The advantage of the use of the epr spectrum is that it allows the unequivocal identification of the ${}^1\Delta$ state as well as some estimate of the amount of the species present. Together with the gas-phase experiments described in the following communication,[10] the resonance measurements bring strong support to the intermediacy of excited oxygen in chemical reactions.

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Gas-Phase Reactions of Singlet Oxygen from a Chemical Source

Sir:

There have now been a number of reports which describe chemical oxygenations in which the oxidizing agent involved appears to be molecular oxygen in an excited singlet state.[1-7] In addition strong evidence has been given[4,8-13] that excited singlet oxygen is also the active species in sensitized photooxidations.

In the solution work[7] the failure to bleach rubrene at −78° with a 250-fold excess of the phosphite–ozone adduct had been taken as reasonable evidence that the adduct itself was not responsible for the chemistry observed. This possibility is not rigorously excluded, however, and prompted the present gas-phase oxidation work.

We have now found that the product gas from the decomposition of the triphenyl phosphite–ozone adduct[7,14] can react with a typical singlet oxygen acceptor *in the gas phase.* Furthermore this same product gas has been shown to contain O_2 $({}^1\Delta_g)$ by epr absorption measurements as described in the accompanying communication. These observations provide further compelling evidence that the oxidizing agent involved in this and the previously reported *in situ* chemical oxygenations is most likely excited singlet oxygen.

The triphenyl phosphite–ozone adduct (0.01 mol) was prepared at −78° as previously described[7] except that dichlorodifluoromethane (150–200 ml) was used as the reaction medium. A small amount (3–4 ml) of pentane was used to facilitate transfer of the phosphite to the cold dichlorodifluoromethane. The resulting reaction mixture was a fine suspension which gave almost complete solution upon ozonization. Following ozonization and nitrogen purging, solvent was completely removed *in vacuo* to give the solid phosphite–ozone adduct which was stable at low temperatures. It was advantageous to add sand or chalk (~100 g of moderator/0.01 mol of adduct) as a moderator prior to solvent removal. In the absence of the moderator decomposition of the solid adduct upon warm-up occurs in an uncontrolled manner with the resultant splattering causing contamination of the gas-mixing chamber.

The flask containing the solid adduct was attached to a high vacuum line while maintained at −78°. Pumping was then continued until the pressure in the system was $<10^{-3}$ mm. The vacuum line was equipped with a product trap (−196°) as well as a trap (−78°) between the gas-mixing chamber and the flask containing the adduct. The latter trap ensures that new materials found in the product trap did not result from contact between gaseous acceptor and solid adduct but were true gas-phase products. The distance traveled by the evolved oxygen prior to encountering the acceptor was ~20 in. Slow introduction of the acceptor, either 2,3-dimethylbutene-2 or 1,3-cyclohexadiene, was then begun. The temperature of the adduct was first raised to −35°, using a methanol–ice bath, producing a momentary rise in pressure. When the pressure had returned to $<10^{-3}$ mm, water was slowly added to the cooling bath to permit slow warming to ~0°, after which the bath was removed and the adduct allowed to warm to ambient temperature. The pressure rose gradually to ~0.2–0.6 mm as decomposition proceeded smoothly. Complete decomposition was evidenced by the pressure again dropping to $<10^{-3}$ mm after 40–50 min. Triphenyl phosphate could be recovered in quantitative yield.

The material in the product trap was analyzed by flame ionization gpc. In the cyclohexadiene case the major product had gpc retention times on two different columns which were identical with those for authentic 5,6-dioxabicyclo[2.2.2]octene-2. The yield was very low (~0.01%),[15a] as expected from the low concentrations of O_2 $({}^1\Delta_g)$ found in the esr experiments (~1%).[15b] While the yield is too low to permit use of the usual product identification procedures, the gpc results combined with the esr results[15] and the control experiments lead us to conclude that we are observing the product which has been used to diagnose the presence of singlet oxygen in solution.[1-9] At the present time we cannot comment on the possible distribution of the initially produced singlet oxygen between the ${}^1\Sigma_g{}^+$ and ${}^1\Delta_g$ states,[11,12] although the major product observed is that usually attributed to the ${}^1\Delta_g$ state.

The tetramethylethylene case is less conclusive. Here we were unable to remove all traces of the singlet oxygen product, 2,3-dimethyl-3-hydroperoxybutene-1, from the starting olefin. We are not able to say with any degree of certainty that the amount of this material increased as a result of the gas-phase oxidation. In this connection it is interesting to note that while Winer and Bayes were able to observe gas-phase singlet oxygen oxidation

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[1] C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, **86**, 3879 (1964).

