

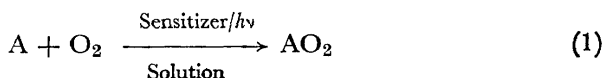
MECHANISM AND STEREOSELECTIVITY OF PHOTOSENSITIZED OXYGEN TRANSFER REACTIONS

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INTRODUCTION

Reactions of molecular oxygen with substrates, A, in solution forming compounds of the composition AO_2 can be sensitized by the presence of a sensitizer, S, and light according to the overall reaction



These reactions can occur *via* different reaction mechanisms.

Two types of chemical relay mechanisms of sensitization are fairly well understood at the present time^{1, 2}. In both cases S in its ground state S_0 is electronically photo-excited by unpairing two electrons, thus forming photo-biradicals, $\cdot S \cdot$ (1S , 3S). Type 1 and Type 2 mechanisms differ in the propagation and termination reactions.

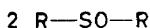
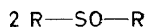
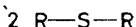
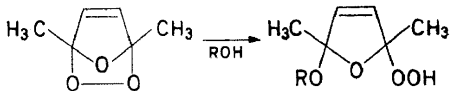
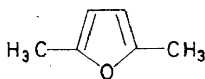
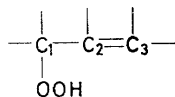
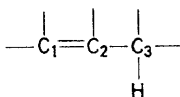
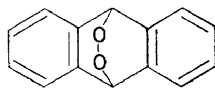
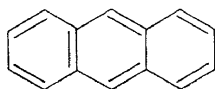
Type 1: Here, monoradicals are involved in the propagation and termination reactions. This is due to the primary chemical reaction of $\cdot S \cdot$ with hydrogen donors, AH, *e.g.* isopropanol, to give rise to pairs of monoradicals $\cdot SH$ and $\cdot A$. In further propagation reactions hydroperoxides AOOH, *e.g.* isopropanol hydroperoxide^{3, 4}, are formed by $\cdot A + O_2 \rightarrow AOO \cdot$, $AOO \cdot + AH \rightarrow AOOH + \cdot A$. In the termination step S_0 is regenerated by $AOO \cdot + \cdot SH \rightarrow AOOH + S_0$. Type 1 sensitization of autoxidation may be called "Bäckström-type photosensitized autoxidation" or "primary dehydrogenation photosensitized reaction with oxygen".

Type 2: In reactions which proceed by the Type 2 mechanism only biradicals take part. Here, $\cdot S \cdot$ adds oxygen to give a short-lived sensitizer-oxygen adduct $\cdot SOO \cdot$, which transfers its oxygen to unsaturated substrates A to AO_2 and the sensitizer in the ground state. This reaction type is called "photosensitized oxygen transfer".

Both these mechanisms are also valid for photosensitized reactions in which compounds other than oxygen are involved; *e.g.*, the photosensitized AH-addition of isopropanol and maleic acid to form terebic acid proceeds by Type 1 sensitization⁵, and the photosensitized cyclo-addition of maleic anhydride to benzene or toluene occurs by Type 2 sensitization⁶⁻⁸.

Only photosensitized oxygen transfer reactions will be discussed here.

The most convenient and thoroughly studied oxygen acceptors are the acenes⁹⁻²⁵, cyclohexadiene derivatives^{9, 26-35}, olefins with isolated double bonds and allylic hydrogen atoms³⁶⁻⁵⁰, furans⁵¹⁻⁵⁵, sulphides⁵⁶, and sulfoxides⁵⁷. These compounds are oxidized to endoperoxides, allylic hydroperoxides, ozonides of the yet unknown cyclobutadienes (which in polar solvents such as alcohols react spontaneously to alkoxyhydroperoxides)⁵⁵, sulphoxides, and sulphones, respectively.



Acenes are able to act as sensitizers as well as substrates. Therefore, in most experiments with these compounds no extra-sensitizers were added. Consequently these reactions are, strictly speaking, unsensitized. Nevertheless, as the mechanism of these "photo-oxidations" requires two acene molecules to take part in the reaction, one acting as a light absorber and oxygen carrier, and the other acting as the substrate, these reactions belong to the class following the Type 2 mechanism. In order to distinguish those cases in which the sensitizer and the substrate are identical molecules, and those in which they are different, we may refer to these reactions as occurring *via* "eigen relay mechanisms" and "foreign relay mechanisms", respectively.

In the photosensitized oxygen transfer reactions at least three short-lived intermediates take part which give rise to a number of very fast monomolecular and bimolecular reactions. These short-lived intermediates

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are the sensitizer in the first excited singlet state and in the lowest excited triplet state, which may be considered from a chemical point of view as a biradical^{6, 58, 59} and an oxygen-containing species which in our opinion⁶⁰ is the excited sensitizer-oxygen adduct with a biradical structure $\cdot\text{SOO}\cdot$ rather than some excited oxygen molecule, *e.g.*, in its lowest excited singlet state⁶¹⁻⁶⁵.

Independently of the problem of the nature of the third intermediate we are able to investigate the effectiveness of fluorescein and fluorescein derivatives as sensitizers of the photosensitized oxygen transfer reaction, and to investigate the intrinsic mechanism of the oxygen transfer to olefins which contain isolated double bonds and allylic hydrogen atoms. The nature of the oxygen transferring species will also be discussed.

EFFECTIVENESS OF FLUORESCHEIN AND DERIVATIVES AS SENSITIZERS

In *Figure 1* all the individual reaction steps are shown which lead to the formation of AO_2 and which decrease the quantum yield of the formation of AO_2 by side reactions.

