# Excitation of chemiluminescence in a model reaction of diphenylmethane oxidation. Evaluation of the efficiency and semiempirical calculations*

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The absolute yields ($\Phi^*$) of excitation of the triplet benzophenone, a product of disproportionation of peroxyls in the chemiluminescent oxidation reaction of diphenylmethane, were measured. The $\Phi^*$ value is independent of the temperature and viscosity of the medium, but decreases with increase in its polarity: it is 0.003 in $CCl_4$ and 0.0015 in MeCN. Semiempirical MNDO calculations of the structure of intermediates and the energy profile of their decomposition were carried out. A conclusion was made that the excitation of the $^3n\pi^*$ state of the ketone occurs during the decomposition of the intermediate tetroxide $Ph_2CHOOOOCHPh_2$ after the transition state, but before isolation of the $Ph_2COOO$ biradical, which thereafter decomposes to benzophenone and $O_2$.

**Key words:** hydrocarbon oxidation; peroxyl radicals; chemiluminescence; electronic excitation.

Alcohol ROH, dioxygen, and ketone $R_{-H}{=}O$ form in the chain oxidation of hydrocarbons RH at the stage of chain termination, *i.e.*, when peroxyl radicals $ROO^{\bullet}$ disproportionate (Scheme 1). The enthalpy of this reaction is ~100 kcal mol$^{-1}$. In this case, the $O_2$ and $R_{-H}{=}O$ molecules can form in their singlet ($^1\Delta_g$, 22 kcal mol$^{-1}$) and triplet ($^3n\pi^*$, 69 kcal mol$^{-1}$ in the case of benzophenone) electronic-excited states, respectively, as evidenced by the chemiluminescence emission of ketone in the visible region[1] and that of oxygen in the IR region.[2]

**Scheme 1**

| | |
|---|---|
| Initiation | $AIBN\ (+O_2,\ RH) \xrightarrow{W_i} R^{\bullet}$ |
| Chain | $R^{\bullet} + O_2 \xrightarrow{k_1} ROO^{\bullet}$ |
| | $ROO^{\bullet} + RH \xrightarrow{k_2} ROOH + R^{\bullet}$ |
| Chain | $ROOH \xrightarrow{k_3} RO^{\bullet} + OH^{\bullet}$ |
| Chain termination | $R^{\bullet} + R^{\bullet} \xrightarrow{k_4} R_2$ |
| | $ROO^{\bullet} + R^{\bullet} \xrightarrow{k_5} ROOR$ |
| | $ROO^{\bullet} + ROO^{\bullet} \xrightarrow{k_6} ROH + O_2 + R_{-H}{=}O$ |
| Chemiexcitation | $ROO^{\bullet} + ROO^{\bullet} \xrightarrow{\Phi^* k_6} ROH + O_2 + {}^3R_{-H}{=}O$ |
| Chemiluminescence | ${}^3R_{-H}{=}O \xrightarrow{k_p,\ \Phi_p} R_{-H}{=}O + h\nu$ |
| Quenching | ${}^3R_{-H}{=}O \xrightarrow{1/\tau_p} R_{-H}{=}O$ |

The excitation of chemiluminescence, *i.e.*, a radiationless transition of the reacting system from the potential energy surface (PES) of the ground state to the PES of the electronic-excited state, is a reverse process relative to quenching. The transition occurs at a reaction coordinate intermediate between the starting reagent and the end product. The probability of the transition, *i.e.*, the chemiexcitation yield ($\Phi^*$), can be defined as the ratio of the formation rate of the excited product to the total rate of a given reaction. $\Phi^*$ is the most important characteristic of chemiluminescence, since it determines the probability of transformation of the chemical energy into the electronic energy. In the case of a complex reaction it is of great interest to identify

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[*] Dedicated to Professor Waldemar Adam, to his 60th birthday.

[†] Deceased.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 2464—2470, October, 1996.

**Table 1.** Chemiluminescence yields ($\Phi = I/(0.5\ W_i)$) and yields of chemiluminescence excitation ($\Phi^* = \Phi/\Phi_A$) in the reaction of diphenylmethane (10%) oxidation at 60 °C

