 1121.

(14) Goodwin, H. A.; Sylva, R. N. *Aust. J. Chem.* **1967**, *20*, 629.

(15) Goolsby, A. D.; Sawyer, D. T. *Anal. Chem.* **1967**, *34*, 411.

(16) Sawyer, D. T.; Roberts, J. L., Jr. "Experimental Electrochemistry for Chemists"; Wiley-Interscience: New York, 1974.

(17) Khan, A. U.; Kasha, M. *J. Chem. Phys.* **1963**, *39*, 2105.

(18) Khan, A. U.; Kasha, M. *J. Chem. Phys.* **1964**, *40*, 605.

(19) Khan, A. U. Kasha, M. *J. Am. Chem. Soc.* **1970**, *92*, 3293.

Table II. Yield of $O_2(^1\Delta_g)$ from the Oxidation and the Dismutation of $O_2^{-}\cdot$ in Dimethylformamide Solutions[a]

conditions	% yield of $O_2(^1\Delta_g)$[b]	% yield, cor[c]	no. of trials
5.00 mM NaOCl + 6.35 mM H_2O_2 + 0.98 mM DPBF (H_2O)[d]	98.3		1
1.05 mM $O_2^{-}\cdot$ + 1.01 mM $[FeCp_2]BF_4$ + 1.05 mM DPBF	13.4 ± 3.21	11.3	3
1.00 mM $O_2^{-}\cdot$ + 0.96 mM $Fe(ClO_4)_3$ + 1.05 mM DPBF	2.13 ± 1.21	0.0	2
1.05 mM $O_2^{-}\cdot$ + 1.00 mM $HClO_4$ + 1.00 mM DPBF	3.80 ± 2.07	1.7	2
1.00 mM $O_2^{-}\cdot$ + 1.16 mM DPBF	1.65 ± 0.54		2
1.02 mM $O_2^{-}\cdot$ + 0.97 mM DPBF	0.486		1

[a] 1,3-Diphenylisobenzofuran (DPBF) serves as the specific chemical trap for $^1O_2$. [b] Actually, these data represent the percentage of conversion of DPBF. [c] $O_2(^1\Delta_g)$ percent yields corrected for the interaction of $^3O_2$ and $O_2^{-}\cdot$ with DPBF in DMF. [d] Water used as the solvent rather than DMF.

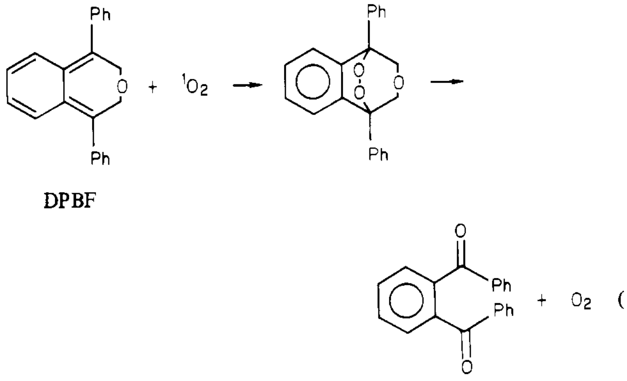
test tube that is adjacent to a photomultiplier tube which, in turn, is connected to a quantum photometer. Integration of plots of photons per second vs. time provides a measure of the photon yield.

Table I summarizes the photon yields that result from the combination of NaOCl and H_2O_2 in water[20] and from the oxidation of electrogenerated $O_2^{-}\cdot$ by $[FeCp_2]^+$, Fe^{3+}, $[Mn(phen)_2O]_2^{4+}$, and $[Mn(bpyO_2)_3]^{3+}$ in dimethylformamide (DMF). The light produced by the proton-induced dismutation of $O_2^{-}\cdot$ in DMF and the oxidation of 3,5-di-*tert*-butyl-*o*-semiquinone (DTBQ$^{-}\cdot$) by $[FeCp_2]^+$ in DMF also are tabulated. Under all conditions more light is obtained when filter 2-73 is present. The oxidation of $O_2^{-}\cdot$ by $[FeCp_2]^+$ and $[Mn(bpyO_2)_3]^{3+}$ generates more light than the NaOCl–H_2O_2 reaction. However, the $O_2^{-}\cdot$ oxidations have been carried out in DMF rather than in the aqueous medium of the NaOCl–H_2O_2 reaction. Moreover, measurements of emission rates indicate that the chemiluminescence process is more persistent when the experiments are performed in DMF (1 s as compared to 0.5 s).

