THE JOURNAL OF Organic Chemistry®

VOLUME 45, NUMBER 22

© Copyright 1980
by the American Chemical Society

OCTOBER 24, 1980

Controlled Generation of Singlet Oxygen at Low Temperatures from Triphenyl Phosphite Ozonide[1]

Paul D. Bartlett,*[2] G. David Mendenhall,[3] and Dana L. Durham

Departments of Chemistry, Harvard University, Cambridge, Massachusetts 02138, and Texas Christian University, Fort Worth, Texas 76129

Received April 24, 1980

The usefulness of triphenyl phosphite ozonide for generating singlet oxygen is greatly increased by the use of pyridine in methanol as solvent, which permits the controlled thermal generation of singlet oxygen at temperatures as low as −100 °C without significant diminution in the yield. Among bases of similar ionization potential or of similar basic strength, pyridine shows unusually low quenching power for singlet oxygen.

Introduction

In investigating the important and complex phenomena associated with singlet molecular oxygen,[4] there is frequent use for a nonphotochemical reference source of this excited species. Triphenyl phosphite ozonide[5] has gained favor as a thermal source of singlet oxygen ($^1\Delta_g$), chiefly because of its usefulness in a variety of solvents, availability of starting materials, good yields of singlet oxygen, and near absence of competing side reactions.

Up to the present, however, triphenyl phosphite ozonide (TPPO) has suffered from an inflexibility in the temperature at which it can be used as a singlet oxygen source; being thermally stable below −25 °C, it cannot serve as a thermal standard for direct comparison with the many important reactions of photochemically generated singlet oxygen carried out at −78 °C and below. In the region where TPPO is thermally stable, there is also a slow direct reaction of the ozonide with olefinic substrates which mimics the reaction of singlet oxygen in some but not all respects, requiring discriminating interpretation of experiments in this temperature region.[6,7]

We now report a simple procedure by which good yields of singlet oxygen products can be obtained from TPPO at temperatures as low as −100 °C.

Results

It has been known for some time that amines, even in catalytic amounts, bring about the decomposition of TPPO to triphenyl phosphate and oxygen but that the oxygen so produced is in the usual triplet ground state. From the effects of amines on photosensitized singlet oxygen reactions,[8] it is clear that even if singlet oxygen were initially produced in this reaction of TPPO, it would be promptly quenched by even small amounts of many amines. We therefore began by searching for a base that would cause the phosphite ozonide to decompose without quenching the singlet oxygen.

In reaction with triphenyl phosphite ozonide at −78 °C, less than stoichiometric quantities of amines completely decompose the ozonide, and the amount of oxygen evolved is the same within experimental error whether excess or less than equivalent amine is present.[9] Aliphatic amines are especially active; tetra-*n*-butylammonium hydroxide, pyridine, and *N*,*N*-dimethylaniline exert a moderate catalysis, and triphenylamine is inert.[6]

A survey was made of the quenching effect of a series of bases when present during the normal thermal generation of singlet oxygen from TPPO at 25 °C. In this series of tests rubrene and the quencher were dissolved in one portion of 2:1 (v/v) methanol–benzene at 25 °C and TPPO was dissolved in another at −50 °C so that, on mixing, the concentrations of rubrene, TPPO, and quencher would be 0.001, 0.0036, and 0.01 M, respectively. In each case the rubrene color faded rapidly to a value which remained constant. The amount (x) of oxidation of the rubrene in

---

(1) Presented in part before the Organic Division at the American Chemical Society Centennial Meeting, New York, 1976, Abstr no. 12.

(2) Address inquiries to this author at Texas Christian University.

(3) Present address: Department of Chemistry and Chemical Engineering, Michigan Technological University, Houghton, MI 49931.

(4) For recent reviews, see: (a) Schaap, A. P. "Singlet Oxygen"; Dowden, Hutchinson and Ross, Inc.: Stroudsburg, PA, 1979. (b) Wasserman, H. H.; Murray, R. W. "Singlet Oxygen"; Academic Press: New York, 1979.

(5) (a) Thompson, Q. E. *J. Am. Chem. Soc.* **1961**, *83*, 845. (b) Murray, R. W.; Kaplan, M. L. *J. Am. Chem. Soc.* **1968**, *90*, 537; *Ibid.* **1969**, *91*, 5358. (c) Wasserman, E.; Murray, R. W.; Kaplan, M. L.; Yager, R. W. A. *J. Am. Chem. Soc.* **1968**, *90*, 4160.

(6) Mendenhall, G. D., Thesis, Harvard University, 1970.

(7) (a) Bartlett, P. D.; Mendenhall, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 210. (b) Bartlett, P. D.; Mendenhall, G. D.; Schaap, A. P. *Ann. N.Y. Acad. Sci.* **1970**, *171*, 79. (c) Schaap, A. P.; Bartlett, P. D. *J. Am. Chem. Soc.* **1970**, *92*, 6055. (d) Bartlett, P. D.; Chu, H.-K. *J. Org. Chem.* **1980**, *45*, 3000.

