Table VI. Rate Constant Ratios for the PAQ–Stilbene Reaction

System	k_4/k_6	k_4/k_5	$\dfrac{k_6}{k_4 + k_6}$	K_3	K_7	K_{10}
Stilbene	0.89 ± 0.05	0.7 ± 0.1	0.5 ± 0.1	0.98 ± 0.06	0.14 ± 0.01	0.53 ± 0.03
α,α'-Stilbene-d_2	0.70 ± 0.04				0.17 ± 0.01	

bene. The data further indicate that all the processes which deactivate the PAQ triplet proceed at comparable rates. Since the decay of X is heavily in favor of the formation of the p state ($K_8 = 0.86$), adduct formation can be viewed as a minor deactivating path, and the nonspectroscopic excitation of stilbene occurs at about the same rate as the classical energy transfer. The small temperature dependence of K_7 (cf. Table II) indicates that the decay of X to p and Q is favored at higher temperature and hence involves some activation energy. The temperature variation of the ratio $K_7 k_4/(k_4 + k_6)$ is in the same direction as that of K_7, but the magnitude is too small to detect a significant influence of $k_4/(k_4 + k_6)$.

The stationary *trans/cis* ratio, $R_S = 0.7$, is close to that reported for high-energy sensitizers.[5] However, in the present case it represents a balance between the rate of isomerization and the rate of addition. Since the addition of PAQ to *cis*-stilbene is faster than to *trans*-stilbene, it is clear that for isomerization only R_S would be much smaller than 0.7.

Since the association complex X resembles the transition state of thermal reactions, the appearance of secondary deuterium isotope effect in adduct formation is not surprising. The formation of X may not only involve the appearance of torsional freedom about the central C–C bond of the olefin, but may also cause the geometry at the central carbon atoms to change from that appropriate for an sp² hybridization

to a configuration between sp² and sp³. In this case $(k_4)_D > (k_4)_H$ is expected,[33] but the data indicate that $(k_4/k_6)_D < (k_4/k_6)_H$. Consequently there is a strong implication that $(k_6)_D > (k_6)_H$, *i.e.*, that the classical energy transfer occurs at less than the diffusion-controlled rate and is subject to an isotope effect.[34] That $(K_7)_D > (K_7)_H$ can be readily accommodated if the olefinic carbon configuration in X is closer to sp² than to sp³, and if the configuration in X and p are similar. Under these circumstances $(k_8)_D \approx (k_8)_H$ and $(k_7)_D > (k_7)_H$. These arguments imply that an activation energy is involved in the formation of X and in its passage into adduct.

(33) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, Co., New York, N. Y., 1960.

(34) G. W. Robinson and R. P. Fosch, *J. Chem. Phys.*, **38**, 1187 (1963), predict on theoretical grounds that only a very small isotope effect can be expected if the energy difference between the initial and final states is small.

Excited Singlet Molecular Oxygen in Photooxidation

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Abstract: Competitive photooxidation of three pairs of unsaturated compounds yields a single set of relative reactivities, whether sensitized by a dye (methylene blue or rose Bengale) or by the aromatic substrates themselves. This result seems, except in case of a remarkable coincidence, uniquely consistent with excited singlet oxygen as the reactive species and inconsistent with a series of biradical-like "moloxides" which would be different for each sensitizer. In pyridine, the relative reactivities with singlet oxygen are as follows: tetramethylethylene, 1.0; 9,10-dimethylanthracene, 1.0; 9,10-diphenylanthracene, $\sim$0.2; rubrene, 2.25; and 1,3-diphenylisobenzofuran, 38.5. Direct addition to the triplet state of these acceptors is undetectable, with the possible exception of the last one where its contribution would be small. Energy considerations would indicate that the active molecules are in the $^1\Delta_g$ state.