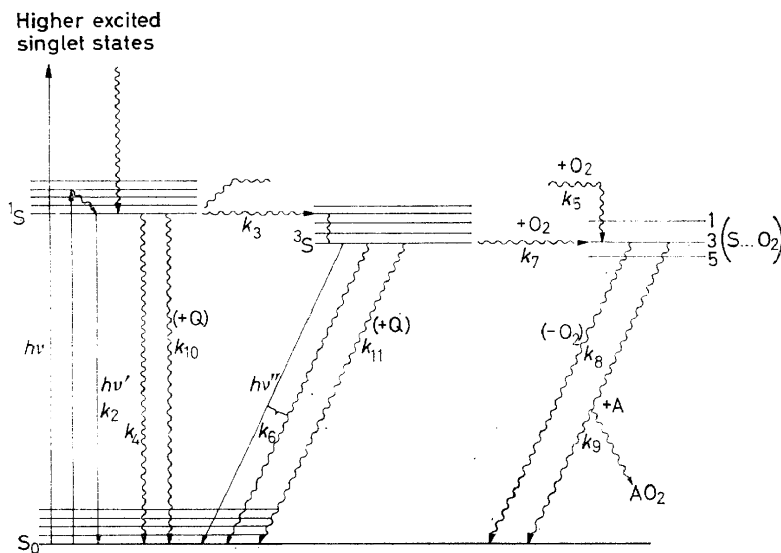


Figure 1. Term scheme; S_0 = sensitizer in the singlet ground state; 1S = sensitizer in the first excited singlet state; 3S = sensitizer in the lowest excited triplet state; $\frac{1}{3}(S \dots O_2)$ = sensitizer-oxygen adduct (described as a Mulliken charge transfer complex in either the singlet-, triplet-, or quintuplet state); A = substrate; Q = quencher; straight arrows = reactions taking place under absorption ($h\nu$) or emission of light ($h\nu'$ = fluorescence, $h\nu''$ = phosphorescence); curly arrows = radiationless mono- and bimolecular reactions

The absorption of polychromatic light by the sensitizer S_0 leads to higher excited singlet states and to higher vibrational levels of the first excited singlet state. The radiationless transitions from all these levels to the zero vibrational level of the first excited singlet state, $^1S(0)$, take place in a time which is short compared with the lifetime of $^1S(0)$ ^{66, 67}. Therefore practically all

the processes such as fluorescence, internal conversion to the ground state, intersystem crossing to the triplet state, and bimolecular reactions, occur from the $^1S(0)$ level. For example, it was shown⁶⁸ that with fluorescein and tetrabromo-fluorescein the excess vibrational energy of 1S is dissipated within 10^{-10} to 10^{-11} sec so that the fluorescence occurs only from the $^1S(0)$ level. Consequently, the quantum yield of fluorescence, γ_f , as well as the quantum yield of the photosensitized oxygen transfer, γ_{AO_2} , is independent of the exciting wavelength, at least with fluorescein dyes as sensitizers.

The intersystem crossing from $^1S(0)$ leads to a triplet excited molecule in a higher vibrational level. From this level two paths for transformation exist: (i) intersystem crossing back to $^1S(0)$, (ii) transition to the zero level of the triplet state, $^3S(0)$, by dissipation of the excess vibrational energy. By absorption of thermal energy the $^3S(0)$ molecule can reach the crossing point and by path (i) the $^1S(0)$ state; delayed fluorescence can then occur. This transition is not shown in *Figure 1* because the probability of path (i) compared with path (ii) is ten thousand times smaller in the case of tetrabromofluorescein in ethanol⁶⁹.

As well as $^1S(0)$, the triplet excited sensitizer in the $^3S(0)$ state can undergo a radiationless transition to S_0 and/or a transition to the ground state by emission of a photon (phosphorescence). As both transitions are accompanied by a change of multiplicity these transitions are quasi-forbidden, and consequently the life time of $^3S(0)$ is much longer than the life time of $^1S(0)$. Therefore the probability of bimolecular reactions with $^3S(0)$ is some orders of magnitude greater than those with $^1S(0)$. Nevertheless, if the concentration of the reactant such as O_2 or Q is sufficiently high, reactions with $^1S(0)$ have to be taken into account.

In our opinion reactions of $^1S(0)$ and $^3S(0)$ with O_2 form some sensitizer-oxygen adducts, $\cdot SOO\cdot$, rather than produce excited oxygen molecules by mere physical energy transfer⁶¹⁻⁶⁵. This adduct may be interpreted as a Mulliken charge transfer complex in either the excited singlet-, triplet-, or quintuplet state⁷⁰ which can undergo a transition to the ground state according to $\frac{1}{5}(S \dots O_2) \rightarrow {}^3(S_0 \dots O_2) \rightleftharpoons S_0 + O_2$, or may react with the substrate A to give $AO_2 + S_0^\ddagger$.

For the mechanism shown in *Figure 1* the quantum yield of the oxygen transfer reaction is given by

$$\gamma_{AO_2} = \frac{[O_2]}{k_2 + k_3 + k_4 + k_5 [O_2] + k_{10} [Q]} \left(k_5 + k_3 \frac{k_7}{k_6 + k_7 [O_2] + k_{11} [Q]} \right) \frac{k_9 [A]}{k_8 + k_9 [A]} \quad (2)$$

We investigated the dianions of fluorescein, tetrabromo-, tetraiodo-, and tetraiodo-tetrachloro-fluorescein as sensitizers of the photosensitized oxygen transfer to 2,5-dimethylfuran. For these sensitizers in methanol at 20° the absolute rate constants have been determined in the following way[†]:

[†] It may be assumed that Q also reacts with $^1S(0)$ or $^3S(0)$ to form similar adducts which then decompose to Q and S_0 ^{71, 72}.

[‡] Experimental details are given in references 73, 74.

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The natural lifetimes, τ_e , of the sensitizers in the $^1S(0)$ state were calculated from the absorption spectra and the O-O-transitions, which for all the dyes are shifted to longer wavelengths by about 400 cm^{-1} , using the expression (3).

$$1/\tau_e = k_2 = \frac{8\pi n^2 (\ln 10)c}{N'} F_{\tilde{\nu}} (\text{sec}^{-1})^{75} \quad (3)$$

where

$n = 1,3288$ (refractive index of methanol at 20°)

$c = 3 \times 10^{10} \text{ cm/sec}$ (velocity of light)

$$F_{\tilde{\nu}} = \int_0^{\infty} \frac{(2\tilde{\nu}_0 - \tilde{\nu}_a)^3}{\tilde{\nu}_a} \times \epsilon(\tilde{\nu}_a) d\tilde{\nu} \text{ cm}^{-1}/\text{mmole} \quad (\text{area of the absorption band at the long wavelength side})$$

$\tilde{\nu}_0$ = wavenumber of the O-O-transition, cm^{-1}

$\tilde{\nu}_a$ = wavenumber (absorption spectrum), cm^{-1}

$\epsilon(\tilde{\nu}_a)$ = molar extinction coefficient (absorption spectrum), cm^2/mmole .

The quantum yields of fluorescence, γ_f , in methanol were measured by comparing the intensities of fluorescence in methanol with those in aqueous alkaline⁷⁶⁻⁸⁰ or ethanolic^{69, 80} solutions for which the quantum yields are known.

