sixth coordination position in cytochrome *c* peroxidase is surrounded by tryptophan, histidine, and arginine;[20] the last is an obvious candidate for the site of protonation in reduction, coordination of anions, and activation of H_2O_2. The most likely sites for coupled proton uptake in the physiological range are therefore the side chains of lysine and arginine (RNH_2, as in our model and possibly peroxidase), serine, threonine, and tyrosine (RO^-, as in cytochrome c_2); less likely are cysteine (RS^-, too readily oxidized), histidine, and tryptophan (heterocyclic anions, charge too diffuse; neutral histidine, p*K* too low).

Further work with other substituted imidazoles will be reported elsewhere.

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Formation of Superoxide Ion from Singlet Oxygen. On the Use of a Water-Soluble Singlet Oxygen Source

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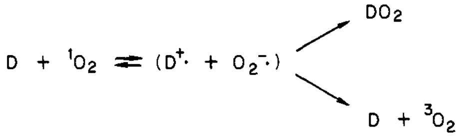
Received August 13, 1980

An electron-transfer mechanism giving rise to a radical cation–superoxide ion pair or charge-transfer complex has been proposed in the singlet oxygenations of electron-rich substrates (D) and the quenching process of singlet oxygen ($^1O_2$) by certain quenchers.[1] These examples include (1) [2 + 2] cycloaddition of $^1O_2$ to enamines proposed by Foote,[2] (2) reactions with phenols,[3] sulfides,[4] and azines,[5] and (3) quenching of $^1O_2$ by phenols,[3a] sulfides,[4] amines,[1a,6] and NADH.[7] Schaap et al.[8] have reported that [2 + 2] cycloaddition of $^1O_2$ to vinyl ethers does not seem to involve electron transfer. However, the evidence for the formation of superoxide ion ($O_2^-\cdot$) from $^1O_2$ has not been obtained so far in either the reaction or the quenching process.[9] The radical cation–$O_2^-\cdot$ pair would be short-lived because of the rapid reverse electron transfer and chemical reaction within a cage. One of the most effective methods for detecting such short-lived $O_2^-\cdot$ would be an enzymic assay utilizing superoxide dismutase (SOD), owing to its highly specific and rapid ($k = 2 \times 10^9\ M^{-1}\ s^{-1}$) reaction with $O_2^-\cdot$.[12] A highly polar aqueous solvent would also be preferable for such an electron-transfer reaction. For this purpose, a water-soluble chemical source[13] that can generate $^1O_2$ under mild conditions (up to 40 °C) and gives no significant effect on the enzyme activity is highly desirable. Photochemical methods can be used as $^1O_2$ sources only with special precaution, since illumination of dye photosensitizers in the presence of oxygen may often produce $O_2^-\cdot$ with the intervention of photoreduced dyes.[11] We report herein the first observation of $O_2^-\cdot$ from the reaction of $^1O_2$ with aromatic amines by using SOD and a newly developed water-soluble $^1O_2$ source.



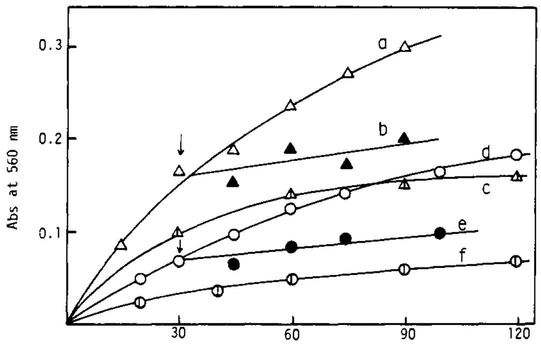


Figure 1. Reduction of NBT during incubation of the endoperoxide (**2**) and *N,N*-dimethyl-*p*-anisidine (**5**) in the presence and absence of SOD. A solution containing **2** (2 mM), **5** (1 mM), and NBT (1 mM) was shaken at 35 °C. After incubation dimethylformamide was added to dissolve the precipitated diformazan, and absorbance change at 560 nm was measured: curve (a) △, (b) ▲, and (c) ▲ in $NaHCO_3$ saturated aqueous solution (pH 8.3); curve (d) ○, (e) ●, and (f) ⦶ in phosphate buffer (pH 7.5). SOD (32 μg/mL) was added at the point indicated by arrow (b, e) or prior to the incubation (c, f).

