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INTERACTIONS OF SINGLET OXYGEN WITH 2,5-DIMETHYL-2,4-HEXADIENE IN POLAR AND NON-POLAR SOLVENTS EVIDENCE FOR A VINYLOG ENE-REACTION

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Abstract: 2,5-Dimethyl-2,4-hexadiene (1) was studied as a singlet oxygen acceptor in various solvents. 1 undergoes concomitantly the three well-known modes of singlet oxygen reactions: (1) the ene-reaction to give the allylic hydroperoxide 3, (2) the (4+2)-cycloaddition to give the endoperoxide 4, and (3) the (2+2)-cycloaddition to give the dioxetane 2. Beyond that (and in contrast to simple olefins), there are (4) "physical" quenching and (5) a "vinylog ene-reaction" to give the twofold-unsaturated hydroperoxide 5. The latter reaction represents a novel mode of singlet oxygen interaction with a substituted 1,3-diene. - Kinetic analysis shows that "physical" quenching, endoperoxide and vinylog ene-product formations proceed with solvent-independent rates; the rates of dioxetane and ene-product formations, however, are solvent-dependent. - A mechanism (Scheme 3) is proposed, according to which endoperoxide formation is due to a concerted singlet oxygen reaction with the s-cis-conformational isomer 1b; with the s-trans-isomer 1a, "physical" quenching and the vinylog ene-reaction proceed via a non-polar singlet diradical intermediate, whereas the ene-product formation occurs via a per-epoxide-like transition state. In aprotic solvents, the dioxetane is mainly formed via a "tight-geometry intermediate", in methanolic solution via a solvent-stabilized zwitterion; the latter is also responsible for the formation of the methanol-addition product 6.

In a recent paper[1] we have shown that of the three types of singlet oxygen reactions with olefins, only the (2+2)-cycloaddition (CA) reaction (with benzvalene) is clearly dependent on solvent polarity. The ene-reaction (with 2-methyl-2-butene and 2,3-dimethyl-2-butene) is slightly dependent, whereas the (4+2)-CA reaction (with 1,3-cyclohexadiene) is practically independent of solvent polarity. "Physical" quenching of singlet oxygen by these olefins is negligible in polar as well as in non-polar solvents.

In another paper[2] we showed that, besides a (4+2)-CA reaction, cis,trans-2,4-hexadiene undergoes an isomerization reaction to trans,trans-2,4-hexadiene by interaction with singlet oxygen. Thus, "physical" quenching of singlet oxygen by an acyclic conjugated diene is not only substantial but is also accompanied by a chemical (cis to trans) reaction. Now we chose to investigate the interactions of singlet oxygen in polar and non-polar solvents with a molecule like 2,5-dimethyl-2,4-hexadiene (1) which we expected to undergo all three types of reactions as well as "physical" quenching.

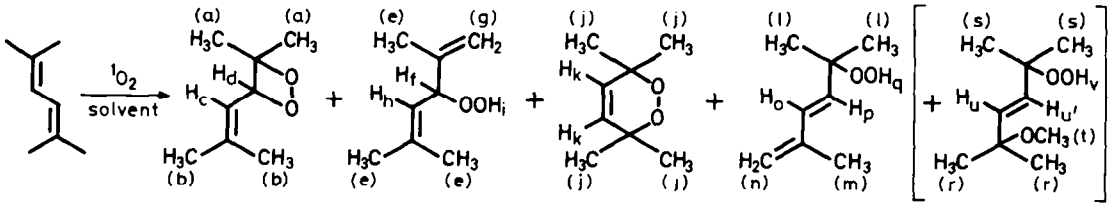
Some years ago, Hasty and Kearns[3] studied the reaction of singlet oxygen with 1. They found that two main products were formed, a dioxetane (2) and an allylic hydroperoxide (3), the ratio of which changed from 2/3 = 2.6 in methanol (MeOH), to 0.2 in acetone (Me_2CO), to 0.1 in CH_2Cl_2, and to 0.01 in acetonitrile (MeCN). After completion of our study, two papers by Foote and co-workers[4,5] appeared on singlet oxygen reactions with 1 in some solvents. Their results and con-

clusions, which deviate from ours in some respects, prompt us to report our results on singlet oxygen interactions with 1 in polar and in non-polar solvents.

RESULTS

Products of Rose Bengal and Tetraphenylporphin Photosensitized Oxygenation Reactions. In each oxygen-saturated solvent, 1 consumed one molecule of oxygen when irradiated in the presence of a typical singlet oxygen-sensitizer such as rose bengal (RB) (in MeOH, MeCN, and Me_2CO) and tetraphenylporphin (TPP) (in benzene and chlorinated solvents). In aprotic solvents, four products, 2 to 5, were obtained; an additional product (6) was formed in the protic solvent MeOH. No other products, especially no polymers, could be detected. Product distributions are shown in Table 1.

Table 1: Product Distributions of Singlet Oxygen Reactions with 2,5-Dimethyl-2,4-hexadiene in Polar and Non-Polar Solvents at 13°C



1 2 3 4 5 6

solvent	(%)	(%)	(%)	(%)	(%)
CCl_4	7	26	23	44	–
C_6H_6	3	33	19	45	–
$CHCl_3$	3	61	6	30	–
CH_2Cl_2	3	64	4	29	–
Me_2CO	8	84	3	5	–
MeCN	3	89	4	4	–
MeOH	53	21	4	2	20

3,3-Dimethyl-4-(2-methyl-1-propenyl)-1,2-dioxetane (2), the (2+2)-CA product, was isolated from the reaction mixture in MeOH by distillation of the residue at -15 to -10°C/10^{-4} Torr into a trap cooled to -78°C, after 4 was filtered off and MeOH was removed at 0°C/10 Torr. The ^{1}H-NMR signal (in $CDCl_3$) at 1.52 ppm (s) is distinctive of the two CH_3-groups (a) at the dioxetane ring of 2. This singlet is used for the quantitative determination of 2 (see below and Experimental section).

2,5-Dimethyl-3-hydroperoxy-1,4-hexadiene (3), the ene-product, was obtained from the irradiation mixture of 1 in MeCN. After removal of 4 by filtration and of the solvent by distillation at 20°C/10 Torr, 3 was isolated by distillation at 108°C/0.1 Torr and identified by its ^{1}H- and ^{13}C-NMR-spectra. The ^{1}H-NMR chemical shifts of the three CH_3-groups (e) appear at 1.73 ppm (m), i.e. in a region between 1.7 and 1.8 ppm where the methyl groups CH_3 (b) and (m) of compounds 2 and 5, respectively, appear. This region is used for quantitative determination of 2 + 3 + 5.

1,2-Dioxa-3,3,6,6-tetramethyl-4-cyclohexene (4), the (4+2)-CA product, precipitates from MeOH and MeCN solutions. It was isolated from the reaction mixtures obtained in MeOH and MeCN as well as from mixtures in other solvents after these solvents were removed by distillation and the resulting residues were treated with MeOH. 4 was identified by its ^{1}H- and ^{13}C-spectra. The singlet at

1.27 ppm (^{1}H-NMR) is distinctive of the four identical CH_3-groups (j) and is used for quantitative determination of 4 in the reaction mixtures.

trans-2,5-Dimethyl-5-hydroperoxy-1,3-hexadiene (5), the vinylog ene-product, was obtained from benzene solutions together with 3 in a 2:1 ratio by distillation at 96°C/0.15 Torr after the solvent was removed at 20°C/10 Torr. The ^{1}H- and ^{13}C-NMR spectra of this mixture allowed to determine the chemical shifts of 5. The singlet at 1.33 ppm (^{1}H-NMR) is distinctive of the two CH_3-groups (l) and is used for quantitative determination of 5 in the reaction mixtures. The characteristic double doublets of H_o and H_p at 5.64 and 6.20 ppm, respectively, with $J_{o,p}$ = 16 cps are easily observed in the ^{1}H-NMR spectra of the reaction mixtures obtained in CCl_4, benzene, $CHCl_3$, and CH_2Cl_2 after removal of the solvents and dissolution of the residues in $CDCl_3$. The other ^{1}H-NMR chemical shifts of 5 appear at 1.78 (m, $3H_m$), 5.01 (m, $2H_n$), and 7.97 (s, broad, H_q).