If O_2 and Q are absent γ_f is given by

$$\gamma_f = \frac{k_2}{k_2 + k_3 + k_4} \quad (4)$$

As k_2 is known the sum of $k_3 + k_4$ can be calculated. In the presence of Q we get

$$\gamma_f^Q = \frac{k_2}{k_2 + k_3 + k_4 + k_{10}[Q]} \quad (5)$$

Only with fluorescein and the tetrabromo derivative could an influence of Q (= Cyclo-octatetraene, COT) on γ_f be obtained. Although the concentration of Q was as high as 1 mole/l. no influence on γ_f was observed with either of the tetraiodo compounds.

The lifetimes of the triplet excited sensitizers, $\tau_{3S} = 1/k_6$, and the rate constant k_{11} of the reaction $^3S(0) + Q \rightarrow S_0 + Q$ (with $Q = \text{COT}$) were determined by means of flash photolysis techniques⁸¹⁻⁸³.

In the absence of Q , and with dimethylfuran as the substrate, A , the quantum yield of the oxygen transfer reaction, γ_{AO_2} , was independent of the concentration of A with $[A] > 2 \times 10^{-3} \text{ mole/l.}$; i.e. $k_9[A] \gg k_8$ and $k_9[A]/(k_8 + k_9[A]) = 1$.

Consequently

$$\gamma_{AO_2} = \frac{[O_2]}{k_2 + k_3 + k_4 + k_5[O_2]} \left(k_5 + k_3 \frac{k_7}{k_6 + k_7[O_2]} \right) \quad (6)$$

Furthermore, γ_{AO_2} was independent of the oxygen concentration with

$[\text{O}_2] > 2 \times 10^{-3}$ mole/l. in the case of tetraiodo- and tetraiodo-tetrachloro-fluorescein as sensitizers. At such high oxygen concentrations $k_6 \ll k_7[\text{O}_2]$ because generally k_7 is found to be of the order of 10^8 to 10^{10} l./mole sec^{21, 23, 84-87}. Therefore equation (6) is reduced to

$$\gamma_{\text{AO}_2} = \frac{k_3 + k_5[\text{O}_2]}{k_2 + k_3 + k_4 + k_5[\text{O}_2]} \quad (7)$$

which allows two interpretations of the fact that there is no oxygen concentration dependence of γ_{AO_2} :

either $k_5[\text{O}_2] \gg k_2 + k_3 + k_4$ and $\gamma_{\text{AO}_2} = 1$

or $k_5[\text{O}_2] \ll k_3$ and $\gamma_{\text{AO}_2} < 1$.

If the first alternative were true, k_5 has to be of the order of 10^{12} to 10^{13} l./mole sec (because $k_2 + k_3 + k_4 = 2.3 \times 10^9$ sec⁻¹), which is much greater than the maximum value of about 10^{11} l./mole sec. Furthermore, γ_{AO_2} is in every case smaller than unity. We are, therefore, forced to assume that $k_5[\text{O}_2] \ll k_3$. This assumption is supported by the fact that γ_I was always found to be independent of $[\text{O}_2]$ ^{75, 88, 89}. Consequently, we arrive at the expression

$$\gamma_{\text{AO}_2} = \frac{k_3}{k_2 + k_3 + k_4} = \gamma_{3S} \quad (8)$$

By this method it is possible to determine the quantum yield of the triplet formation, γ_{3S} , by measuring the quantum yield of the photosensitized oxygen transfer reaction. The sum of $k_3 + k_4$ being known, the absolute rate constants k_3 and k_4 can be calculated[†].

In the case of fluorescein and tetrabromo-fluorescein there was a slight dependence of γ_{AO_2} on the oxygen concentration. By equation (7) k_5 was determined, though the limits of error were great.

In the presence of COT as the quencher Q, the quantum yield γ_{AO_2} depends on both the quencher and oxygen concentration. With the quencher concentrations used (from 1×10^{-2} to 6×10^{-2} mole/l.) the quantum yields of fluorescence, γ_I , were not affected. $\gamma_{\text{AO}_2}^0$ for the inhibited reaction is given by

$$\gamma_{\text{AO}_2}^0 = \gamma_{3S} \frac{1}{1 + k_{11}[\text{Q}]/k_7[\text{O}_2]} \quad (9)$$

which is correct in the case of the two tetraiodo-fluoresceins and nearly so for the tetrabromo-fluorescein. As required by equation (10)

$$\gamma_{\text{AO}_2}/\gamma_{\text{AO}_2}^0 = 1 + \frac{k_{11}}{k_7[\text{O}_2]}[\text{Q}] \quad (10)$$

[†] According to Noyes⁹⁰ there exists no experimental evidence for the assumption of a radiationless transition $^1\text{S}(0) \rightarrow \text{S}_0$. With the sensitizers used in our work the sums of $\gamma_I + \gamma_{3S}$ are found to be from 0.7 to nearly 1 (Table I). On account of the difficulties involved in quantum yield determinations there is some doubt whether the $^1\text{S}(0) \rightarrow \text{S}_0$ radiationless transitions really exist. Nevertheless, our preliminary results with rhodamin 3B as a sensitizer gave $\gamma_{\text{AO}_2} = 0.02$, $\gamma_{3S} < 0.02$, and $\gamma_I = 0.65$ in methanol at 20°C which seems to support the existence of some path for the radiationless transition $^1\text{S}(\text{O}) \rightarrow \text{S}_0$.

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straight lines are observed for each oxygen concentration by plotting the ratio of the γ 's against $[Q]$. From the slope of the lines $k_{11}/k_7[O_2]$ is calculated. As k_{11} and $[O_2]$ are known k_7 can be determined for each sensitizer.

The results of our measurements and calculations are shown in *Table 1*.

