# Decay kinetics of benzophenone oxide in the liquid phase

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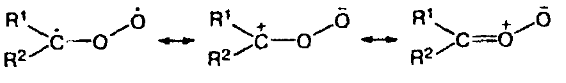
The kinetics of self-termination of benzophenone oxide (BPO) in the liquid phase was studied by flash photolysis. The extinction coefficient of BPO ($\varepsilon$) was found to be virtually independent of the solvent nature, $\varepsilon = (1.9\pm0.1) \cdot 10^3$ L mol$^{-1}$ cm$^{-1}$. The rate constant of the BPO self-termination increases from $1.8 \cdot 10^7$ (MeCN) and $7.4 \cdot 10^7$ ($C_6H_6$) to $1.5 \cdot 10^9$ ($n$-decane) and $2.0 \cdot 10^9$ L mol$^{-1}$ s$^{-1}$ ($n$-pentane) at 293±2 K. Solvation of BPO promotes a polar state of the molecule in MeCN and $C_6H_6$. In nonpolar hydrocarbons, a great contribution is made by the biradical structure resulting in an increase in the rate constant and a shift of the absorption maximum to the long-wave region (from 410 nm in MeCN to 425 nm in $n$-pentane). In solutions of benzene and acetonitrile, benzophenone oxide reacts with the parent diazo compound with a rate constant of $(2-4) \cdot 10^5$ L mol$^{-1}$ s$^{-1}$ (293±2 K) along with the self-termination.

**Key words:** kinetics, flash photolysis, carbonyl oxides.

The chemistry of carbonyl oxides (COx), labile intermediates of olefin ozonolysis



has recently been under intense study.[1,2] At the same time, published data on the rate constants of reactions between carbonyl oxides are rather limited.[3,4] In these works, the recombination rate constant of ROO (R = $Ph_2C$) in an acetonitrile solution was determined, and the extinction coefficient of benzophenone oxide ($\varepsilon_{ROO}$) obtained previously was used.[3]

In this work, we determined the extinction coefficients and decay rate constants of $Ph_2COO$ in solutions of MeCN, $C_6H_6$, $n$-$C_5H_{12}$, and $n$-$C_{10}H_{22}$ (293±2 K) by flash photolysis and kinetic spectrophotometry.

## Experimental

Experiments were carried out on a flash photolysis setup, its parameters are presented in the work published previously.[5] Quartz cells with an optical path length of 10 cm (MeCN, $C_6H_6$, and $n$-$C_5H_{12}$) or 16 cm ($n$-$C_{10}H_{22}$) and diameter of ~1 cm were used as the reactors. Solvents were purified according to known procedures,[6] and diphenyldiazomethane ($RN_2$) was synthesized and purified by a standard procedure.[7] The content of the latter in solutions was determined by spectrophotometry at $\lambda_{max}$ = 525 nm; its extinction coefficient at this wavelength was the same ($\varepsilon_{RN_2}$ = 130±5 L mol$^{-1}$ cm$^{-1}$) in all solvents used.

## Results and Discussion

***Preparation and absorption spectra of ROO.*** Benzophenone oxide was prepared by two methods.[1,2]

In the first case (the main method), air- or oxygen-saturated solutions of $RN_2$ ($10^{-5}$—$10^{-3}$ mol L$^{-1}$) were subjected to flash photolysis with the filtered light, and benzophenone oxide was obtained due to the following sequence of transformations:

$$RN_2 \xrightarrow{h\nu} {}^1R + N_2 \rightleftharpoons {}^3R \xrightarrow{O_2} ROO.$$

For photolysis of $RN_2$ in MeCN, $C_6H_6$, and $n$-$C_5H_{12}$, a UFS-2 light filter was used (transmission region is 240—400 nm); for photolysis in $n$-$C_{10}H_{22}$, an SZS-23 light filter (300—700 nm) or an aqueous solution of $K_2CrO_4$—$Na_2CO_3$ (290—340 nm) were used.[4]

Under the conditions indicated above, benzophenone oxide is formed quantitatively in a solution of MeCN.[3,4] The same conclusion can be drawn for the reaction in $C_6H_6$. In a medium of $n$-alkanes RH containing relatively weak C—H bonds, the process can be accompanied by the reaction of triplet carbene with the solvent:[8]

$${}^3R + RH \longrightarrow RH^{\cdot} + R^{\cdot},$$

due to which the yield of ROO decreases.

