very powerful oxidants. In particular they are very powerful O atom donors in which respect they resemble certain monooxygenase enzymes.[18] Since the parent dioxirane has been indentified as a product of gas-phase ozonolysis of ethylene, it also seems likely that dioxiranes could be involved in air pollution chemistry and particularly the environmental health aspects of this chemistry.

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(17) (a) Edwards, J. O.; Pater, R. H.; Curci, R.; DiFuria, F. *Photochem. Photobiol.* **1979**, *30*, 63–70. (b) Gallopo, A. R.; Edwards, J. O. *J. Org. Chem.* **1981**, *46*, 1684–1688. (c) Cicala, G.; Curci, R.; Fiorentino, M.; Laricciuta, O. *J. Org. Chem.* **1982**, *47*, 2670–2673, (d) Curci, R.; Fiorentino, M.; Troisi, L.; Edwards, J. O.; Pater, R. H. *J. Org. Chem.* **1980**, *45*, 4758–4760. (e) Murray, R. W.; Ramachandran, V. *Photochem. Photobiol.* **1979**, *30*, 187–189. (f) Lovas, F. J.; Suenram, R. D. *Chem. Phys. Lett.* **1977**, *51*, 453–456, (g) Martinez, R. I., Huie, R. E., Herron, J. T. *Chem. Phys. Lett.* **1977**, *51*, 457–459. (h) Suenram, R. D.; Lovas, F. J. *J. Am. Chem. Soc.* **1978**, *100*, 5117–5122. (i) Talbott, R. I.; Thompson, P. G.; U.S. Patent 3 632,606. dated Jan 4, 1972. (j) Ganzer, G. A.; Sheridan R. S. *Abstracts of Papers*, 190th National Meeting of the American Chemical Society, Chicago, IL; American Chemical Society: Washington, DC, 1985; ORGN 148.

(18) Orrenius, S.; Ernster, L., *Molecular Mechanisms of Oxygen Activation*: Hayaishi, O., Ed.; Academic: New York, 1974; p 215.

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## Generation of ${}^1\Delta_g$ $O_2$ from Triethylsilane and Ozone

E. J. Corey,* Mukund M. Mehrotra, and Ahsan U. Khan

*Department of Chemistry, Harvard University*
*Cambridge, Massachusetts 02138*

*Received September 12, 1985*

Trialkylsilanes are known to react with ozone at 0 to –60 °C in inert organic solvent to form trialkylsilanols as major products by a pathway that is thought to involve trialkylsilyl hydrotrioxides as intermediates.[1] We became interested in this reaction as a possible chemical method for the generation of ${}^1\Delta_g$ $O_2$ at sufficiently low temperatures to allow the synthesis of unstable endoperoxides since it seemed that the silyl hydrotrioxide → silanol + $O_2$ reaction could be a source of singlet dioxygen. Despite the existence of an extensive literature on the reaction of ozone with silanes,[1] the possible production of ${}^1\Delta_g$ $O_2$ in this process has not been proposed. Physical and chemical evidence is presented herein that triethylsilyl hydrotrioxide can be generated at –78 °C by the reaction of ozone with triethylsilane and that it decomposes to give ${}^1\Delta_g$ $O_2$ in preparatively useful yield.