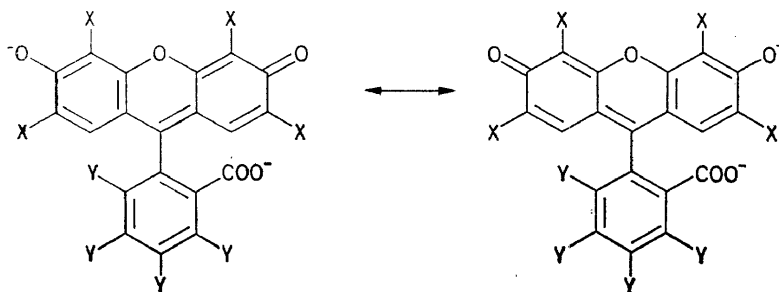


Table 1. Rate constants, γ_t , γ_{3s} , and γ_{AO_2} ; sensitizers: fluorescein, tetrabromo-, tetraiodo-, and tetraiodo-tetrachloro-fluorescein

| | Fluorescein X = H Y = H | Tetrabromo- X = Br Y = H | Tetraiodo- X = I Y = H | Tetraiodo-tetrachloro- X = I Y = Cl |
|-----------------------|-------------------------------|--------------------------------|------------------------------|---|
| k_2 | 2.2 | 2.2 | 1.8 | $1.8 \times 10^8 \text{ sec}^{-1}$ |
| k_3 | 0.08 | 0.88 | 14.1 | $17.3 \times 10^8 \text{ sec}^{-1}$ |
| k_4 | 0.09 | 0.42 | 6.8 | $3.6 \times 10^8 \text{ sec}^{-1}$ |
| γ_t | 0.93 | 0.63 | 0.08 | 0.08 |
| γ_{3s} | 0.03 | 0.3 | 0.6 | 0.76 |
| k_8 | | 2.2 | 5.8 | $6.5 \times 10^3 \text{ sec}^{-1}$ |
| k_5 | ~ 1 | ~ 5 | | $\times 10^9 \text{ l./mole sec}$ |
| k_7 | | 1.2 | 1.2 | $1.2 \times 10^9 \text{ l./mole sec}$ |
| k_{10}^{COT} | ~ 4.5 | ~ 3.5 | | $\times 10^8 \text{ l./mole sec}$ |
| k_{11}^{COT} | | 1.4 | 1.1 | $0.5 \times 10^9 \text{ l./mole sec}$ |
| γ_{AO_2} | 0.1 | 0.4 | 0.6 | 0.76 |

Schenck and Koch² determined the lifetime of the triplet state of tetraiodo-tetrachloro-fluorescein in oxygen saturated methanol at 20° to be less than 2×10^{-7} sec. With $k_7 = 1.2 \times 10^9$ l./mole sec and $[O_2] = 1.057 \times 10^{-2}$ mole/l., this lifetime should be $1/k_7[O_2] = 0.9 \times 10^{-7}$ sec.

As was already mentioned γ_{AO_2} is independent of A when $[A] > 2 \times 10^{-3}$ mole/l. (A = dimethyl furan). This permits us to estimate the minimum lifetime of the sensitizer-oxygen-adduct. Assuming k_9 to be a diffusion-controlled rate constant $k_9 = 8RT/3000\eta \approx 10^{10}$ l./mole sec ($\eta = 0.584 \times 10^{-2}$ erg sec/cm³ for methanol at 20°). Because of $k_8 \ll k_9[A]$ we get $1/k_8 \gg 5 \times 10^{-8}$ sec. Measurements of the lifetime of the sensitizer-oxygen-adduct with the sensitizers tetrabromo- and tetraiodo-tetrachloro-fluorescein led to lifetimes $1/k_8 < 13 \times 10^{-8}$ and $< 20 \times 10^{-8}$ sec, respectively².

The dependence of γ_{AO_2} on the oxygen concentration is given by

$$\gamma_{AO_2} = \gamma_{3S} \frac{k_7[O_2]}{k_6 + k_7[O_2]} \quad (11)$$

for tetraiodo- and tetraiodo-tetrachloro-fluorescein. With the rate constants of *Table 1* γ_{AO_2} is found to be $\frac{1}{2}\gamma_{3S}$ at $[O_2] = 6 \times 10^{-6}$ mole/l. Experiments on the determination of this "half-value concentration of oxygen" were carried out very recently by Franken in our laboratory. His preliminary results show this particular oxygen concentration to be between 5×10^{-6} and 2×10^{-5} mole/l.

With the assumption that triplet excited tetrabromo-fluorescein in ethanol at -196° decays exclusively by emission of phosphorescence light quanta Parker and Hatchard⁶⁹ calculated $\gamma_{3S} = 0.025$ at 25° in ethanol. With the same sensitizer in methanol and ethanol at 20° we found (by the method discussed) $\gamma_{3S} = 0.3$. In our opinion this discrepancy indicates that even at -196° the radiationless transition ${}^3S(0) \rightarrow S_0$ is very effective.

Adelman and Oster⁷⁸ investigated a series of fluorescein dyes in aqueous solution. They found that all the γ_{3S} 's had approximately the same values while the γ_I 's decreased in the same order as they do in our experiments. The authors concluded that only the radiationless transitions ${}^1S(0) \rightarrow S_0$ are enhanced by halogenation of the fluorescein molecule. Similar results were obtained by Forster and Dudley⁹¹. This is in contrast to the behaviour of these sensitizers in alcoholic solutions.

As is shown in *Table 1* there is nearly no influence of halogenation on the k_2 -values (or natural lifetimes $1/k_2$) of the different sensitizers. On the other hand substitution of $X = H$ by $X = Br$ and $X = I$ enhances the internal conversion, ${}^1S(0) \rightarrow S_0$, as well as (somewhat more strongly) the inter-system crossing, ${}^1S(0) \rightarrow {}^3S(0)$. Consequently, γ_{3S} is increased by the introduction of "heavy" halogen atoms into the fluorescein molecule. This effect of heavy halogen atoms is due to enhanced spin-orbit coupling which causes some mixing of singlet and triplet states⁹²⁻⁹⁵.

As a consequence of the very short lifetime of ${}^1S(0)$ the oxygen transferring intermediate is exclusively (or nearly exclusively) formed by the reaction of ${}^3S(0)$ with oxygen.

MECHANISM OF OXYGEN TRANSFER TO OLEFINS CONTAINING ISOLATED DOUBLE BONDS

In considering the termination stage of the photosensitized oxygen transfer reactions we restrict our discussion to the reactions of the oxygen transferring species with olefins which contain isolated double bonds and allylic hydrogen atoms.

Since the discovery of this particular reaction³⁶⁻³⁸ no exception from the rule given in *Figure 2* has been found:

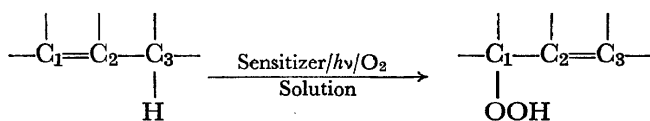
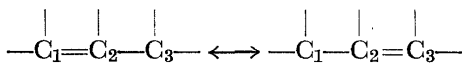


Figure 2

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i.e., when oxygen in a photosensitized reaction is transferred to olefins the oxygen is added to one carbon atom of the double bond (in this case to C-1), the double bond is shifted into the allyl position (with formation of the double bond C₂=C₃), and the allylic hydrogen atom at C-3 is moved to the oxygen atom which is not attached to a carbon atom. As will be shown later this reaction takes place as a concerted reaction^{48, 73, 74, 96}.