The purpose of this note is to present additional experimental evidence for a mechanism *via* excited singlet oxygen molecules for the photooxidation in solution of organic compounds (acceptors) such as the polyacenes, in which a transannular peroxide is formed. This type of reaction has attracted much attention.[1] It is generally agreed that it does not pro-

ceed by direct addition of a ground-state oxygen molecule to a singlet excited molecule of the acceptor during the fluorescence quenching step. On the basis of the complex kinetic data previously accumulated, three
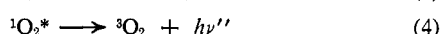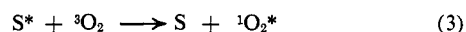
(1) For recent discussions of photooxidation, see E. J. Bowen, *Advan. Photochem.*, **1**, 23 (1963); and C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, **86**, 3880 (1964).

main mechanisms have been proposed, differing in the reactive intermediates assumed: (a) the triplet state of the acceptor reacting with ground-state oxygen, (b) a hypothetical transient "moloxide" of the acceptor or of the sensitizer that later transfers its oxygen to the acceptor, or (c) "active" oxygen reacting with ground-state acceptor. A strong argument for the latter can be inferred, by analogy, from the recent work of Corey[2] and Foote[3] on the reactivity of electrically or chemically excited molecular oxygen in a singlet state (here $^1O_2^*$).

In the present work, the competitive photoxidation of a mixture of two acceptors has been investigated. It shows that the hypothesis (a) above of a reaction of the triplet state of the acceptor can be ruled out in such cases as the photooxidations of rubrene, 9,10-dimethylanthracene, or 9,10-diphenylanthracene, which all give transannular peroxides. The results are consistent with a singlet oxygen mechanism. They will be presented at first exclusively on that basis, in anticipation of the Discussion where it will be shown that a Schenck-like interpretation by a moloxide-type of reaction (b) meets with difficulties. A method is outlined by which relative rate constants of the reactions of singlet oxygen with different acceptors can be obtained.

It is obvious that if the energies required to excite the first triplet as well as the first singlet excited states of an acceptor are greater than the energy absorbed by the sensitizer, the efficient participation in the oxidation of any excited states of the acceptor can be excluded. Such an acceptor, if photosensitized, acts unambiguously as a captor of singlet oxygen. Tetramethylethylene (TME) fits the energy and reactivity requirements for this role of $^1O_2^*$ captor. It reacts with chemically produced singlet oxygen, mainly to give 2,3-dimethyl-3-hydroperoxybutene-1 (TMEO$_2$) identical with the photooxidation product.[3] Its first triplet state is about 83 kcal above ground state,[4] yet it has been found here that its photooxidation proceeds readily when sensitized by methylene blue at 640 mμ, corresponding to quanta of 44.6 kcal only.

Methylene blue as sensitizer (S) must transfer its excitation energy to an oxygen molecule, which in turn reacts with TME to form its hydroperoxide.[5]

$$S + h\nu \longrightarrow S^* \tag{1}$$

$$S^* \longrightarrow S + h\nu' \tag{2}$$

$$S^* + {}^3O_2 \longrightarrow S + {}^1O_2^* \tag{3}$$

$${}^1O_2^* \longrightarrow {}^3O_2 + h\nu'' \tag{4}$$

$${}^1O_2^* + TME \longrightarrow TMEO_2 \tag{5}$$

If tetramethylethylene acts as an inhibitor of the sensitized photooxidation of another acceptor (A), it is evidence that the photooxidation of the latter also proceeds *via* singlet oxygen, by the same sequence of reactions with an additional step (6).

$${}^1O_2^* + A \longrightarrow AO_2 \tag{6}$$
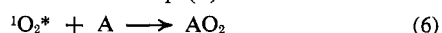
(2) E. J. Corey and W. O. Taylor, *J. Am. Chem. Soc.*, **86**, 3881 (1964).

(3) (a) C. S. Foote and S. Wexler, *ibid.*, **86**, 3879 (1964); (b) C. S. Foote, S. Wexler, and W. Ando, *Tetrahedron Letters*, No. 46, 4111 (1965).

(4) Its exact value is not known but has been estimated at 3.6 ev, *i.e*, 3 ev below the first excited singlet state of TME: see C. A. Coulson and E. T. Stewart in "The Chemistry of Alkenes," E. Patai, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, pp 137, 144.