| Solvent | $\varepsilon$ ($T$/°C)[a] | $\eta_{60°}$ /cP[b] | $W_i \cdot 10^{-9}$ /mol L$^{-1}$ s$^{-1}$ | $I \cdot 10^{-8}$ /photon mL$^{-1}$ s$^{-1}$ | $\Phi \cdot 10^4$ | $\Phi_A$ | $\Phi^* \cdot 10^3$ |
|---|---|---|---|---|---|---|---|
| $CCl_4$ | 2.2 (50) | 0.585 | 3.62[c] | 10.43 | 9.56 | 0.34 | 2.80 |
| | | | | 10.87 | 9.97 | | 2.93 |
| | | 3.21[c] | | 9.80 | 10.30 | | 3.03 |
| | | | | 10.03 | 10.40 | | 3.06 |
| PhH | 2.2 (60) | 0.389 | 4.20 | 11.34 | 8.10 | 0.28 | 2.86 |
| | | | 4.28 | 12.80 | 8.97 | | 3.17 |
| | | | 4.76 | 10.66 | 7.43 | | 2.63 |
| PhBr | 5.0 (50) | 0.720 | 4.90 | 9.91 | 6.72 | 0.23 | 3.00 |
| | | | 4.80 | 8.90 | 6.17 | | 2.75 |
| | | | 4.80 | 11.95 | 6.90 | | 3.07 |
| PhCl | 5.1 (60) | 0.520 | 4.68 | 8.40 | 5.95 | 0.25 | 2.40 |
| | | | 4.68 | 9.55 | 6.78 | | 2.70 |
| | | | 4.70 | 8.78 | 6.20 | | 2.45 |
| | | | 4.83 | 9.53 | 6.55 | | 2.60 |
| $Me_3COH$ | 7.0 (60) | 1.133 | 4.02[c] | 7.52 | 6.21 | 0.23 | 2.70 |
| | | | | 7.70 | 6.35 | | 2.76 |
| | | | 4.42[d] | 8.53 | 6.40 | | 2.80 |
| | | | | 8.67 | 6.50 | | 2.83 |
| MeCN | 32.7 (55) | 0.252 | 4.57 | 3.81 | 2.50 | 0.175 | 1.43 |
| | | | 4.40 | 4.25 | 2.91 | | 1.67 |
| | | | 4.70 | 4.24 | 2.72 | | 1.56 |
| | | | 4.80 | 4.16 | 2.87 | | 1.64 |
| $Ph_2CH_2$ | 2.5 (50) | 1.527 | | | | | |

[a] Dielectric constants of pure solvents were taken from Refs. 11—14. [b] The $Ph_2CH_2$ viscosity was measured in this work, that of $Me_3COH$ was taken from Ref. 15 (p. 31), those for the rest of the substances were taken from Ref. 11 (p. 108). [c,d] Because of the low solubility of the chelate in $CCl_4$ and $Me_3COH$, it was dissolved to $4.45 \cdot 10^{-3}$ mol L$^{-1}$ in a $Ph_2CH_2$/AIBN/PhBr[c] (or $Ph_2CH_2$/AIBN/PhH[d]) mixture and added to 5 mL of the reaction mixture with an increment of 0.1 mL which resulted in a change in the mixture composition: the concentration of PhBr (or PhH) increased to 6—9 vol.%.

the intermediate, which is a direct precursor of the chemiexcited product.

Recently, the kinetic parameters of oxidation of diphenylmethane have been measured in a number of solvents at different temperatures.[3] In this work, the absolute yields of excitation of chemiluminescence were measured under the same conditions. Semiempirical calculations of the structure and energetic terms of a number of intermediates were carried out and a qualitative picture of chemiexcitation upon disproportionation of peroxyl radicals was given.

## Experimental

The procedures of preparation and carrying out the experiments were analogous to those previously described.[3] The oxidation was initiated by the thermal decomposition of azobis(isobutyro)nitrile (AIBN). (1,10-Phenanthroline)europium(III) tris(thenoyltrifluoroacetonate), (Eu(TTA)$_3$phen), was used to increase the chemiluminescence. The effect of viscosity was studied either by dissolution of diphenylmethane or by varying the temperature; the viscosity was measured on an Ubbelohde viscosimeter.

The reaction mixture was placed into a thermostated vertical flat-bottomed glass cylinder (i.d. 17 mm, height 55 mm) equipped with a reflux condenser. The Hastings—Weber "cocktail", i.e., the radioluminescing solution calibrated against light flux,[4] was placed into the same vessel. This allowed us to exclude the geometric factor in the expression for the chemiluminescence intensity and (after a spectral correction was made) to calibrate the chemiluminometer scale in absolute intensities.

The initiation rate $W_i$ (mol L$^{-1}$ s$^{-1}$) was measured directly in the reaction mixture using the kinetics of quenching by an inhibitor and the subsequent recovery of the chemiluminescence intensity (the photocurrent i in relative units):

$$W_i = 2[\mathrm{InH}]_0/\int(1 - \mathrm{i})\mathrm{d}t \text{ or } W_i = 2[\mathrm{InH}]_0/\tau_i,$$

where $[\mathrm{InH}]_0$ is the concentration of the inhibitor (chroman $C_1$) introduced into the solution; $\int(1 - \mathrm{i})\mathrm{d}t = \tau_i$ is the "stolen" light sum, i.e., the area over the kinetic curve of the normalized chemiluminescence intensity. The "induction period" $\tau_i$ was chosen in real experiments as the time between the moment of InH introduction and the moment of 50% recovery of the initial chemiluminescence intensity.[5]

The sensitivity of the chemiluminometer ($10^4$—$10^5$ photon s$^{-1}$) allowed us to record chemiluminescence at $W_i = 10^{-13}$—$10^{-12}$ mol L$^{-1}$ s$^{-1}$; however, in order to increase the accuracy of measurements, $W_i \sim 10^{-9}$ mol L$^{-1}$ s$^{-1}$ was used in most experiments.