Methylene blue sensitized photooxygenation of 3-(4-methyl-1-naphthyl)propionic acid[14] (**1**, 0.15 M) in dichloromethane–methanol (8:5) at 0 °C followed by rapid column chromatography (silica gel, $CHCl_3$) gave the naphthalene 1,4-endoperoxide **2**[15] (80%) (Scheme I). The endoperoxide **2** was soluble in phosphate buffer or $NaHCO_3$ saturated aqueous solution.[16] Warming the solution to 35 °C produced **1** quantitatively with the liberation of $^1O_2$.[17,18] In phosphate buffer at pH 7.5, **2** reverted with a half-life of 23 min (E_a = 17 kcal/mol) at 35 °C to **1** and $^1O_2$. The formation of $^1O_2$ was confirmed by the reaction of α-lipoic acid[13] or imidazole–nitrosodimethylaniline,[19] both of which are known to react with $^1O_2$ in water. The effectiveness of **2** in singlet oxygenation in aqueous solvent is also illustrated by the successful isolation of *N*-formylkynurenine (**3**, 23%) and **4**[20] (42%) from the

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(9) Hematoporphyrin sensitized photooxidation of NADH has been reported to produce $O_2^-\cdot$.[10] However, the interaction between photoexcited sensitizer and oxygen resulting in production of $O_2^-\cdot$ directly[11] could contribute to confusion in such experiments.[7]

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(11) (a) Usui, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 440. (b) Beauchamp, C.; Fridovich, I. *Anal. Biochem.* **1971**, *44*, 276. (c) Srinivasan, V. S.; Podolski, D.; Westrick, N. J.; Neckers, D. C. *J. Am. Chem. Soc.* **1978**, *100*, 6513. (d) Cox, G. S.; Whitten, D. G. *Chem. Phys. Lett.* **1980**, *67*, 511.

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(15) KI-starch test, positive; ^1H NMR ($CDCl_3$) δ 1.9 (s, 3 H, Me), 2.70–2.85 (m, 4 H, CH_2CH_2), 6.7 (s, 2 H, CH=CH), 7.2–7.4 (m, 4 H, aromatic H), 9.2 (br, s, 1 H, COOH); ^{13}C NMR ($CDCl_3$–CD_3OD) δ 14.8, 24.2, 27.2, 77.8, 79.3, 119.3, 119.4, 125.8, 125.9, 136.0, 139.2, 139.6, 140.2, 174.5.

(16) **2** was soluble up to 10 mM in 0.26 M phosphate buffer (pH 7.5) and up to 40 mM in $NaHCO_3$ saturated aqueous solution (pH 8.3) at 25 °C.

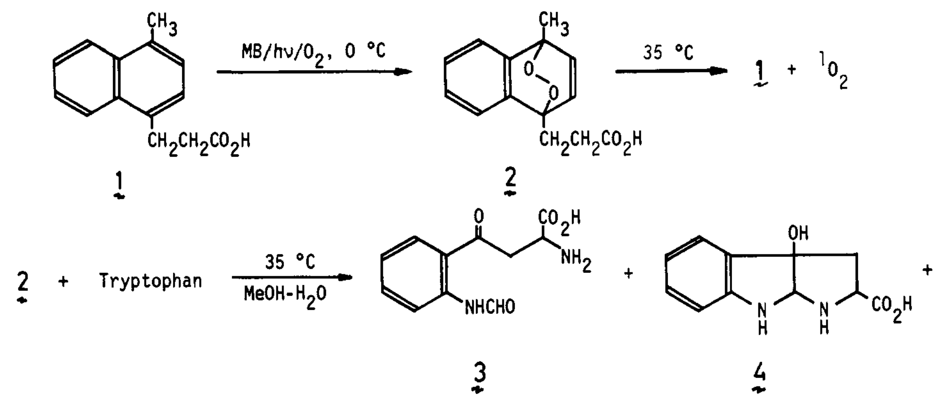
(17) Wasserman, H. H.; Larsen, D. L. *J. Chem. Soc., Chem. Commun.* **1972**, 253. See also: Saito, I.; Matsuura, T., ref 1b, p 511.

(18) A trapping experiment with the singlet oxygen acceptor, diphenylisobenzofuran, in methanol has shown that $^1O_2$ is formed in more than 82% yield.

(19) Kraljič, I.; Mohsni, S. El. *Photochem. Photobiol.* **1978**, *28*, 577.

0002-7863/81/1503-188$01.00/0

Scheme I



reaction of **2** (2.8 mM) and tryptophan (0.4 mM) in aqueous methanol.