This reaction type differs considerably from that of the Type 1 autoxidation which is initiated, *e.g.*, by the decomposition of peroxides or by irradiation. In the Type 1 autoxidation reaction⁹⁷⁻⁹⁹ the allylic hydrogen atom at C-3 is abstracted by an initiator radical to give a mesomeric monoradical



O₂ is then attached at both radical sites, C₁ and C₃, and the peroxy radicals thus formed abstract hydrogen from the C-3 position of the olefin to give hydroperoxides and a new mesomeric monoradical. In contrast to the photosensitized oxygen transfer reaction a chain propagation can occur.

With (+)-limonene (Ia) and (+)-carvomenthene (Ib) (Figure 3), both these reactions were studied in detail^{46, 100-102}.

In addition to other products, *cis* and *trans* carveyl hydroperoxides and carvotanacetyl hydroperoxides respectively are formed in both oxidation

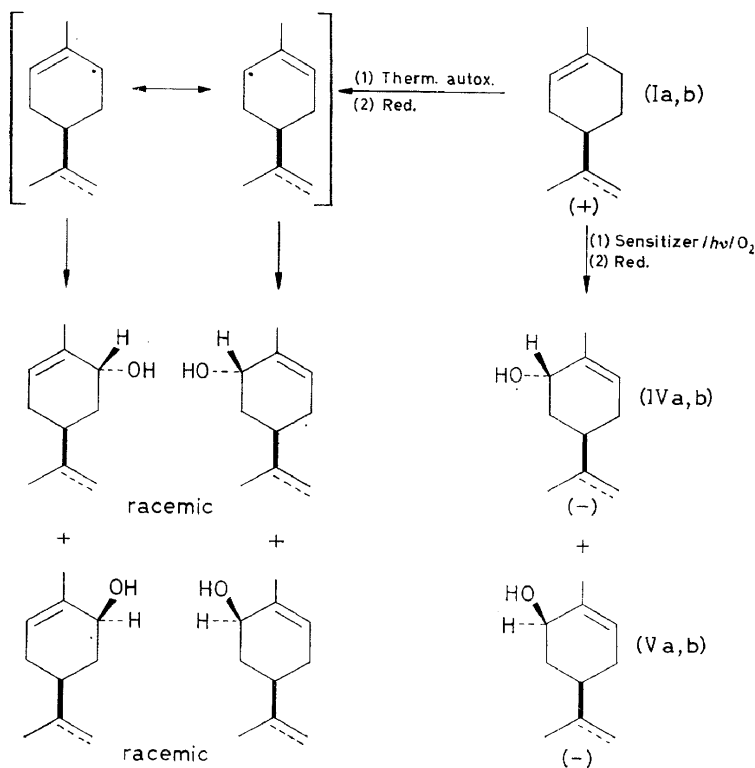


Figure 3

reactions. After reduction of the hydroperoxides with retention of configuration, the corresponding carveols and carvotanacetols respectively show a remarkable difference: those obtained from the photosensitized oxygen transfer reaction are optically active, those obtained from the thermal autoxidation reaction are optically inactive (racemic) (*Figure 3*).

Furthermore, the exclusive formation of (–)-*cis*- and (–)-*trans*-carveols and of (–)-*cis*- and (–)-*trans*-carvotanacetols respectively shows that, in the photosensitized oxygen transfer reaction, there is no insertion of oxygen between the carbon atom α to the double bond and the allylic hydrogen atom; if there were, the (+)-carveols and the (+)-carvotanacetols respectively would be formed.

According to *Figure 2* four other products of the photosensitized transfer of oxygen to (+)-limonene and (+)-carvomenthene are formed in addition to the carveols and carvotanacetols respectively†.

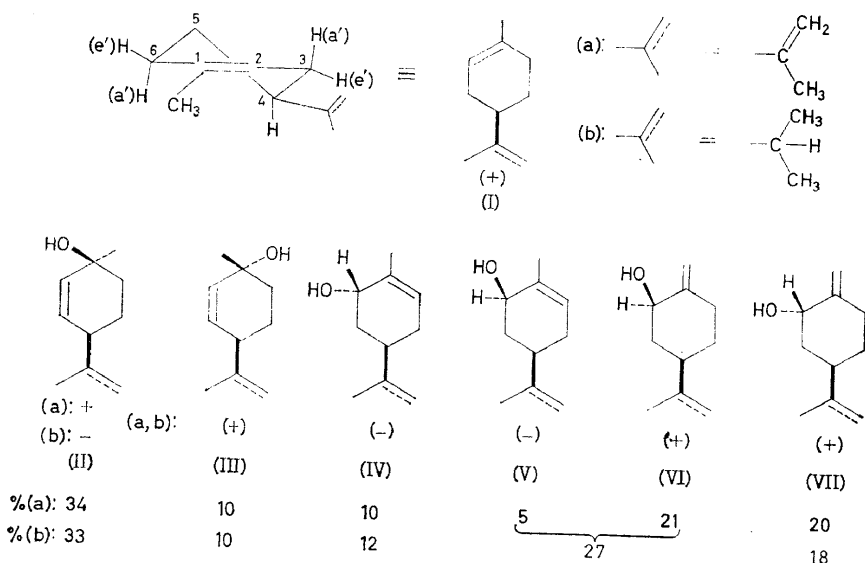


Figure 4

As can be seen from *Figure 4* the products are not formed in a statistical manner. If this were the case there should be 25 per cent of both the tertiary alcohols and 12.5 per cent of each of the four secondary alcohols. The deviations from the statistical product distribution can be explained by conformational analysis. According to these results¹⁰³ the most probable conformations of limonene and carvomenthene at room temperature are those in which the largest substituents are in an equatorial position as shown in *Figure 4*. In these conformations the allylic hydrogen atoms at C-3 and C-6 are in quasi-axial (a') and quasi-equatorial (e') positions. In

† The Δ^8 -double bond of limonene is not attacked under the conditions used. This is in accord with the rule that oxygen is transferred much faster to tri- and tetra-substituted ethylenes than to disubstituted ethylenes^{10, 51, 55, 73, 74}.

