Volume 27
Number 12
June 15, 1988

Inorganic Chemistry

Communications

Chemical Sources of Singlet Oxygen. 2.[1,2] Quantitative Generation of Singlet Oxygen from Hydrogen Peroxide Disproportionation Catalyzed by Molybdate Ions

Sir:

Although "spontaneous" disproportionation of hydrogen peroxide into water and singlet oxygen $^1\Delta_g$ (eq 1) is possible on

$$2H_2O_2 \rightarrow 2H_2O + {}^1O_2 \qquad (1)$$

thermodynamic grounds[3] and from spin-conservation rules,[4] it is well-known that if this reaction occurs, its rate is extremely low at room temperature.[4,5]

However, a recent report strongly suggests that this reaction can be efficiently catalyzed by molybdate ions.[1b] Chemical evidence is presented herein that MoO_4^{2-} reacts catalytically with H_2O_2 in aqueous basic solution to form $^1O_2$ quantitatively through the intermediacy of a diperoxomolybdate anion, MoO_6^{2-}.

Evidences for $^1O_2$ Generation. The formation of an endoperoxide of a polycyclic aromatic compound during an oxidation process already is a telling test for $^1O_2$ involvement.[1b] This test is even more convincing when it is coupled with the deuterium solvent effect resulting from the 14 ± 1 times longer lifetime of $^1O_2$ in D_2O than in H_2O.[7] In presence of a nonquenching chemical trap A, singlet oxygen arising from reaction 1 can either be quenched by water (eq 2) or react with the trap (eq 3).

$$^1O_2 + \text{water} \xrightarrow{k_d = 1/\tau} {}^3O_2 \qquad (2)$$

$$^1O_2 + A \xrightarrow{k_r} AO_2 \qquad (3)$$

Under stationary-state conditions and after integration between zero time and t, we obtain the following expression for the cumulated amount of $^1O_2$.[1b,8]

$$[^1O_2]_t = [A]_0 - [A]_t + (k_d/k_r)\ \ln\ ([A]_0/[A]_t)$$

Hence, if A is introduced at a concentration well below k_d/k_r, a minimum 10-fold enhancement of ln $([A]_0/[A]_t)$ should be observed when D_2O is used as a solvent instead of H_2O. Such a trapping experiment was previously carried out under nonoptimum conditions with tetrapotassium 9,10-diphenylanthracene-2,3,6,7-tetracarboxylate (DPATC) and led to a deuterium effect of only 3.2.[1b] The same experiment has now been performed at pH 10.5 to accelerate reaction 1 and in the presence of ethylenediaminetetraacetate (EDTA) to suppress the decomposition of H_2O_2 by impurities.[9] Under these conditions the isotope effect increased to 13 ± 1 in agreement with the theoretical value.

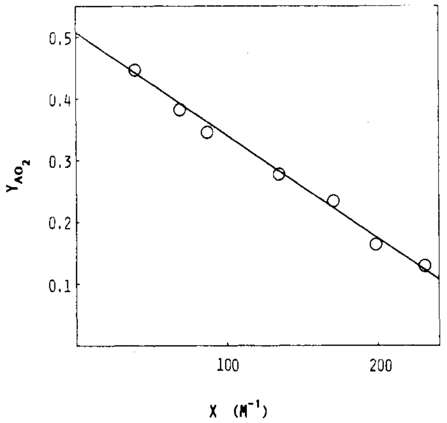

Figure 1. Competitive trapping of singlet oxygen. Conditions: 20 mM H_2O_2, 1 mM MoO_4^{2-}, 0.1 mM EDTA, phosphate buffer pH 10.5, 1.6–16 mM RTC, 25 °C, t = 1 h. Formation of $RTCO_2$ and loss of RTC were monitored by HPLC. H_2O_2 was titrated with permanganate.

Another reliable test is based on competition experiments between two acceptors of different reactivities. Thus, we have checked that the relative rates of peroxidation of DPATC and disodium 9,10-diphenylanthracene-2,7-disulfonate[6] were identical whether $^1O_2$ was produced by photosensitization or by the system H_2O_2/MoO_4^{2-}.