Semiempirical calculations were carried out by the MNDO method.[6] All configurations built on five molecular orbitals, three of the highest occupied and two of the lowest unoccupied orbitals, were taken into account.

## Results and Discussion

The radical-chain reaction of oxidation of hydrocarbons RH (R = Rh$_2$CH for diphenylmethane) and chemiluminescence (the light emission by ketone) are shown in Scheme 1.[7]

At moderate temperatures one can neglect the decomposition of peroxide. The chain reaction determines the rate of accumulation of ROOH, but has no effect on the rate of chain termination. The latter occurs solely due to the ROO$^·$ radicals, since the reaction of R$^·$ with dioxygen is very fast, and the stationary concentration of radicals R$^·$ is negligible.[7] Therefore, the rate of loss of peroxyl radicals $k_6[\mathrm{ROO}^·]^2$ and the initiation rate $W_i$ become equal under stationary conditions, and the total photon flux, or the quantum intensity ($I$/photon s$^{-1}$), is defined by the following expression:

$$I_p = \Phi_p\Phi^* \ (0.5W_i). \qquad (1)$$

The chemiexcitation yield $\Phi^*$ can be determined if the yield of the ketone phosphorescence, $\Phi_p = k_p\tau_p$, is known from independent photophysical experiments. However, this value is extremely small ($140 \cdot 7 \cdot 10^{-8} \approx 10^{-5}$)[8] and is strongly affected by impurities. Therefore, it is difficult to measure under the conditions (the composition of the solution, temperature, viscosity) in which chemiluminescence is studied. Another approach consisting of the energy transfer to the luminophore, which serves as the chemiluminescence enhancer (or activator), for instance, Eu(TTA)$_3$phen, is more convenient and reliable:

$$^3R_{-H}{=}O + A \xrightarrow{k_{et},\ \Phi_{et}} R_{-H}{=}O + A^*,$$

$$A^* \xrightarrow{\Phi_A} A + h\nu.$$

The quantum intensity of the activated chemiluminescence is:

$$I_A = \Phi_A\Phi_{et}\,\Phi^* \ (0.5\ W_i), \qquad (2)$$

where $\Phi_A$ is the quantum yield of the A photoluminescence (for Eu(TTA)$_3$phen the value of $\Phi_A$ is 0.2—0.3; Table 1), $\Phi_{et} = k_{et}\tau_p\,[A]$ is the yield of the energy transfer, $k_{et}$ is the rate constant of the energy transfer, limited by diffusion ($k_{et}$ is ~$10^{10}$ L mol$^{-1}$ s$^{-1}$ at 60 °C), $\tau_p = \tau_p^0(1 + k_{et}\tau_p^0[A])^{-1}$ is the lifetime of the benzophenone triplet in the presence of A, and $\tau_p^0$ is the lifetime of the benzophenone triplet in the absence of A ($7 \cdot 10^{-8}$ s)[8]. The activator Eu(TTA)phen emits light in a narrow band at 613 nm where the sensitivity of the photomultiplier with the multialkali cathode is high.

It follows from Eqs. (1) and (2) that the europium complex increases the chemiluminescence $\Phi_A\Phi_{et}/\Phi_p^0$ times (*i.e.*, by 4 orders of magnitude at $[A] = 5.0 \cdot 10^{-4}$ mol L$^{-1}$), and it can be measured with high accuracy. The absolute yield of the excitation $\Phi^*$ is determined from the limiting (at $\Phi_{et} = 1$, *i.e.*, at $[A] = \infty$) intensity of the activated chemiluminescence, *i.e.*, from the intercept on the ordinate axis of the linear dependence $I_A^{-1}$ on $[A]^{-1}$:

$$\frac{1}{I_A} = \frac{1}{\Phi_A\Phi^*(0.5\ W_i)}\left\{1 + \frac{1}{k_{et}\tau_p^0[A]}\right\}. \qquad (3)$$

The total yields of the activated chemiluminescence, $\Phi = \Phi_A\Phi^*$, are listed in Table 1. To calculate the excitation yield, one must know the *absolute* yield $\Phi_A$ in the mixture in question and at a given temperature. The effect of the composition of the mixture and that of temperature on the *relative* quantum yield of the Eu(TTA)$_3$phen photoluminescence has been studied in detail previously[9]; the value of the *absolute* yield ($\Phi_A$) in acetone at 25 °C has been reliably measured;[10] it is 0.56±0.08. Combining these data, one can readily obtain the absolute values of $\Phi_A$ for the mixtures of diphenylmethane with solvents and then calculate the value of the chemiexcitation yield of benzophenone $\Phi^*$.