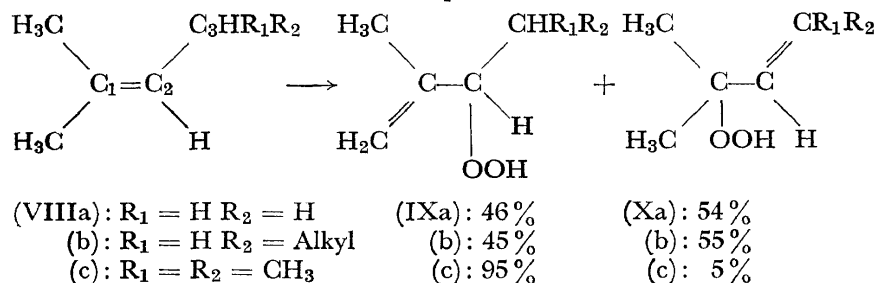
contrast to this the allylic hydrogen atoms of the CH_3 -group are equally present on both sides of the molecule because of the free rotation of this group. If we further take into account the results of Nickon and Bagli^{47, 48}, who found that with cyclohexene derivatives only the allylic hydrogen atom is used which is *cis* to the oxygen attack, we are able to correlate the product distribution with the availability of allylic hydrogen atoms.

With the product pairs (II/III) and (IV/V) it is easily seen that (II) and (IV) are formed in a reaction in which quasi-axial allylic hydrogen atoms at C-3 and C-6, respectively, are used. On the other hand (III) and (V) which are formed in smaller amounts, arise from reactions in which quasi-equatorial allylic hydrogen atoms at C-3 and C-6, respectively, should have been used. In agreement with the theory (VI) and (VII) are formed in equal amounts.

The fact that (VI) is formed in the same amount as (VII), and that the yield of (II) is more than three times that of (III), excludes a steric effect of the substrates. Otherwise the yields of (II) and (VI), formed by an oxygen attack *cis* to the side-chain at C-4, would have been smaller than those of (III) and (VII), respectively.

We therefore conclude that the stereoselectivity of the photosensitized oxygen transfer to limonene and carvomenthene arises from the different availability of allylic hydrogen atoms.

This effect was also shown in the aliphatic series⁵⁵.



While in (VIIIa) and (VIIIb) there is always an "axial" allylic hydrogen atom of the freely rotating $\text{C}_3\text{HR}_1\text{R}_2$ group available, this is no longer the case with (VIIIc). An inspection of Stuart-Briegleb models shows that in (VIIIc) the free rotation of the $\text{CH}(\text{CH}_3)_2$ group is strongly hindered. Furthermore, the most stable conformation of this molecule is that in which the H atom lies in the plane of the double bond ("equatorial"). As a consequence of the "equatorial" position of this allylic hydrogen atom (IXc) is found in 95 per cent yield although C_2 is more shielded against an oxygen attack than C_1 .

The stereoselectivity of photosensitized oxygen transfer is also influenced by the steric effect of bulky groups in the substrate molecule. This is demonstrated in Figure 5 with (+)- Δ^3 -carene (XI) as a substrate^{44, 104}.

The equilibrium of the two conformations of (+)- Δ^3 -carene, (XIa) and (XIb), at room temperature is not known. From the ease of interconversion of Dreiding models of (XIa) and (XIb), the equilibrium constant is probably near unity. The allylic hydrogen atoms at C-2 and C-5 possess "axial" positions when they are *cis* to the dimethyl cyclopropane ring in (XIa), and when

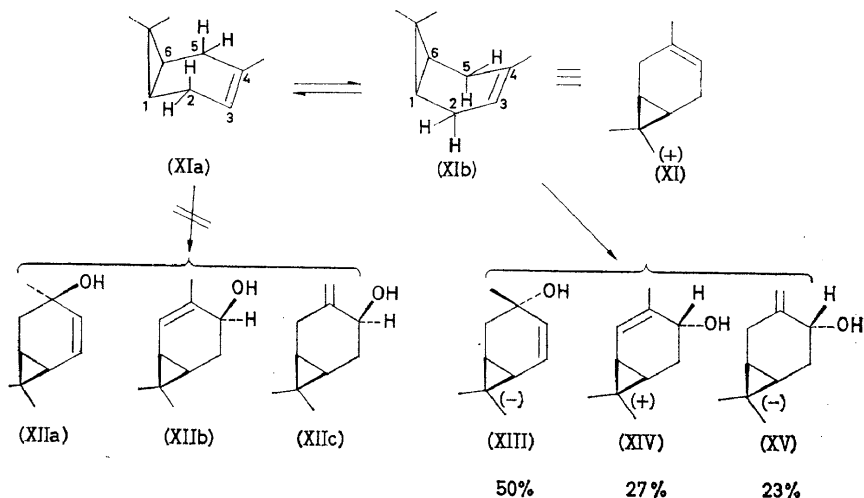
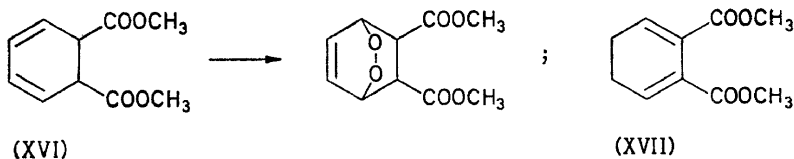


Figure 5

they are *trans* to this ring in (XIb). Therefore, all these hydrogen atoms should be as available as those of the freely rotating CH_3 group. This should give rise to a product containing equal amounts of tertiary and secondary alcohols; *i.e.* 25 per cent of each of the tertiary, and 12.5 per cent of each of the secondary alcohols. In fact only the *trans* alcohols (XIII–XV) are formed. Nevertheless, our assumption on the equal availability of the allylic hydrogen atoms seems to be correct as is seen from the 2 : 1 : 1 ratio of the products formed. Consequently, the absence of the formation of *cis* alcohols must be due to the complete inhibition of a *cis* oxygen attack due to the bulky dimethyl cyclopropane ring⁴⁵.

A factor which influences the ease of photosensitized oxygen transfer to ethylene compounds as well as to cyclohexadiene derivatives, is the electron density of the double bonds^{73, 74}. In the cyclohexadiene series, for example, the formation of an endoperoxide occurs only with (XVI). No reaction takes place with (XVII)⁵¹.



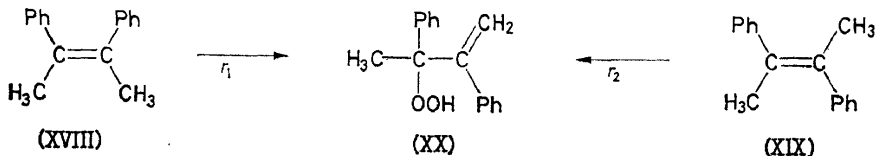
With olefins an increase in the quantum yield is observed in the order 1,2-dimethylethylene < trimethylethylene < tetramethylethylene, and cyclohexene < 1-methylcyclohexene < 1,2-dimethylcyclohexene^{40, 55, 105}. This increase is due to the enhanced electron densities caused by the electron-donating methyl groups^{73, 74}.