The color of a cold (–78 °C), saturated methylene chloride solution of ozone (ca. 0.04 M) was discharged within 45 s upon treatment with 2 equiv of triethylsilane (TES). Addition of a methylene chloride solution (at –78 °C) of excess 2,5-diphenyl-3,4-benzofuran (DPBF) at once and further reaction at –78 °C for 1 h produced (after warming to 0 °C and analysis by HPLC) 45% yield of *o*-dibenzoylbenzene (based on $O_3$).[2] In a parallel preparative experiment[3] *o*-dibenzoylbenzene was isolated in 91% yield,[4a] using 1 equiv of ozone, 2 equiv of TES, and 0.33 equiv of DPBF. This chemical evidence for the generation of ${}^1\Delta_g$ $O_2$ was further confirmed by the demonstration of a number of characteristic transformations including α-terpinene → ascaridole (90% yield),[4b] 9,10-dimethylanthracene → 9,10-endoperoxide (92%),[4c] 1,3-cyclohexadiene → 1,4-endoperoxide (46%),[4d] tetraphenylcyclopentadienone → (*Z*)-1,2-dibenzoylstilbene (62%),[4e] tetramethylethylene → 3-hydroperoxy-2,3-dimethyl-1-butene (40%),[4f] citronellol → 1:1 mixture of 3,7-dimethyloct-5-ene-1,7-diol and 3,7-dimethyloct-7-ene-1,6-diol (after reduction with $NaBH_4$–$CH_3OH$, 25%),[4g] and 2-[(trimethylsilyl)oxy]bicyclo[2.2.1]hept-2-ene → 3-[(trimethylsilyl)peroxy]bicyclo[2.2.1]heptan-2-one (50%).[4h,5]

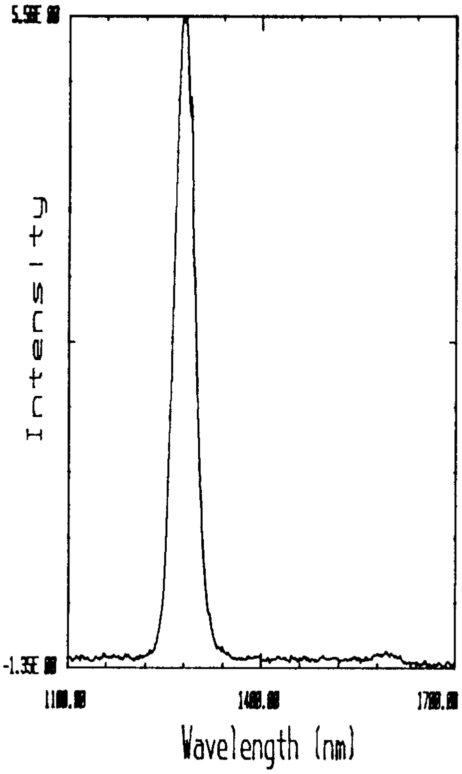

**Figure 1.** Near-infrared emission spectrum from decomposition of triethylsilyl hydrotrioxide at –60 °C in $CH_2Cl_2$.

The approximate rate of decomposition of the intermediate which gives rise to ${}^1\Delta_g$ $O_2$, clearly best formulated as triethylsilyl hydrotrioxide, was evaluated at –78 °C by generating the hydrotrioxide at that temperature, adding an excess of DPBF (in $CH_2Cl_2$ at –78 °C) at varying time intervals, and determining the extent of oxidation of DPBF to *o*-dibenzoylbenzene by HPLC analysis. In this way a half-life of a few minutes could be estimated. Equation 1 summarizes the process of ${}^1\Delta_g$ $O_2$ generation.

$$(C_2H_5)_3SiH + O_3 \xrightarrow[45\ \mathrm{s}\ (CH_2Cl_2)]{-78\ ^\circ C} (C_2H_5)_3SiOOOH \xrightarrow[t_{1/2}\ \mathrm{ca.}\ 150\ \mathrm{s}]{\mathrm{ca.}\ -60\ ^\circ C} (C_2H_5)_3SiOH + {}^1\Delta_g\ O_2 \quad (1)$$

The formation of ${}^1\Delta_g$ $O_2$ from triethylsilyl hydrotrioxide was also demonstrated spectroscopically. Solutions of ozone and triethylsilane were mixed in a small Pyrex Dewar vessel cooled by a dry-ice cold finger (to a temperature of ca. –60 °C) and placed before the entrance slit of an ultrasensitive near-infrared

