



changed, except for viscosity broadening, from -40 to -115° . Thus the ion shows no evidence of collapse to a less symmetric structure such as $10'$ or $10''$; if the ion does not have the pyramidal structure 14 , equilibration between less symmetric structures must be rapid at -115° .

Nucleophiles could react with the apical carbon of 14 in either of two ways, giving 15 or 16 . When solutions of the ion were quenched (sodium carbonate suspension in pentane, followed by water) alcohol 6 was isolated in 60% yield; quenching with methanol gave a nearly quantitative yield of the corresponding methyl ether. The path leading to products of type 15 seems to be favored, and this result can be rationalized on energetic grounds.¹⁴

(14) NOTE ADDED IN PROOF. Nucleophile could also attack 14 (or its equivalent in equilibrating ions) at a basal carbon. After this paper was submitted, R. K. Lustgarten, *J. Amer. Chem. Soc.*, **94**, 7602 (1972), described labeling results on the solvolysis of *endo*-4-*psin*tricyclic tosylate which indicate that an ion analogous to 14 may be involved. However, the apical and basal carbons were all secondary, and product was derived from nucleophilic attack at basal carbon, the site of lowest electron density.

The tosylate of demethylated 6 has been studied solvolytically (R. M. Coates and K. Yano, *Tetrahedron Lett.*, 2289 (1972)), but the possibility of an intermediate analogous to 14 was not considered. We are investigating the behavior of this parent system in strong acid.

We are actively elaborating these initial studies.¹⁵

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for their generous financial support.

(15) NOTE ADDED IN PROOF. The ^{13}C nmr spectrum of our ion has been determined and permits the following unambiguous assignment of chemical shifts, in parts per million from CS_2 : apical carbon, 188.2; framework basal carbons, 133.5; basal methyls, 183.5; framework bridgehead carbons, 143.6; remaining framework carbon, 135.4. The remaining two sets of methyl carbons appear at 178.2 and 186.0. Long-range proton- ^{13}C coupling was so extensive as to prohibit the determination of any of the coupling constants. The apical carbon is at highest field and the basal framework carbons are at lowest field, supporting the conclusion from the pmr spectrum that most of the positive charge is in the basal positions. We express our appreciation to Dr. Philip W. Westerman (Case Western Reserve University) for running the spectrum and help in interpreting it, and to Professor George A. Olah for making his facilities available to us.

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Singlet Oxygen ($^1\Delta_g$) Quenching in the Liquid Phase by Metal(II) Chelates

Sir:

Relatively few classes of compounds have been shown to quench the reactions of singlet oxygen ($^1\Delta_g$), $^1\text{O}_2$. Known quenchers include various dialkyl sulfides¹ and amines,^{2,3} some of which are also oxidized by $^1\text{O}_2$,^{1,2b} and carotenoids.¹ Since Pfeil⁴ has shown that the ^3E state of several Cr(III) complexes can be quenched by oxygen ($^3\Sigma_g^-$) to give $^1\text{O}_2$, we have investigated the occurrence of the reverse process, $^1\text{O}_2$ quenching by metal chelates, and have found that some Ni(II) compounds are efficient $^1\text{O}_2$ quenchers.

Quenching experiments were performed with rubrene (9,10,11,12-tetraphenylanthracene) as the $^1\text{O}_2$ receptor; bleaching of the rubrene absorption at 520 nm was used to follow the rubrene oxidation to the *endo*-peroxide. $^1\text{O}_2$ was generated by three separate methods. In method a, air-saturated rubrene solutions were photolyzed at $520 \pm 20 \text{ nm}$,⁵ and initial rates of rubrene consumption calculated. In method b, a solution of triphenyl phosphite ozonide⁶ at -70° was added to a rubrene solution (at 25°) to give an initial ozonide concentration in the range 2.4×10^{-3} – $0.94 \times 10^{-3} M$. The rubrene solution contained small percentages of methanol and pyridine so as to catalyze a virtually instantaneous $^1\text{O}_2$ evolution.⁷ In method c, oxygen (6 Torr) was fed through a microwave discharge (2450 MHz, 70 W) in a quartz tube and atomic oxygen, ozone, and $^1\Sigma_g^+$ oxygen were removed.⁸ The $^1\text{O}_2$ stream was split into two identical gas streams each of which passed over a stirred solution (2.0 ml), one with quencher and one quencher free. This procedure allowed parallel experiments to be performed

(1) C. S. Foote, R. W. Denny, L. Weaver, Y. Chang, and J. Peters, *Ann. N. Y. Acad. Sci.*, **171**, 139 (1970).