Furthermore, in situ singlet oxygen chemiluminescence often corresponds to the fluorescence of an organic molecule.[19,21] Because all of the experiments, except the NaOCl–H_2O_2 reaction, have been performed in DMF, the solvent may enhance the number of photons counted and shift the number of photons counted in the presence of the two filters to the filter which transmits at higher energy, i.e., filter 2-73 (see Table I). Khan and Kasha[19,21] suggest that the dimeric singlet states of oxygen can be used as a quantum ladder for sensitizing luminescence of organic molecules. Ogryzlo and Pearson,[22] on the other hand, suggest a mechanism that involves the stepwise energy transfer from two singlet oxygen molecules to the organic substrate, in which the first energy-transfer collision excites the organic molecule to its triplet state and the second to its singlet excited state. That the chemiluminescence persists for longer time periods in DMF that it does for the NaOCl–H_2O_2 reaction in water is consistent with the strong quenching of singlet oxygen by aqueous media (the intrinsic half-life of the $^1\Delta_g$ species is reduced from 45 min in the gas phase to 2 μs in water).[23]

The bottom entry in Table I represents the photon count for a system in which no $O_2(^1\Delta_g)$ or $O_2(^1\Sigma_g^+)$ can be generated and illustrates the extent of photoemission by other chemical processes. With the subtraction of the number of counts for the $[FeCp_2]^+$–DTBQ$^{-}\cdot$ system in DMF from the remaining systems in DMF, an approximate correction is made for the chemiluminescence by excited species other than the singlet states of O_2. Such a subtraction gives the "corrected counts" of Table I. DTBQ$^{-}\cdot$ has been used because, like $O_2^{-}\cdot$, it is a one-electron reducing agent and is roughly equivalent to $O_2^{-}\cdot$ as a reducing agent (E_{pa} = −0.73 V vs. SCE for $O_2^{-}\cdot$; E_{pa} = −0.45 V vs. SCE for DTBQ$^{-}\cdot$).

Chemical Trapping. As an additional measure of the yield of singlet oxygen from the oxidation and dismutation of $O_2^{-}\cdot$, 1,3-diphenylisobenzofuran (DPBF) has been used as a specific trapping agent.[11] Its reaction with $^1O_2$ involves an addition step followed by formation of dibenzoylbenzene (DBB).



DPBF

DBB

(1)

Because DPBF reacts to a limited extent with triplet-state oxygen,[24] all solutions have been deaerated with argon and protected from light.

The electronic spectrum of DPBF exhibits three dominant bands at 414 mm (ε 24 700 M^{-1} cm^{-1}), 324 nm (ε 7900), and 311 nm (ε 8030). The peak at 414 nm has been used to determine the yield of $O_2(^1\Delta_g)$ because it has the largest molar absorptivity and the least amount of interference from ferrocene and dibenzoylbenzene (DBB). Cyclic voltammetry of DPBF in DMF at a Pt electrode indicates that the oxidation of DPBF is irreversible with E_{pa} = +0.835 V vs. SCE; the reduction of DPBF is quasi-reversible with E_{pc} = −1.875 V and E_{pa} = −1.800 V vs. SCE for the reverse scan.