To test for generation of $O_2^{-}\cdot$ from the reaction of $^1O_2$ with aromatic amines, a combination of *p*-nitro blue tetrazolium (NBT)[11b,21] and SOD[12,22] was used as a detecting reagent for $O_2^{-}\cdot$. When an anaerobic solution of **2** (2 mM), *N*,*N*-dimethyl-*p*-anisidine (**5**, 1 mM), and NBT (1 mM) in 0.26 M phosphate buffer (pH 7.5) was shaken at 35 °C for 2 h, NBT was reduced to diformazan which was readily detectable by its characteristic UV absorption at 560 nm. The superoxide inhibiting enzyme, SOD, substantially inhibited the formation of diformazan, whether it was added during or prior to the reaction (Figure 1). From the known stoichiometry of the NBT reduction by $O_2^{-}\cdot$,[11b,23] the yield of the $O_2^{-}\cdot$ trapped by NBT is estimated to be 1.1% on the basis of **5** (37% on the basis of consumed **5**) after 2-h reaction (Scheme II). The yield of $O_2^{-}\cdot$ was further confirmed by the reduction of ferricytochrome *c* in place of NBT under the same conditions.[24,25] SOD again inhibited the reduction of cytochrome *c*.

The following control experiments have demonstrated that both $^1O_2$ and aromatic amine **5** are indispensable for the formation of $O_2^{-}\cdot$: (i) Incubation of **2** and NBT in the absence of **5** under the conditions did not produce $O_2^{-}\cdot$. (ii) Autoxidation of **5** (1 mM) in phosphate buffer (pH 7.5) under oxygen bubbling was negligibly slow, and the addition of NBT (1 mM) to the system produced only a small amount of diformazan even after prolonged reaction (4 h).[26] (iii) The decomposition rate of **2** was first order (k = 4.9 × 10^{-4} s^{-1} at 35 °C) and independent of the concentrations of **5** and NBT, eliminating a bimolecular reaction between **2** and **5** or NBT.[27] (iv) Diformazan was not formed when H_2O_3 (2.5 mM) was added to the solution containing **5** (1 mM) and NBT (1 mM) under the specified conditions (35 °C, 2 h). (v) Incubation of the solution (**2**, **5**, NBT) below 20 °C, where the generation of $^1O_2$ is suppressed, never produced diformazan. These results strongly suggest that $O_2^{-}\cdot$ is produced by a direct reaction of $^1O_2$ with **5**. In fact, addition of a $^1O_2$ quencher, NaN_3 (15 mM), to the reaction system inhibited 60% of the $O_2^{-}\cdot$ formation.[28] Hydrogen peroxide is not responsible for the formation of $O_2^{-}\cdot$ since addition of catalase to the system (**2**, **5**, NBT) did not inhibit the diformazan formation. The possibility that $O_2^{-}\cdot$ is formed by the decomposition of hydroperoxidic products formed via a $^1O_2$-initiated radical chain autoxidation[5,29] of **5** under the conditions is ruled out by the following facts: (i) Addition of N_2O[30] or 2-propanol (up to 2 M) as a radical scavenger to the system did not affect the formation of $O_2^{-}\cdot$ appreciably.[31] (ii) The yield of $O_2^{-}\cdot$ was not changed whether the reaction was carried out under anaerobic conditions or under oxygen bubbling.

Young et al.[16] have demonstrated that $^1O_2$ undergoes physical quenching by a series of substituted *N*,*N*-dimethylanilines, including **5** (k_q = 2.09 × 10^8 M^{-1} s^{-1}), via partial charge-transfer intermediates in methanol, and they suggested that the rate constant for quenching should be more than 100 times greater than any possible photooxidation of these amines. In fact, reaction of **2** (2 mM), **5** (1 mM), and NBT (1 mM) at 35 °C for 2 h resulted in only 3% conversion of the amine **5**, with the decomposition of **2** being more than 80%.[32,33] Thus, it seems likely that major portion of the $O_2^{-}\cdot$ formed results from the quenching process of $^1O_2$ by **5**. The formation of $O_2^{-}\cdot$ may most reasonably be explained in terms of one electron-transfer reaction from **5** (E_{ox}, 0.49 V vs. SCE)[34] to $^1O_2$. Such an electron transfer seems to be at least energetically feasible in highly polar aqueous solution.[35] Under conditions which produced $O_2^{-}\cdot$ in 1.1% yield with **5**, the reaction with *N*,*N*-dimethyl-*p*-toluidine (E_{ox}, 0.65 V vs. SCE)[37] gave only 0.3% of $O_2^{-}\cdot$. Substrates having higher oxidation potentials (E_{ox}, 0.65 V vs. SCE), such as *N*,*N*-dimethylaniline (0.71 V),[37] *N*,*N*-dimethylbenzylamine (0.92 V),[38] Dabco (0.68 V),[39] and

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[25] The reduced form of cytochrome *c* has been shown to be an efficient quencher of $^1O_2$.[7]

[26] The yield of diformazan was less than 0.2% based on **5** after 4-h reaction. Note that the system (**2**, **5**, NBT) produced 4.4% of diformazan within 2 h.