(2) (a) C. Ouannès and T. Wilson, *J. Amer. Chem. Soc.*, **90**, 6527 (1968); (b) W. F. Smith, *ibid.*, **94**, 186 (1972).

(3) J. P. Dalle, R. Magous, and M. Mousseron-Canet, *Photochem. Photobiol.*, **15**, 411 (1972).

(4) A. Pfeil, *J. Amer. Chem. Soc.*, **93**, 5395 (1971).

(5) T. Wilson, *ibid.*, **88**, 2898 (1966).

(6) R. W. Murray and M. L. Kaplan, *ibid.*, **91**, 5358 (1969).

(7) G. D. Mendenhall, Ph.D. Thesis, Harvard University, 1970.

(8) M. L. Kaplan and P. G. Kelleher, *Science*, **169**, 1207 (1970).

Table I. Singlet Oxygen ($^1\Delta_g$) Decay (k_d) and Quenching Rate Constants (k_q) in Various Solvents^a

Quencher	Rubrene $\xrightarrow{h\nu}$ ^b		(PhO) ₃ P-O ₃ decompn ^e		Microwave discharge ^d	
	Isooctane	CH ₂ Cl ₂	Isooctane ^e	CH ₂ Cl ₂ ^f	Hexadecane	2-Butoxyethanol ^g
None	4.0 ^h	N.D. ⁱ	$k_d \times 10^{-4} \text{ sec}^{-1}$ 5.0	0.73	9.0 ^h	38 ^h
Dabco			$k_q \times 10^{-8} M^{-1} \text{ sec}^{-1}$ 0.35	0.33		
Nickel(II) bis(2-hydroxy-5-methoxy-phenyl- <i>N-n</i> -butylaldimine)		>10	35		2.0	
Nickel(II) di- <i>n</i> -butyldithiocarbamate	70			>10 ^j	9.0	
Nickel(II) <i>n</i> -butylamine[2,2'-thiobis-(4- <i>tert</i> -octyl)phenolate]	1.8		2.7		0.80	2.8
Nickel(II) bis[2,2'-thiobis(4- <i>tert</i> -octyl)phenolate]	1.3		2.0		1.3	
Nickel(II) acetylacetonate						0.75
Nickel(II) bis(butyl-3,5-di- <i>tert</i> -butyl-4-hydroxybenzyl phosphonate)		0.14		0.10		0.34
NiCl ₂ ·6H ₂ O						3.1
CoCl ₂ ·6H ₂ O						0.48
MnCl ₂ ·4H ₂ O						<0.01

^a At 25° unless specified. ^b Initial rubrene concentration $1.0 \times 10^{-4} M$; 50% rubrene oxidation in ~3.5 min in absence of quencher. Quencher concentrations $4.0 \times 10^{-3} M$. ^c Quencher concentration $2.4 \times 10^{-3} M$. ^d Initial rubrene concentration $1.9 \times 10^{-4} M$. Exposures 5 or 10 min. Without quencher, ~50% rubrene consumption in ~3 min. Quencher concentrations $4.0 \times 10^{-3} M$. ^e Methanol-pyridine-isooctane mixture (3:3:94% by volume); rubrene concentration $4.0 \times 10^{-4} M$. ^f Methanol-pyridine-methylene chloride mixture (3:3:94% by volume); rubrene concentration $6.0 \times 10^{-4} M$. ^g At 0°. ^h Calculated from $k_q(\text{Dabco}) = 3.4 \times 10^7 M^{-1} \text{ sec}^{-1}$, from method b. ⁱ Assumed $0.73 \times 10^4 \text{ sec}^{-1}$, from method b. ^j Interference by chelate-ozonide reaction to give colored products.

so as to compensate for fluctuations in the $^1\text{O}_2$ concentration. Effective quenchers and the solvents used for each method are listed in Table I.