(8) Foote, C. S., ref 4b, pp 157–159.

(9) Koch, E. *Tetrahedron* **1970**, *26*, 3503.

0022-3263/80/1945-4269$01.00/0 © 1980 American Chemical Society

Table I. Quenching of Singlet Oxygen[a] by Bases

base	x^b	IP[c]	k_q/k_{ox}[d]
p-$(CH_3)_2NC_6H_4N(CH_3)_2$	0	6.9	
NaN_3	0.03		13.4
$C_6H_5N(CH_3)_2$	0.20	7.14	1.67
$C_6H_5NHCH_3$	0.52	7.34	0.390
Et_3N	0.54	7.50	0.361
$H_2NNH_2 \cdot H_2O$	0.58	9.56	0.296
Et_2NH	0.58	8.01	0.296
NH_3	0.64	10.15	0.241
$C_6H_5NH_2$	0.80	7.69	0.110
$(C_6H_5)_2NH$	0.92	7.25	0.040
nitroxide[e]	0.95		0.025
$(C_6H_5CH_2)_3N$	0.98		0.010
$(C_6H_5)_3N$	1.00	6.86	
pyridine	1.00	9.23	

[a] $^1O_2$ generated thermally from $(PhO)_3PO_3$ (0.0036 M) in 2:1 (v/v) methanol–benzene at 25 °C in the presence of 0.001 M rubrene and 0.01 M quencher. [b] Relative extents of oxidation of rubrene with and without base present. [c] Ionization potential: Franklin, J. L., et al., "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions", National Bureau of Standards: Washington, D.C., 1969. [d] Assuming 100% formation of singlet oxygen from ozonide and k_s/k_{ox} = 0.00135. [e] 2,2,6,6-Tetramethyl-4-piperidone-1-oxyl.

each case (relative to that without amine) is recorded in Table I. Since under similar conditions the yield of singlet oxygen from TPPO has been shown to be between 90 and 100%,[10] these results are translated into corresponding values of β (= k_q/k_{ox}), on the assumption that singlet oxygen, equivalent to the TPPO, is consumed in competitive addition to rubrene (k_{ox}), quenching by amine (k_q), and quenching by the solvent with a constant k_s, where k_s/k_{ox} = 0.00135. The measurable scale of relative quenching rates observed in this way extends over a 100-fold range between apparent total quenching and absence of any detectable effect; however, the production of such a 100-fold effect requires a larger range of β values. The concentration (v) of rubrene peroxide formed, the concentration (y) of triplet oxygen resulting from quenching, and the concentration (Q) of quenching amine are related by the eq 1–3 which enable the value of β to be determined

$$v = 0.00867x \tag{1}$$

$$y = (\mathrm{TPPO})_0 - v = 0.0036 - v \tag{2}$$

$$y = (k_s/k_{ox} + k_q(Q)/k_{ox}) \ln \frac{(\mathrm{Ru})_0}{(\mathrm{Ru})_\infty}$$
$$= (0.00135 + 0.01\beta) \ln \frac{0.001}{0.001 - v} \tag{3}$$

from the experimental quantities reported and summarized in Table I. The concentration of singlet oxygen does not appear in these equations, since it is present in both the numerator and denominator of the quantity in parentheses. The value of k_s/k_{ox} is determined in the experiments without added amine, where $(\mathrm{Ru})_0/(\mathrm{Ru})_\infty$ = 7.52.

In Table I pyridine and triphenylamine stand out as having no appreciable quenching effect on singlet oxygen from TPPO. Of the two, pyridine has all the properties we seek as a reagent in the formation of oxygen from TPPO. Both methanol–benzene and pure methanol proved satisfactory solvents for pyridine and TPPO at very low temperatures.