3 as well as the 2:1-mixture of (5 + 3) were converted to the corresponding trimethylsilylperoxy compounds 3a and (5a + 3a). Unfortunately, (5a + 3a), a 2:1-mixture according to ^{1}H-NMR analysis as well as to glass capillary vpc, could not be separated by distillation.

In order to show that the vinylog ene-product 5 is a primary product of a singlet oxygen/1 interaction rather than a rearrangement product of 3, pure 3 was treated thermally as well as irradiated in oxygen-containing benzene in the presence of TPP for about three hours. After removal of benzene, the ^{1}H-NMR showed only the chemical shifts of 3; no trace of 5 was observed. Furthermore, 5 does not originate from 2 or 4 : if 2 is kept for 24 hours at room temperature in a solvent like $CHCl_3$, it is quantitatively cleaved to acetone and ß-methyl-crotonaldehyde, whereas 4 is stable at room temperature in all solvents.

trans-2,5-Dimethyl-2-hydroperoxy-5-methoxy-3-hexene (6) is an additional product in MeOH. Its ^{1}H-NMR signal at 1.26 ppm (s), distinctive of the two CH_3-groups (r), as well as the AB-system of H_u/$H_{u'}$ at 5.65 ppm with $J_{u,u'}$ = 15 cps are used for the quantitative determination of 6.

6 is a primary product of the singlet oxygen/1 interactions in MeOH since methanolysis of any of the other products does not lead to compound 6. If 2 is kept in solution at room temperature for 24 hours in the presence of MeOH, only quantitative decomposition to acetone and ß-methyl-crotonaldehyde is observed. 4 is stable in a Me_2CO/MeOH mixture at room temperature, and 3 as well as 5 do not react with MeOH even if the compounds are irradiated in MeOH in the presence of RB.

Product Distributions were obtained by quantitative ^{1}H-NMR analysis as described in the Experimental section. This method avoided the manipulation of the original reaction mixtures; removal of solvents at low temperatures and reduced pressures followed by dissolution of the residues in $CDCl_3$ or $CDCl_3$/$CFCl_3$-mixtures did not alter the primary products. The ^{1}H-NMR spectra contained no other signals than those which could be attributed to products 2 through 6 indicating that no other products, especially that no appreciable amounts of polymers, were formed.

The relative amounts of products shown in Table 1 are average values from at least five identical runs. The individual values deviate by about ± 2 (in %); in CCl_4, for example, compound 2 appears at (7±2)%, compound 5 at (44±2)%, etc. The error is thus rather appreciable if the products appear below about 10%.

Dioxetane 2, the (2+2)-CA product, becomes a main product only in the protic solvent MeOH; in aprotic solvents, it is always formed in amounts lower than 10%. The yield of the ene-product 3 is substantial in each solvent; it increases with increasing polarity of the aprotic solvents. The endoperoxide 4, the (4+2)-CA product, appears at appreciable amounts only in the most non-polar solvents. The vinylog ene-product 5 becomes the main product in CCl_4 and benzene; its formation decreases with increasing polarity. These observations, however, do not allow to draw any conclusions with respect to the mechanistic pathways involved in product formation. In order to do this, kinetic studies are inevitable.

Kinetic Studies. In photosensitized singlet oxygen reactions, the rate of oxygen consumption is given by equ.(1)

$$v_{O_2} = I_a \cdot \Phi(^1O_2) \cdot \eta \qquad (1)$$

with v_{O_2} = number of oxygen molecules consumed per unit time, I_a = number of photons absorbed by the sensitizer per unit time, $\Phi(^1O_2)$ = quantum yield of singlet oxygen formation by interaction of $^3O_2$ with the electronically excited sensitizer, and η = efficiency with which singlet oxygen interacts with a substrate to give oxygenated products[6].

If 2,5-dimethylfuran (DMF) is used as a substrate at concentrations larger than about $5 \cdot 10^{-4}$ M in MeOH[1,6] and about $5 \cdot 10^{-6}$ M in CCl_4[1], the efficiency becomes $\eta = 1$[6,7] and thus

$$v_{O_2}^{DMF} = I_a \cdot \Phi(^1O_2) \qquad (2)$$

It is important to note that DMF yields an endoperoxide as the primary product in all the solvents used and that the subsequent thermal reactions of the endoperoxide do not interfere with the singlet oxygen reaction[8,9].

We applied DMF in each solvent at initial concentrations of 10^{-2} M. If the sensitizer concentrations were larger than $2 \cdot 10^{-4}$ M, the resulting oxygen-uptake rate in a given solvent was independent of the sensitizer concentration and constant until DMF was consumed to more than 95%. The limiting (or maximum) oxygen-consumption rate (equ.(2)) is thus easily determined. In order to check the stability of the whole irradiation arrangement (especially the constant output of photons from the irradiation source), two runs with DMF in the respective sensitizer/solvent combinations were performed before and two runs were executed after the runs with 1 were made. The values of $v_{O_2}^{DMF}$ were found to be better than ±2%.

Since 1 does not appear to quench the triplet state of RB and TPP, the following reaction steps subsequent to singlet oxygen formation should be considered[1]:

(a) $^1O_2 \longrightarrow {}^3O_2$; $k_d = 1/\tau_{so}$; spontaneous deactivation;

(b) $^1O_2 + A \longrightarrow$ products AO_2; k_r = rate constant of A-disappearance or oxygen consumption = sum of partial rate constants of product formation;

(c) $^1O_2 + A \longrightarrow {}^3O_2 + A$; k_q^A; "physical" quenching of singlet oxygen by A;

(d) $^1O_2 + \text{sens} \longrightarrow {}^3O_2 + \text{sens}$; k_q^S; "physical" quenching of singlet oxygen by the sensitizer;

with τ_{so} = lifetime of singlet oxygen in a given solvent, A = singlet oxygen-acceptor, and sens = sensitizer. In our case, A = 1, $k_r = k_2 + k_3 + k_4 + k_5$ (+ k_6), and sens = RB and TPP.

The rate of oxygen consumption by A is given by equ.(3)

$$v_{O_2}^A = I_a \cdot \Phi(^1O_2) \cdot k_r[A] / [(k_r + k_q^A)[A] + k_d + k_q^S[\text{sens}]] \qquad (3)$$

We applied 1 in each solvent at initial concentrations between $2 \cdot 10^{-2}$ and $4 \cdot 10^{-2}$ M. The oxygen-uptake rate decreased continuously during a run until it became zero when 1 had taken up one molecule of oxygen per molecule of 1. The recorded oxygen-uptake/time curves thus allowed to determine $v_{O_2}^A$ as a function of the concentration of 1 (= A).

Division of equ.(2) by equ.(3) leads to equ.(4)

$$v_{O_2}^{DMF}/v_{O_2}^A = (1 + k_q^A/k_r) + (k_d/k_r + k_q^S[\text{sens}]/k_r)[A]^{-1} \qquad (4)$$

which shows that a plot of $v_{O_2}^{DMF}/v_{O_2}^A$ vs. $[A]^{-1}$ should be linear and therefore allow to determine the value of k_q^A/k_r from the intercept and $(k_d/k_r + k_q^S[\text{sens}]/k_r)$ as the slope.

If $v_{O_2}^{DMF}/v_{O_2}^{A}$ turns out to be independent of the sensitizer concentration, the slope of equ.(4) is equal to k_d/k_r. If, however, the slope of equ.(4) depends on the sensitizer concentration, a plot of the slope-values of equ.(4) vs. [sens] allows to determine k_d/k_r from the intercept and k_q^S/k_r from the slope of equ.(5):

$$\text{slope-values of equ.(4)} = k_d/k_r + (k_q^S/k_r)\cdot[\text{sens}] \qquad (5)$$

The ß-value[6] of a singlet oxygen acceptor, defined as k_d/k_r (in M), is thus determined by extrapolation to zero sensitizer concentration. According to equations (4) and (5), the ratios of k_q^A/k_r and k_d/k_r are separated such that they are determined as values which are independent of eachother. It seems to be important to point this out since Foote[5] recently criticized certain ß-value determinations as leading sometimes to k_d/k_r-, at other times to $k_d/(k_r + k_q^A)$-values.