For methods b and c, integrated forms of the rate equations were used in the derivation of the pseudo-unimolecular rate constants (k_d) for the decay of $^1\text{O}_2$ and the $^1\text{O}_2$ quenching rate constants (k_q), whereas the direct rate equation was employed for method a.⁹ The rate constant for the $^1\text{O}_2$ oxidation of rubrene (k_{ox}) was assumed to be $7 \times 10^7 M^{-1} \text{ sec}^{-1}$.¹⁰ In method b, a quantitative yield of $^1\text{O}_2$ was assumed from the ozonide⁷ and this then allowed the k_d values in each solvent to be calculated directly from the rubrene concentration changes in the absence of quenchers. For methods a and c, k_d had to be derived indirectly from 1,4-diazabicyclo[2.2.2]octane (Dabco) quenching data, using k_q for Dabco calculated from the results of

(9) Method a is

$$k_q = \frac{k_{ox}[\text{R}\ddot{\text{u}}]_0 + k_d \left[\frac{(d[\text{R}\ddot{\text{u}}]/dt)^0}{(d[\text{R}\ddot{\text{u}}]/dt)^Q} - 1 \right]}{[\text{Q}]}$$

Method b is

$$k_q = \frac{k_{ox} \left(\frac{[(\text{PhO})_3\text{PO}_3]_0 - [\text{R}\ddot{\text{u}}]_0 + [\text{R}\ddot{\text{u}}]_t}{\ln [\text{R}\ddot{\text{u}}]_0/[\text{R}\ddot{\text{u}}]_t} \right) - \frac{k_d}{k_{ox}}}{[\text{Q}]}$$

Method c is

$$k_q = \frac{k_{ox}([\text{R}\ddot{\text{u}}]_t^Q - [\text{R}\ddot{\text{u}}]_0^Q) + k_d \ln [\text{R}\ddot{\text{u}}]_t^Q/[\text{R}\ddot{\text{u}}]_0^Q}{[\text{Q}] \ln [\text{R}\ddot{\text{u}}]_0/[\text{R}\ddot{\text{u}}]_t^Q}$$

where [Q] = quencher concentration, $[(\text{PhO})_3\text{O}_3]_0$ = initial ozonide concentration, $[\text{R}\ddot{\text{u}}]_0$ = initial rubrene concentration (unchanged by the presence of quencher), $[\text{R}\ddot{\text{u}}]_t$ = final rubrene concentration, and $-(d[\text{R}\ddot{\text{u}}]/dt)_0$ = initial rate of rubrene loss. Superscripts Q and 0 indicate the presence or absence of quencher.

(10) Calculated from the following literature values: $k_{ox}(\text{rubrene}) = 3.0k_{ox}(2,3\text{-dimethyl-2-butene})$,¹¹ $k_{ox}(2,3\text{-dimethyl-2-butene}) = 50k_{ox}(2\text{-methyl-2-pentene})$,¹² and $k_{ox}(2\text{-methyl-2-pentene}) = 5 \times 10^5 M^{-1} \text{ sec}^{-1}$, since $k_q(\beta\text{-carotene})/k_{ox}(2\text{-methyl-2-pentene}) \approx 2 \times 10^4$ ¹³ in benzene-methanol solutions and quenching by β -carotene is diffusion controlled ($k_q = 1 \times 10^{10} M^{-1} \text{ sec}^{-1}$ from the modified Debye equation).

(11) B. E. Algar and B. Stevens, *J. Phys. Chem.*, **74**, 3029 (1970).

(12) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

(13) C. S. Foote and R. W. Denney, *J. Amer. Chem. Soc.*, **90**, 6233 (1968).

method b (Table I) which was assumed solvent independent.¹⁴ The k_d values for methods a, b, and c are shown in Table I together with k_q values for quenching by the effective compounds, calculated from the appropriate k_d values and the above assumptions.