(5) The electronic states involved are left unspecified here, but will be considered in the Discussion. The nature of the deactivating processes (eq 2 and 4) does not need to be specified here; radiative transitions are written for simplicity.

Total inhibition at a high enough ratio of concentration of the captor TME to that of the acceptor A rules out the contribution to the oxidation of A of a side path involving, for example, the reaction of triplet $^3A^*$ with $^3O_2$ (reaction 7, with the competitive radiative or rationless deactivation of $^3A^*$).

$$^3A^* + {}^3O_2 \longrightarrow AO_2 \tag{7}$$

$$^3A^* \longrightarrow A + h\nu \tag{8}$$
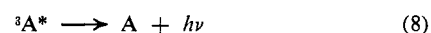
Assuming steady states for S* and $^1O_2^*$ and assuming that reaction 4 is negligible[6] compared to reactions 5 and 6, one arrives at the following linear relation between the reciprocal of the rate of oxidation of the acceptor and the concentration of TME

$$\frac{1}{\dfrac{d[AO_2]}{dt}} = \frac{k_5}{kk_6[A]}[TME] + \frac{1}{k} \tag{9}$$

with $k = (k_1k_3[S][^3O_2])/(k_2 + k_3[^3O_2])$ for a series of runs at constant light intensity and constant initial concentrations of oxygen, acceptor, and sensitizer, the values of which determine k.

A study of the direct photooxidation where the acceptor acts as its own sensitizer provides a way of checking the validity of the proposed mechanism (1 to 6). With the following reaction sequence now replacing reactions 1, 2, and 3, relation 9 should still be observed, with a

$$A + h\nu \longrightarrow A^* \tag{1'}$$

$$A^* \longrightarrow A + h\nu' \tag{2'}$$

$$A^* + {}^3O_2 \longrightarrow A + {}^1O_2^* \tag{3'}$$
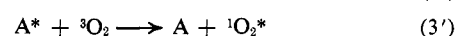
different value of k.

Experimental Section

Pyridine was used as solvent when not otherwise specified. Bromobenzene was the solvent in one series of runs with 9,10-dimethylanthracene.

Oxygen at pressure of 180 mm was admitted to an outgassed stirred solution of the acceptors. The course of the reaction induced by monochromatic light, from a Bausch and Lomb 33.86.-26.07 grating monochromator, at about 10° was checked by the absorption of oxygen; plots of the pressure against time were nearly linear during the reaction times. The rates of oxidation were determined photometrically with a Beckman DU2 from the initial and final concentrations of the acceptors after appropriate dilution. Final concentrations of TME were not measured.

Solvents and reagents were of high commercial grade, used without further purification; their absorption spectra and extinction coefficients agree with the literature values. The samples of 9,10-dimethylanthracene and 1,3-diphenylisobenzofuran were kindly provided by Miss B. Kaski. Control tests were performed to make sure that dark reactions were negligible, and that in the absence of oxygen no photochemical reaction took place.

Results

1. Rubrene (R). Tetramethylethylene acts indeed as an inhibitor of the photooxidation of rubrene[7] sensitized by methylene blue at 640 mμ, as well as of its direct photooxidation at 540 mμ (Figure 1). The inhibition is total when TME is present at an initial concentration about 100 times that of rubrene, the oxygen being then absorbed by the solution exclusively to oxidize TME.

Figure 2 shows that the results fit the linear relation 9. It gives for the ratio k_5/k_{6R} the value of 0.42 for the