At least five runs were executed with 1 for each sensitizer concentration (see Exp. sect.) in a given solvent. Linear plots of $v_{O_2}^{DMF}/v_{O_2}^{A}$ vs. $[A]^{-1}$ were obtained; only with TPP in chlorinated solvents were the slopes of equ.(4) dependent on the sensitizer concentration. ß-values, k_q^A/k_r and k_q^S/k_r were determined by applying the method of least squares. The experimental values, shown in Table 2, are of the 98% confidence level with standard deviations of ±2%.

Table 2: Effect of Solvent on Singlet Oxygen/1-Interactions

Solvent	$\frac{\varepsilon - 1}{2\varepsilon + 1}$	$10^{-4}k_d$ (s^{-1}) a)	Experimental Values: k_q^S/k_r	$k_q^A/k_r + 1$	k_d/k_r (mM)	Calculated Values: $10^{-7}k_q^S$ ($M^{-1}s^{-1}$)	$10^{-6}k_q^A$ ($M^{-1}s^{-1}$)	$10^{-6}k_r$ ($M^{-1}s^{-1}$)	$10^{-6}k_r$ ($M^{-1}s^{-1}$) b)	$k_r/(k_r + k_q^A)$	$k_r/(k_r + k_q^A)$ b)
CCl_4	0.222	0.14	220	10.81	14.3	2.2	0.98	0.10	--	0.09	--
C_6H_6	0.232	4.20	-	10.74	238	-	1.75	0.18	<0.25	0.09	<0.07
$CHCl_3$	0.356	0.40 c)	40	2.86	8.3	1.9	0.90	0.48	--	0.35	--
CH_2Cl_2	0.420	0.95	28	3.21	11.0	2.4	1.90	0.86	1.40	0.31	0.25
Me_2CO	0.465	3.80	-	2.44	51.2	-	1.07	0.74	0.74	0.41	0.19
MeCN	0.480	3.30	-	1.91	24.0	-	1.26	1.38	1.60	0.52	0.25
MeOH	0.477	14.30	-	1.45	59.4	-	1.09	2.41	2.50	0.69	0.96

a) ref. 11 ; b) ref. 4 ; c) ref. 12 and 13 .

In order to calculate absolute rate constants, the choice of the reported singlet oxygen lifetimes that has to be made may become rather critical. To make k_r, k_q^A and k_q^S comparable to rate constants reported earlier for other substrates[1,10], we use the singlet oxygen lifetimes obtained by Merkel and Kearns[11], except for $CHCl_3$ where the more recent value determined by Byteva[12] and Schuster[13] was applied. Foote's[4] new values of singlet oxygen lifetimes agree very well with the Merkel/Kearns-values for benzene and MeOH, and deviate by no more than a factor of two for CH_2Cl_2, Me_2CO and MeCN.

The k_q^S-values for singlet oxygen quenching by TPP in chlorinated solvents agree very well with those obtained earlier when other substrates of singlet oxygen reactions were studied[1]. Tanielian and co-workers[14,15] reported recently on singlet oxygen quenching by a sensitizer. Their value of $7.3\cdot10^8$ $M^{-1}s^{-1}$ for chlorophyll in benzene[15] is about 30-times larger than our value for TPP in CCl_4. To which extent "physical" quenching contains "chemical" quenching, for example product formation between singlet oxygen and TPP, is not known. However, if it occurs, the quantum yield of this process should be rather small because we did not observe any appreciable oxidative bleaching of this sensitizer.

Table 3: Effect of Solvent on Partial Rate Constants of Product Formation in Singlet Oxygen Reactions with 1

Solvent	$10^{-5}k_2$ ($M^{-1}s^{-1}$)	$10^{-5}k_3$ ($M^{-1}s^{-1}$)	$10^{-5}k_4$ ($M^{-1}s^{-1}$)	$10^{-5}k_5$ ($M^{-1}s^{-1}$)
CCl_4	0.07	0.25	0.23	0.42
C_6H_6	0.05	0.59	0.34	0.81
$CHCl_3$	0.14	2.98	0.29	1.45
CH_2Cl_2	0.26	5.50	0.34	2.50
Me_2CO	0.59	6.22	0.22	0.37
MeCN	0.41	12.28	0.55	0.55
MeOH[a]	12.77	5.06	0.96	0.48

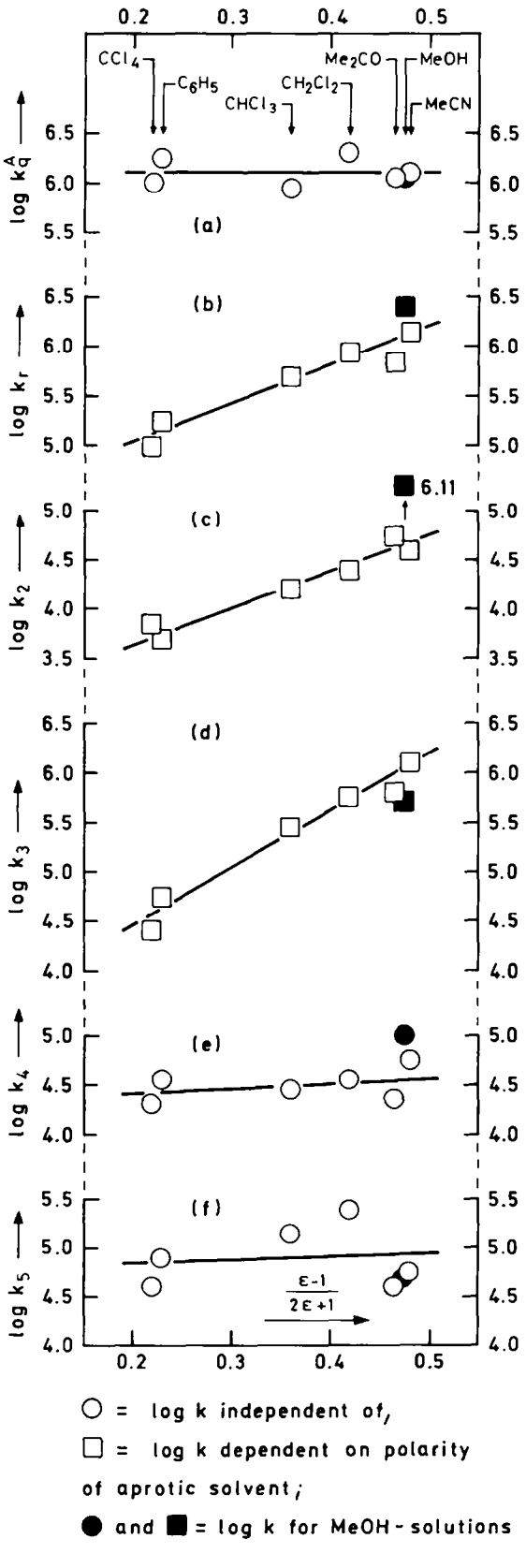
a) $k_6 = 4.83 \cdot 10^5\ M^{-1}s^{-1}$.

"Physical" quenching of singlet oxygen by 1 is appreciable in all solvents. Plotting log k_q^A vs. the polarity function (Fig. 1a) shows that "physical" quenching is solvent-independent with an average value of $\bar{k}_q^A = (1.28 \pm 0.39) \cdot 10^6\ M^{-1}s^{-1}$. (In Fig. 1a-f, the linear plots of log k vs. the polarity function were obtained by applying the method of least squares by disregarding the log k-values determined for methanolic solutions; for numerical values, see Table 4, Exp. section).