The variations in $^1\text{O}_2$ decay constants with solvent type (Table I) are in good agreement with published $^1\text{O}_2$ lifetimes.¹⁶ Similarly, the k_q values for Dabco (Table I) are also in good agreement with the literature value in benzene-methanol ($1.6 \times 10^7 M^{-1} \text{ sec}^{-1}$).¹ $^1\text{O}_2$ quenching did not appear to involve chelate reaction since exposure (30 min) of the effective chelates in rubrene-free solutions to $^1\text{O}_2$ from the microwave discharge resulted in negligible change in the uv spectra of the chelates. Although all three methods of $^1\text{O}_2$ generation are open to question,¹⁷ the fair agreement in observed k_q values for the various methods (Table I) indicates that nickel(II) chelates are true quenchers of $^1\text{O}_2$. The k_q values derived for several of the metal chelates (Table I) are approaching diffusion-controlled values, similar to that found for *N*-phenyl-*N'*-cyclohexyl-*p*-phenylenediamine³ ($k_q \sim 5 \times 10^9 M^{-1} \text{ sec}^{-1}$ if $k_d \sim 4 \times 10^5 \text{ sec}^{-1}$, as found for 2-butoxyethanol, Table I) but still somewhat slower than β -carotene ($k_q \sim 3 \times 10^{10} M^{-1} \text{ sec}^{-1}$).¹

From the data in Table I, it is possible to speculate on mechanisms for $^1\text{O}_2$ quenching by the chelates. The

(14) Combination of the k_d/k_q values of Foote, *et al.*,¹⁵ for Dabco quenching in methanol and in benzene with the $^1\text{O}_2$ lifetimes in these solvents derived experimentally by Merkel and Kearns¹⁶ indicates that k_q for Dabco is solvent independent.

(15) C. S. Foote, E. R. Peterson, and K.-W. Lee, *J. Amer. Chem. Soc.*, **94**, 1032 (1972).

(16) P. B. Merkel and D. R. Kearns, *ibid.*, **94**, 1029 (1972).

(17) Method a because of possible quenching of the rubrene triplet (which is probably the chief precursor of $^1\text{O}_2$ formation¹¹), method b because of some direct reaction between the ozonide and the chelates, and method c because of the possibility of residual oxygen atoms being present in the discharge.¹⁸

(18) K. Furukawa and E. A. Ogryzlo, *Chem. Phys. Lett.*, **12**, 370 (1971).

quenching effect appears to be a property of the Ni(II) chelate as a whole, or of the Ni(II) nucleus, since the ligand 2,2'-thiobis(4-*tert*-octylphenol) failed to quench $^1\text{O}_2$ whereas Ni(II) chelates of this ligand are effective (Table I). The chelate coordination and magnetism also appear to be unimportant, since an octahedral (paramagnetic) complex, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$,¹⁹ quenches $^1\text{O}_2$ with a similar k_q to that of a square planar (diamagnetic) complex (the nickel aldimine¹⁹ or nickel di-*n*-butyldithiocarbamate,²⁰ for example), yet nickel acetylacetonate (an octahedral trimer)¹⁹ is less efficient. Heavy atom effects have previously been precluded in $^1\text{O}_2$ quenching.¹ The marked increase in k_q on going from Mn(II) to Co(II) to Ni(II) for the hydrated chlorides (Table I) is probably significant since both $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ have electronic absorptions corresponding to energy levels of 8000–9000 cm^{-1} ,¹⁹ whereas all transitions of the unpaired d^5 electrons of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ are forbidden.¹⁹ Since the fluorescence emission for the $^1\Delta_g \rightarrow ^3\Sigma_g^-$ transition occurs at ~ 8000

(19) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, Chapter 28.

(20) C. K. Jorgensen, "Inorganic Complexes," Academic Press, London, 1963.

cm^{-1} (22.5 kcal/mol),¹ transfer from $^1\text{O}_2$ to the Ni(II) and Co(II) chelates is possible either *via* a collisional process as suggested for β -carotene,¹ or by a long-range energy-transfer mechanism. However, other possible $^1\text{O}_2$ quenching mechanisms might include charge or electron transfer processes (*cf.* amines²¹), which occur between some chelates and oxy radicals,²² and chelate- $^1\text{O}_2$ complex formation with the Ni(II) d^8 chelates, analogous to those reported to be formed with ground-state oxygen by Ni(0) complexes²³ or by d^8 complexes of iridium.²⁴

(21) I. B. C. Matheson and J. Lee, *J. Amer. Chem. Soc.*, **94**, 3310 (1972).

(22) T. V. Liston, H. G. Ingersoll, and J. Q. Adams, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **14** (4), A83 (1969).

(23) S. Otsuka, A. Nakamura, Y. Tatsuno, and M. Miki, *J. Amer. Chem. Soc.*, **94**, 3761 (1972).