(6) This follows from the observation that the rate of oxidation is independent of the acceptor concentration in the range studied.
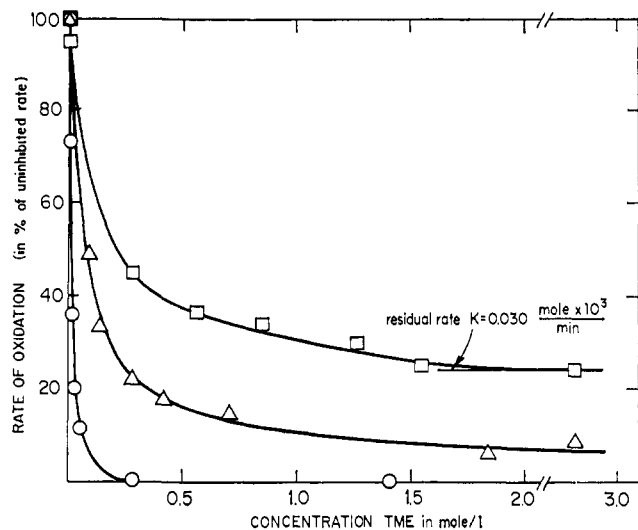
(7) 9,10,11,12-Tetraphenylnaphthacene.

Figure 1. Effect of tetramethylethylene (TME) on photooxidation: O, rubrene at 540 mμ (initial concentration 3.4 × 10^{-3} mole/l.); □, diphenylisobenzofuran (DPBF) at 425 mμ (initial concentration 2.6 × 10^{-3} mole/l.); △, diphenylisobenzofuran (DPBF) at 575 mμ (initial concentration 2.6 × 10^{-3} mole/l.).
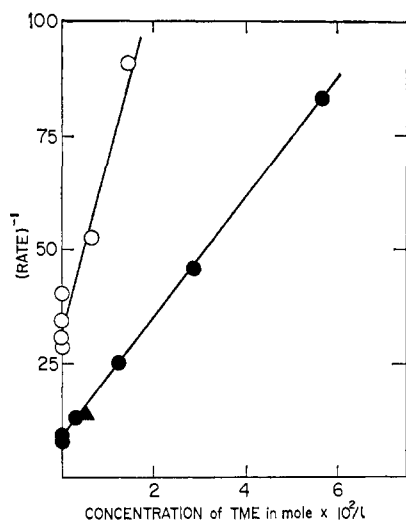

Figure 2. Effect of tetramethylethylene (TME) on the photooxidation of rubrene: ●, rubrene at 540 mμ (initial concentration 3.4 × 10^{-3} mole/l.); O, sensitized rubrene at 640 mμ (initial concentration 3.8 × 10^{-3} mole/l.); ▲, with 9,10-dimethylanthracene (DMA instead of TME (same units of concentration).

sensitized reaction, and 0.47 for the direct oxidation. Thus, the photooxidation of rubrene proceeds entirely via $^1O^*_2$. It reacts with $^1O_2^*$ about twice as fast as TME.

2. 9,10-Dimethylanthracene (DMA). TME inhibits the photooxidation of DMA sensitized by methylene blue at 640 mμ in pyridine, as well as its direct photooxidation at 403 mμ in bromobenzene. Figure 3 shows that the results fit relation 9, with $k_5/k_{6_{DMA}} = 1.0$, both at 640 and at 403 mμ.

Changing the solvent from pyridine to bromobenzene, which could have been expected to have a heavy-atom influence, is shown to affect neither the rate of photooxidation of pure DMA, nor the ratio $k_5/k_{6_{DMA}}$.

As in rubrene, the photooxidation of 9,10-dimethylanthracene proceeds entirely via $^1O_2^*$; it reacts with $^1O_2^*$ at about the same rate as TME.

This suggests that the effect of DMA on the photooxidation of rubrene should be identical with that of
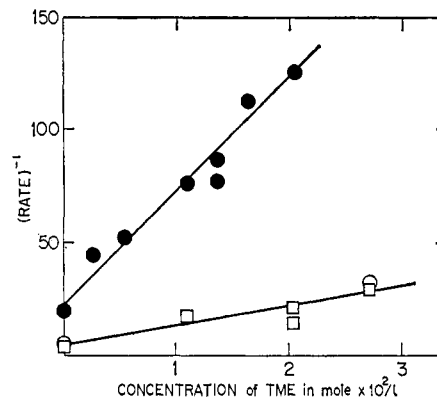

Figure 3. Effect of tetramethylethylene (TME) on the photooxidation of 9,10-dimethylanthracene (DMA): ●, in pyridine at 640 mμ (initial concentration 4.4 × 10^{-3} mole/l.); O, in pyridine at 403 mμ (initial concentration 5.3 × 10^{-3} mole/l.); □, in bromobenzene at 403 mμ (initial concentration 5.0 × 10^{-3} mole/l.).