"Chemical" quenching (k_r) of singlet oxygen by 1 depends on the solvent and obviously increases with solvent polarity (Fig. 1b). (Similar plots are obtained if the E_T-values[16] are used instead of the ε-function). Therefore, the fraction of the total singlet oxygen/1-interactions which leads to products, $k_r/(k_r + k_q^A)$ of Table 2, increases from about 10% in the most non-polar aprotic solvents (CCl_4 and benzene) to about 50% in the most polar aprotic solvent (MeCN) and to about 70% in the polar protic solvent MeOH. This trend was also observed by Manring and Foote[4], and the agreement between our and their absolute values of k_r is remarkably good.

The solvent dependence of k_r rests mainly on the solvent dependence of the ene-product (3) formation (Table 3, Fig. 1d). If we apply the Kirkwood-Laidler-Eyring model[17] with $\mu(^1O_2) = 0$ D and $\mu(1) = 0$ D, the dipole moment of the transition state leading to 3 is calculated to be 5.9 D (Table 4, Exp. section). This value is distinctly larger than that determined

Figure 1: Dependence of Rate Constants on Solvent Polarity



for the transition state dipole moment of ene-reactions with mono-olefins such as 2,3-dimethyl-2-butene and 2-methyl-2-butene[1].

In spite of the rather large error in the quantitative determination of dioxetane 2 in aprotic solvents, there is clearly a trend of k_2-values to increase with increasing solvent polarity. A transition state dipole moment of 4.7 D is calculated which is somewhat smaller than the value of 6.7 D recently obtained for benzvalene-dioxetane formation[1].

The production of the (4+2)-CA product 4 is independent of solvent polarity; a similar result was recently observed with 1,3-cyclohexadiene[1]. The average value is $\bar{k}_4 = (0.33 \pm 0.12).10^5$ $M^{-1}s^{-1}$ (Table 3, Fig. 1e).

The formation of primary product 5 exhibits a rather peculiar solvent dependence (Fig. 1f). The average value of k_5 appears to be solvent-independent with $\bar{k}_5 = (0.53 \pm 0.18).10^5$ $M^{-1}s^{-1}$ in CCl_4, benzene, Me_2CO, MeCN (and MeOH),but seems to be distinctly larger in $CHCl_3$ and CH_2Cl_2. In a first approximation, however, we may consider the formation of 5 as occurring in a solvent-independent manner(see Table 4, Exp. section).

We may then summarize our results shown in Tables 2 and 3 and Figure 1a-f as follows: in aprotic solvents, the rates of singlet oxygen/1-interactions leading to dioxetane 2 and ene-product 3 are solvent polarity-dependent; the rates leading either to "physical" quenching or to endoperoxide 4 and vinylog ene-product 5 are solvent polarity-independent. MeOH plays a special role since it favors dramatically the dioxetane formation and, furthermore, gives rise to a MeOH-addition product 6 at a rate comparable to that of the ene-reaction.

DISCUSSION

The reaction of 2,5-dimethyl-2,4-hexadiene (1) with singlet oxygen gives rise to four products, 2 to 5, in non-polar as well as in polar aprotic solvents. In the protic solvent MeOH, the solvent-addition product 6 is formed in addition to 2-5.

Three of these products, namely 2, 3 and 4, may be expected to appear, since (2+2)-CA reactions leading to dioxetanes, ene-reactions affording allylic hydroperoxides with a shifted double bond, and (4+2)-CA reactions yielding endoperoxides are the three well-established types of singlet oyxgen reactions with olefins[18].

Hasty and Kearns[3] found that the product ratio of 2/3 is rather solvent-dependent, being 2.6 for MeOH, 0.2 for Me_2CO, 0.1 for CH_2Cl_2, and 0.01 for MeCN. Foote[4] confirmed these product ratios for MeOH (2.4) and MeCN (0.03), and our own values for these product ratios agree very well too : 2.5 for MeOH, 0.1 for Me_2CO, 0.05 for CH_2Cl_2, and 0.03 for MeCN.

Only for methanolic solutions was the formation of endoperoxide 4 considered to be important, with a product ratio of $4/3 < 0.1$[4]. Our results (Table 1) indicate that endoperoxide formation is indeed restrained in solvents like those used by Kearns[3] and Foote[4], but that appreciable amounts are formed in benzene and CCl_4 giving rise to 4/3 ratios of 0.6 and 0.9, respectively.

There is, however, a fourth product formed, the trans-2,5-dimethyl-5-hydroperoxy-1,3-hexadiene (5), which was not expected to occur[19]. Since none of the products 2, 3 and 4 could be transformed into 5 under our reaction conditions, we consider this product as being formed in direct singlet oxygen/1 interactions. This new type of singlet oxygen reaction with a 1,3-diene should be termed "vinylog ene-reaction". In the case of 1, the vinylog ene-reaction can compete successfully with the other reactions in CH_2Cl_2 and $CHCl_3$, and even more so in benzene and CCl_4 in which 5 becomes the main product with 5/3 ratios of 1.4 and 1.7, respectively[21].

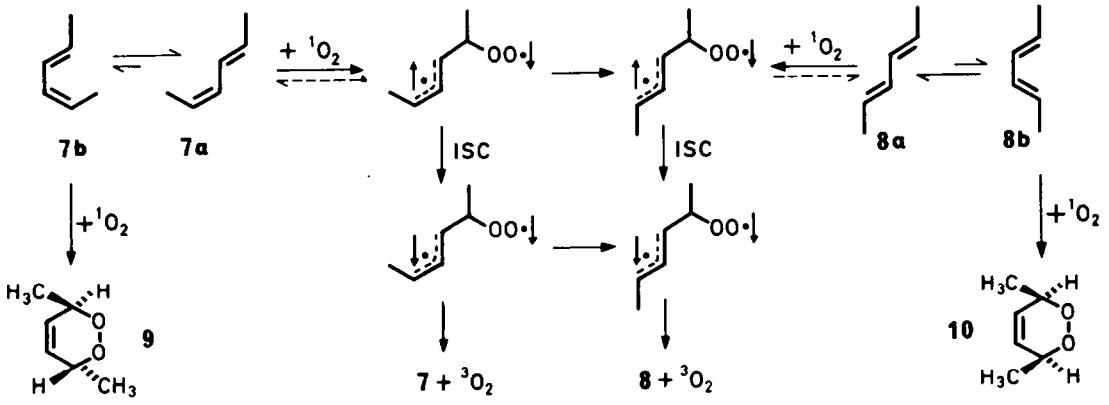
The kinetic analysis revealed that "physical" quenching of singlet oxygen by 1 is actually the major reaction in all the solvents. This result is in contrast to those obtained with simple mono-olefins where "physical" quenching of singlet oxygen by the substrate is negligible[1,4].

However, we did observe "physical" quenching with other 1,3-dienes such as cis,trans-

2,4-hexadiene (7) and trans,trans-2,4-hexadiene (8) and showed that singlet oxygen-quenching by 7 occurred concomitantly with cis-to-trans-isomerization of 7 to 8, probably via (7-singlet oxygen)- and (8-singlet oxygen)-exciplexes[2]. Of course, such a "chemical" contribution to "physical" quenching is not observable with 1 since educt and product would be identical.

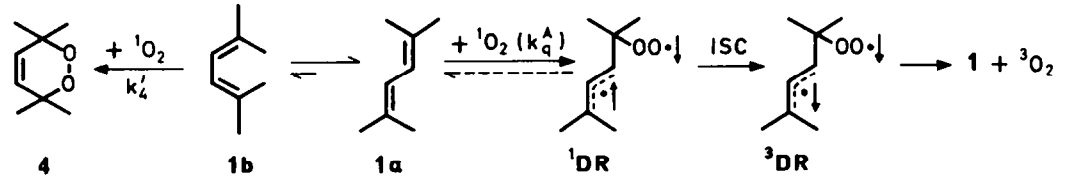
We argued furthermore that the relatively small apparent rate constant of the formation of 10 is due to the fact that 8 is present in the s-cis conformation (8b) to only about 1% and that only this conformational isomer gives rise to the (4+2)-CA product 10 in a concerted reaction with singlet oxygen.