In the second case, only for studying absorption spectra of benzophenone oxide in MeCN, the sensitizer

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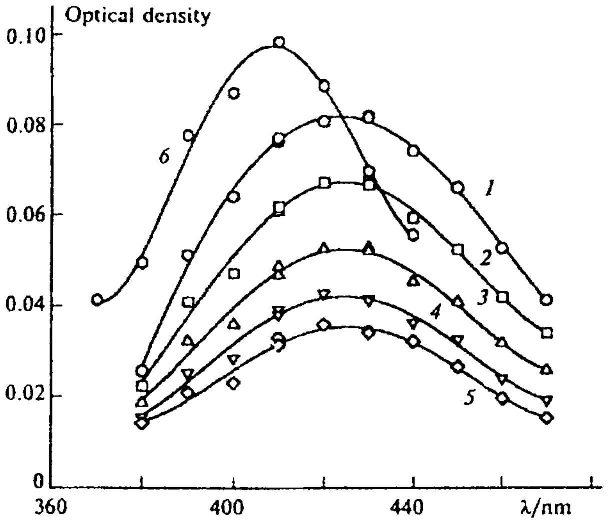


**Fig. 1.** Optical spectra of benzophenone oxide in solutions of *n*-pentane (*1—5*) and acetonitrile (*6*); immediately after pulse (*1*, *6*); 0.05 ms (*2*), 0.1 ms (*3*), 0.15 ms (*4*), and 0.2 ms (*5*) after pulse.

methylene blue (MB) was used for the generation of ROO:

$$\mathrm{MB} \xrightarrow{h\nu} \mathrm{MB}^{\bullet} \xrightarrow{O_2} {}^1O_2 \xrightarrow{RN_2} \mathrm{ROO} + N_2.$$

Flash photolysis of the $RN_2$—MB—$O_2$—MeCN system was performed by light with $\lambda > 560$ nm (the OS-14 light filter) at the initial concentrations $[RN_2]_0 \approx 1 \cdot 10^{-4}$ and $[MB]_0 = 5 \cdot 10^{-7}$ mol $L^{-1}$.

In all cases, to prevent the photochemical decomposition of $RN_2$, the intensity of the probing beam was weakened by the SS-15 light filter, which absorbs in the region of 300—520 nm.

The absorption spectra of intermediates formed due to flash photolysis of the $RN_2$—$O_2$—MeCN and $RN_2$—MB—$O_2$—MeCN systems are almost identical and characterized by $\lambda_{max}$ = 410 nm (Fig. 1), which indicates unambiguously the formation of benzophenone oxide in both cases.[3,4]

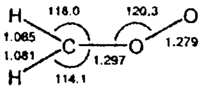
In solutions of benzene, *n*-decane, and *n*-pentane, the maxima of the absorption band of benzophenone oxide $\lambda_{max}$(ROO) are 415, 420, and 425 nm, respectively. For all solvents, the position of the maximum and shape of the absorption spectrum remain unchanged in time (the change in the absorption spectrum in time for the reaction in *n*-pentane is presented in Fig. 1 for comparison). This indicates that under the conditions of our experiments, the signal observed is related to the single intermediate, benzophenone oxide.

The shift of $\lambda_{max}$(ROO) to the short-wave region on going from nonpolar alkanes to polar MeCN can be related to the more efficient solvation of the ground state of carbonyl oxide as compared to that of the electron-excited state. To verify this assumption for $H_2COO$, we calculated the dipole moments of the ground and excited states of carbonyl oxide.