TME. One run with a mixture of rubrene and DMA confirms this prediction, thereby supporting a simple mechanism via $^1O_2^*$ for these acceptors (Figure 2).

3. 9,10-Diphenylanthracene (DPA). The direct photooxidation of DPA at 400 mμ is much slower than that of DMA. Its inhibition by TME is already total when TME is present at half the concentration of DPA; this creates less satisfactory experimental conditions because of the rapid change with time of the small concentrations of TME needed.

Four runs at an initial concentration of DPA of 1.4 × 10^{-2} mole/l. gave a value of $k_5k_{6_{DPA}}$ of the order of 5.6 (±1.3).

4. 1,3-Diphenylisobenzofuran (DPBF). The situation is somewhat different in the case of the direct photooxidation of DPBF at 425 mμ.[8] The addition of TME has an inhibiting effect on the rate of oxidation, but higher concentrations of TME are necessary, and the inhibition is never total (Figure 1) no matter how much TME is present. More explicitly, it is found that the final concentration of DPBF is always smaller than the initial concentration, as it would be if some of the DPBF were oxidized in spite of the TME. However, as only DPBF concentrations were measured in these runs instead of the final amount of the oxidized products, it is impossible without further experiments to ascertain the significance of this residual rate of change K of DPBF (Figure 1, $K = 0.030 × 10^{-3}$ mole/min).[9] It could be the effect of the solvent cage surrounding the DPBF and the singlet oxygen just formed, if the probability of reaction of $^1O_2^*$ with DPBF were comparable to the probability of diffusion of oxygen out of the cage.[10] It could also, however, result from a second concurrent path of oxidation, not proceeding via excited oxygen molecules and therefore

(8) The sensitized photooxidation of DPBF is believed to yield first a transannular, ozonide-like peroxide (DPBFO$_2$), which then rearranges into o-dibenzoylbenzene: see G. O. Schenck, Ann., **584**, 156 (1953); A. Le Berre and R. Ratsinbazafy, Bull. Soc. Chim. France, 229 (1963); and references therein cited. The peroxidation of DPBF by externally generated singlet oxygen is very fast, according to Corey.[2]

(9) There is no significant autoxidation of DPBF in the dark and no reaction of DPBF with TME in the dark or at 425 mμ, in the time scale and at the temperature of these runs. There does seem to be some photodecomposition of pure DPBF at 425 mμ in pyridine, but not enough to account for more than about one-third of the residual rate observed.

(10) The author is grateful to one of the referees for suggesting this interpretation.

insensitive to the presence of TME, such as a reaction of DPBF in a triplet state with $^3O_2$ (reactions 7 and 8 above). In any case, the rate of photooxidation as a function of TME can be expressed as the sum of two terms, one being this constant rate K, the other resulting from the usual sequences (1′ to 6) via singlet oxygen. By analogy with (9), and substituting for the experimental value of K

$$\frac{1}{\dfrac{d[\text{DPBFO}_2]}{dt} - 0.03} = \frac{k_5}{k'k_{6_{DPBF}}}[\text{TME}] + \frac{1}{k'} \quad (10)$$

Figure 4 gives $k_5/k_{6_{DPBF}} = 0.026$. Thus DPBF reacts about 20 times faster with $^1O_2{}^*$ than rubrene does, and at least 75% of its photooxidation proceeds via $^1O_2{}^*$.

On the basis of the cage effect mentioned above, any sensitizer could be expected to suppress the residual rate. Such seems to be the situation at 575 mμ with rose Bengale as a sensitizer. The inhibition by tetramethylethylene is now almost total (Figure 1) (nearly within the limits of errors of these measurements), yet the results agree well with the value of $k_5/k_{6_{DPBF}}$ obtained above at 425 mμ (Figure 4). However, this sensitizer effect could also be interpreted on the basis of a direct reaction of DPBF in its triplet state. One could indeed expect the residual rate to be smaller at a longer wavelength, where the incident energy may be below the triplet level of DPBF or inefficiently transferable to it. Further experiments are needed to clarify this point.