Reaction Stoichiometries. In moderately alkaline solutions (pH 8–12), MoO_4^{2-} acts as a catalyst[10] and is left unchanged when the dismutation is completed. We have measured the singlet oxygen yield $Y = [^1O_2]_t/([H_2O_2]_0 - [H_2O_2]_t)$ in trapping experiments with various concentrations of tetrapotassium rubrene-2,3,8,9-tetracarboxylate[11] (RTC); formation of $RTCO_2$ and loss of RTC were monitored by HPLC. When endoperoxide yields $Y_{AO_2} = ([A]_0 - [A]_t)/([H_2O_2]_0 - [H_2O_2]_t)$ are plotted against $X = \ln\ ([A]_0/[A]_t)/([H_2O_2]_0 - [H_2O_2]_t)$, a straight line was

---

[1] (a) This article is dedicated to the memory of Professor G. Rio. (b) Part 1: Aubry, J. M. *J. Am. Chem. Soc.* **1985**, *107*, 5844–5849.

[2] The work reported herein is taken in part from: Cazin, B. Thèse de Docteur Ingénieur, Paris VI, 1986. It was supported by a grant from Roussel Uclaf Co., which is gratefully acknowledged.

[3] Koppenol, W. H. *Nature (London)* **1976**, *262*, 420–421.

[4] Evans, D. F.; Upton, M. W. *J. Chem. Soc., Dalton Trans.* **1985**, 2525–2529.

[5] Smith, L. L.; Kulig, M. J. *J. Am. Chem. Soc.* **1976**, *98*, 1027–1029.

[6] This acceptor was a generous gift of Professor G. Rio. It can be prepared by sulfonation of 9,10-diphenylanthracene: Etienne, A.; Lepeley, J. C.; Heymès, R. *Bull. Soc. Chim. Fr.* **1949**, *16*, 835–840.

[7] (a) Ogilby, P. R.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 3423–3430. (b) Rodgers, M. A. J. *J. Am. Chem. Soc.* **1983**, *105*, 6201–6205. (c) Rodgers, M. A. J.; Snowden, P. T. *J. Am. Chem. Soc.* **1982**, *104*, 5541–5543.

[8] Wilkinson, F.; Brummer, J. G. *J. Phys. Chem. Ref. Data* **1981**, *10*, 809–999.

[9] 0.2 mM DPATC was allowed to react with 0.2 mM MoO_4^{2-}, 0.1 mM EDTA and 10 mM H_2O_2 at pH 10.5 and 35 °C during 8 h in H_2O or D_2O; HPLC and UV analysis showed 16% and 89% peroxidation of the trap in H_2O and D_2O, respectively.

[10] (a) Spitalsky, E.; Funck, A. *Z. Phys. Chem., Stoechiom. Vermandtschaftsl.* **1927**, *126*, 1–23. (b) Baxendale, J. H. *Adv. Catal.* **1952**, *4*, 31–86. (c) Sahin, M.; Berkem, A. R. *Chim. Acta Turc.* **1977**, *5*, 311–331.

[11] Aubry, J. M.; Rigaudy, J.; Ngyuen Kim Cuong. *Photochem. Photobiol.* **1981**, *33*, 149–153.