The quantum-chemical *ab initio* calculations were performed in the 6-31G(d) basis set in terms of the Meller—Plesset second-order perturbation theory and by the method of generalized valence bonds (GVB) using the GAMESS program[9] adapted for an IBM PC Pentium. Polarization functions of the d-type 0.72 for the C atom and 1.28 for the O atom were used.

The ground state ($S_0$) was calculated with complete optimization of geometric parameters. The equilibrium geometry of $H_2COO$ was determined in the MP2/6-31G(d) basis set, which described correctly the structure and properties of COx.[10] The excited states ($T_1$ and $S_1$) were calculated for the fixed geometry by the GVB/6-31G(d) method in the vertical transition approximation.

The results of the calculations are presented below:



| | $E_{tot}$/au | μ/D |
|---|---|---|
| $S_0$ | −189.05381 | 5.35 |
| $T_1$ | −188.53947 | 1.78 |
| $S_1$ | −188.53188 | 1.80 |

The excited states have pronounced biradical properties, and the values of their dipole moments are characteristic of peroxy radicals.[11] The ground state is considerably more polar and, hence, it can be solvated considerably more efficiently. As a result, the energy of the ground state decreases, which leads to an increase in the energy of the π—π*-transition and a shift of the absorption band in polar solvents to the short-wave spectral range, which is observed in experiments.

The calculated dipole moment of the ground state of $H_2COO$ agrees satisfactorily with the value $\mu$ = 4.0 D, which was experimentally determined for benzophenone oxide.[12]

***Decay kinetics of ROO.*** The benzophenone oxide formed reacts as follows:[3,4,13]

$$\mathrm{ROO} + \mathrm{RN_2} \longrightarrow 2\ \mathrm{R{=}O} + N_2, \qquad (1)$$

$$\mathrm{ROO} + \mathrm{ROO} \longrightarrow 2\ \mathrm{R{=}O} + O_2. \qquad (2)$$

The consumption rate (*W*) of ROO is given by the expression

$$-d[\mathrm{ROO}]/dt = k_1[\mathrm{RN_2}][\mathrm{ROO}] + 2k_2[\mathrm{ROO}]^2 \qquad (3)$$

or, going to optical density values (*A*),

$$W = -dA/dt = k_1[\mathrm{RN_2}] \cdot A + 2k_2/(\varepsilon_{\mathrm{ROO}} \cdot l) \cdot A^2. \qquad (4)$$

In solutions of $n$-$C_5H_{12}$ and $n$-$C_{10}H_{22}$, the kinetic curves of changes in the optical density in the maximum of the absorption spectra of ROO are linearized in coordinates of the second-order equation (1/*A* =

$1/A_0 + k_{exp}t$) and make it possible to determine the effective rate constants ($k_{exp}$).

In the studied range of reagent concentrations, the empirical constant $k_{exp}$ is independent of $[RN_2]_0$, *i.e.*, reaction (1) can be neglected. The $2k_2/\varepsilon_{ROO}$ value was determined from the experimental data.

However, when the process occurs in MeCN or $C_6H_6$, reaction (1) should be taken into account by the equation

$$W_0/A_0 \cdot [RN_2]_0 = k_1 + 2k_2/(\varepsilon_{ROO} \cdot l) \cdot A_0/[RN_2]_0, \quad (5)$$

which follows from expression (3). The dependences of the initial rates $W_0 = (-dA/dt)_{t=0}$ on $[RN_2]_0$ in benzene and acetonitrile solutions are presented in Table 1. It was established by the analysis that for $C_6H_6$ and acetonitrile the following correlations are fulfilled with the correlation coefficients 0.991 and 0.995, respectively:

$$W_0/A_0 \cdot [RN_2]_0 = (4\pm19) \cdot 10^5 + (3.86\pm0.37) \cdot 10^3(A_0/[RN_2]_0), \quad (6)$$

$$W_0/A_0 \cdot [RN_2]_0 = (2.4\pm2.0) \cdot 10^5 + (9.36\pm0.50) \cdot 10^2(A_0/[RN_2]_0). \quad (7)$$

Thus, the $2k_2/(\varepsilon_{ROO} \cdot l)$ values in solutions of $C_6H_6$ and MeCN were determined. The results of the calculation of the parameter $2k_2/\varepsilon_{ROO}$ for all solvents studied are presented in Table 2.