[27] Reaction of endoperoxides with *N*,*N*,*N'*,*N'*-tetramethylphenylenediamine, see: Boyd, J. D.; Foote, C. S.; Imagawa, D. K. *J. Am. Chem. Soc.* **1980**, *102*, 3641.

[28] A similar result has been obtained with the use of 1,4-diazabicyclo[2.2.2]octane (Dabco) as $^1O_2$ quencher.

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[30] Hopkins. T. R.; Lumry, R. *Photochem. Photobiol.* **1972**, *15*, 555.

[31] The yield of $O_2^{-}\cdot$ was 1.0% in the presence of 2-propanol (2 M) and 0.8% in N_2O saturated solution after 2-h reaction.

[32] In this run 1.1% of $O_2^{-}\cdot$ based on **5** was detected. The disappearance of **2** and **5** was monitored by high-performance LC.

[33] It should be noted that incubation of **2** and **5** in the absence of NBT did not produce any detectable products. See also: ref 17 and Saito, I.; Abe, S.; Takahashi, Y.; Matsuura, T. *Tetrahedron Lett.* **1974**, 4001.

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[35] The free-energy change (ΔG) for an electron-transfer reaction is calculated from the Weller equation ($\Delta G = 23.06\ [E(A/A^{+}\cdot) - E(O_2^{-}\cdot/O_2) - e^2/\epsilon\alpha] - \Delta E_{0,0}$) by using the oxidation potential of **5** in CH_3CN,[34] the reduction potential of ground-state oxygen in the same solvent (−0.82 V vs. SCE),[36] the excitation energy of $^1O_2$, and 1.3 kcal/mol for $e^2/\epsilon\alpha$. The calculated ΔG for electron transfer from **5** to $^1O_2$ is 6.4 kcal/mol in CH_3CN. Much smaller or negative ΔG value may be expected for the electron-transfer reaction in alkaline aqueous solution, although neither oxidation potential of **5** nor the reduction potential of O_2 was measured under our experimental conditions. The following ΔG values (CH_3CN) are obtained for other amines; *N*,*N*-dimethyl-*p*-toluidine (10 kcal/mol) *N*,*N*-dimethylaniline (11.4 kcal/mol), Dabco (10.8 kcal/mol), and *N*,*N*-dimethylbenzylamine (16.7 kcal/mol).

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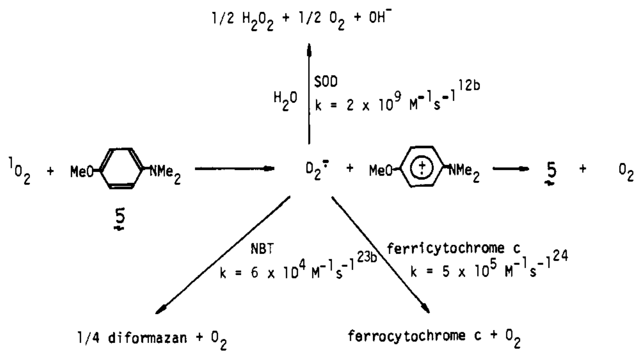
Scheme II



n-propylamine, did not produce $O_2^-\cdot$ by the reaction of **2** under similar conditions.[40] Note that *N*,*N*-dimethylbenzylamine[42] and *n*-propylamine[43] are known to be readily oxidized by $^1O_2$, leading to α-oxidation products probably via hydroperoxidic intermediates. Grossweiner[44] has proposed that the reaction of tryptophan with $^1O_2$ may proceed via an electron-transfer process. However, the reaction of tryptophan (3 mM), **2** (2.5 mM), and NBT (1 mM) in phosphate buffer (pH 7.5) under the specified conditions never produced diformazan. Likewise, Jefford and Boschung[45] have suggested the formation of $O_2^-\cdot$ by the reaction of $^1O_2$ with rose bengal. Under our conditions the reaction of **2** (2 mM) and rose bengal (0.045 mM) did not produce any trace of diformazan. These observations might imply that an electron-transfer reaction giving rise to $O_2^-\cdot$ is only possible for substrates with oxidation potentials *less than ~0.5 V vs. SCE in highly polar aqueous solvent*.

