which permit over-all energy transfer as the molecules separate (progression from center to far right of Figure 1). On the other hand, crossing between degenerate states in forbidden processes results in configurations which cannot lead to energy transfer (Figure 2).

Although these considerations appear to be useful in explaining the present results as well as recent results of others,[8] we wish to emphasize that orbital symmetry will generally be secondary in importance to energy in determining the rate of energy-transfer processes. Thus exothermic energy transfer is expected to occur in general with or without orbital symmetry conservation, and control by orbital symmetry is expected only when there is a competition between different energy-transfer processes.

[8] Orbital symmetry requirements in fluorescence quenching have recently been reported (G. S. Hammond, 20th National Organic Chemical Symposium, Burlington, Vt., June 18–22, 1967).

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Electron Paramagnetic Resonance of ${}^1\Delta$ Oxygen from a Phosphite–Ozone Complex

Sir:

The identification of electronically excited oxygen as a product of organic chemical reactions is usually based on its subsequent reaction with unsaturated organic molecules.[1-3] The evidence is usually the observation of products which have also been obtained with photosensitized oxidations or with microwave discharged oxygen.[4,5] While the physical evidence is unequivocal for both ${}^1\Delta$ and ${}^1\Sigma$ oxygen in the discharge,[6] similar support for the chemical production of these states has been confined to their electronic emission spectra arising with some inorganic reactions.[7] To determine if excited oxygen is, in fact, produced in one of the organic reactions which had been suggested as a source, we have examined the epr spectrum of the oxygen produced by the decomposition of a triphenyl phosphite–ozone complex.[3] The presence of ${}^1\Delta$ oxygen has been demonstrated by its characteristic absorptions.

The epr of ${}^1\Delta$ O_2 in a discharge was first observed and characterized by Falick, *et al.*[8] We may regard these absorptions as arising from the magnetic moment due to the orbital motion of the two π^* electrons. In a corresponding ${}^1D$ state of an atom, the pure orbital motion produces a $g = 1$, and epr absorption would be near 6000 G at 9 Gc. In the ${}^1\Delta$ O_2 the component of orbital angular momentum along the internuclear axis is $2\hbar$. This knowledge of one component of the total angular momentum J implies, by the uncertainty principle, that the direction of J is off the axis. We may view the internuclear axis as tumbling about J so that, on the average, only the component of the orbital magnetic moment parallel to J remains to interact with the external magnetic field. The reduced moment is equivalent to $g = 4/(J(J + 1))$.[8,9] For the lowest rotational state of the molecule $J = 2$, a value which arises from the orbital motion. For this state $g = {}^2/_3$ and absorption is expected at $\sim$9000 G. The higher rotational states have a smaller g factor, and resonance will occur only at fields beyond the upper limit of the magnet (15 kG). Consequently we see only the four $\Delta m_J = 1$ transitions of $J = 2$. These transitions are split by a second-order interaction, and four absorptions at intervals of $\sim$100 G are observed.[8]

In a typical run, 0.01 mol of the solid triphenyl phosphite–ozone complex,[3] diluted with sand to moderate the decomposition,[10] was allowed to decompose at $\sim -20°$. The oxygen produced traversed a quartz tube which passed through a Varian V-4535 large-access cavity. Large diameters ($\sim$20 mm) were used in the system to minimize the time interval between the production of the O_2 and its entrance into the cavity. The oxygen pressure in the tube was kept in the range of 0.2–2 mm. The higher pressure was associated with collisional broadening, and most experiments were done at 0.3–0.6 mm. The intensity of the absorptions paralleled the rate of oxygen evolution by the complex. The strong signals characteristic of ${}^3\Sigma$ O_2 were easily detected. In addition, the weaker absorptions of the ${}^1\Delta$ O_2 were observed. These were identified by comparison with the spectrum observed with oxygen which had experienced a microwave discharge and then passed through the same cavity. The positions of the lines agreed within 1 G. For both the chemically and electrically produced ${}^1\Delta$ O_2 the inner two lines are about 50% stronger than the outer, as expected for a ${}^1\Delta$ state.[9]

The relative intensities of the ${}^3\Sigma$ and ${}^1\Delta$ were also measured for discharged and for chemically produced oxygen. Assuming that the discharge contains 10% ${}^1\Delta$,[8,11] the gas from the complex contained $\sim$1% ${}^1\Delta$ when it was in the cavity. Implicit in this determination is the assumption that both sources of ${}^1\Delta$ have the same relative amount of the $J = 2$ state, the one rotational state observed in the resonance experiments. At 300°K, in thermal equilibrium, some 3% of the oxygen is in $J = 2$. Significant departures from equilibrium in one sample could invalidate the comparison, but we do not feel that large differences are likely.

Although the ${}^1\Delta$ is observed, we do not wish to imply that this must be the state originally produced on decomposition of the complex. Another possibility is that ${}^1\Sigma$ is the first product, but would, of course, not be detectable in the epr experiment. Relaxation to the ${}^1\Delta$ and also to the ${}^3\Sigma$ state would then allow their observation. Relaxation of the original excited state could occur as it diffuses out of the reaction mixture and travels to the cavity, although direct production of ${}^3\Sigma$ in the decomposition is also possible.

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[11] In our experiments the concentration of ${}^1\Delta$ in the discharge was largely independent of the microwave discharge power except at the lowest power levels. A decrease of the ${}^3\Sigma$ signal of 7–8% was observed with the initiation of the discharge.

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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