In acetonitrile $k_1 = (2.4\pm2.0) \cdot 10^5$ L mol$^{-1}$ s$^{-1}$, which agrees well with the data presented previously.[4] In benzene the rate constant value $k_1 \approx (4\pm19) \cdot 10^5$ L mol$^{-1}$ s$^{-1}$ should be considered only as an estimate; the high error of determination of this rate constant is related to the insignificant contribution of reaction (1) to the overall process.

**Table 1.** Dependence of $W_0$ on $[RN_2]_0$ ($l$ = 10 cm)

| $[RN_2]_0 \cdot 10^4$ /mol L$^{-1}$ | $A_0$ | $W_0 \cdot 10^{-2}$ /s$^{-1}$ | $[RN_2]_0 \cdot 10^4$ /mol L$^{-1}$ | $A_0$ | $W_0 \cdot 10^{-2}$ /s$^{-1}$ |
|---|---|---|---|---|---|
| | | In $C_6H_6$ solution | | | |
| 0.60 | 0.417 | 7.26 | 1.70 | 0.743 | 20.70 |
| 1.00 | 0.515 | 9.82 | 1.70 | 0.811 | 29.40 |
| 1.00 | 0.533 | 11.70 | 5.00 | 0.433 | 8.77 |
| 1.00 | 0.600 | 12.60 | 10.00 | 0.380 | 6.48 |
| 1.00 | 0.608 | 13.40 | 50.00 | 0.198 | 2.39 |
| 1.70 | 0.576 | 14.30 | | | |
| | | In MeCN solution | | | |
| 0.40 | 0.444 | 1.990 | 3.87 | 0.353 | 1.440 |
| 0.53 | 0.522 | 2.420 | 8.40 | 0.081 | 0.152 |
| 0.65 | 0.104 | 0.136 | 8.40 | 0.086 | 0.158 |
| 0.69 | 0.540 | 2.880 | 8.40 | 0.335 | 1.320 |
| 0.89 | 0.372 | 1.260 | 8.40 | 0.347 | 1.260 |
| 0.94 | 0.102 | 0.189 | 10.50 | 0.084 | 0.178 |
| 1.00 | 0.105 | 0.183 | 10.50 | 0.092 | 0.200 |
| 3.87 | 0.075 | 0.147 | 10.50 | 0.338 | 1.190 |
| 3.87 | 0.081 | 0.174 | 10.50 | 0.348 | 1.390 |
| 3.87 | 0.330 | 1.230 | | | |

**Table 2.** Dependences of optical properties of ROO ($\varepsilon$/L mol$^{-1}$ cm$^{-1}$) and rate constant ($2k_2$/L mol$^{-1}$ s$^{-1}$) on the nature of the solvent

| Solvent | $\lambda_{max}$ /nm | $\varepsilon_{ROO}$ | $(2k_2/\varepsilon_{ROO} \cdot l) \cdot 10^{-4}$ /s$^{-1}$ | $2k_2 \cdot 10^{-8}$ |
|---|---|---|---|---|
| $n$-$C_5H_{12}$ | 425 | 1810±270 | 10.5±1.1 | 20.0[a] |
| $n$-$C_{10}H_{22}$ | 420 | 1860±30 | 4.8±0.6[b] | 15.0[a] |
| $C_6H_6$ | 415 | 2010±240 | 0.39±0.04 | 0.74[a] |
| MeCN | 410 | 1500±60 | 0.094±0.005 | 0.18[a] |
| MeCN | 410[c] | 1850±450[c] | — | 0.6[c] |
| MeCN | 410[d] | — | 0.144±0.001[d] | 0.27[d] |

[a] Calculated using the average (for all solvents) value $\varepsilon_{ROO} = (1.9\pm0.1) \cdot 10^3$ L mol$^{-1}$ s$^{-1}$. [b] $l$ = 16 cm. [c] According to data in Ref. 3 at 300 K. [d] According to data in Ref. 4.