There is much current interest in uncovering chemical processes which could give rise to $O_2^-\cdot$ in vivo.[21,46] The results described here clearly demonstrate that the generation of $O_2^-\cdot$ from $^1O_2$ in the presence of electron donors is a viable process, although a definite conclusion on the electron-transfer process must await further studies. Furthermore, the newly developed water-soluble endoperoxide **2** may be used as a convenient, mechanistically less complicated, singlet oxygen source for the singlet oxygen reactions of biological systems in aqueous system under mild conditions. We are currently studing the electron-transfer reaction between $^1O_2$ and other electron-rich substrates of biological interests.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan. K.I. is indebted to the Japan Society for the Promotion of Science for financial support.

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(40) The diformazan formation from the reaction of **2**, NBT, and *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine (0.22 V vs. SCE)[41] could not be measured accurately because of the rapid formation of colored Würster salt from the reaction of the amine with ground-state oxygen.

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Metal-Hydrogen Bond Energies in Protonated Transition-Metal Complexes

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Received July 14, 1980

Existing data for transition-metal-hydrogen bond dissociation energies of neutral complexes are few and controversial.[1-8] For the ion BH^+, the homolytic bond energy $D(B^+–H)$ can be determined readily and accurately from the proton affinity (PA) and adiabatic ionization potential (IP) of the base B, as shown in the thermodynamic cycle of Scheme I, which yields the relationship given in eq 1.

Scheme I

$$\begin{tikzcd}
BH^+ \arrow[r, "D(B^+\text{-}H)"] \arrow[d, "PA(B)"'] & B^+ + H \\
B + H^+ \arrow[r, "IP(B)"'] & B^+ + H^+ + e^- \arrow[u, "-IP(H)"']
\end{tikzcd}$$

$$D(B^+\text{-}H) = PA(B) + IP(B) - IP(H) \qquad (1)$$

We report the proton affinities of 20 organotransition-metal complexes in the gas phase. For 16 of these complexes protonation occurs on the metal center, and the corresponding metal-hydrogen homolytic bond dissocation energies are determined. These data are summarized in Table I.

All proton affinities were determined by the techniques of ion cyclotron resonance spectroscopy,[9] by examining proton-transfer reactions in mixtures with compounds of known base strength. Ionization potentials are taken from a variety of sources and experimental procedures, as noted in Table I. The site of protonation in several of these compounds has been determined by either gas-phase or solution-phase studies; these results are also presented in Table I. For the cases indicated, ligand protonation corresponds to carbon-hydrogen, rather than metal-hydrogen, bond formation.

The following points emerge from the data presented in Table I:

(1) An average metal-hydrogen bond energy of 68 kcal/mol is computed from the 16 compounds for which protonation on the metal center is indicated. The enormous range of energies, from 53 kcal/mol for $D[CpFe(CO)_2CH_3^+–H]$ to 87 kcal/mol for $D[(CO_5)MnH^+–H]$, would suggest this average should be used only with extreme caution to predict the thermochemistry or reactivity of metal hydrides.

(2) Despite the wide range of bond strengths, periodic trends are apparent. In the first-row transition-metal carbonyls, the metal-hydrogen bond energy is a maximum for $D[(CO)_5Fe^+–H]$. On proceeding from a first-row compound to its second-row homologue, the metal-hydrogen bond energy increases. A difference of 7 kcal/mol is seen between $D[(CO)_6Cr^+–H]$ and $D[(CO)_6Mo^+–H]$ and between $D[CpCo(CO)_2^+–H]$ and $D[CpRh(CO)_2^+–H]$. A more substantial increase is evident with $D[Cp_2Ru^+–H]$, for which the bond energy is 25 kcal/mol stronger than $D[Cp_2Fe^+–H]$. There does not seem to be an increase in bond energy on proceeding from second- to third-row metals; however, the only example is $D[(CO)_6Mo^+–H]$ compared to $D[(CO)_6W^+–H]$. The 6 kcal/mol difference between $D[(CO)_5MnCH_3^+–H]$ and $D[(CO)_5ReCH_3^+–H]$ is consistent with these observations.

(3) Typically within a "homologous" series of compounds, the homolytic bond energy $D(B^+–H)$ remains constant.[11] It is clear on examining the three iron complexes listed in Table I that they do not constitute "homologous" molecules. We suggest that compounds with higher oxidation states of the same metal atom have substantially weaker metal-hydrogen bonds. Formation of several σ bonds causes changes in the electron density and orbital

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