SCHEME 1



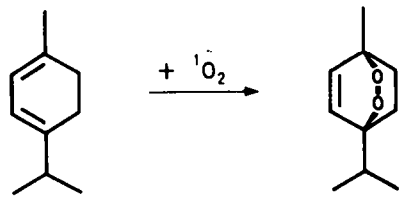
If the assumed exciplexes give rise to the corresponding singlet diradicals and if these species undergo efficient intersystem crossing (ISC) to the corresponding triplet diradicals followed by C-O bond splitting to yield triplet molecular oxygen and 7 (or 8), the mechanism outlined in Scheme 1 does not only explain our findings with 7 and 8 rather satisfactorily, but may be applied also to the case of singlet oxygen/1 interactions (Scheme 2) with the following results:

SCHEME 2



1 should exist in solution as an equilibrium mixture of s-trans(1a)- and s-cis(1b)-conformational isomers. Due to the "extra" methyl groups in positions 2 and 5 of the 2,4-hexadiene derivative 1, the conformational isomer 1b should be present in the 1a/1b equilibrium to a much smaller extent (say, to about 0.1%) than 7b is in the 7a/7b equilibrium (about 1%[2]). Because of the rather strong repulsion of the two interfering methyl groups of 1b, one may expect a rather small effect of solvent polarity on the 1a/1b equilibrium. If, furthermore, the interaction of $^1O_2$ with 1b leads to endoperoxide 4 in a concerted reaction, k_4' and, consequently, k_4, the apparent rate constant of endoperoxide formation, should be solvent-independent, as we indeed observed.

If α-terpinene (11) is a model for the s-cis-conformational isomer 1b, k_4' should be of the same order of magnitude as k_r(11) (= $5.7 \cdot 10^7$ $M^{-1}s^{-1}$ in MeOH), the rate constant for the ascaridole (12) formation. Thus, with k_4 = $9.6 \cdot 10^4$ $M^{-1}s^{-1}$ and k_4' = $5 \cdot 10^7$ $M^{-1}s^{-1}$, 1b should be present at about 0.2% at 13°C, which seems to be a reasonable value with respect to the s-cis/s-trans ratio reported for 1,3-butadiene[22,23].



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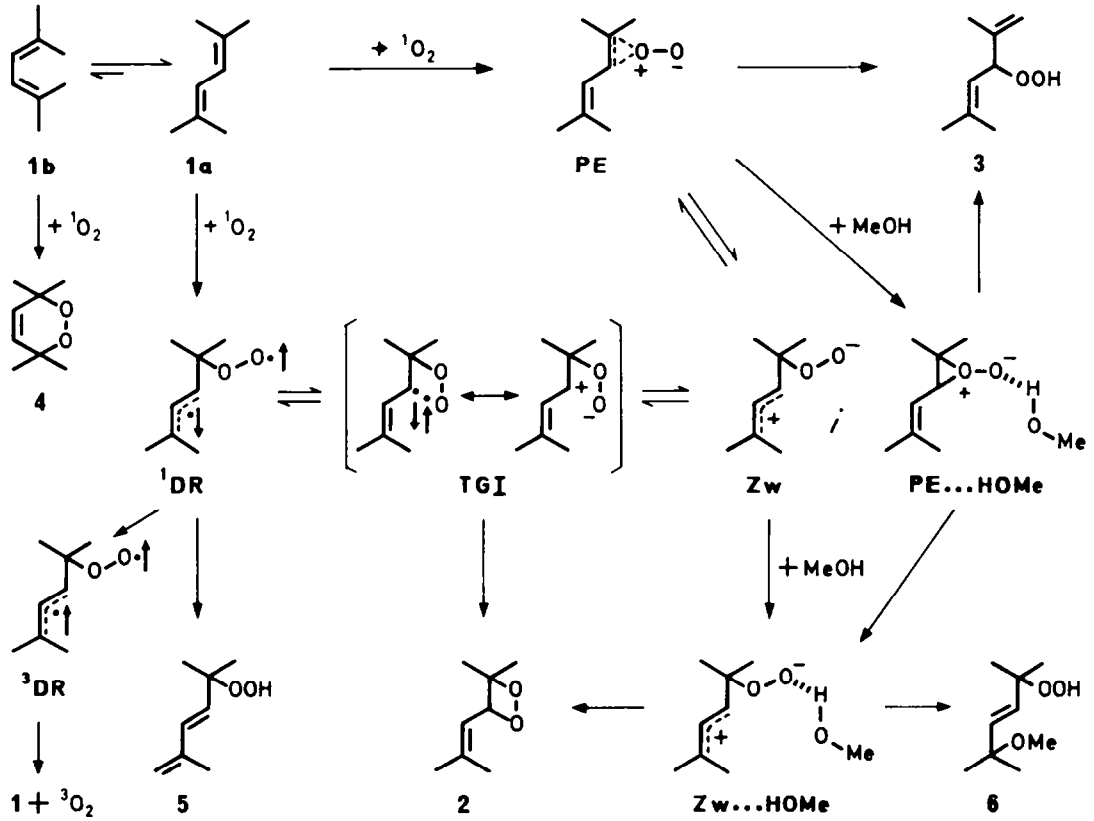
"Physical" quenching of singlet oxygen by 1 can successfully compete with endoperoxide (4) formation because 1 exists as the s-trans-conformational isomer 1a to an extent of about 99.8% (see above). Interaction of 1a with singlet oxygen leads to the singlet diradical (^{1}DR) which may undergo intersystem crossing to the triplet diradical (^{3}DR); the latter may then decompose into triplet molecular oxygen and 1 in an efficient spin-allowed process.

Interaction of singlet oxygen with 1 may, however, yield a resonance hybrid of ^{1}DR and the corresponding zwitterion (Zw) rather than a "pure" singlet diradical. Foote[4] has explained at some length that, in the limiting case, ^{1}DR should easily undergo ISC whereas Zw should not.

We prefer to consider the interaction between ^{1}DR and Zw as occurring via the "tight-geometry intermediate" (TGI)[24] which represents a resonance hybrid of a non-polar singlet 1,4-diradical and a polar 1,4-zwitterion in a conformation in which the radical sites are close to C-O-bond distance (Scheme 3).

SCHEME 3



According to Scheme 3, "physical" quenching via the non-polar ^1DR and ^3DR should be little (if at all) influenced by solvent polarity. As stated above, the vinylog ene-product 5 appears to be formed in a solvent-independent manner (k_5/k_q^A = 0.04), if we neglect chloroform and methylene chloride solutions (k_5/k_q^A = 0.14). We propose, therefore, that deactivation of ^1DR not only yields "physical" quenching but also results in a hydrogen shift to give 5.

The formation of TGI via ^1DR should become increasingly important with increasing solvent polarity. TGI should undergo bond closure to give dioxetane 2 rather efficiently, and thus even that portion of dioxetane formation that occurs via the ^1DR intermediate should increase with increasing solvent polarity. Since the ratio of k_2/k_q^A never exceeds 0.05 in the aprotic solvents (in MeOH, it is about one), the solvent polarity effect is practically absent for the "physical" quenching process.

So far, we have considered the solvent-independent reactions of singlet oxygen with 1b to give 4 and with 1a to give ^1DR. However, there should be another pathway available by which the ene-product (3) is formed via a solvent-dependent transition state and/or intermediate. The most likely candidate for such a transition state or intermediate is the perepoxide (PE) of Scheme 3[10,26-28].The dipole moment of about 6 D, determined for the transition state that leads to ene-product 3, appears to be in accord with the assumption of a PE-like transition state[28-30] as well as with a PE-intermediate[31]. The assumption of passing a PE-like transition state (without the subsequent formation of a PE-intermediate) may suffice to explain the production of 3 in the aprotic solvents. In this case, H-shift from the allylic position and C-O bond formation at position 3 to give 3 occur concomitantly in a concerted process. C-O bond formation at position 2 and "ring opening" to give zwitterion Zw with subsequent dioxetane formation is obviously disfavored in comparison with ene-product formation. However, some dioxetane (2) formation may occur via the pathway PE-Zw-TGI, too.