[2] C. S. Foote, S. Wexler, and W. Ando, *Tetrahedron Letters*, 4111 (1965).

[3] C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *J. Am. Chem. Soc.*, **90**, 975 (1968).

[4] E. McKeown and W. A. Waters, *J. Chem. Soc., B*, 1040 (1960).

[5] H. H. Wasserman and J. R. Scheffer, *J. Am. Chem. Soc.*, **89**, 3073 (1967).

[6] J. A. Howard and K. U. Ingold, *ibid.*, **90**, 1956 (1968).

[7] R. W. Murray and M. L. Kaplan, *ibid.*, **90**, 537 (1968).

[8] C. S. Foote and S. Wexler, *ibid.*, **86**, 3880 (1964).

[9] E. J. Corey and W. C. Taylor, *ibid.*, **86**, 3882 (1964).

[10] T. Wilson, *ibid.*, **88**, 2898 (1966).

[11] D. R. Kearns, R. A. Hollins, A. U. Khan, R. W. Chambers, and P. Radlick, *ibid.*, **89**, 5455 (1967).

[12] D. R. Kearns, R. A. Hollins, A. U. Khan, and P. Radlick, *ibid.*, **89**, 5456 (1967).

[13] K. R. Kopecky and H. J. Reich, *Can. J. Chem.*, **43**, 2265 (1965).

[14] Q. E. Thompson, *J. Am. Chem. Soc.*, **83**, 846 (1961).

[15] (a) Yield based on phosphite–ozone adduct. (b) E. Wasserman, R. W. Murray, M. L. Kaplan, and W. A. Yager, *ibid.*, **90**, 4160 (1968).

of tetramethylethylene using a microwave discharge,[16] Corey and Taylor[6] were unable to observe this oxidation using a similar source. It is conceivable that the "ene" reaction, which requires relocation of a hydrogen atom, is more sensitive to the differences between gas-phase and solution conditions than is the diene reaction. This could lead to a different order of reactivities for gas-phase and solution singlet oxygen oxidations.

In a separate experiment the adduct was permitted to decompose so that the product gas passed through a column of silica gel which had been impregnated with leuco malachite green and was protected from light by aluminum foil. The initial color of the adsorbed dye was pale blue even when carefully prepared. After decomposition of the adduct, the bottom portion of the column had turned dark blue-green in color, presumably due to the formation of the oxidation product.[17]

Control experiments in which a pressure rise comparable to that obtained by decomposition of the adduct was produced by the introduction of ground-state O_2 gave none of the oxidation products from the olefins nor caused a color change in the adsorbed dye experiment.

The phosphite–ozone adduct is representative of a large number of potential singlet oxygen sources in ozone chemistry. The possibility, suggested by the results reported here, that these sources can be responsible for gas-phase reactions of singlet oxygen is of particular significance to the air pollution problem. That singlet oxygen may play an important role in air pollution was discussed recently by Khan, Pitts, and Smith.[18] These authors suggest that singlet oxygen, to be used in accomplishing the important conversion of NO to NO_2 in smog production, is produced by photosensitization of ground-state O_2. They have proposed that polynuclear aromatic hydrocarbons, present as atmospheric contaminants, may act as one such type of photosensitizer.

The results reported here coupled with the known high concentrations of ozone in polluted atmospheres suggest that the required singlet oxygen[18] may be produced by reactions of ozone with other atmospheric contaminants. Such contaminants could include tertiary amines, sulfides, sulfoxides, phosphines, phosphites, and some olefins, all of which are known to react with O_3 in such a way that one oxygen atom is retained in the oxidized product. The other product is molecular oxygen which it now appears is almost certainly in an excited singlet state.[19]

[16] A. M. Winer and K. D. Bayes, *J. Phys. Chem.*, **70**, 302 (1966).

[17] H. Kautsky, *Trans. Faraday Soc.*, **35**, 216 (1939).

[18] A. U. Khan, J. N. Pitts, Jr., and E. P. Smith, *Environ. Sci. Technol.*, **1**, 656 (1967).

[19] NOTE ADDED IN PROOF. We have also observed the conversion of α-terpinene to ascaridole by singlet oxygen in the gas phase.