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(1) (a) *Ozonation in Organic Chemistry*; Bailey, P. S., Ed.; Academic Press: New York. 1982; Vol. II, p 329. (b) Aleksandov, Yu. A.; Tarunin, B. I. *Russ. Chem. Rev. (Engl. Transl.)* **1977**, *46*, 905. (c) Spialter, L.; Pazdernik, L.; Bernstein, S.; Swansiger, W. A.; Buell, G. R.; Freeburger, M. E. *Adv. Chem. Ser.* **1972**, *No. 112*, 65. (d) For studies of the formation of carbon hydrotrioxides from the reaction of activated C–H bonds with ozone and the thermal decomposition of such C-hydrotrioxides, see: Stary, F. E.; Emge, D. E.; Murray, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 1880. Pryor, W. A.; Ohto, N.; Church, D. F. *Ibid.* **1982**, *104*, 5813.

(2) HPLC analysis was performed under air-free conditions (because of facile air oxidation of DPBF), using a Du Pont Zorbax silica gel column with 3% tetrahydrofuran in hexane as solvent.

(3) Yield based on the limiting substrate. In preparative experiments the ratio of TES to $O_3$ was generally 2. The ratio of $O_3$ to substrate ($O_3$/S ratio) was 5 unless otherwise indicated.

(4) (a) Howard, J. A.; Mendenhall, G. D. *Can. J. Chem.* **1975**, *53*, 2199. (b) Schenck, G. Ziegler, K. *Naturwissenschaften* **1944**, *32*, 157. (c) Corey, E. J.; Taylor, W. C. *J. Am. Chem. Soc.* **1964**, *86*, 3881. (d) Kaneko, C.; Sugimoto, A.; Tanaka, S. *Synthesis* **1974**, 876. (e) Wilcox, C. F., Jr.; Stevens, M. P. *J. Am. Chem. Soc.* **1962**, *84*, 1258. (f) Schenck, G. O.; Schult-Elte, K. *Ann. Chem.* **1958**, *618*, 185. (g) Ohloff, G.; Klein, E.; Schenck, G. O. *Angew. Chem.* **1961**, *73*, 578. (h) Jefford, C. W.; Rimbault, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 6437.

(5) Products were identified unambiguously by spectral and chromatographic comparisons with authentic samples prepared as previously described.[4] In all these reactions the material balance was excellent, the remainder being starting material.

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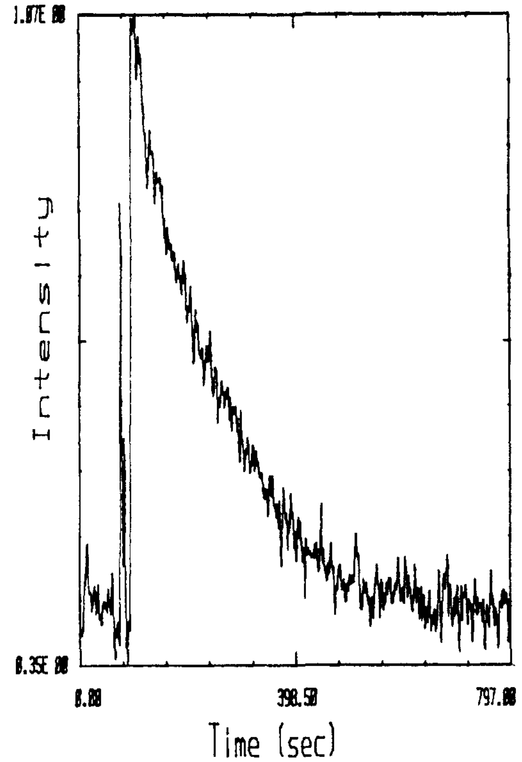

**Figure 2.** Near-infrared emission at 1278 nm as a function of time for the decomposition of triethylsilyl hydrotrioxide at −60 °C in $CH_2Cl_2$($t_{1/2}$ 150 s).

spectrometer.[6] Figure 1 shows the emission spectrum obtained which is as expected for $^1\Delta_g\ O_2 \rightarrow {}^3\Sigma_g\ O_2$ with a strong 0,0 peak at 1278 nm and a weak 0,1 peak at 1594 nm.[7] It is clear that these emissions originate from free $^1\Delta_g\ O_2$ molecules because of their wavelength and relative intensities, the latter being very similar to the gas-phase Franck–Condon factors.[7] The intensity of $^1\Delta_g\ O_2$ emission is one of the strongest observed to date from any chemical source.