The following stoichiometric equation was used to determine the extinction coefficient of benzophenone oxide:

$$[ROO]_0 = A_0/(\varepsilon_{ROO} \cdot l) = [RN_2]_0 - [RN_2] = \Delta[RN_2]. \quad (8)$$

Since after the irradiation of the reaction mixture with one pulse the $\Delta[RN_2]$ value is low, the solution was subjected to several (usually ~10) pulses. Then the difference $\Delta[RN_2]$ and the corresponding sum of the initial values of the optical density ($\Sigma A_0$) of carbonyl oxide were determined, and $\varepsilon_{ROO}$ was calculated:

$$\varepsilon_{ROO} = \Sigma A_0/(\Delta[RN_2] \cdot l).$$

For selection of experimental conditions, it should be taken into account that Eq. (8) is valid when two conditions are simultaneously fulfilled: (1) the only channel of consumption of $RN_2$ is its decay under the light pulse action and (2) the yield of ROO per consumed $RN_2$ is quantitative. Thus, it is difficult to determine $\varepsilon_{ROO}$ in $C_6H_6$ and MeCN because of the side reaction of consumption of $RN_2$ (1), and in hydrocarbons it is difficult due to the reaction of $^3R$ with RH resulting in a decrease in the yield of ROO.

It follows from Eqs. (6) and (7) that the process should be performed at $A_0/[RN_2]_0 \gg 1 \cdot 10^2$ L mol$^{-1}$ ($C_6H_6$) or $A_0[RN_2]_0 \gg 3 \cdot 10^2$ L mol$^{-1}$ (MeCN) to decrease to the maximum extent the contribution of reaction (1) in solutions of $C_6H_6$ and MeCN; taking into account these requirements, we carried out experiments at $A_0/[RN_2]_0 \approx (2-3) \cdot 10^3$ ($C_6H_6$) and $\sim 3 \cdot 10^3$ L mol$^{-1}$ (MeCN).

For experiments in the RH medium, we established that the $\varepsilon_{ROO}$ values in air and oxygen are almost equivalent, the same concerns the values of the kinetic parameters $2k_2/\varepsilon_{ROO}$. Therefore, under our conditions, the reaction of $^3R$ with RH can be neglected.

The $\varepsilon_{ROO}$ values obtained in this work and in Ref. 3 are presented in Table 2, which shows that in terms of experimental error, the $\varepsilon_{ROO}$ values almost coincide, *i.e.*, they are weakly affected by the solvent nature. The $\varepsilon_{ROO}$ value determined for the reaction in MeCN is underestimated by approximately 10% due to the comparatively great contribution of reaction (1) to the overall consumption of ROO. Taking this into account, we obtain the average value $\varepsilon_{ROO} = (1.9\pm0.1)\cdot10^3$ L mol$^{-1}$ cm$^{-1}$.

The rate constants $2k_2$ calculated from the average value of the extinction coefficient are presented in Table 2. It is noteworthy that the dependence of the recombination rate constant on the solvent nature is very strong: the rate constants in *n*-pentane and acetonitrile differ by two orders of magnitude. It is likely that the solvation of ROO favors a more efficient charge separation in the molecule and, hence, stabilization of the zwitterionic state. In nonpolar hydrocarbon solvents, benzophenone oxide has a more pronounced biradical character and reacts with the high rate constant characteristic of diffusion-controlled homorecombination of alkyl radicals[14] and cross recombination of alkyl and peroxide radicals.[15]

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