Although the solvent polarity of MeCN equals that of MeOH, the ratio of k_2/k_3 is dramatically enhanced by a factor of nearly a hundred from 0.03 to 2.5 by changing the solvent from MeCN to MeOH. We interpret this change by assuming that in MeOH a hydrogen-bonded PE intermediate, PE...HOMe, is formed which undergoes ring-opening and H-shift from the allylic position to give 3 as well as ring-opening to the MeOH-stabilized zwitterion Zw...HOMe. The latter, already discussed by Manring and Foote[4] as the important intermediate in methanolic solution, may then give rise to the dioxetane 2 and to the MeOH-addition product 6. Formation of 2 in methanol thus proceeds mainly via this pathway in accord with the observed "jump" of the k_2-value when the solvent is changed from MeCN to MeOH (see Table 3).

If $k_3/(k_q^A + k_2 + k_3 + k_4 + k_5)$ represents the fraction of the polar pathway in aprotic solvents and $(k_2 + k_3 + k_6)/(k_q^A + k_2 + k_3 + k_4 + k_5 + k_6)$ in MeOH, the polar pathway is used increasingly from 2% in CCl_4 and 3% in benzene to 22% in $CHCl_3$ and 20% in CH_2Cl_2, to 34% in Me_2CO and 47% in MeCN, to 65% in MeOH.

Figure 2: Reaction Profile of Endoperoxide (4) Formation from the s-cis Conformational Isomer 1b of 2,5-Dimethyl-2,4-hexadiene (1)

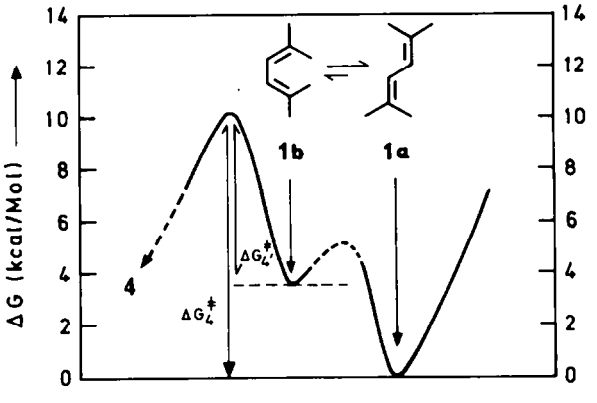
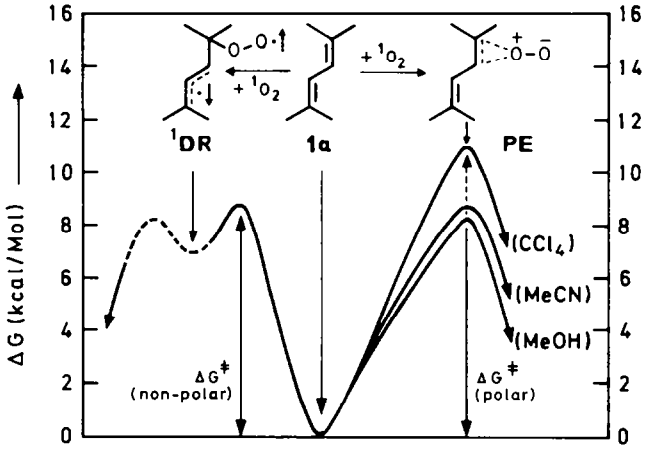


Figure 3: Reaction Profile of Singlet Oxygen Reactions with the s-trans Conformational Isomer 1a of 2,5-Dimethyl-2,4-hexadiene (1)



Figures 2 and 3 represent the reaction profiles of singlet oxygen reactions with 1 at 13°C in the solvents studied. In Figure 2, endoperoxide (4) formation is separated from all the other reactions since its formation is considered as occurring from the s-cis conformational isomer 1b; the enhanced energy content of 1b as compared with the s-trans conformational isomer 1a is given by $\Delta\Delta G = \Delta G_4^{\ddagger} - \Delta G_4^{\ddagger}$, = 3.6 kcal/mol.

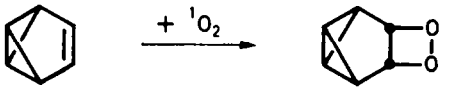
In Figure 3, the reactions of singlet oxygen with the s-trans conformational isomer 1a are considered. With the assumptions made above for the non-polar and polar pathways in aprotic solvents and in methanol, $\Delta G^{\ddagger}$ (non-polar) is calculated to be (8.8±0.1) kcal/mol for all solvents; $\Delta G^{\ddagger}$ (polar), however, decreases from 11.0 (in CCl_4) to 8.8 (inMeCN) to 8.4 kcal/mol (in MeOH), indicating an increasing stabilization of the PE-like transition state with increasing solvent polarity. Since the polarities of MeCN and MeOH are equal, the increased stability of the PE-like transition state by only 0.4 kcal/mol shows that hydrogen-bonding of the transition state is negligible (but becomes prominent for the subsequent intermediates).

Our results and conclusions are somewhat different from those of Manring and Foote[4]. The main difference is that these authors consider the ene-reaction as being insensitive to conditions which is just opposite to our results. In their mechanism, in which they do not consider, of course, the formation of the vinylog ene-product 5[21] and in which they neglect the production of endoperoxide 4, "physical" quenching, ene-product (3) and dioxetane (2) formation are assumed to proceed via a common PE-like transition state or via a common PE intermediate. According to our results, however, the main reaction, i.e. the "physical" quenching, is insensitive to solvent polarity whereas the ene-reaction is certainly dependent on it. The difference between Foote's and our results may in part be due to the fact that we studied the singlet oxygen interactions with 1 in two more solvents (CCl_4 and $CHCl_3$) and that we did not manipulate the product mixtures before we determined the product distributions.

The mechanism outlined in Scheme 3 allows to draw the following conclusions for olefins which should principally be able to undergo the ene-reaction: (1) if a 1,3-diene is fixed in the s-cis conformation, endoperoxide formation should always be so much preferred that other reactions such as "physical" quenching and ene-reaction generally have no chance to occur; examples are found with 1,3-cyclohexadiene[1] and α-terpinene (11)(see above); (2) if neither a stabilized diradical (^{1}DR) nor a stabilized zwitterion (Zw) can form, only the ene-reaction will occur and there will be no "physical" quenching; examples are found with simple olefins such as 2,3-dimethyl-2-butene and 2-methyl-2-butene[1]; (3) if a stabilized zwitterion can form but not a stabilized diradical, dioxetane formation may become prominent, but "physical" quenching should be negligible; depending on the zwitterion stabilization, dioxetane formation may surpass the ene-reaction; enamines such as N,N-dimethylisobutenylamine may be an example as was discussed by Foote[4]; (4) if

a stabilized diradical can form but not a stabilized zwitterion, "physical" quenching may become an important process, but dioxetane formation may become negligible and should have a chance only in rather polar solvents; an example is 2,5-dimethyl-2,4-hexadiene (1) in aprotic solvents; (5) special structural conditions are probably necessary for the vinylog ene-reaction to occur, one being a fixed s-trans conformation in order to avoid endoperoxide formation (see point (1)); in order to avoid competition by the ene-mode of reaction, the use of the most non-polar solvents seems to be suggested.

Finally, there may exist a pathway that leads directly to the "tight-geometry-intermediate" TGI. In the case of singlet oxygen/benzvalene (13) interactions, we observed dioxetane (14) formation as the only mode of reaction the rate of which increased with solvent polarity; "physical" quenching was negligible in all solvents[1]. Formation of ^{1}DR and Zw intermediates from 13 appears to be rather unlikely, and ene-product formation should be impossible because allylic bridge-head hydrogens do not participate in ene-reactions[10]. TGI formation with subsequent ring-closure to the dioxetane (in a "quasi-concerted" reaction) seems to be a possibility.