The stability of the $^1\Delta_g\ O_2$ precursor, triethylsilyl hydrotrioxide, was measured by monitoring the decay in emission at 1278 nm with time. The value of $t_{1/2}$ obtained for the solution in methylene chloride at ca. −60 °C was 150 s (Figure 2). Parallel experiments performed with the same components in carbon disulfide solution at ca. −60 °C gave a $t_{1/2}$ of 10 s. The lifetime of $^1\Delta_g\ O_2$ in carbon disulfide solution is known to be considerably longer than in methylene chloride as solvent, but far less than in the gas phase.[8] Presumably carbon disulfide interacts less with $^1\Delta_g\ O_2$ than methylene chloride or benzene. It would appear that methylene chloride stabilizes the silyl hydrotrioxide, perhaps through hydrogen bonding, more than does carbon disulfide and that such stabilization results in the slower rate of decomposition observed in methylene chloride. The effect of more polar solvents (e.g., methanol) on the stability of the hydrotrioxide is of considerable interest in light of these results.

The above described experiments demonstrate the feasibility of a new approach to the chemical generation of singlet dioxygen from ozone which has both practical and mechanistic implications.[9]

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[6] (a) Khan, A. U. *J. Photochem.* **1984**, *25*, 327. (b) Khan, A. U.; Kasha, M. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 6047.

[7] The apparent shift of 10 nm to longer wavelength for both 0,0 and 0,1 from values obtained in the gas phase may be due to uncompensated monochromoter–detector characteristics. Khan, A. U. In *Singlet $O_2$*; Fimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. I, p 39.

[8] (a) Foote, C. S.; Peterson, E. R.; Lee, K.-W. *J. Am. Chem. Soc.* **1972**, *94*, 1032. (b) *Singlet Molecular Oxygen, Benchmark Papers in Organic Chemistry*; Schaap, A. P., Ed.; Dowden, Hutchinson and Ross: Stroudsberg, PA, 1976; Vol. V.

[9] This work was assisted financially by the National Science Foundation and the National Foundation for Cancer Research. (Grant to the Institute of Molecular Biophysics, Florida State University, in support of A.U.K.). We thank Dr. Thérèse Wilson for her help.

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# Radical Cation Acidities in Dimethyl Sulfoxide Solution

Frederick G. Bordwell* and Mark J. Bausch

*Department of Chemistry, Northwestern University*
*Evanston, Illinois 60201*

*Received December 13, 1985*

Radical cations have been implicated as intermediates in the oxidation of a wide variety of organic molecules, and proton loss from radical cations is a common route to the formation of radicals and products derived therefrom.[1] The acid–base equilibrium constants for the dissociation of radical cations have been measured or estimated in only a few instances, however.[1,2] In this paper we describe a potentially general method for estimating acidities of radical cations by combination of the $pK_{HA}$ value of a given acid in $Me_2SO$ solution with its oxidation potential, $E_{ox}$(HA), and that of its conjugate base, $E_{ox}(A^-)$. The thermodynamic cycle involved[7] is shown in eq 1–4.

$$HA \rightleftarrows H^+ + A^- \qquad pK_{HA} \tag{1}$$

$$A^- \rightleftarrows A\cdot + e^- \qquad E_{ox}(A^-) \tag{2}$$

$$HA^{+\cdot} + e^- \rightleftarrows HA \qquad -E_{ox}(HA) \tag{3}$$

$$HA^{+\cdot} \rightleftarrows H^+ + A\cdot \tag{4}$$

The $pK_{HA}$ values for phenothiazine and its 2-MeO, 2-Cl, and 2-$CF_3$ derivatives together with their oxidation potentials and those for their conjugate bases, all in $Me_2SO$ solution, are summarized in Table I. Similar data for fluorene and its 2-MeO and 2,7-$(MeO)_2$ derivatives are also given, together with the $pK_{HA^{+\cdot}}$ constants for all seven of the corresponding radical cations.

