

From an estimate of the steady-state concentration of $^1\Delta$ oxygen generated during the irradiation and a measurement of the effective lamp output we find that the quantum yield for the formation of $^1\Delta$ is of the order 0.5 ± 0.3 , assuming a $^1\Delta$ lifetime of ~ 1 sec in the cell.⁶ While we consider this number uncertain, it indicates that a significant fraction of the excitation energy is utilized to generate $^1\Delta$. Furthermore, if the value of ~ 0.5 could be established, sensitization by the naphthalene triplet would be indicated. This result tends, therefore, to support the theoretical work of Kawaoka, Khan, and Kearns,³ who predicted that the oxygen quenching of triplet-state molecules proceeds primarily by energy transfer to oxygen. To verify this point, however, a careful study of the pressure dependence of the $^1\Delta$ resonance intensity will be required. Preliminary measurements indicate that over a range of oxygen pressures from 0.1 to 0.3 mm the steady-state concentration of $^1\Delta$ is still increasing with increasing O_2 pressure. A detailed study of this point is in progress and will be presented elsewhere.

(8) K. Kawaoka, A. U. Khan, and D. R. Kearns, *J. Chem. Phys.*, **46**, 1842 (1967).

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Electron Paramagnetic Resonance of $^1\Delta$ Oxygen Produced by Gas-Phase Photosensitization with Naphthalene Derivatives

Sir:

We have observed the formation of $^1\Delta-O_2$ on uv irradiation of vapor-phase mixtures of oxygen with naphthalene and some of its derivatives. Under steady-state conditions as much as 70% of the total oxygen can be converted to the excited form so that the systems could serve as convenient sources of $^1\Delta$ for gas-phase reactions. The excited oxygen was detected by its characteristic epr spectrum, a procedure which had been previously used in demonstrating its formation on decomposition of a triphenyl phosphite-ozone complex.¹ These photosensitization experiments may be regarded as giving strong support to Foote's hypothesis that many photooxidations involve excited oxygen as the reactive intermediate, this upper state being produced from ground-state oxygen by energy transfer from the photosensitizer.² To our knowledge, the first direct physical evidence for this transfer has been the very recent report of Snelling who observed the near-infrared emission of $^1\Delta$ oxygen produced by benzene photosensitization.³ Our experiments, and the similar ones by Kearns, *et al.*, described in the ac-

(1) E. Wasserman, R. W. Murray, M. L. Kaplan, and W. A. Yager, *J. Am. Chem. Soc.*, **90**, 4160 (1968).

(2) C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *ibid.*, **90**, 975 (1968), and references cited therein.

(3) D. R. Snelling, *Chem. Phys. Letters*, **2**, 346 (1968).

companying communication,⁴ give additional evidence using other sensitizers and another method of detection which allows direct measurements of concentrations. Also, our results lead to quite high $^1\Delta$ concentrations, some two orders of magnitude larger than the benzene system.³

The experiments were performed by including a few crystals or drops of the naphthalene derivative in a quartz tube of ~ 24 mm o.d. containing from 0.1 to 1.0 mm of oxygen. Irradiation was accomplished with unfiltered medium or high-pressure mercury or xenon lamps of 150–500 W through a Supersil window. The characteristic four-line epr spectrum of $^1\Delta-O_2$, due to the orbital magnetic moment of the π^* electrons, was readily observed during irradiation between 9–10 kG at X-band. The origin of the spectrum was established by comparison with that observed with a microwave discharge in O_2 as first reported by Falick, *et al.*,⁵ and with that observed in the phosphite-ozone decomposition.¹ The concentrations of the $^1\Delta$ and $^3\Sigma$ were established by comparing the intensities of the epr absorptions with those of discharged oxygen where the $^1\Delta$ concentration is 7–10%.^{1,5}

Naphthalene (I), 1- (II) and 2-fluoronaphthalene (III), and octafluoronaphthalene (IV) were used as sensitizers. With I–III, steady-state $^1\Delta$ concentrations of 3–6% were readily obtained. Sensitizer, O_2 , and light must all be present if $^1\Delta$ is to be observed. With I, and somewhat less readily with II and III, irradiation was also associated with the largely irreversible disappearance of the $^3\Sigma$ oxygen within a period of tens of minutes. While ground state I is supposedly inert to reaction with $^1\Delta-O_2$, the conditions of our experiment are such that collisions are likely between excited I and excited oxygen, so that reaction may well occur. With IV the irreversible removal of O_2 was slower, and we have concentrated on IV- O_2 mixtures for a more detailed study.