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Acknowledgment: Support by Fonds der Chemischen Industrie, Frankfurt/Main, Germany, is gratefully acknowledged.

EXPERIMENTAL

Chemicals. 2,5-Dimethyl-2,4-hexadiene (1) (Ega) was purified by distillation (131-134°C/730 Torr). 2,5-Dimethylfuran (DMF)(Fluka) was purified by distillation (91-94°C/730 Torr). Solvents (Fluka, puriss. p.a.) were used without further purification; only chloroform was purified by filtration over alumina. Rose bengal (RB) (Ega), purified by extraction with methanol, and tetraphenylporphin (TPP), prepared after ref. 32 and purified by chromatography on neutral alumina in hot $CHCl_3$[33], were used as sensitizers. - Spectra. Proton-NMR were recorded on a Bruker WP-80-CW-spectrometer using tetramethylsilane (TMS) as internal standard. ^{13}C-NMR were recorded at 80 MHz on a Bruker WP-80-FT-spectrometer using TMS is internal standard. Solvents for NMR-spectroscopy were $CDCl_3$ or or mixtures of $CDCl_3/CFCl_3$. IR-spectra were taken on a Perkin-Elmer-IR-spectrometer 125 as thin films.

Irradiation. A 25 ml irradiation unit with automatic O_2-consumption recording system[7,34] was used for preparative and kinetic studies. A 150 W Halogen-Bellaphot lamp (Osram) and a band filter transparent between 480 and 570 nm (Hoya) was used for electronic excitation of RB and TPP. Both sensitizers were applied at $5\cdot10^{-4}$ and 10^{-3} M concentrations in preparative runs; in kinetic runs, concentrations of 10^{-4}, $2\cdot10^{-4}$, $4\cdot10^{-4}$, $6\cdot10^{-4}$, $8\cdot10^{-4}$, and 10^{-3} M were applied. The solvents containing the sensitizer and 1 (or DMF) were saturated with oxygen before irradiation. The irradiation unit, the oxygen burette and the tubing connecting the unit with the burette were kept at (13 ± 0.1)°C by cooling with water; thermostat JULABO-P.

Products. 3,3-Dimethyl-4(2-methyl-1-propenyl)-1,2-dioxetane 2 : A solution of 500 mg of 1 (4.55 mM) in 25 ml of MeOH containing $5\cdot10^{-4}$ M RB was irradiated for three hours after which time 4.55 mM of O_2 were consumed; no O_2-consumption occurred under further irradiation. - After 40 mg of a precipitate (= 4, see below) was filtered off, about 90% of the solvent was removed by distillation at 0°C/10 Torr. The residue was cooled to -78°C and the pressure reduced to 10^{-4} Torr. When the residue was warmed up slowly, distillation of MeOH into a trap cooled to -78°C occurred at -25

to -20°C. Further warming to -10°C resulted in the distillation of a yellow oil which crystallized when it entered the cool trap. After separation from MeOH, the solid phase was slowly warmed up; the resulting yellow oil, 150 mg of 2 corresponding to a yield of 23%, was immediately dissolved in $CDCl_3$. ^{1}H-NMR (at 20°C): δ = 1.52 (s, $6H_a$); 1.69 (d, $3H_b$, $J_{b,c}$ = 1 cps) and 1.79 (d, $3H_b$, $J_{b,c}$= 1 cps); 5.55 (d-sept., H_c, $J_{b,c}$ = 1 cps, $J_{c,d}$ = 9 cps); 5.95 (d, H_d, $J_{c,d}$ = 9 cps), the ^{1}H-NMR in accord with that reported[3]. Further evidence for structure 2 is obtained by taking the ^{1}H-NMR-spectra at lower temperatures in $CDCl_3/CFCl_3$(2:1): instead of one singlet for the two CH_3 (a)-groups at room temperature, there appear two different CH_3 (a)-groups at lower temperatures; the shift difference between the two groups increases with decreasing temperature: $\Delta\delta$ = 2.2 cps at + 10°C, 3.7 cps at -10°C, 5.4 cps at -30°C, and 7.2 cps at -70°C, indicating decreasing skeletal vibrations of the dioxetane ring with decreasing temperature.

A sample of 2 in $CDCl_3/CFCl_3$ (2:1) was kept at room temperature for 24 hours. Another sample of 2 in $CDCl_3/CFCl_3$ (2:1) was diluted with MeOH (2 : MeOH = 1:5) and also kept at room temperature for 24 hours. The ^{1}H-NMR-spectra of both solutions showed that 2 was completely transformed into acetone (δ = 2.01) and ß-methyl-crotonaldehyde, δ = 1.97 (d, 3H, J_{H,CH_3} = 1 cps); 2.16 (d, 3H, J_{H,CH_3} = 1 cps); 5.87 (d-sept., H, J_{H,CH_3} = 1 cps, $J_{H,H}$ = 8 cps); 9.92 (d, H, $J_{H,H}$=8 cps). In the MeOH-containing sample, there were no signals that could be attributed to (cis- or trans)-2,5-dimethyl-2-hydroperoxy-5-methoxy-3-hexene (6).

2,5-Dimethyl-3-hydroperoxy-1,4-hexadiene 3 : A solution of 1 g of 1 (9.09 mM) in 25 ml of MeCN containing $5\cdot10^{-4}$ M RB was irradiated until the oxygen-consumption ceased (i.e., after 9.09 mM of oxygen was taken up). The endoperoxide 4 (see below) precipitated from MeCN and was removed by filtration. The filtrate was subjected to distillation at 20°C/10 Torr; MeCN and ß-methyl-crotonaldehyde were thus removed since 2 was quantitatively decomposed under these conditions. The residue yielded 400 mg of colorless 3 (= 31% yield) by distillation at 108°C/0.1 Torr. ^{1}H-NMR: δ = 1.73 (m, $9H_e$); 4.83 (m, H_f); 4.9 (m, $2H_g$); 5.07 (d-sept., H_h, $J_{e,h}$ = 1 cps, $J_{f,h}$ = 8 cps); 8.27 (s, broad, H). - ^{13}C-NMR: 18.53 (q); 24.50 (q); 25.96 (q); 85.84 (d); 113.04 (t); 120.73 (d); 139.78 (s); 143.87 (s). - IR: 3500, 2970, 2920, 1700, 1652, 1450, 1370, 1132, 964, and 895 cm^{-1}. C calc.: 67.57, found :67.21; H calc.: 9.92, found: 9.43.

A sample of 3 was dissolved in benzene and irradiated for 3 hours in the presence of TPP. The ^{1}H-NMR-spectra of the irradiated solution did not show any signal that could be attributed to 2,5-dimethyl-5-hydrperoxy-1,3-hexadiene (5).

A sample of 3 was dissolved in MeOH and irradiated for 1 hour in the presence of RB. The ^{1}H-NMR-spectra of the irradiated solution did not show any signal that could be attributed to 2,5-dimethyl2-hydroperoxy-5-methoxy-3-hexene (6).

2,5-Dimethyl-3-trimethylsilylperoxy-1,4-hexadiene 3a : A solution of 450 mg of 3 (3.17 mM) and 252 mg of pyridine (3.17 mM) in 20 ml of CH_2Cl_2 was added slowly to a solution of 350 mg of trimethyl chlorosilane (3.22 mM) in 10 ml of n-pentane cooled to 0°C. After stirring the reaction mixture for 30 min. at room temperature, the precipitate (pyridinium hydrochloride) was filtered off; the solvent was removed at 25°C/10 Torr and the residue, distilled at 81-82°C/10 Torr, gave 310 mg of a colorless liquid 3a (= 46% yield). ^{1}H-NMR: δ = 0.15 (s, 9H); 1.70 (m, 9H); 4.77 (m, H); 4.89 (m, 2H); 5.05 (m, H). - ^{13}C-NMR: -1.69 (q); 18.03 (q); 24.29 (q); 25.54 (q); 85.27 (d); 112.32 (t); 121.01 (d); 137.79 (s); 143.61 (s). - C calc.: 61.63, found: 61.65; H calc.: 10.24, found: 9.83.