It can be seen from Fig. 1 that $\Phi^*$ depends neither on the temperature nor on the composition of the mixture. The viscosity changes are 2—3 times but the value of $\Phi^*$ (~0.003) remains constant. The values of $\Phi^*$ for a number of mixtures at 60 °C are given in Table 1; it also follows from these data that the excitation yield is independent of viscosity; however, its value decreases as the dielectric constant of the medium increases.

Let us consider the results obtained with allowance for the mechanism of the reaction in which chemiexcitation occurs. According to Russell,[16] the chain termination proceeds *via* tetroxide which forms from two peroxyl radicals (Scheme 2) and is in equilibrium

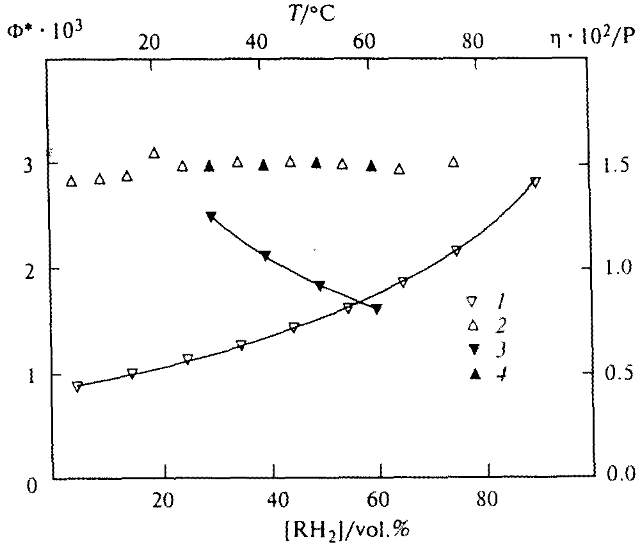

**Fig. 1.** The dependences of viscosity (*1*) and the absolute yield of chemiexcitation $\Phi^*$ (*2*) on the diphenylamine concentration in benzene at 60 °C, and temperature dependences of viscosity (*3*) and the yield $\Phi^*$ (*4*) at the diphenylamine concentration of 55 vol.%.

with them. Hence, the empirical-constant of the chain termination rate can be written as

$$k_6 = Kk_b = (k_a/k_{-a})k_b,$$

where $K$ is the equilibrium constant; $k_{-a}$ and $k_b$ are the rate constants of reversible ($a$) and irreversible ($b$) decomposition of tetroxide. Correspondingly, the effective activation energy is $E_6 = E_b - Q$ (Fig. 2). The irreversible decomposition proceeds *via* the rigid six-membered transition state ROOOOR$^{\#}$, where the rotations about C(1)—O(2), O(2)—O(3), O(3)—O(4), and O(4)—O(5) bonds are hindered. This decreases the entropy of decomposition activation (by ~14 cal mol$^{-1}$ deg$^{-1}$),[17] and the pre-exponential factor of the rate constant $k_b$ becomes 3 orders of magnitude lower than that of $k_{-a}$. Because of this, the equilibrium between peroxyls and tetroxide remains though the effective activation energy $E_6$ approaches zero or is negative.

The constant $k_6$ does not depend on temperature in the reaction of the diphenylmethane oxidation,[3] *i.e.*, $E_6 \approx 0$. The absolute value of $k_6$ is $3 \cdot 10^8$ L mol$^{-1}$ s$^{-1}$, *i.e.*, it approaches the formal diffusion limit $(1/4)k_d$ ($k_d = RT/2000\eta \approx 6 \cdot 10^9$ L mol$^{-1}$ s$^{-1}$; 1/4 is the spin-statistical factor introduced under the assumption that the correlation of the radical spins persists during the total encounter time). Nevertheless, $k_6$ is independent of viscosity and, hence, the reaction proceeds in the kinetic rather than in the diffusion region.

The same regularities are also observed for $\Phi^*$ (see Table 1 and Fig. 1). Thus, the contribution of chemiexcitation ($\Phi^* k_6$; see Scheme 1) to the overall rate constant of the chain termination $k_6$ is insignificant and constant; the excitation is not an independent channel and requires no additional thermal activation ($\Delta E^*$ in Fig. 2); the nonadiabatic jump to the potential energy surface (PES) of the excited state occurs after the system passes through the activation barrier of the tetroxide decomposition rather than before this transition.