5. Mixtures of Rubrene and DPBF. From the ratios of rate constants k_5/k_{6_R} and $k_5/k_{6_{DPBF}}$ one predicts $k_{6_{DPBF}}/k_{6_R} = 17.3$. Therefore, rubrene and DPBF should inhibit each other's photooxidation by competing for the available singlet oxygen. Light of 540 mμ that excites rubrene was used to induce both the direct oxidation of rubrene and the rubrene-sensitized oxidation of DPBF. As the initial and final concentration of both rubrene and DPBF can be measured, the ratio $k_{6_{DPBF}}/k_{6_R}$ can be calculated from eq 11, based on reaction 6 for R and for DPBF and on assuming a steady state for $^1O_2{}^*$. Three runs gave the following

$$\log \frac{[\text{DPBF}]_0}{[\text{DPBF}]} = \frac{k_{6_{DPBF}}}{k_{6_R}} \log \frac{[\text{R}]_0}{[\text{R}]} \quad (11)$$

values for $k_{6_{DPBF}}/k_{6_R}$: 20.0, 20.7, and 25.0; one run in which none of the rubrene was oxidized gave a lower limit of 10. (No attempt was made here to correct for the so-called residual rate.) These results can be considered in adequate agreement with the value of $k_{6_{DPBF}}/k_{6_R} = 17.3$ deduced from the effect of TME on rubrene and on DPBF separately.

6. Experiments with Gaseous Singlet Oxygen. In order to check further the $^1O_2{}^*$ mechanism for the photooxidations, a few rough runs were carried out on the competitive oxidation of rubrene and DPBF by metastable oxygen externally generated by Corey's electrodeless discharge; they gave rate ratios similar to the photochemical ones in order of magnitude. Two runs with a pyridine solution of rubrene and DPBF shielded from light gave $k_{6_{DPBF}}/k_{6_R}$ between 9 and 73, by eq 9. This is compatible with a value of 20 obtained above for the photochemical reactions. In another pair of runs, no oxidation of rubrene was detectable after 20 min in a solution containing TME, whereas
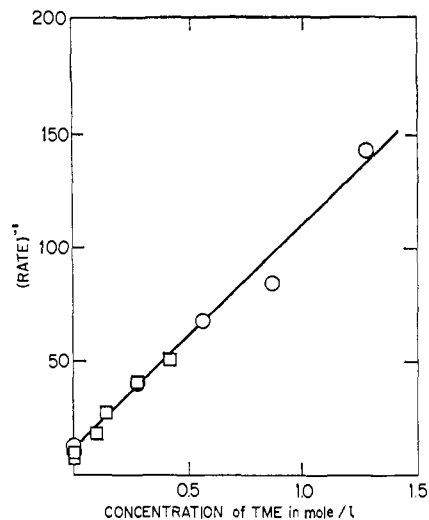

Figure 4. Effect of tetramethylethylene (TME) on the photooxidation of 1,3-diphenylisobenzofuran (DPBF) (initial concentration 2.6×10^{-3} mole/l.): O, at 425 mμ (Y axis represents reciprocal of corrected rates (rate − 0.03)$^{-1}$); □, sensitized at 575 mμ.

rubrene was 90% oxidized in a run without TME. Such a total inhibition was observed in the photooxidation when the same concentration of TME was present (3.10^{-1} mole/l.). This experiment also illustrates the sensitivity of rubrene as a photometric detector of oxidation via $^1O_2{}^*$.
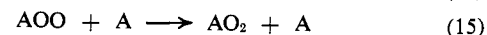
Discussion

All the data presented here on the competitive photooxidation of rubrene, dimethyl- and diphenylanthracenes, and tetramethylethylene are entirely consistent with a mechanism via singlet oxygen, thus ruling out any significant role of the triplet excited state of these acceptors in the peroxide-forming step. Anthracene itself has not been investigated here, because of its even slower rate of oxidation and its tendency to dimerize. There is no reason to suspect that it would not behave like the substituted anthracene as far as the mechanism of its photooxidation is concerned. Although the case of DPBF is more complex, $^1O_2{}^*$ is the main reactive intermediate.