The oxidation potentials for all four phenothiazines are reversible, indicating that loss of an electron in the oxidative step to form the radical cation is not followed by rapid loss of a proton to the solvent, as occurs with radical cation phenols.[12] The oxidation potentials for the conjugate bases of the phenothiazines are irreversible, suggesting that the radicals formed undergo rapid dimerization, or other reactions.[15]

The spin density in the phenothiazine radical cations **1** is

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[1] (a) Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *12*, 115–278. (b) Hammerich, O.; Parker, V. D. *Ibid.* **1984**, *20*, 55–189. (c) Nelsen, S. F.; Parmelee, W. P.; Gobl, M.; Hiller, K.-O.; Veltwisch, D.; Amus, K.-D. *J. Am. Chem. Soc.* **1980**, *102*, 5606–5610.

[2] For example, in water, $pK_{HA^{+\cdot}}$ is −2 for $PhOH^{+\cdot}$, 4–5 for phenothiazine$^{+\cdot}$,[4] 6.5–7.5 for $Me_2NH^{+\cdot}$,[5] 7 for $PhNH_2^{+\cdot}$,[6] and −11 for $PhCH_3^{+\cdot}$ (calcd).[7]

[3] Dixon, W. T.; Murphy, D. *J. Chem. Soc., Faraday Trans.* **1976**, *72*, 1221–1230.

[4] Alkaitas, S. A.; Beck, G.; Gratzel, M. *J. Am. Chem. Soc.* **1975**, *97*, 5723–5728.

[5] Fessenden, R. W.; Neta, P. *J. Phys. Chem.* **1972**, *76*, 2857–2859.

[6] Land, E. J.; Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2027.

[7] Nicholas, A. M. de P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165–2189.

[8] Bordwell, F. G.; Hughes, D. L. *J. Am. Chem. Soc.* **1984**, *106*, 3234–3239.

[9] Bordwell, F. G.; McCollum, G. J. *J. Org. Chem.* **1976**, *41*, 2391–2395.

[10] We have observed that reversible $E_{ox}$(HA) values in $CH_3CN$ and $Me_2SO$ differ by no more than 40 mV, in agreement with literature observations on solvation effects,[11] but the differences may be somewhat larger for irreversible $E_{ox}$(HA) values.

[11] Svaan, M.; Parker, V. D. *Acta Chem. Scand., Ser B* **1984**, *B38*, 759–765.

[12] For example, in water 2,4,6-$(t\text{-Bu})_3C_6H_2OH^{+\cdot}$ loses a proton during cyclic voltammetry, and the resulting radical is then oxidized further to the cation.[13] Radical cation formation from 3,6,7-trimethoxyfluoren-2-ol in $CH_3CN$ has also been shown to be accompanied by deprotonation and cation formation.[14]

[13] Richards, J. A.; Whitson, P. E.; Evans, D. H. *J. Electroanal. Chem.* **1975**, *63*, 311–327. Evans, D. H. *Acc. Chem. Res.* **1977**, *10*, 313–319.

[14] Nilsson, A.; Palmquist, U.; Roulân, A.; Parker, V. D. *J. Am. Chem. Soc.* **1975**, *97*, 3540–3541.

[15] There is evidence that the $E_{ox}(A^-)$ values obtained provide a good measure of relative $e_T^-$ ability, however, since they give an excellent correlation with the rate constants for single electron transfer to the 1,1-dinitrocyclohexane electron acceptor.[16]

[16] Bausch, M. J. Ph.D. Dissertation, Northwestern University, Evanston, IL, Nov, 1984.

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