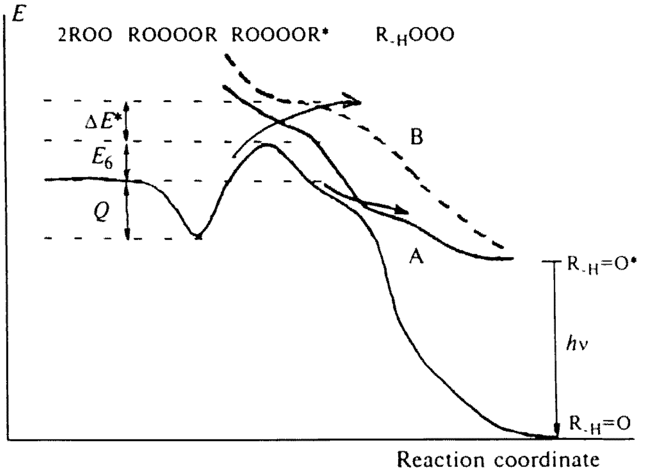

**Fig. 2**. The qualitative digram of the PES section along the coordinate of the reaction of disproportionation of the peroxyl radicals (see Scheme 2) if an additional activation energy is not required (A) or required (B) for chemiexcitation of the product (ketone).

The polarity effect on $\Phi^*$ (not on $k_6$) can mean that the dipole moment of the key (for the excitation) structure in the ground state is greater than that in the excited state; the polar medium increases the splitting between the PES and, therefore, according to the Landau—Zener model,[18] the probability of nonadiabatic transition to the PES of the electronic-excited state decreases.

No experimental procedures of studying the PES are available for such complex molecules. We carried out semiempirical calculations of the structure of intermediates. The simplest and real tetroxides, intermediate biradicals, and the end products are presented in Scheme 2. Stages of formation of tetroxide ($a$), six-membered transition state ($b$), biradical ($c$), and products ($d$) are indicated by arrows. Numbering of atoms used in semiempirical calculations is given. The intermediate of the ethylbenzene oxidation, PhMeCHOOOOCHPhMe, containing a lesser number of atoms and calculations of which require less computing time, was investigated instead of PhPhCHOOOOCHPhPh. In addition to the bond lengths and angles, the values of bond orders

**Scheme 2**

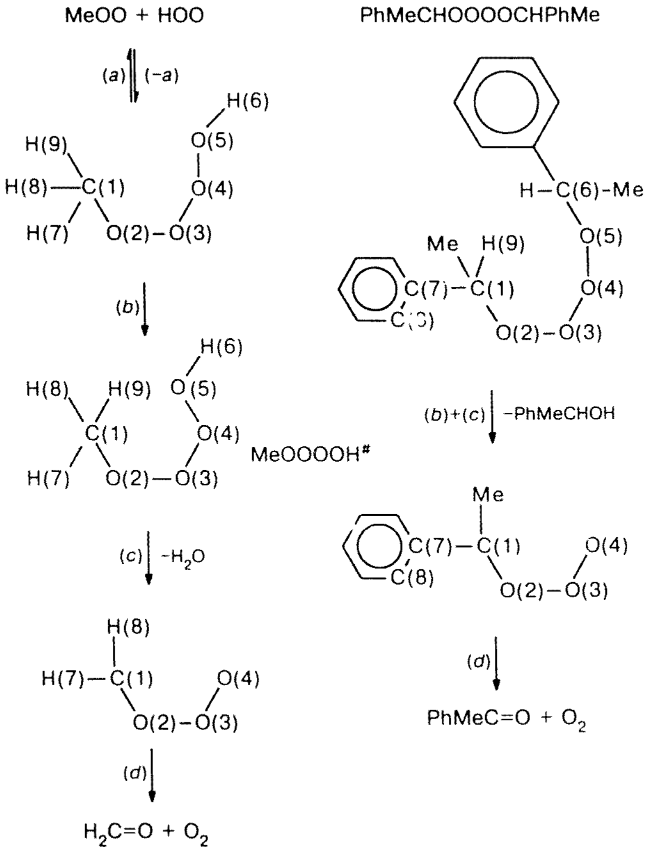

**Table 2.** Geometric parameters of equilibrium conformations of tetroxides MeOOOOH and PhMeCHOOOOCHPhMe and of PhMeCOOO biradical (see Scheme 2) calculated by the MNDO method