The kinetic data, thus presented, do not completely rule out the alternative but unnecessary hypothesis of a moloxide of the sensitizer or of the acceptor (SOO or AOO).[11] Reactions 5 and 6 could conceivably be replaced by reactions 12 and 13 in the photosensitized oxidation

$$\text{SOO} + \text{TME} \longrightarrow \text{TMEO}_2 + \text{S} \quad (12)$$
$$\text{SOO} + \text{A} \longrightarrow \text{AO}_2 + \text{S} \quad (13)$$
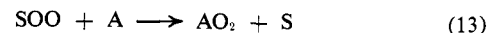
or by reactions 14 and 15 in the direct photooxidation of the same acceptor.

$$\text{AOO} + \text{TME} \longrightarrow \text{TMEO}_2 + \text{A} \quad (14)$$
$$\text{AOO} + \text{A} \longrightarrow \text{AO}_2 + \text{A} \quad (15)$$

However, no moloxide has been isolated yet or physically characterized in any way. Besides, the relative rates for two different acceptors were found to be independent of the sensitizer used (i.e., $k_{12}/k_{13} = k_{14}/k_{15}$). Thus, the

(11) For a recent discussion of the moloxide hypothesis, see K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964). See also the arguments of Foote.[8b]
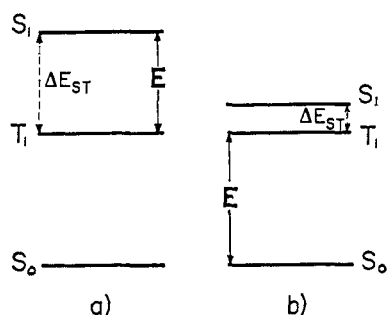
Figure 5. Energy diagrams illustrating the energy (E) available for excitation of oxygen through a triplet–triplet transfer (a) or through a triplet–triplet annihilation (b). Case a is typical of the configuration of energy levels in a polyacene, case b in a dye.

tendency of a given sensitizer–oxygen moloxide to give away its oxygen to one acceptor rather than another must depend solely on the nature of the acceptors involved, and not at all on the relationship between sensitizer and acceptor. In the case of a direct photooxidation where the acceptor is also the sensitizer, one does not quite see why a transfer of oxygen should be necessary at all, and why the moloxide could not be internally rearranged in the peroxide form at the occasion of collisions with the solvent molecules (hence $k_{14}/k_{15} < k_{12}/k_{13}$), for instance.[12] Moreover, no adduct between oxygen and sensitizer can be invoked in the "dark" experiments carried out with gaseous $^{1}O_2^*$; yet they behave very much like the photochemical ones.

Returning to the singlet oxygen mechanism, the energy transfer reactions 3 and 3′ appear quite remarkable in their efficiency, no matter what the amount of energy present in the excited sensitizer. The electronic states in which the participating molecules are, is of course not directly known. Because of spin conservation, only a triplet–triplet transfer (eq 16) or a triplet–triplet annihilation (eq 17) could be responsible for the excitation of oxygen (the donor D represents either the sensitizer S or the acceptor A above). Both

$$^{1}D^* + {}^{3}O_2 \longrightarrow {}^{3}D^* + {}^{1}O_2^* \tag{16}$$

$$^{3}D^* + {}^{3}O_2 \longrightarrow {}^{1}D + {}^{1}O_2^* \tag{17}$$
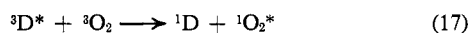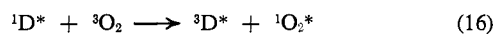
should be frequent events in the unusual situation existing here due to the triplet ground state of oxygen. Therefore, it may very well be that both play a part in the excitation of oxygen, with relative efficiencies depending on the energy levels of the donor present (Figure 5).