Cis and *trans* dimethylstilbene (XVIII and XIX, respectively) give the same oxidation product (XX)⁵⁵, but the rate of oxygen transfer, r_1 , with (XVIII) is considerably larger than that, r_2 , with (XIX).

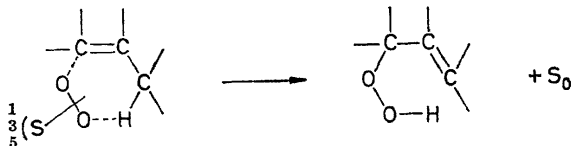
The higher oxidation rate of (XVIII) seems again to be due to the enhanced electron density in the *cis* compound as compared with the *trans*.

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It is most interesting that the rate r_1 is not changed to r_2 , nor is the rate r_2 changed to r_1 , during the reactions of (XVIII) or (XIX), respectively. These observations, together with the fact that the oxygen transferring species is not able to isomerize *cis* stilbene into the *trans* compound and *vice*



*versa*⁵⁵, provide strong support for our view that the photosensitized oxygen transfer reactions occur as concerted reactions *via* a cyclic transition state^{48, 73, 74, 96}. With olefins the transition state consists of the two carbon atoms of the double bond, the carbon atom α to this double bond, the allylic hydrogen atom at C- α , and the oxygen molecule.



NATURE OF THE OXYGEN TRANSFERRING SPECIES

In this part we are concerned with the problem of the nature of the third intermediate in the photosensitized oxygen transfer reactions.

Two possible mechanisms were soon excluded for spectroscopic, kinetic, energetic, and chemical reasons^{58, 60-65, 106, 107}: the "acceptor activation mechanism" proposed by Gaffron^{14, 15}, in which the electronic energy of the excited sensitizer is transferred to the substrate, and the mechanism proposed by Weiss¹⁰⁸⁻¹¹⁰, in which an electron is transferred from the excited sensitizer to the oxygen molecule. So we are left with the question: is the oxygen transferring species an excited oxygen molecule in its lowest excited singlet state as was proposed by Kautsky⁶¹⁻⁶⁵, or is it an excited oxygen-sensitizer adduct (complex) as was independently proposed by Schönberg^{12, 13} Terenin^{106, 107}, and Schenck⁵⁸?

As the very effective quenching of the fluorescent state, $^1\text{S}(0)$, of polycyclic hydrocarbons such as anthracene cannot be brought about by the energy transfer reaction $^1\text{S}(0) + ^3\text{O}_2 \rightarrow \text{S}_0 + ^1\text{O}_2$, on account of the violation of the spin conservation rule, Terenin¹⁰⁶ proposed a "paramagnetic" quenching of oxygen of the type $^1\text{S}(0) + ^3\text{O}_2 \rightarrow ^3\text{S}(0) + ^1\text{O}_2$: "The main feature of such a "paramagnetic" quenching is that not only an active O_2 molecule is formed during this process, but that the second partner, *i.e.* the aromatic molecule, has also acquired chemical reactivity, having been transformed into the biradical $^3\text{S}(0)^\dagger$. We expect therefore, that "paramagnetic"

† The electronic states such as the triplet state *etc.* are given in this and other citations in the notation of the present authors.

quenching will be accompanied by association or dimerization processes, induced by the biradical $^3S(0)$. In the first place, the latter can easily react with O_2 before they separate, according to the mechanism: $^1S(0) + ^3O_2 \rightarrow ^3(S..O_2)$, with the formation of a more-or-less stable peroxide, which, certainly, will be produced in one step, and is already in the transition complex formed by a suitable encounter of O_2 with the excited molecule". The existence of such an unstable addition product was proved by an extensive study of the photoconductivity of solid dye films¹⁰⁶.

In a thorough investigation of intramolecular and intermolecular energy conversion involving change of multiplicity Porter and Wright¹¹¹ concluded that, in the reaction of a triplet state, or biradical state, molecule with a paramagnetic quencher such as oxygen, a collision complex is formed which should have a stability of several kcal. Spin-spin interaction will therefore be strong and the complex may have a considerable life. These authors further concluded: "It is to be expected that the radiationless transition probability is increased in the presence of an efficient paramagnetic quencher only by an amount corresponding to the difference between a spin-forbidden and a spin-allowed transition, *i.e.* by a factor of about 10^4 . Now the lifetime of triplet anthracene in *n*-hexane in the absence of quenchers is 10^{-3} sec so that its lifetime when the spin restriction is removed should be about 10^{-7} sec. The average lifetime of the collision complex between triplet anthracene and oxygen, nitric oxide, or a second triplet state, should therefore also be about 10^{-7} sec which is much longer than the duration of an encounter not involving chemical interaction and is in accordance with kinetic studies of anthracene photosensitized oxidation".

It may be stated that our own results fit very well with the last statement: with tetraiodo-tetrachloro-fluorescein we found

$$\tau_{3S} = 1.5 \times 10^{-4} \text{ sec and } 5 \times 10^{-8} \text{ sec} < \tau_{\frac{3}{2}(S..O_2)} < 2 \times 10^{-7} \text{ sec}$$

Linschitz and Pekkarinen¹¹², as well as Tsubomura and Mulliken⁷⁰, explain the quenching of excited singlet and triplet states by molecules like oxygen as due to the formation of short-lived charge transfer adducts. In the theory of the latter authors there exists in addition to the $\frac{1}{2}(S..O_2)$ state given in *Figure 1* a triplet charge transfer state, 3CT , with a great probability of interaction of both these states. Mulliken describes the reaction of excited molecules with oxygen with respect to Kautsky's theory as follows: "the energy difference between the singlet and triplet states of the donor is dissipated as thermal energy (vibrational first), and no excitation of the oxygen molecule to its metastable states is necessarily involved". Although the Mulliken theory has one feature in common with the Weiss theory in relating the quenching action of oxygen to charge transfer "such a complete electron transfer as he (Weiss) proposes is very unlikely in non-polar solutions, where the present theory of the mechanism of quenching seems to be much more adequate". Similar theories were also proposed by Murrell¹¹³ and Hoijtink¹¹⁴.