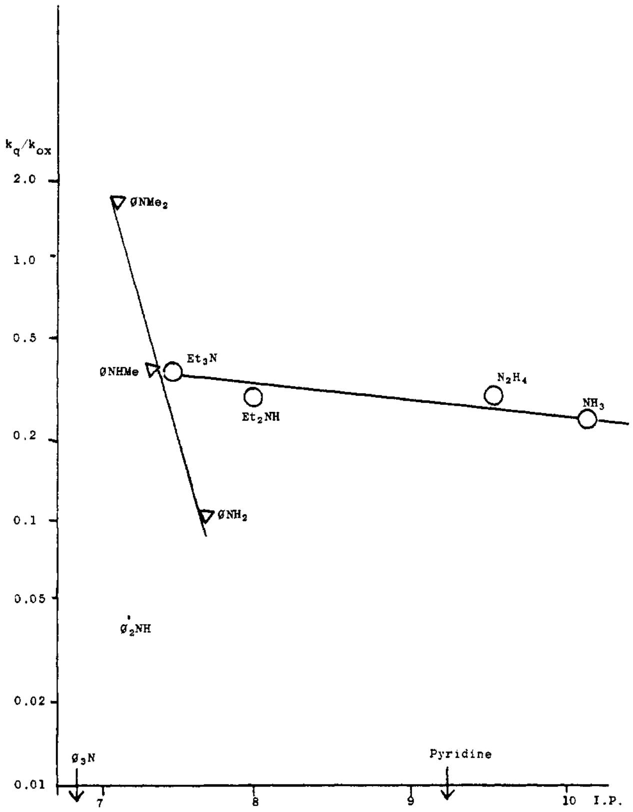


Figure 1. Logarithmic plot of k_q/k_{ox} for some amines vs. their ionization potentials in the reaction of singlet oxygen with rubrene in methanol–benzene (2:1 v/v) at 25 °C: triangles, anilines; circles, nonaromatic bases.

Within a structurally related group of amines there is a correlation between logarithm of quenching power for singlet oxygen and ionization potential of the amine (Figure 1), but the plot for the anilines has a very much greater slope than that for the aliphatic amines. Diphenylamine, triphenylamine, and pyridine do not fall on the correlation line for either anilines or aliphatic amines. As in many other cases of quenching, it is clear that electron-donor or -acceptor character is only one of the predisposing factors. There is also a strong leveling effect of solvent on the quenching power of the aliphatic amines compared to the quenching rate constants in the gas phase measured by Ogryzlo and Tang,[11] whose log slope is ten times ours in a plot like that of Figure 1.

The low quenching power of 2,2,6,6-tetramethyl-4-piperidone-1-oxyl is in accord with many other examples, showing that inhibitors of chain reactions are not in general quenchers of singlet oxygen.

Having established that pyridine exerts no quenching effect on the singlet oxygen, we did a series of experiments on the effect of solvent on the accelerated generation of singlet oxygen from TPPO. It soon developed that, unlike the more destructive amines, pyridine does not cause oxygen evolution from TPPO in rigorously pure, dry aprotic solvents, although in most actual cases the addition of pyridine will cause a short-lived effervescence. However, in a methanol or part-methanol solvent, pyridine brings about smooth liberation of singlet oxygen at temperatures as low as −100 °C, and the singlet oxygen under these conditions adds to substrates present in solution to produce the same products and yields as in photosensitized

---

(10) Murray, R. W.; Lin, J. W.-P.; Kaplan, M. L. *Ann. N.Y. Acad. Sci.* **1970**, *171*, 121.

(11) Ogryzlo, E. A.; Tang, C. S. *J. Am. Chem. Soc.* **1970**, *92*, 5034.

(12) Wieringa, J. H.; Strating, J.; Wynberg, H.; Adam, W. *Tetrahedron Lett.* **1972**, 169.

oxygenation under the same conditions.[13] This procedure extends greatly the usefulness of TPPO as a reagent for the thermal generation of singlet oxygen. A typical procedure is as follows.

Triphenyl phosphite ozonide was prepared in the usual way by passing a stream of dry ozone through cold methylene chloride (−78 °C) while slowly adding 0.0232 g (0.074 mmol) of triphenyl phosphite at such a rate as to maintain the deep blue color of the ozone solution. After addition of the phosphite was complete (30–45 min) the solution was purged of ozone by passing a stream of dry nitrogen through it for 30 min. A separate solution of 10 mg (0.037 mmol) of biadamantylidene (Ad=Ad) was prepared in 1.5 mL of methylene chloride at −78 °C. This solution was added to that of the phosphite ozonide, followed by 1.0 mL of a 50:50 mixture of methanol–pyridine, also at −78 °C.

Under these conditions, in the absence of a singlet oxygen acceptor, oxygen bubbles off rapidly. In the presence of Ad=Ad but without the methanol–pyridine, no direct reaction occurs between Ad=Ad and TPPO.[7d] Under the present conditions, when the highly colored rubrene is used instead of Ad=Ad, the rubrene color is discharged within minutes after addition of the methanol–pyridine.

In the present experiment, TLC indicated no remaining Ad=Ad after about 5 min of reaction. The solution was then allowed to warm to room temperature, the solvent was removed, and the remaining syrup was subjected to preparative TLC, yielding 0.0102 g (91.1%) of the dioxetane of biadamantylidene.[12] The purified dioxetane decomposes at about 150 °C. The adamantanone produced remelts at 250–255 °C. A mixture of the dioxetane and 9,10-dibromoanthracene (DBA) on heating to 150 °C shows the blue luminescence characteristic of Ad=Ad dioxetane.