1,2-Dioxa-3,3,6,6-tetramethyl-4-cyclohexene 4 : 40 mg of a precipitate obtained as described above (see under 2) was twice recrystallized from MeOH and dried over silica gel, m.p. 55-57°C (decomp.), (ref. 4: 57-58°C). - Mol.weight: 142 (calc.), 148 (osmometric in benzene). - ^{1}H-NMR: δ = 1.27 (s, $12H_j$); 5.66 (s, $2H_k$): - ^{13}C-NMR: 25.11 (q); 79.90 (s); 133.73 (d): - C calc.: 67.57, found: 67.28; H calc.: 9.92, found: 9.62.

4 was also isolated from runs in MeCN (see above), as well as from runs in CH_2Cl_2 and CCl_4 by removing the solvents by distillation and dissolving the residue in MeOH (from which 4

precipitated).

A solution of 45 mg of 4 in 10 ml of Me_2CO and 20 ml of MeOH was stirred for 24 hours at 20°C. The solvent was removed by distillation and the residue dissolved in $CDCl_3$. The ^{1}H-NMR-spectra showed no signals that could be attributed to 6.

trans-2,5-Dimethyl-5-hydroperoxy-1,3-hexadiene 5 : A solution of 750 mg of 1 (6.83 mM) in 25 ml of benzene containing $4 \cdot 10^{-4}$ M TPP was irradiated until the oxygen-consumption ceased (i.e., after 6.83 mM of oxygen were taken up). The solvent was removed by distillation at 20°C/10 Torr; the residue yielded a 2:1-mixture of 5 and 3 (according to ^{1}H-NMR) as a colorless liquid after distillation at 90-96°C/0.15 Torr. We did not succeed in separating 5 from 3 by distillation. Comparison of the ^{1}H-NMR-spectra of pure 3 (see above) and that of the 5/3-mixture yielded the ^{1}H-NMR of 5 : δ = 1.33 (s, $6H_l$); 1.78 (m, $3H_m$); 5.01 (m, $2H_n$); 5.64 (d, H_o, $J_{o,p}$ = 16 cps); 6.20 (d, H_p, $J_{o,p}$ = 16 cps); 7.97 (s, broad, H_q). Similarly, the ^{13}C-NMR of 5 was obtained: 18.08 (q); 24.50 (q); 82.20 (s); 117.07 (t); 132.85 (d); 133.15 (d); 141.48 (s).

A sample of the 5/3-mixture (2:1) was irradiated for 1 hour in MeOH in the presence of RB. The solvent was removed and the residue dissolved in $CDCl_3$. The ^{1}H-NMR-spectra showed no occurrence of signals that could be attributed to 6.

trans-2,5-Dimethyl-5-trimethylsilylperoxy-1,3-hexadiene 5a : 500 mg of a 2:1-mixture of 5/3 was dissolved in a mixture of 20 ml of CH_2Cl_2 and 270 mg of pyridine (3.43 mM). 365 mg of trimethylsilyl chloride (3.36 mM) dissolved in 10 ml of n-pentane was added. After 2 hours of stirring, pyridinium chloride was filtered off; the residue was distilled at 76-83°C/10 Torr. The colorless liquid is a 2:1-mixture of 5a/3a according to ^{1}H-NMR as well as to glass capillary vpc (50 m; 25°C; N_2 (1.5 bar, 2 ml min^{-1}); inlet: 40°C; flame detector: 75°C; T_r(3a) = 40 s; 36%; T_r (5a) = 36 s; 64%). - Comparison of the ^{1}H-NMR-spectra of pure 3a (see above) and that of the 5a/3a-mix- yielded the ^{1}H-NMR of 5a : δ = 0.08 (s, 9H); 1.32 (s, 6H); 1.81 (m, 3H); 5.09 (m, 2H); 5.66 (d, H, $J_{H,H}$ = 16 cps); 6.16 (d, H, $J_{H,H}$ = 16 cps). - ^{13}C-NMR: -1.53 (q); 17.62 (q); 24.29 (q); 81.54 (s); 116.07 (t); 131.31 (d); 133.52 (d); 141.18 (s).

trans-2,5-Dimethyl-2-hydroperoxy-5-methoxy-3-hexene 6 : A solution of 1 in MeOH containing RB was irradiated as described above (see under 2). After 4 was filtered off and after MeOH was completely removed by distillation at 0°C/10 Torr, the residue was dissolved in $CDCl_3$ and a ^{1}H-NMR taken. The signals of 6 do not interfere with those of 2 and 3. ^{1}H-NMR of 6: δ = 1.26 (s, $6H_r$); 1.34 (s, $6H_s$); 3.13 (s, $3H_t$); 5.65 (AB-system, H_u + $H_{u'}$, $J_{u,u'}$ = 15 cps); 8.31 (s, H_v). The ^{1}H-NMR of 6 agrees with that of the corresponding alcohol[4].

Determination of Product Ratios. Immediately after the oxygen-consumption ceased, the solvent was removed at low temperatures and reduced pressure. The residue was dissolved in $CDCl_3$ or $CFCl_3$-mixtures and the ^{1}H-NMR-spectra were taken. Integration of the singlets at 1.52, 1.27 and 1.33 ppm, distinctive of the methyl groups (a) of 2, (j) of 4, and (l) of 5, respectively, allowed to determine the ratio of 2:4:5. To re-examine the ratio, the doublet at 6.20 ppm of 5 was used instead of the singlet at 1.33 ppm. Integration over the signals between 1.7 and 1.8 ppm, where the methyl groups (b) of 2, (m) of 5, and (e) of 3 appear, allowed to determine the relative amount of 3. To re-examine the ratio of 3:5, the residue was treated with trimethylsilyl chloride; the trimethylsilylperoxy compounds 3a/5a were isolated by distillation (see above) and dissolved in $CDCl_3$. The singlets at 1.70 and 1.32, distinctive of 3a and 5a, respectively, were used. In the special case of MeOH and MeCN as solvents, 4 was filtered off, dried and weighed. Finally, the relative amount of 6 was determined by using the singlet at 1.26 ppm, distinctive of the methyl group (r), as well as the AB-system at 5.65 ppm of the protons $H_u/H_{u'}$.

Kinetic Data. The method of determination of relative and absolute rate constants is described under "Results; Kinetic Studies". - According to the Kirkwood-Laidler-Eyring model, the dipole moment of the transition state is given as

$$\mu^{\ddagger} = (r_{\ddagger}^3 \cdot 2.303 \cdot k_B T \cdot \alpha)^{0.5} \quad \text{(in Debye-units)}$$

(since $\mu(\underline{1}) = 0$ D and $\mu(^1O_2) = 0$ D), with $r^{\dagger}$ = radius of $\underline{1} + {}^1O_2$ at the transition state, calculated from the sum of the mole volumina of $\underline{1}$ and singlet oxygen minus a double-bond increment of 3 cm^3 ; $r^{\dagger} = 4.09$ Å ($r(\underline{1}) = 3.84$ Å, $r(^1O_2) = 2.23$ Å); $k_B = 1.38 \cdot 10^{-4}$ $D^2 Å^{-3} K^{-1}$; $T = 286$ K; and α = slope of straight lines of Figures 1a-f calculated for

$$\log k = \log k_0 + \alpha(\varepsilon - 1)/(2\varepsilon + 1)$$

by applying the method of the least squares.

Table 4. Transition State Dipole Moments of Singlet Oxygen Reactions with $\underline{1}$

k	log k_0	α	$\mu^{\dagger}$	k	log k_0	α	$\mu^{\dagger}$
k_q^A	6.09 ± 0.22	0.02 ± 0.60	0.35	k_3	3.34 ± 0.23	5.61 ± 0.60	5.90
k_r	4.28 ± 0.18	3.76 ± 0.48	4.83	k_4	4.32 ± 0.23	0.48 ± 0.60	1.73
k_2	2.94 ± 0.16	3.62 ± 0.42	4.74	k_5	4.83 ± 0.54	0.19 ± 1.43	1.09

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