| Molecule (μ/D) | n | Bond | d/Å | Bond angle | ω /deg | Dihedral angle | φ /deg |
|---|---|---|---|---|---|---|---|
| MeOOOOH | 0.96 | H(7)—C(1) | 1.11 | H(7)—C(1)—O(2) | 111 | H(7)—C(1)—O(2)—O(3) | 90 |
| (2.13) | 0.95 | C(1)—O(2) | 1.43 | C(1)—O(2)—O(3) | 116 | C(1)—O(2)—O(3)—O(4) | −113 |
| | 0.99 | O(2)—O(3) | 1.29 | O(2)—O(3)—O(4) | 112 | O(2)—O(3)—O(4)—O(5) | 98 |
| | 0.98 | O(3)—O(4) | 1.30 | O(3)—O(4)—O(5) | 112 | O(3)—O(4)—O(5)—H(6) | 99 |
| | 1.00 | O(4)—O(5) | 1.29 | O(4)—O(5)—H(6) | 110 | | |
| | 0.93 | O(5)—H(6) | 0.96 | | | | |
| PhMeCHOOOOCHPhMe | 1.37 | C(8)—C(7) | 1.40 | C(8)—C(7)—C(1) | 119 | C(8)—C(7)—C(1)—O(2) | −123 |
| (2.43) | 0.96 | C(7)—C(1) | 1.53 | C(7)—C(1)—O(2) | 106 | C(7)—C(1)—O(2)—O(3) | 160 |
| | 0.94 | C(1)—O(2) | 1.44 | C(1)—O(2)—O(3) | 116 | C(1)—O(2)—O(3)—O(4) | −116 |
| | 0.99 | O(2)—O(3) | 1.29 | O(2)—O(3)—O(4) | 111 | O(2)—O(3)—O(4)—O(5) | 96 |
| | 0.99 | O(3)—O(4) | 1.30 | O(3)—O(4)—O(5) | 112 | O(3)—O(4)—O(5)—C(6) | 104 |
| | 0.99 | O(4)—O(5) | 1.29 | O(4)—O(5)—C(6) | 116 | | |
| | 0.94 | O(5)—C(6) | 1.44 | | | | |
| PhMeCOOO | 1.27 | C(8)—C(7) | 1.43 | C(8)—C(7)—C(1) | 123 | C(8)—C(7)—C(1)—O(2) | 6 |
| (1.73) | 1.18 | C(7)—C(1) | 1.44 | C(7)—C(1)—O(2) | 116 | C(7)—C(1)—O(2)—O(3) | 125 |
| | 1.12 | C(1)—O(2) | 1.39 | C(1)—O(2)—O(3) | 113 | C(1)—O(2)—O(3)—O(1) | 165 |
| | 0.81 | O(2)—O(3) | 1.30 | O(2)—O(3)—O(1) | 113 | | |
| | 1.36 | O(3)—O(1) | 1.19 | | | | |

reflecting the electron density transfer along the bonds (*i.e.*, their weakening of strengthening) are given in Table 2. A comparison shows the close mutual position of the key fragments of MeOOOOH and PhMeCHOOOOCHPhMe, and one can expect that the structure of the central part will be the same as that of the intermediate PhPhCHOOOOCHPhPh in question.

The dihedral angle in PhMeCHOOOOCHPhMe is −123°; the order of the C(7)—C(1) bond is equal to 0.96. The four bonds at C(1) atom virtually correspond to $sp^3$ hybridization, and their orders are close to unity. In the equilibrium conformation of the PhMeCOOO biradical the dihedral angle C(8)—C(7)—C(1)—O(2) is equal to 6° and, hence, the phenyl ring nearly lies in the same plane (see Scheme 2) as the C(7), C(1), and O(2) atoms. The C(1)—Me bond deviates from the plane C(7)—C(1)—O(2) only by 10°, and it can be expected that p-AO of the unpaired electron of C(1) atom is nearly perpendicular to the figure plane (angle of ~95°; hybridization close to $sp^2$) and, hence, it is partially conjugated with the π-system of the phenyl ring. In fact, the order of the C(7)—C(1) bond is 1.18.

The dihedral angle between the planes, where p-AO of the C(1) atom and the cleaved O(2)—O(3) bond lie, is ~30° while the O(3)—O(2)—C(1) angle is 113°, *i.e.*, it is close to the tetrahedral angle. Thus, the AO overlap is sufficiently large to afford the formation of the C—O π-bond. The values of the bond orders and the lengths of C(1)—O(2), O(2)—O(3), and O(3)—O(4) bonds show that the equilibrium conformation of the PhMeCOOO biradical is, to a some extent, prepared to a decay to form acetophenone and dioxygen. (Note that according to calculations the $H_2COOO$ biradical is unstable and decomposes into $H_2CO$ and $O_2$.)

In contrast to the complex rearrangement of the nuclei in reactions (*b*) and (*c*), the biradical decomposition (process (*d*)) reduces to the lengthening of the only O(2)—O(3) bond; in this case the computation program optimizes the remaining geometric parameters so that the energy (the formation enthalpy) becomes minimal. Energetic profiles of the PES along the *r*(PhMeCO—OO) coordinate are shown in Fig. 3. A shallow potential well corresponds to the equilibrium conformation of the biradical. At *r*(PhMeCO—OO) < 1.9 Å, the lowest state is singlet, whereas at ~1.9 Å level inversion occurs and the system, moving on the singlet PES, is not in the ground, but in an excited level corresponding to a