The absolute concentration $^1\Delta-O_2$ was independent of the original O_2 pressure in the range of 0.2–1.0 mm for a given set of irradiation conditions. The independence implies that effectively all excited IV transferred energy to O_2 before deactivation. Consistent with this conclusion is the observation that even with the more powerful lamps the concentration of the $^1\Delta$ was linearly proportional to the intensity of light irradiating the sample. At the lower O_2 pressures, with the higher proportions of $^1\Delta$, we could easily see the immediate decrease in $^3\Sigma$ associated with rise of $^1\Delta$ on initial illumination. Blocking the light produced a corresponding rise in $^3\Sigma$ and disappearance of $^1\Delta$. In most experiments, the $^3\Sigma$ and $^1\Delta$ changes balanced one another, although in some the loss of $^3\Sigma$ on illumination was greater than the amount of $^1\Delta$ produced. The oxygen balance in the majority of experiments indicates that a substantial amount of O_2 is not present in some metastable form other than $^1\Delta$. These results do not imply that the $^1\Delta$ must be formed immediately on sensitization. The $^1\Sigma$ might be formed first but would

(4) D. R. Kearns, A. U. Khan, C. K. Duncan, and A. H. Maki, *J. Am. Chem. Soc.*, **91**, 1039 (1969). The simultaneous publication of the two communications is possible through the gracious withholding, by Drs. Maki and Kearns and their coworkers, of the previously submitted manuscript.

(5) A. M. Falick, B. H. Mahan, and R. J. Meyers, *J. Chem. Phys.*, **42**, 1837 (1965).

be expected to deactivate rapidly to the $^1\Delta$ on collision.⁶

On continued irradiation the $^3\Sigma$ concentration decreases with time, presumably due to irreversible reactions of O_2 with the sensitizer. The $^1\Delta$ also decreases with the total pressure but more slowly. It is possible that at the lower pressures the excited naphthalenes are not completely scavenged by the $^3\Sigma$ to produce $^1\Delta$. At quite low O_2 pressures, ~ 0.01 mm, the $^1\Delta$ concentrations can be higher than that of the $^3\Sigma$. We have obtained O_2 -IV mixtures in which 70% of the total O_2 is converted to $^1\Delta$. Such an inverted population can occur because we are not producing the $^1\Delta$ by direct absorption of light by the $^3\Sigma$ but rather through an intermediate excited aromatic.

One significant point is that the energy transfer we are observing in the above experiments is essentially that postulated by Khan, *et al.*, to explain how significant concentrations of $^1\Delta$ could arise in an atmosphere which contained some aromatic compounds.⁷ Direct excitation from the $^3\Sigma$ would not be feasible because of the low transition probabilities. The apparently high efficiencies of the transfer even at low O_2 pressures make the process particularly likely. It would thus appear that substantial amounts of $^1\Delta$ might be available in a polluted atmosphere and could serve as a reactant in subsequent oxidations.

The following compounds have also been found to be sensitizers. The figures given are percentages of $^3\Sigma$ converted to $^1\Delta$: quinoxaline, 3.5%; 1-naphthaldehyde, 2.5; biphenyl, 2.4; 1-acetonaphthone, 0.9; 1-chloronaphthalene, 0.4; phenanthrene, 0.4; anthracene, 0.3; 2-acetonaphthone, 0.2; dibenzfuran, 0.2; anthraquinone, 0.1; phenanthridine, 0.1.

(6) S. J. Arnold, M. Kubo, and E. A. Ogryzlo, *Progr. Reaction Kinetics*, in press.

(7) A. U. Khan, J. N. Pitts, Jr., and E. B. Smith, *Environ. Sci. Technol.*, **1**, 656 (1967). We are indebted to Drs. R. W. Murray and P. R. Story for bringing this reference to our attention.