By monitoring the loss in absorbance of the 414-nm band of DPBF, it is possible to estimate the percentage yield of $O_2(^1\Delta_g)$ for the oxidation and dismutation reactions of $O_2^{-}\cdot$. The results for such experiments are summarized in Table II. The control experiments with DPBF in the presence of $O_2(^3\Sigma_g^-)$ or $O_2^{-}\cdot$ indicate that DPBF is susceptible to oxidation by these molecules, which is in agreement with previous work.[24] Cyclic voltammetric measurements, however, establish that the reduction or oxidation of DPBF by $O^{2-}\cdot$ is thermodynamically impossible and that $O_2^{-}\cdot$ is stable in the presence of DPBF. Thus, the conversion of DPBF in the presence of $O_2^{-}\cdot$ may only reflect the oxidation of DPBF by $^3O_2$, which arises from the autodismutation process.

Reference to Table II indicates that the NaOCl–H_2O_2 and the $[FeCp_2]^+$–$O_2^{-}\cdot$ systems give substantial yields of $O_2(^1\Delta_g)$, 98.3% and 11.3%, respectively, but the Fe^{3+}–$O_2^{-}\cdot$ and H^+–$O_2^{-}\cdot$ systems do not. Indeed, the yields from the latter two systems are within the experimental limits of the measurements,[25] ±1.72% and ±2.93%, respectively. Because ferrocenium ion decomposes in DMF,[26] the experiments have been performed by dissolving it in DMF immediately before the addition of $O_2^{-}\cdot$.

---

(20) Foote, C. S.; Wexler, S.; Ando, W.; Higgins, R. *J. Am. Chem. Soc.* **1968**, *96*, 975.

(21) Khan, A. U.; Kasha, M. *J. Am. Chem. Soc.* **1966**, *88*, 1574.

(22) Ogryzlo, E. A.; Pearson, A. E. *J. Phys. Chem.* **1968**, *72*, 2913.

(23) Khan, A. U. *J. Phys. Chem.* **1976**, *80*, 2219.

(24) LeBerre, A; Ratsimbasafy, R. *Bull. Soc. Chim. Fr.* **1963**, *5*, 229.

(25) At the 90% confidence level.

(26) Prins, R.; Korswagen, A. R.; Kortbeek, A. G. T. G. *J. Organomet. Chem.* **1972**, *39*, 335.

In the presence of protons or Fe^{3+} ion $O_2^-\cdot$ is rapidly destroyed. Cyclic voltammetry and spectroscopy conform that in the presence of protons $O_2^-\cdot$ is dismutated to O_2 and H_2O_2, and in the presence of Fe^{3+} ion $O_2^-\cdot$ is oxidized to O_2 while Fe^{3+} ion is reduced to Fe^{2+} ion. In both cases, O_2 is a product; however, the data of Table II indicate that the yield of $O_2(^1\Delta_g)$ is extremely low.

When $O_2^-\cdot$ is combined with $[FeCp_2]BF_4$ in DMF, cyclic voltammetry and spectroscopy confirm that $O_2^-\cdot$ is oxidized to O_2 and ferrocenium ion is reduced to ferrocene. The chemical trapping experiments (Table II) indicate that a significant yield of $O_2(^1\Delta_g)$ is formed. This is consistent with the findings of Mayeda and Bard.[1,3] Although they observed a much higher conversion of DPBF (based on product isolation and analysis for *o*-dibenzoylbenzene (DBB)), this was accompanied by increased DPBF conversion in their control experiments with $^3O_2$. The present in situ studies minimize the exposure of DPBF to $^3O_2$.

The interaction of $[Mn(phen)_2O]_2^{4+}$ and $[Mn(bpyO_2)_3]^{3+}$ complexes with $O_2^-\cdot$ cannot be monitored by DPBF because both complexes react with DPBF in the absence of $O_2^-\cdot$. The reduction potential for the $[Mn(phen)_2O]_2^{4+}$ complex occurs at +1.34 V vs. SCE,[27] and the reduction potential for the $[Mn(bpyO_2)_3]^{3+}$ complex occurs at +0.87 V vs. SCE;[28] DPBF is oxidized at +0.83 V vs. SCE. Hence, DPBF is directly oxidized by these materials and interferes with their oxidation of $O_2^-\cdot$.