Acknowledgment. We thank the National Science Foundation, the National Institutes of Health, and the Robert A. Welch Foundation for support of this work.

Registry No. Triphenyl phosphite ozonide, 29833-83-8; biadamantylidene, 30541-56-1; dioxetane of biadamantylidene, 35544-39-9; adamantanone, 700-58-3; oxygen, 7782-44-7; sodium azide, 26628-22-8; *N*,*N*-dimethylbenzamine, 121-69-7; *N*-methylbenzamine, 100-61-8; *N*,*N*-diethylethanamine, 121-44-8; hydrazine, 302-01-2; *N*-ethylethanamine, 109-89-7; ammonia, 7664-41-7; benzenamine, 62-53-3; *N*-phenylbenzenamine, 122-39-4; 2,2,6,6-tetramethyl-4-piperidine-1-oxyl, 2896-70-0; *N*,*N*-bis(phenylmethyl)benzenemethanamine, 620-40-6; *N*,*N*-diphenylbenzenamine, 603-34-9; pyridine, 110-86-1; *N*,*N*,*N*′,*N*′-tetramethyl-1,4-benzenediamine, 100-22-1.

---

(13) As these observations imply, the role of the pyridine is to enhance reactivity of the hydroxylic solvent, which replaces successive phenoxy groups from the TPPO, each replacement increasing the thermal lability of the ozonide (Lonzetta, C. M. Ph.D. Thesis, Harvard University, 1976; Bartlett, P. D.; Lonzetta, C. M., forthcoming paper).

The Steric Effect of a Bulky Group: The Stereochemistry of 1,4-Di-*tert*-butyl-1,4-dihydronaphthalene and 1-*tert*-Butyl-1,4-dihydronaphthalene

Norman L. Holy,* Howard P. Vail, Abdol-Hossein Nejad, and Su-Jen Huang

Department of Chemistry, Western Kentucky University, Bowling Green, Kentucky 42101

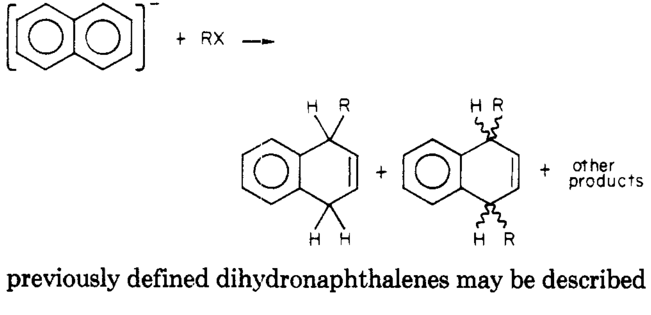
James L. Marshall,* Oya Saracoglu, and Cato R. McDaniel, Jr.

Department of Chemistry, North Texas State University, Denton, Texas 76203

Received March 20, 1980

The stereochemistry of the mono- and di-*tert*-butyldihydronaphthalene derivatives was investigated with the aid of ^{1}H NMR, ^{13}C NMR, and the LAOCOON III program of the parent hydrocarbons and of an epoxide derivative. The di-*tert*-butyl derivative is distinguished by a nearly planar cyclohexadiene ring in which the *tert*-butyl groups are trans. In the mono-*tert*-butyl derivative, the cyclohexadiene ring is unusual because the ring appears to be twisted, presumably to permit relief of steric strain.

A good deal of interest has been shown in the reactions of the naphthalene radical anion with alkyl halides.[1] Whereas the mechanism of the reaction has attracted a great deal of attention, the stereochemistry of the products has received little attention. The stereochemistry of previously defined dihydronaphthalenes may be described in terms of a cyclohexadiene ring which is either a "flattened boat" or "highly puckered", or some intermediate structure.[2] Because there is interest both in radical anion reactions and the stereochemistries of cyclohexadienes containing bulky groups, we undertook a study of the mono- and di-*tert*-butyl derivatives of dihydronaphthalene. While this study was underway, a report appeared[3] which described the alkylation of 1-alkyl-1,4-dihydronaphthalenes with akyl halides; this report claimed that the methylation of 1-methyl-1,4-dihydronaphthalene gave exclusively cis 1,4-dialkylated product, while the isopropylation of 1-isopropyl-1,4-dihydronaphthalene gave only trans 1,4-dialkylated product. These assignments were made on the basis of trends in the mixed dialkyl products, which in turn were stereochemically assigned by



---

(1) For leading references, see J. F. Garst, *Acc. Chem. Res.*, 4, 400 (1971).

(2) For a recent review, see P. W. Rabideau, *Acc. Chem. Res.*, 11, 141 (1978).

(3) P. W. Rabideau and E. G. Burkholder, *J. Org. Chem.*, 44, 2354 (1979).

0022-3263/80/1945-4271$01.00/0