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Studies on the Mechanism of Squalene Biosynthesis. Presqualene, a Pyrophosphorylated Precursor to Squalene

Sir:

Recently an intermediate in the biosynthesis of squalene from farnesyl pyrophosphate was isolated, and, on the basis of isotopic evidence, a tentative structure was proposed.¹ This structure has since been shown to be incorrect by Corey and Ortiz de Montellano,² who synthesized the compound and found it to be inactive in squalene synthesis. We now report chemical and spectroscopic evidence on this interme-

(1) H. C. Rilling, *J. Biol. Chem.*, **241**, 3233 (1966).

(2) E. J. Corey and P. Ortiz de Montellano, *Tetrahedron Letters*, 5113 (1968). We wish to thank Professor Corey for communicating these results to us prior to publication.

diate and on some of the derivatives which permits a revised formulation of its structure (I).

This intermediate was enzymatically prepared from farnesyl-1,1- t_2 pyrophosphate.^{1,8} Butanol extracts of the incubation mixtures were concentrated and chromatographed on Dowex-1.⁸ Fractions containing the intermediate were combined and, after the addition of NH_4OH , lyophilized. The residue was dissolved in benzene and precipitated with ammoniacal methanol. Thin-layer chromatography showed one major radioactive component with traces of nonradioactive contaminants.

This compound was stable to strong base and labile to dilute acid and could be enzymatically converted to squalene in the presence of NADPH. The nmr spectrum⁴ of I had, as does squalene, resonances at δ 5.3 (broad multiplet, olefinic H), 2.0 (methylene envelope), and 1.6 and 1.69 (incompletely resolved methyl singlets). In addition, there is a δ 4.07 multiplet (CH_2O) and a 1.16 broad singlet (at least 5 H) presumably due to the cyclopropyl methyl overlapped by the complex splitting of the cyclopropyl hydrogens. The later resonances are in reasonable agreement with the nmr spectrum of a model compound, III ($Y = POP$).

Since I is an unstable and nonvolatile pyrophosphate ester, most of the structural work was performed on reduction products from I. Treatment with $LiAlH_4$ gave a mixture of hydrocarbons (25%) and an alcohol (25%), II ($X = H$), whose homogeneity was established as follows. Chromatography of the alcohol on a 1×20 cm column of silica gel G with benzene as a solvent revealed a single radioactive component. This material was found to be homogeneous by tlc (cyclohexane-ethyl acetate 70:30, R_f 0.50) and by glpc on 3% SE 30 and 3% OV-1 with retention times of 1.47 and 1.78 relative to squalene. Acetylation of II yielded a single product as evidenced by tlc (R_f 0, hexane; 0.35, benzene; and 0.66, cyclohexane-ethyl acetate 70:30). Glpc of II-acetate showed a major component with retention times of 1.90 and 1.86 relative to squalene on OV-1 and SE-30. Substantial decomposition of II-acetate occurred during glpc.

The following experiment established that rearrangements had not occurred during the formation of II. Tritiated II was mixed with farnesol as a carrier and pyrophosphorylated,⁵ and the products were separated by ion-exchange chromatography. The yield of II-pyrophosphate was 14% while that of farnesyl pyrophosphate was 25%. The II-pyrophosphate had chromatographic properties (ion exchange and tlc) identical with those of I and could be enzymatically converted to squalene in 65% yield.

The nmr spectrum of II ($X = H$) was similar to that of I except the signal due to the methylenoxy hydrogens was shifted to δ 3.82 and the cyclopropyl methyl singlet was relatively sharp at δ 1.15 with other ill-defined absorption at δ 0.9 and 1.26, presumably due to the cyclopropyl H and to CH_2 adjacent to cyclopropane. The

(3) S. Sofer and H. C. Rilling, *J. Lipid Res.*, in press.

(4) A Varian A-56/60 spectrometer was used in conjunction with a C-1024 time-averaging computer. Because of the small amounts of material available, each sample was scanned a minimum of 300 times. Deuteriochloroform was used as the solvent. The nmr spectra of *cis*- and *trans*-III ($Y = H$) were obtained from Professor R. B. Bates, whom we wish to thank.

(5) A. H. Kandutsch, H. Paulus, E. Levin, and K. Bloch, *J. Biol. Chem.*, **239**, 2507 (1964).