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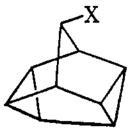
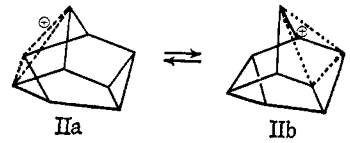
Reactivity and Degenerate Rearrangement in the Solvolysis of 9-Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane *p*-Nitrobenzoate

Sir:

The carbonium ion produced by solvolysis of the 9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane derivative I has unique structural and symmetry properties which could result in multiple degeneracy. Since I is a polycyclic analog of *cis*-3-bicyclo[3.1.0]hexyl tosylate, the carbonium ion is capable of threefold degeneracy by means of a homocyclopropyl carbinyl rearrangement (I → IIa).[1] In addition, there is the possibility of a bridge-flip rearrangement (*e.g.*, IIa ⇄ IIb) which again regenerates a cation identical with the original. If both processes were to operate concurrently, all positions become interchangeable and, hence, all nine carbon atoms could become equivalent. We now report the synthesis of the functionalized pentacycle I[2] and the results of a preliminary study on its solvolytic reactions.



I



IIa

IIb

The key intermediate in our synthetic plan was the unsaturated, tetracyclic alcohol III since a photochemical bond reorganization of III homologous to the norbornadiene–quadricyclene transformation[3] should produce I-OH.[2,4] Epoxide V[5] was secured from the readily available hydrocarbon IV (deltacyclene)[6] by perbenzoic acid treatment (30 min at 0°, 78%). The reaction of V in chloroform with 48% hydrobromic acid produces mainly the rearranged bromohydrin VI [48%; mp 73–74°; τ 5.82 (2 d, J = 3 and 7 Hz) and 5.75 (s, $h_{1/2}$ = 4 Hz)] in addition to lesser amounts of the *exo,exo* vicinal isomer VII [31%; mp 50–51°; τ 5.40 (d, J = 6 Hz) and 5.90 (d, J = 6 Hz)].[8] With anhydrous hydrogen bromide in ether, however, the reaction proceeds with little rearrangement, VII and its *exo,endo* isomer VIII [mp 82–83°, τ 5.70 (2 d, J = 1.5 and 4 Hz) and 5.90 (d, J = 1.5 Hz)] being the major products. Dehydrobromination of VI (KO-*t*-Bu–DMSO, 3 hr at 25°) gives rise to 8-tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonen-5-ol (III) [83%, bp 74–78° (2 mm); ν_{max} 700 cm^{-1}; τ 4.08 (m, 2 H) and 6.04 (t, J = 2 Hz, 1 H)].[9]

The structure of III has been confirmed by an independent synthesis. The diazo ketone IX, obtained from 7-norbornadienecarboxylic acid,[10] affords (Cu–THF, reflux 2 hr) the tetracyclic ketone X [~50%; ν_{max} 1750 and 1764 cm^{-1}; τ 3.80 (t, J = 2 Hz, 2 H)][9] also

[1] S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron Suppl.*, 8 [II], 621 (1966), and references cited.

[2] The parent hydrocarbon I (X = H) has recently been synthesized by three different routes: (a) H. Prinzbach and D. Hunkler, *Angew. Chem. Intern. Ed. Engl.*, **6**, 247 (1967); (b) P. K. Freeman and D. M. Balls, *J. Org. Chem.*, **32**, 2354 (1967); (c) E. Wiskott and P. von R. Schleyer, *Angew. Chem. Intern. Ed. Engl.*, **6**, 694 (1967).

[3] W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961); G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

[4] C. F. Huebner, E. Donoghue, L. Dorfman, E. Wenkert, W. E. Streth, and S. W. Donelly, *Chem. Commun.*, 419 (1966).

[5] All new compounds have been fully characterized by satisfactory spectral and microanalytical data (IX, spectra only).

[6] Prepared (62%) from the norbornadiene dimers[7] by the method of L. G. Cannell, *Tetrahedron Letters*, 5967 (1966).

[7] J. J. Mrowca and T. J. Katz, *J. Am. Chem. Soc.*, **88**, 4012 (1966).

[8] For similar homocyclopropyl rearrangements, *cf.* P. K. Freeman and D. M. Balls, *Tetrahedron Letters*, 437 (1967); R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967).

[9] Professor P. von R. Schleyer has informed us that III (and X) has also been prepared in his research. Comparison of the nmr spectra of III and X, kindly proffered by Professor Schleyer, has established the identity of the compounds from both laboratories.

[10] G. W. Klump and F. Bickelhaupt, *Tetrahedron Letters*, 865 (1966).