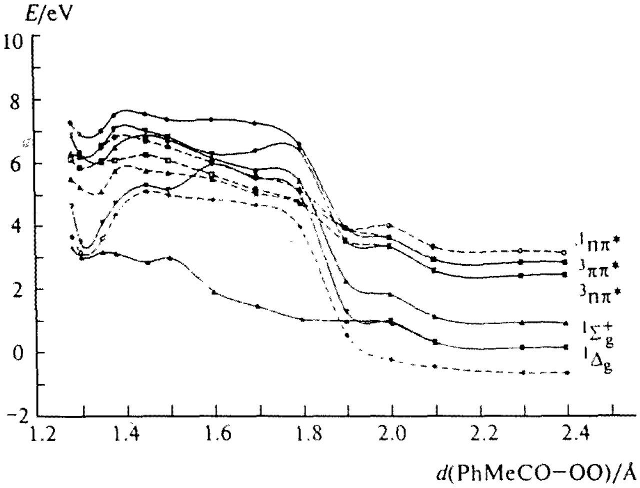

**Fig. 3.** The dependences of the relative energies of five singlet (solid lines) and four triplet (dotted lines) states on the coordinate of the decay reaction of the PhMeCOOO biradical (the O(2)—O(3) bond length). Calculations by the MNDO method. The states of the same multiplicity are enumerated in order of increasing the energy (they are considered as the states of the same symmetry and, hence, are not intersected[18]).

combination of the $S_0$ ketone state and the degenerate $^1\Delta_g + {}^1\Delta'_g$ state of dioxygen. Thus, $^1O_2$ forms at the end of the reaction and the conditions of its generation are hardly dependent on the substituents at C(1). Actually, the values of $\Phi^*(^1\Delta_g)$ change only from 0.03 to 0.14 upon disproportionation of secondary peroxyls, while they are equal for $Ph_2CHOO$ and $Ph_2CDOO$ (0.11 and 0.12, respectively).[2]

It is seen in Fig. 3 that the excitation of ketone upon the decomposition of PhMeCOOO is impossible as the ground S- and the second T terms do not intersect and the gap between them is too large. We expected (not found) "the external effect of the heavy atom" on transitions with changing spin, known in photochemistry: the $\Phi^*(^3n\pi^*)$ yield does not depend on the presence of Cl and Br atoms in the solvent molecules. It is possible that the transition to the PES corresponding (in the products region) to $PhMeC{=}O(^3n\pi^*)$ occurs at the stage of the tetroxide decomposition that includes changes in many coordinates. A study of this problem is the object of a further investigation. In this work its consideration will be qualitative and simplified.

Two structures of the biradical differing in the dihedral angles C(7)—C(1)—O(2)—O(3) are shown in Scheme 3. It is evident that the electron in the p-AO of C(1) in the left structure and the electron released upon the cleavage of the O(2)—O(3) bond form a π-bond, *i.e.*, the ketone is in the $S_0$ state. As mentioned above, the AO overlap in the optimized biradical is favorable for the formation of a C—O π-bond. On the contrary, the electron in the p-AO of C(1) in the right structure interacts with the unshared pair of O(2). This leads to the excitation: two of the three electrons form a π-bond; the third electron passes to π*-MO; the electron participated in the O(2)—O(3) bond remains single in a nonbonding (n) orbital. It is just an excited nπ*-state.

Thus, the probability of chemiexcitation must depend on the value of the dihedral angle C(7)—C(1)—O(2)—O(3) in the *nonthermalized* biradical at the moment of the O(2)—O(3) bond cleavage; it is most likely that this conformation, "pre-biradical," must have originated at an earlier stage, *i.e.*, upon abstraction of the alcohol from ROOOOR#. The fraction of such conformations is likely to be small and the yield of the ketone chemiexcitation in the self-reaction of peroxyls is correspondingly low (see Ref. 20 and this work).

The effect of the C(7)—C(1)—O(2)—O(3) angle is demonstrated in Table 3, where two nonequilibrium structures, obtained by twisting about the C(1)—O(2) bond, are compared with the equilibrium structure of the biradical. The energies are given for the ground state geometry. Were the structure of PhMeCOOO in its excited states optimized, the energy splittings would be smaller. However, the nonoptimized values are more consistent with the studied problem since chemiexcitation should be considered as the fast Franck—Condon transition from the ground state to the excited state at fixed nuclear coordinates (excluding some which are components of the "reaction coordinate"). It follows from Table 3 that the levels of the nonequilibrium conformation are brought closer and even their sequence differs in multiplicity as compared to the equilibrium conformation. It means that a crossing or an avoided crossing of the PES occurs in a given area of hyperspace, which undeniably favors chemiexcitation. The increased dipole moments of the ground state of the biradical structure can be a cause for the polarity effect on the chemiexcitation yield discussed above.