0020-1669/88/1327-2013$01.50/0

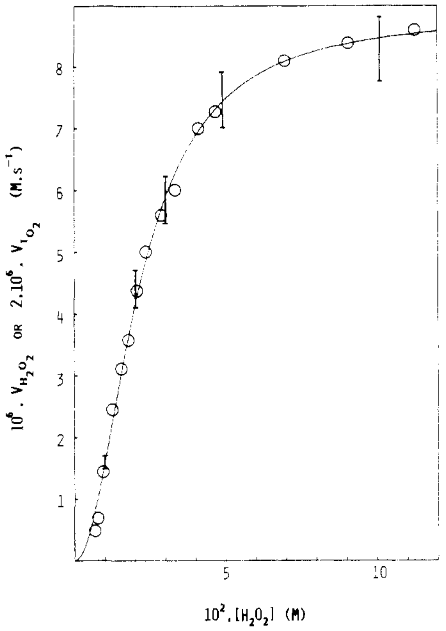

Figure 2. H_2O_2 dependence of the reaction rate. Conditions: 1 mM MoO_4^{2-}, 0.1 mM EDTA, ionic strength 0.1 M (phosphate), pH 10.5, 25 °C. Circles represent experimental $v_{H_2O_2}$, bars represent experimental $v_{^1O_2}$, and the line represents the theoretical curve, assuming rate and equilibrium parameters given in the text.

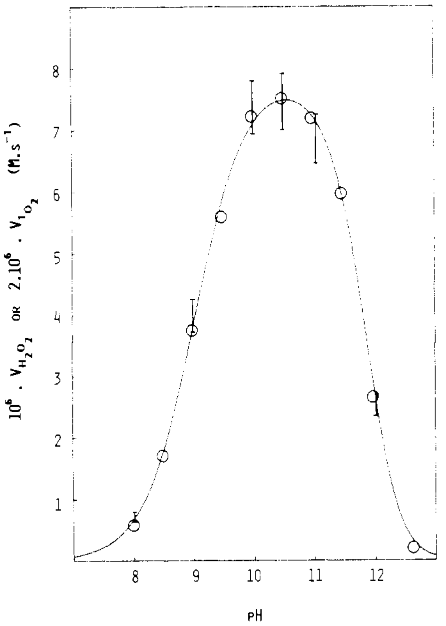

Figure 3. Acidity dependence of the reaction rate. Conditions: 1 mM MoO_4^{2-}, 50 mM H_2O_2, 0.1 mM EDTA, ionic strength 0.1 M (phosphate), 25 °C. Circles represent experimental $v_{H_2O_2}$, bars represent experimental $v_{^1O_2}$, and the line represents the theoretical curve, assuming rate and equilibrium parameters given in the text.

obtained; its intercept with the Y_{AO_2} axis provides the $^1O_2$ yield, and its slope provides the quenching ratio, k_d/k_r.[12] Representative data are given in Figure 1, and the extrapolated singlet oxygen yield ($Y \simeq 0.50$) indicates the formation of one $^1O_2$ molecule per two molecules of H_2O_2; the quenching ratio ($k_d/k_r \simeq 1.6 \times 10^{-3}$ M at 25 °C) is in good agreement with the value determined by the photosensitization method (1.5×10^{-3} M at 20 °C).[13,14]

Order of the Reaction with Respect to MoO_4^{2-} and H_2O_2. Reaction rates for the disappearance of H_2O_2 ($v_{H_2O_2}$) and for the formation of $^1O_2$ ($v_{^1O_2}$) were calculated from loss of H_2O_2 (titrated with permanganate) and from appearance of $^1O_2$ (monitored with 0.2 mM RTC by spectrophotometry at 540 nm).[1b] The reaction is first order with respect to MoO_4^{2-} in the concentration range 0.2 mM–2 mM, as has been reported previously.[10] The rate law is more complex with regard to H_2O_2 since the reaction is second order at low concentrations of the peroxide and zero order at concentrations higher than 0.1 M (Figure 2). These results are readily explained in terms of formation (eq 4) and decomposition (eq 5) of a mononuclear diperoxo species, MoO_6^{2-}, according to Baxendale.[10b]

$$2H_2O + MoO_6^{2-} \overset{K_4}{\rightleftharpoons} MoO_4^{2-} + 2H_2O_2 \qquad (4)$$

$$MoO_6^{2-} \xrightarrow{k_5} MoO_4^{2-} + {}^1O_2 \qquad (5)$$

Influence of Acidity. Reaction rates exhibit a strong pH dependence with an asymmetrical bell-shaped curve (Figure 3). Spectrophotometric studies carried out at pH 7 indicate the formation of a mononuclear complex with one proton and two peroxo groups. It was assumed to be $HMoO_6^-$, i.e. the acid corresponding to MoO_6^{2-} (eq 6) and the monomeric form of the well-defined complex $Mo_2O_{11}^{2-}$.[15] In very alkaline solutions, H_2O_2 dissociates (eq 7) and the equilibrium 4 is shifted to the right.