Discussion

Theoretical Assessment of the Energetics for Electron Transfer from $O_2^-\cdot$. The electron-donation properties of superoxide ($O_2^-\cdot$) and the reaction surface associated with the donation of hydrogen by the perhydroxyl radical ($HO_2\cdot$) have been evaluated by use of SCF-MO-INDO theory to aid in the interpretation of the data. The calculations have involved unrestricted open-shell procedures which, to a first approximation, can be used to describe pure spin states.[29] The important aspect of the unrestricted open-shell method is the ability to assign eigenvalues to individual one-electron molecular orbitals. Therefore, qualitative predictions of which electron will be most easily removed, of its specific spin orientation, and of the resultant multiplicity of the molecule once the electron has been removed are possible.

The INDO calculations predict that the highest energy occupied molecular orbital of O_2 is a $\pi_g{}^\beta$ orbital which is more than 0.45 eV (43 kJ/mol) higher in energy than the next highest energy $\pi_g{}^\alpha$ orbital. Accordingly the adiabatic removal of an electron will energetically favor the removal of the $\pi_g{}^\beta$ ($\downarrow$) electron to give triplet oxygen. (Note that there are seven α-spin valence electrons and six β-spin valence electrons in the superoxide ion. The removal of one β electron will produce a triplet state.)

The perhydroxyl radical ($HO_2\cdot$) is an important intermediate in the dismutation of superoxide in the presence of proton donors.[30,31] So that the adiabatic removal of an electron from $O_2^-\cdot$ could be studied, the reaction surface for the abstraction of hydrogen from $HO_2\cdot$

$$HO_2\cdot \rightarrow O_2 + H\cdot \qquad (2)$$

has been calculated. At equilibrium, the hydrogen atom is bonded to the central oxygen atom via equal contributions of σ^α and σ^β orbitals. Accordingly, the total electron density on hydrogen is made up of equal amounts of electrons from the α set and the β set ($P_{HH}{}^\alpha = 0.43$, $P_{HH}{}^\beta + 0.43$, $P_{HH}{}^{tot} = 0.86$). However, when the hydrogen atom is moved away from its equilibrium position in any direction, the calculations indicate that $P_{HH}{}^\alpha$ decreases and $P_{HH}{}^\beta$ and $P_{HH}{}^{tot}$ increase, with the variations in the electron density being relatively smooth functions of position. At sufficiently large OH bond lengths, $P_{HH}{}^\alpha$ drops to zero and $P_{HH}{}^\beta$ and $P_{HH}{}^{tot}$ increase to unity. These effects are illustrated in Figure 1 and indicate that triplet oxygen is produced as a result of hydrogen abstraction from $HO_2\cdot$. Note that Figure 1 demonstrates that triplet oxygen is formed for any surface path followed by the abstraction reaction. Consequently, vibronic and/or nonadiabatic mechanisms are unlikely to favor the formation of singlet oxygen via hydrogen abstraction from $HO_2\cdot$.