In the polyacenes, the singlet–triplet splitting (ΔE_{ST}) is of the order of 30 kcal,[13] which is sufficient to excite the first singlet state of oxygen ($^{1}\Delta_g$ at 22.5 kcal above ground state) via triplet–triplet transfer (eq 16), but too low to excite the next singlet state ($^{1}\Sigma_g^+$ at 37.5 kcal above ground state). In dyes, the singlet–triplet splitting is

much smaller. Unfortunately, no information on the energies of the triplet states of methylene blue or rose Bengale seems available in the literature. But if their ΔE_{ST} is smaller than 10 kcal as is the case with eosin, crystal violet, and various fluorescein derivatives,[14] then a triplet–triplet transfer could clearly not be responsible for the excitation of even the lowest $^{1}\Delta_g$ state of $^{1}O_2^*$. This could only be achieved by a triplet–triplet annihilation (reaction 17) in which the whole of the triplet energy of the sensitizer is available. With rose Bengale as sensitizer ($E_S = 50$ kcal) there would probably be sufficient energy to excite also the $^{1}\Sigma_g^+$ state.

Such a triplet–triplet annihilation could explain as well the autosensitization by such polyacenes as the anthracene derivatives studied here and perhaps rubrene, although the height of its triplet state (as yet unknown) can be expected to be very close to the $^{1}\Delta_g$ state of $^{1}O_2^*$. However, if ΔE_{ST} remains roughly constant along the linear polyacenes series, a triplet–triplet annihilation (reaction 17) could no longer result in excitation of singlet oxygen in pentacene[15] and diphenyl-6,13-pentacene;[16] for example, their triplet level is likely to be well below 20 kcal, yet they are reported to undergo direct photooxidation. A triplet–triplet transfer remains therefore a more generally valid interpretation for the photooxidation of the polyacenes.

Finally, a very indirect clue on the spectroscopic state of the excited oxygen molecules involved may be gathered from the unsensitized photooxidation of rubrene. By either eq 16 or 17 it can only produce singlet oxygen in the $^{1}\Delta_g$ state; yet the relative rates of reactions of rubrene, TME, and DPBF with that "pure" $^{1}\Delta_g$ oxygen are not distinguishable from their relative rates of reactions with other singlet oxygen possibly made of $^{1}\Sigma_g^+$ oxygen. Either the oxidizing properties of $^{1}\Delta_g$ or $^{1}\Sigma_g^+$ singlet oxygen are the same towards the acceptors studied here, or else by the time singlet oxygen reacts it is always mostly in the lowest $^{1}\Delta_g^+$ state. This latter interpretation seems to agree with the findings of Ogryzlo[17] on the predominance of the $^{1}\Delta_g$ state in chemically excited $^{1}O_2^*$ in solution as well as in electrically excited $^{1}O_2^*$ in the gas, from an analysis of their luminescences.

(12) Since these results were obtained, K. R. Kopecky and H. J. Reich, *Can. J. Chem.*, **43**, 2265 (1965), have published data demonstrating that the rates of dye-sensitized photooxidation of olefins are independent of the dye employed, and have similarly used this as an argument in favor of the singlet oxygen hypothesis.

(13) See ref 1 and N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1695, pp 86, 132; G. Porter and N. M. Windsor, *Proc. Roy. Soc.* (London), A245, 238 (1958).

(14) See N. J. Turro, ref 13, p 132; P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, N. Y., 1949; L. S. Foster and D. Dudley, *J. Phys. Chem.*, **66**, 838 (1962).

(15) E. Clar and F. John, *Ber.*, **63**, 2967 (1930).

(16) C. F. H. Allen and A. Bell, *J. Am. Chem. Soc.*, **64**, 1253 (1942).

(17) R. J. Browne and E. A. Ogryzlo, *Proc. Chem. Soc.*, 117 (1964); S. J. Arnold, E. A. Ogryzlo, and H. Witzke, *J. Chem. Phys.*, 40, 1769 (1964).