$$HMoO_6^- \overset{K_6}{\rightleftharpoons} H^+ + MoO_6^{2-} \qquad (6)$$

$$H_2O_2 \overset{K_7}{\rightleftharpoons} H^+ + HO_2^- \qquad (7)$$

Hence, no more peroxo complex can be detected by spectrophotometry, and the catalysis stops.

Assuming that the decomposition of MoO_6^{2-} (eq 5) is slow compared to the attainment of the equilibria (eq 4, 6, and 7), the rate law is

$$v_{^1O_2} = \frac{1}{2}v_{H_2O_2} = \frac{k_5[MoO_4^{2-}]_0[H_2O_2]_0^2}{K\left(1 + \frac{K_7}{[H^+]}\right)^2 + \left(1 + \frac{[H^+]}{K_6}\right)[H_2O_2]_0^2}$$

where $[MoO_4^{2-}]_0$ refers to the starting concentration and $[H_2O_2]_0$ to the total concentration of free hydrogen peroxide. Using the literature value[16] for $pK_7 = 11.6$, we calculate the specific rate constant $k_5 = 4.6 \times 10^{-3}$ s^{-1} and the equilibrium constants $pK_4 = 3.4$ and $pK_6 = 9.1$.[17]

In order to strengthen the hypothesis of a diperoxo complex as a reactive intermediate, we checked by trapping experiments with RTC that both stable diperoxo complexes $K_2Mo_2O_{11}{\cdot}4H_2O$[15b] and $MoO_5{\cdot}HMPT{\cdot}H_2O$[18] did evolve $^1O_2$ in aqueous solution at pH 10.5.

Registry No. H_2O_2, 7722-84-1; O_2, 7782-44-7; MoO_4^{2-}, 14259-85-9.

Laboratoire de Chimie Générale
Faculté de Pharmacie de Lille
59045 Lille Cédex, France
and Laboratoire de Chimie Organique Physique
(UA 351), USTL
59655 Villeneuve d'Ascq Cédex, France
J. M. Aubry*

Laboratoire de Recherches Organiques
(UA 476), ESPCI
75231 Paris Cédex, France
B. Cazin

Received November 4, 1987

---

(12) Caminade, A. M.; El Khatib, F.; Koenig, M.; Aubry, J. M. *Can. J. Chem.* **1985**, *63*, 3203–3209.

(13) Aubry, J. M.; Rigaudy, J.; Nguyen Kim Cuong. *Photochem. Photobiol.* **1981**, *33*, 155–158.

(14) Aubry, J. M. Thèse de Doctorat d'Etat, Université de Paris VI, 1982.

(15) (a) Souchay, P. *Bull. Soc. Chim. Fr.* **1949**, *16*, 122–133. (b) Stomberg, R. *Acta Chem. Scand.* **1968**, *22*, 1076–1090. (c) Le Carpentier, J. M.; Mitschler, A.; Weiss, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr., Crystl Chem.* **1972**, *B28*, 1288–1298.

(16) Evans, M. G.; Uri, N. *Trans. Faraday Soc.* **1949**, *45*, 224–230.

(17) Our value agrees with that of Csânyi (Csânyi, L. J. *Acta Chim. Acad. Sci. Hung.* **1958**, *14*, 79–87 ($pK_6 = 9.1$)) but not with that of Russian workers (Kreingol'd, S. U.; Vasnev, A. N. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1980**, *25*, 1355–1357 ($pK_6 = 8.0$)).

(18) Mimoun, H.; Serée de Roch, I.; Sajus, L. *Bull. Soc. Chim. Fr.* **1969**, 1481–1492.