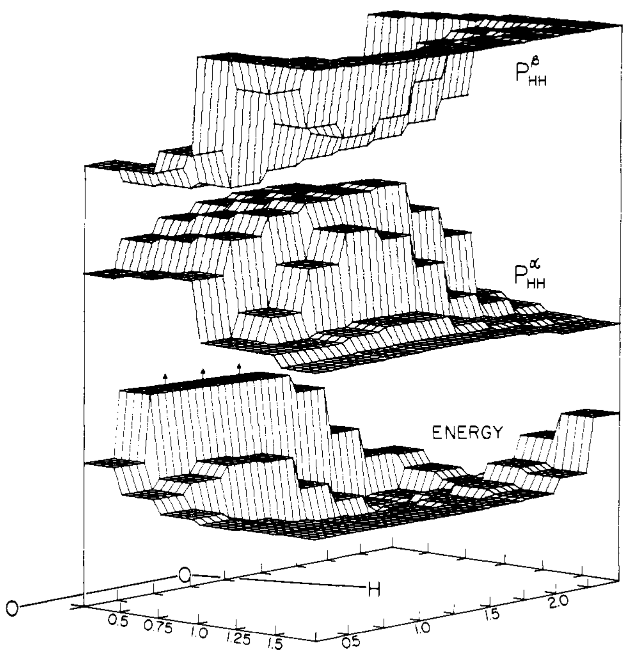


Figure 1. The abstraction of hydrogen from the perhydroxyl radical as calculated by use of SCF-MO-INDO unrestricted open-shell theory. The oxygen atoms are at (0, 0) and (1.198 Å, 0), and the indicated surfaces are calculated for hydrogen atom positions in the range $x = 0.25$–2.5 Å and $y = 0.25$–1.75 Å in 0.25-Å increments. The calculated equilibrium conformation is depicted at the bottom of the figure, and the coordinate matrix calculated for the hydrogen atom is indicated in angstroms. The lowest surface depicts the total electronic energy of the $HO_2\cdot$ radical as a function of hydrogen coordinate; the vertical arrows indicate a truncated region of the surface. The diagonal elements of the α- and β-electron density matrices associated with the 1s orbital of hydrogen are depicted in the center and top surfaces, respectively.

In summary, the calculations indicate that the dismutation of superoxide will form oxygen in its ground triplet ($^3\Sigma_g{}^-$) state whenever the electron is adiabatically removed via one-center (charged) electron sinks. The calculations of Koppenol and Butler,[31] however, indicate that if the oxidation involves the reaction of $O_2^-\cdot$ with a doublet radical, electron transfer may form singlet ($^1\Delta_g$) oxygen. The salient observation is that the multiplicity of the transition state will dictate the multiplicity of the oxygen generated by the dismutation reaction (see below).

Formation of $^1O_2$. Both the photon-counting and the chemical-trapping experiments indicate that a low yield of singlet oxygen arises from the oxidation of $O_2^-\cdot$ by Fe^{3+} ion. This is consistent with the theoretical calculations, which illustrate that the favored transition state of the redox reaction is a triplet (or higher) state that leads primarily to the formation of $O_2(^3\Sigma_g{}^-)$

$$\cdot Fe^{III} + :O_2^-\cdot \rightarrow {}^3[\cdot Fe^{III}:O_2^-\cdot] \rightarrow \cdot Fe^{II}\cdot + \cdot{}^3O_2\cdot \qquad (3)$$

---

(27) Morrison, M. M.; Sawyer, D. T. *Inorg. Chem.* **1978**, *17*, 333.

(28) Morrison, M. M.; Sawyer, D. T. *Inorg. Chem.* **1978**, *17*, 338.

(29) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.

(30) Sawyer, D. T.; Gibian, M. J. *Tetrahedron* **1979**, *35*, 1471.

(31) Kappenol, W. H.; Butler, J. *FEBS Lett.* **1977**, *83*, 1.

Further, this is consistent with the recent report that $O_2^{-}\cdot$ forms an electron-pair donor complex with manganese(II) rather than a singlet reaction complex.[32] In contrast, the high yields of singlet oxygen (based on photon counting) from the oxidaion of $O_2^{-}\cdot$ by $[FeCp_2]^+$, $[Mn(bpyO_2)_3]^{3+}$, and $[Mn(phen)_2O]_2^{4+}$ provide convincing evidence that a singlet transition state is favored in these redox reactions.

$$O_2^{-}\cdot + \cdot FeCp_2^+ \rightarrow {}^1[O_2{:}FeCp_2] \rightarrow {}^1O_2 + {:}FeCp_2 \quad (4)$$