**Scheme 3**

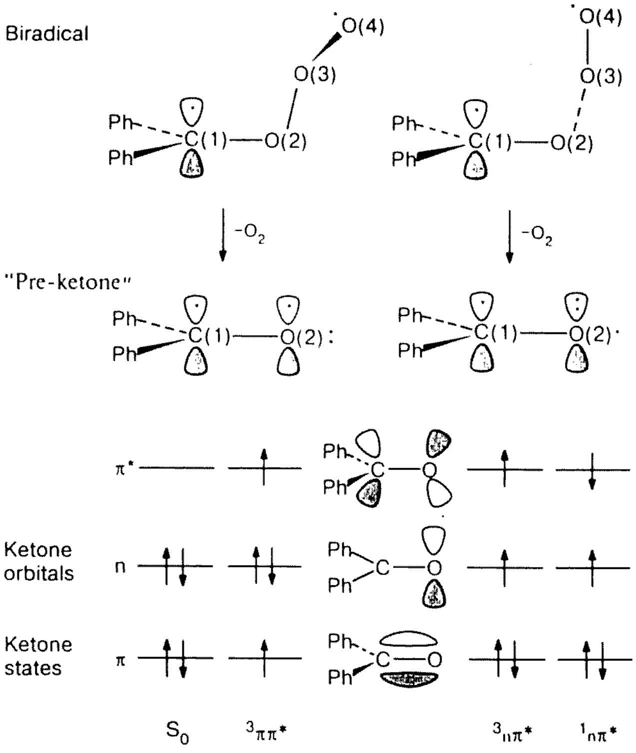

**Table 3.** The effect of the dihedral angle C(7)—C(1)—O(2)—O(3) of the PhMeCOOO biradical on the dipole moment (D) in the ground state and the energies of the vertical transitions from the ground state to the lowest excited singlet (S) and triplet (T) states

| Angle/deg | μ/D | *E*/eV (multiplicity) |
|---|---|---|
| 125 | 1.72 | 0.00 (S), 2.70 (T), 3.42 (T), 3.84 (T), 3.92 (S), 3.98 (T), 4.06 (S) |
| 185 | 4.33 | 0.00 (T), 0.005 (S), 0.84 (T), 0.85 (S), 1.53 (T), 1.80 (T), 1.83 (S) |
| 215 | 6.24 | 0.00 (T), 0.05 (S), 1.563 (T), 1.567 (S), 2.23 (T), 2.93 (S), 2.94 (T) |

Immediately after the reaction, the triplet ketone and $O_2$ are in the same cage and the energy transfer can decrease the measured yield of the ketone excitation and increase the measured yield of $^1O_2$ (this possibility was discussed in Refs. 2, 21). It should be noted that one can solve this problem by comparing the rate constant of quenching ($k_q$) of the ketone triplet at its encounter with $O_2$ with the diffusion constant ($k_d$) of the rate of formation of cages containing $^3R_{-H}{=}O$ and $O_2$.

The cages are the same at chemi- and photoexcitation and, therefore, one can use the data on the quenching of photogenerated triplets by dioxygen (see the summary in Ref. 22, Tables 7.1 and 7.2). All these results (not only for ketones, but also for any organic molecules) show that $k_q$ is an order of magnitude lower than $k_d$. This means that only one collision of ten results in energy transfer to $O_2$ or that the characteristic time of deactivation by dioxygen is by an order of magnitude higher than the lifetime of the cage ($\tau_c = 10^{-10} - 10^{-11}$ s).

According to Kellogg's statement,[21] the value of $\Phi^*$ for the triplet ketone in the reaction ROO + ROO is close to 1, but it is effectively quenched by dioxygen in the cage, so that the measured $\Phi^*$ is $10^8$ times lower than the true one ($\Phi^*_0$). However, not the chemiexcitation yields were compared,[21] but the probabilities of the chemiluminescence emission from the cage and those of quenching of the excited ketone by the energy transfer to $O_2$; in the case of benzophenone the ratio of these probabilities is indeed small ($k_p \cdot 10\tau_c \approx 10^{-7}\div10^{-8}$). We get, for the ratio of the yields, $\Phi^* = \Phi^*_0(1 - k_q/k_d)$, *i.e.*, the measured yield is only insignificantly less than the true one; in this case the probability of observing the ketone chemiluminescence is determined by the fact that the rate constant $k_q$ is appreciably lower than $k_d$.

The yields of the singlet dioxygen due to energy transfer from the *photogenerated* ketone can be much higher than in the case of chemiexcitation: for instance, in the case of fluorenone they are 80—90% and 6—10%, respectively.[2] This should not be surprising: in the absence of quenching competing with the transfer to $O_2$ in the bulk, the yield of $^1O_2$ in the photoprocess can be high even at a low $k_q$ (particularly, at a high concentration of $O_2$ in solution); however, the contribution of the chemigenerated ketone to the $^1O_2$ yield cannot exceed the $\Phi^* k_q/k_d$ value.

The authors express their gratitude to Prof. J. W. Hastings for supplying the radioluminescent solution and the discussion of the procedure of its application.

The work was carried out with the financial support of the Russian Foundation for Basic Research (Projects Nos. 96-03-32544 and 96-03-34142) and the International Science Foundation and the Government of the Russian Federation (Grant JIL 100).

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*Received January 9, 1996;*
*in revised form May 13, 1996*