(24) L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968).

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Book Reviews

Advances in Physical Organic Chemistry. Volume 9. Edited by V. GOLD (King's College, University of London). Academic Press, Inc., New York, N. Y. 1971. ix + 299 pp. \$18.00.

There are four chapters in this volume: "Superacid Systems" (24 pp) by R. J. Gillespie and T. E. Peel; "Turnstile Rearrangement and Pseudorotation in the Permutational Isomerization of Pentavalent Phosphorus Compounds" (102 pp) by F. Ramirez and I. Ugi; "The Hydrogen Abstraction Reaction from O-H Bonds" (57 pp) by M. Simonyi and F. Tüdos; "Vinyl Cations" (96 pp) by G. Modena and U. Tonellato. The reviews are competently done and libraries should add this volume to the others in the series. (The notion of a library acquiring nearly all, but not all, volumes in a continuous series, even for valid reason, is more whimsical than realistic.)

Systems of high proton availability, which have aptly been popularized as superacid, have been known for a long time. The chapter on this subject, essentially completed at the end of 1968, covers a period when the properties of the systems became well understood, but their wide application still lay ahead. Commercially available superacids have since become available and the pace of publication has mounted. I would judge, therefore, that the major portion (80%) of this review, namely on the properties of superacid media, will remain valuable much longer than the material on applications.

Aspects of the pseudorotation of pentavalent phosphorus have been reviewed by the present authors and others both before and after the present work, whose coverage of the literature essentially reaches into 1970. Because of their complementary interests, the authors bring diverse observations to bear on the issues and interpretations. The emphasis on the turnstile rotation (TR) as compared with the Berry pseudorotation (BPR) mechanism is understandable, since these authors discovered TR and had to advocate its consideration in the face of "establishment" opposition. The authors do consider BPR, however, in some detail and this makes for balance in their presentation. (This important research area can use more light and less heat.)

As discussed in this volume, the homolytic reactivity of the O-H group is a selected slice of an enormous field, restricted by choice to second-order bimolecular reactions in the liquid phase. Citations in 1970 are given. Of necessity, the emphasis is on phenols, yet the cleavages of ArO-H bonds in redox reactions, photochemistry, pulse radiolysis, etc., had to be excluded. Nevertheless, the dis-

cussions and compilations of kinetic parameters illustrating substituent, isotope, steric, hydrogen-bonding, and medium effects should be useful to researchers in the free radical field. I did think that the short section on the details of detection of hydrogen bonding was extraneous.

The properties of the once elusive vinyl (or ethenyl) cations are carefully and thoroughly treated in the last chapter. Documentation extends into the 1970's. The authors make chemical connections between the vinyl cation and acetylenes, allenes, propargyl cations, etc., indicating beautifully how broad and significant this area is.

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PMR Spectroscopy in Medicinal and Biological Chemistry. By A. F. Casy (University of Alberta). Academic Press, London and New York. 1972. xvi + 425 pp. \$23.00.

The importance of nmr to the solution of biochemically interesting problems is evidenced by the veritable explosion of papers on this subject within the past three to four years. Therefore, the text written by A. F. Casy, aimed at the reader who has a fundamental knowledge of nmr, is timely since the author wishes to inform medicinal, organic, and pharmacological chemists of past biological work which has been studied by nmr. This book attempts to review a large field and succeeds in some cases and falls short in others. For example, Chapters 3 and 5 which deal with stereochemical problems are well written and clearly show one of the powerful uses of nmr. Within Chapter 3, however, the discussion of the usefulness of the nuclear Overhauser effect is too short since recently this has proven to be a powerful technique for conformational analysis. Chapters 8 and 9 deal with only a small part of the application of nmr to studies of peptides and proteins. No mention is made of the use of paramagnetic probes for the study of molecular interactions by the measurement of longitudinal and transverse relaxation rates of protons. Chapter 9, however, gives an excellent review of nmr studies of carbohydrate conformations and makes the text an excellent source for ideas to stimulate further studies utilizing ^{13}C nmr. Overall, I recommend the book as a reference text and believe it will serve its intended purpose to stimulate medicinal, organic, and pharmacological chemists to further use nmr to study biologically interesting problems.

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