Such a conclusion is further supported by the singlet trapping experiments of Table II as well as by those of Mayeda and Bard.[1]

The yield of singlet oxygen from the proton-induced dismutation of $O_2^{-}\cdot$ is extremely low (see Tables I and II). This result is consistent with previously reported low yields of singlet oxygen from the proton-induced dismutation of $O_2^{-}\cdot$.[33,34] One explanation which has been suggested[35,36] for such low yields is that singlet oxygen is quenched by a rapid ($k = 1.6 \times 10^9$ $M^{-1}\ s^{-1}$) redox reaction with $O_2^{-}\cdot$. However, the conditions of the present experiments are such that this cannot account for the low singlet oxygen yield, especially in view of the high yield from the $[FeCp_2]^+$–$O_2^{-}\cdot$ reaction for comparable concentrations of $O_2^{-}\cdot$. If the proton-induced dismutation of $O_2^{-}\cdot$ occurs via a stepwise mechanism that involves a triplet transition state with electron transfer from $O_2^{-}\cdot$ to $HO_2\cdot$ (eq 5 and 6), then ground-state triplet O_2 should be favored (see Theoretical section). Because erythrocytic superoxide dismutase (SOD) catalyzes the dismutation of $O_2^{-}\cdot$ to ground-state ${}^3O_2$,[37] the enzymic mechanism may also involve a triplet transition state. Alternatively, the oxidation of $O_2^{-}\cdot$ by the oxidized form of SOD may involve a direct adiabatic electron transfer to give $O_2({}^3\Sigma_g^-)$, as predicted by the theoretical calculations.

$$O_2^{-}\cdot + H^+ \rightarrow \cdot O_2H \quad (5)$$

$$\cdot O_2H + O_2^{-}\cdot \rightarrow [\cdot O_2{:}H{:}O_2\cdot]^-_{TS} \rightarrow {}^-O_2H + {}^3O_2 \quad (6)$$

Our experimental results indicate that oxidation of $O_2^{-}\cdot$ by adiabatic electron transfer yields $O_2({}^3\Sigma_g^-)$ and that whether triplet or singlet state O_2 results from other oxidation and dismutation reactions of $O_2^{-}\cdot$ is determined by the multiplicity of the transition state (triplet and singlet, respectively). The results of Table I and II support the conclusions that reactions of $O_2^{-}\cdot$ with protons and $Fe(ClO_4)_3$ result in either triplet transition states or adiabatic electron transfer and that the $[FeCp_2]^+$, $[Mn(bpyO_2)_3]^{3+}$, and $[Mn(phen)_2O]_2^{4+}$ complexes oxidize $O_2^{-}\cdot$ via a singlet transition state.

Acknowledgment. This work was supported by the National Science Foundation under Grant Nos. CHE76-24555 and CHE79-22040, the U.S. Public Health Service—NIH under Grant No. GM-22761, the Research Corp. under Grant No. 50678, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. $O_2^{-}\cdot$, 11062-77-4; O_2, 7782-44-7; $[Fe(Cp)_2]BF_4$, 1282-37-7; $[Mn(bpyO_2)_3](ClO_4)_3$, 75961-56-7; $[Mn(phen)_2O]_2(ClO_4)_4$, 62412-52-6; $Fe(ClO_4)_3$, 13537-24-1; $HClO_4$, 7601-90-3; NaOCl, 7681-52-9; H_2O_2, 7722-84-1; $DTBQ^{-}\cdot$, 18802-82-9; DPBF, 5471-63-6; $HO_2\cdot$, 3170-83-0.

---

(32) Bielski, B. H. J.; Chan, P. C. *J. Am. Chem. Soc.* **1978**, *100*, 1920.

(33) Nilsson, R.; Kearns, D. R. *J. Phys. Chem.* **1974**, *78*, 1681.

(34) Poupko, R.; Rosenthal, I. *J. Phys. Chem.* **1973**, *77*, 1722.