Taking very seriously the theory that triplet and singlet excited molecules have more or less biradical character (compare *e.g.* Porter¹¹⁵) Schenck^{1, 2, 6, 58-60, 71, 72, 116} proposed that electronically excited molecules

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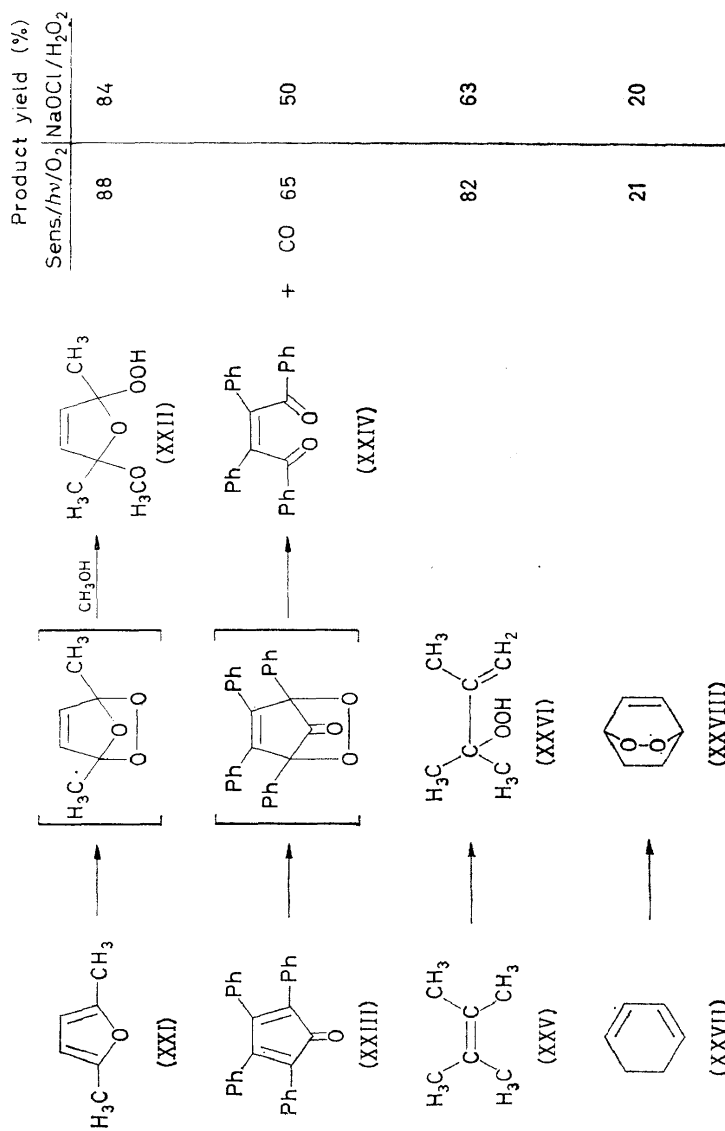


Figure 6

should behave chemically in the manner of free radicals. Therefore, reactions with oxygen should not only be very effective in quenching $^1\text{S}(0)$ and $^3\text{S}(0)$, but should also lead to new biradical molecules in which the oxygen is attached to a former radical site by a normal chemical bond. The effect of steric hindrance to oxygen attack, caused by bulky groups in substrates where these groups are somewhat removed from the reaction centres, led us again to the assumption that the oxygen must have the big sensitizer molecule in close proximity when it reacts with the substrate.

However, the problem of the oxygen transferring species is not yet settled. Very recently the assumption that a sensitizer-oxygen adduct is the oxygen transferring species was severely criticized by Foote and Wexler^{117†}. In the reaction of hypochlorite with hydrogen peroxide excited singlet oxygen in its $^1\Delta_g$ state is formed, at least as an intermediate in the formation of the light emitting species $\text{O}_4^{*118, 119}$. Foote made some experiments with substrates such as dimethylfuran (XXI), tetraphenylcyclopentadienone (XXIII), tetramethylethylene (XXV), and cyclohexadiene (XXVII) in methanol containing hydrogen peroxide (Figure 6). By dropwise addition of hypochlorite to the solution at 10° he succeeded in isolating 2,5-dimethyl-2-hydroperoxy-5-methoxydihydrofuran (XXII), *cis*-dibenzoyl stilbene (XXIV), 2,3-dimethyl-3-hydroperoxybutene-(1) (XXVI), and norascaridol (XXVIII), respectively.

These results are very interesting, and in the case of the cyclic diene compounds no other explanation than that given by Foote seems to be possible for the moment in order to account for the formation of the products isolated. But with the tetramethylethylene (XXV) a normal autoxidation reaction induced by hydrogen abstraction might have taken place.

In order to check Foote's assumption in the case of olefins we carried out some experiments with (+)- α -pinene (XXIX) under the same conditions (in the presence of air) as were used in the experiments cited above, as well as in the presence of nitrogen and oxygen, respectively. The results of these experiments were compared with those obtained by photosensitized oxygen transfer to (XXIX) at $20^{38, 120}$, and by benzoyl peroxide induced autoxidation at $80\text{--}120^{121}$.

As can be seen from Figure 7 the reactions of α -pinene with hydrogen peroxide/sodium hypochlorite are very similar to the thermal autoxidation process in which chain reactions are induced mainly by hydrogen abstraction from C-4, resulting in the formation of the products (XXXIII-XXXVI), and to a smaller degree by hydrogen abstraction from C-7, resulting in the formation of the products (XXX-XXXII).

In our opinion this is a striking proof that in the reactions of olefins with excited singlet oxygen this reactive oxygen has enhanced dehydrogenating properties, as was proposed by Dupont¹²², rather than the properties of the oxygen-transferring species in the photosensitized oxygen transfer reactions.

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† We thank Dr Foote for making his results available to us prior to publication.

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| (XXIX) | (XXX) | (XXXI) | (XXXII) | (XXXIII) | (XXXIV) | (XXXV) | (XXXVI) | (XXXVII) |
|--|-------|--------|---------|----------|---------|--------|---------|----------|
| | | | | | | | | |
| Sens./hv/O ₂ | 94 | | | | | | | |
| Autoxidation | 14 | 13 | | 33 | 9 | | 31 | |
| NaOC1/H ₂ O ₂ in the presence of air | 9 | 10 | | 21 | 10 | | 50 | |
| N ₂ | 12 | 10 | | 23 | 9 | | 46 | |
| O ₂ | 9 | 11 | | 22 | 6 | | 52 | |

Figure 7

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