(35) Giuraud, H. J.; Foote, C. S. *J. Am. Chem. Soc.* **1976**, *98*, 1984.

(36) Khan, A. U. *J. Am. Chem. Soc.* **1977**, *99*, 370.

(37) Zimmerman, R.; Flohe, L.; Weser, U.; Hartmann, H. *FEBS Lett.* **1973**, *29*, 117 .

Contribution from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47401

Studies of Boranes. 47.[1] Synthesis and X-ray Crystallographic Study of Tetradecaborane(20)[2]

JOHN C. HUFFMAN, DAVID C. MOODY, and RILEY SCHAEFFER*

Received April 10, 1980

Tetradecaborane(20) was obtained in low yield by the following synthetic route: $KB_6H_9 + B_8H_{12} \xrightarrow{Et_2O} [KB_{14}H_{21}] \xrightarrow{HCl} B_{14}H_{20} + H_2 + KCl$. The yellow thermochromic compound crystallizes in space group $P2_12_12_1$, with $a = 13.119$ (4), $b = 9.976$ (3), and $c = 8.963$ (3) Å (at −164 °C), with ρ(calcd) = 0.971 g/cm³ for $Z = 4$. The structure was solved by direct methods. Anisotropic least-squares refinement of boron positional parameters and isotropic refinement of hydrogen parameters yielded residuals of $R_1 = 0.047$ and $R_2 = 0.021$. The molecule consists of two B_8H_{12}-type fragments fused in a cis fashion and nearly possesses C_{2v} symmetry in the solid state.

Introduction

Relatively few neutral boron hydrides containing between 11 and 20 borons have been reported. Earlier studies in this area resulted in the synthesis of n-$B_{18}H_{22}$, i-$B_{18}H_{22}$, and $B_{20}H_{16}$.[3] Heřmánek and co-workers later prepared $B_{16}H_{20}$[4] and have reported its controlled hydrolysis to yield the first 14-boron-containing species, $B_{14}H_{18}$.[5] More recently, however, work in this laboratory on the acid–base reactions of boron hydrides has led to a systematic method of preparation of both large and small boranes. In the range of B_{11}–B_{20}, three new hydrides have been obtained: $B_{13}H_{19}$,[6] $B_{14}H_{22}$,[7] and $B_{15}H_{23}$.[7,8]

In this paper we wish to report the planned synthesis and X-ray crystallographic study of a stable new B_{14} hydride, tetradecaborane(20), $B_{14}H_{20}$.[2] The synthesis takes advantage

---

(1) For the preceding paper in this series see David C. Moody and Riley Schaeffer, *Inorg. Chem.*, **15**, 233 (1976).

(2) A preliminary communication of this work has already appeared: John C. Huffman, David C. Moody, and Riley Schaeffer, *J. Am. Chem. Soc.*, **97**, 1621 (1975).

(3) Earl L. Muetterties, "The Chemistry of Boron and Its Compounds", Wiley, New York, 1967.

(4) J. Plešek, S. Heřmánek, B. Štíbr, and F. Hanousek, *Collect. Czech. Chem. Commun.*, **32**, 1095 (1967); **33**, 699 (1968).

(5) S. Heřmánek, K. Fetter, and J. Plešek, *Chem. Ind.*, **5**, 606 (1972).

(6) (a) J. C. Huffman, D. C. Moody, J. W. Rathke, and R. Schaeffer, *J. Chem. Soc., Chem. Commun.*, 308 (1973); (b) Jerome Rathke, David C. Moody, and Riley Schaeffer, *Inorg. Chem.*, **13**, 3040 (1974).

(7) Jerome Rathke and Riley Schaeffer, *Inorg. Chem.*, **13**, 3008 (1974).

(8) Jerome Rathke and Riley Schaeffer, *J. Am. Chem. Soc.*, **95**, 3042 (1973).

0020-1669/81/1320-0741$01.00/0 © 1981 American Chemical Society