Absolute rate constants of decay of aryl-substituted carbonyl oxides

A. M. Nazarov,[a]* *E. M. Chainikova,*[a] *I. A. Kalinichenko,*[a] *S. L. Khursan,*[b]
R. L. Safiullin,[a] *and V. D. Komissarov*[b]

[a] *Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences,*
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 35 6066. E-mail: root@chemorg.ufanet.ru
[b] *Bashkortostan State University, 32 ul. Frunze, 450074 Ufa, Russian Federation.*
Tel.: +7 (347 2) 23 6727

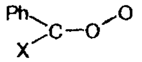
The decay kinetics of a series of carbonyl oxides (CbO) — 4-methylbenzophenone oxide, 2,5-dimethylbenzophenone oxide, 4-chlorobenzophenone oxide, 2-bromobenzophenone oxide, and acetophenone oxide — were studied by the pulse photolysis technique in acetonitrile, benzene, *n*-decane, and *n*-pentane. The absorption spectra were studied, and the absorption coefficients and absolute rate constants of CbO decay were determined. The absorption maxima observed in the spectra of carbonyl oxides range within 405±25 nm. The decay rate constant was found to depend on both the CbO structure and the medium.

Key words: kinetics, pulse photolysis, carbonyl oxides.

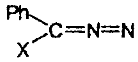
Carbonyl oxides (CbO), being key intermediates in ozonolysis of olefins,[1] have been of interest for researchers for several decades. Benzophenone oxide (**1a**), in particular, its spectral properties, recombination kinetics, and the effect of the medium on it, has been studied in most detail.[2–7]

The decay kinetics of several CbOs have been analyzed[5]; however, data on absolute values of the rate constants are lacking, because absorption coefficients of these CbO are unknown.

In the present work, we used the pulse photolysis and high-performance spectrophotometry (PP-HPS) techniques to determine the absorption coefficients and decay rate constants of 4-methylbenzophenone oxide (**1b**), 2,5-dimethylbenzophenone oxide (**1c**), 4-chlorobenzophenone oxide (**1d**), 2-bromobenzophenone oxide (**1e**), and acetophenone oxide (**1f**) in acetonitrile, benzene, *n*-decane, and *n*-pentane.



1a—f



2a—f

X = Ph (**a**); 4-MePh (**b**); 2,5-Me$_2$Ph (**c**); 4-ClPh (**d**); 2-BrPh (**e**); Me (**f**)

Experimental

Solvents and *n*-butyl alcohol were purified by the known procedures.[8] Diazo compounds (RN$_2$, structures **2a—f**) were synthesized and purified as described previously.[9] The content of RN$_2$ in a solution was measured spectrophotometrically. Absorption coefficients of RN$_2$ were determined by back titration. An excess of benzoic acid was added to the solution, and the unreacted acid was titrated with sodium hydroxide. The absorption maxima and the corresponding absorption coefficients of RN$_2$ in the solvents used are presented in Table 1.

Kinetic studies were carried out on a PP-HPS installation whose structure has been described previously.[10] A quartz cell with an optical length of 10 cm and an inner diameter of ~1 cm was used as the reactor. Photolysis of RN$_2$ was performed by a filtered light (a UFS-2 light filter, transmission region 270—380 nm). To avoid the decomposition of RN$_2$ by

Table 1. Optical properties of diazo compounds Ph(X)CN$_2$

X	Solvent	λ_{max} /nm	ε* /L mol^{-1} cm^{-1}
4-MePh	MeCN	525	82
	C_6H_6	525	88
	$C_{10}H_{22}$	525	84
4-ClPh	MeCN	520	119
	C_6H_6	525	128
	i-C_8H_8	532	112
2-BrPh	MeCN	510	52
	C_6H_6	510	58
	$C_{10}H_{22}$	510	67
Me	MeCN	506	37
	C_6H_6	510	35
	$C_{10}H_{22}$	515	35
2,5-Me$_2$Ph	MeCN	510	43
	C_6H_6	520	48
	$C_{10}H_{22}$	525	44

* The error of determination of ε is at most 10%.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 677—681, April, 1999.

1066-5285/99/4804-0672 $22.00

the probing beam, the absorption region of diazo compounds was cut off by an SS-15 light filter (transmission region 300—520 nm).

Results and Discussion

Pulse photolysis of solutions of RN_2 saturated with air oxygen results in the formation of intermediate species absorbing in the 360—480 nm wavelength region. No signals were observed in this range under similar conditions but in the absence of RN_2. In all cases, the shape of the spectra remains unchanged with time (Fig. 1), *i.e.*, only one species, the corresponding CbO, absorbs the light. The recorded absorption maxima undergo the influence of the nature of CbO and solvent, being within the range of 405±25 nm (Table 2). On going from nonpolar solvents to polar acetonitrile, a hypsochromic shift of λ_{max} is observed for all CbO except for **1c**. As shown[7] for **1a**, this phenomenon is explained by the more efficient solvation of the ground state of CbO than that of the electron-excited state due to the higher polarity of the ground state of CbO.

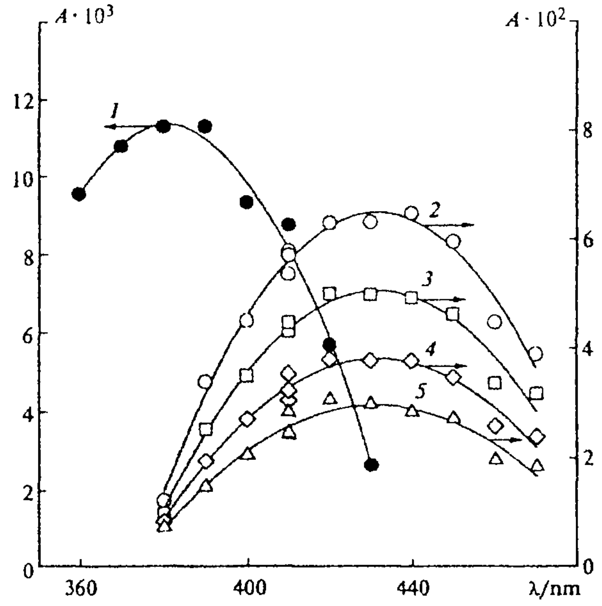


Fig. 1. Optical spectra of solutions of carbonyl oxides **1f** in MeCN (*1*) and **1d** in *n*-pentane (*2*—*5*) immediately after the end of the pulse (*1*, *2*) and 0.1 (*3*), 0.15 (*4*), and 0.2 ms (*5*) after the pulse.

Under the conditions of pulse photolysis, the formation and decay of CbO includes the following main stages[7]:

$$RN_2 \longrightarrow {}^1R\colon + N_2, \qquad (1)$$

$${}^1R\colon \rightleftarrows {}^3R\colon, \qquad (2)$$

$${}^1R\colon + RN_2 \longrightarrow R{-}N{=}N{-}R, \qquad (3)$$

$${}^3R\colon + O_2 \longrightarrow ROO, \qquad (4)$$

$$ROO + RN_2 \longrightarrow 2\,RO + N_2, \qquad (5)$$

$$ROO + ROO \longrightarrow 2\,RO + O_2, \qquad (6)$$

$$ROO + S \longrightarrow \text{Products}, \qquad (7)$$

where S is a solvent.

The time dependence of the optical absorption decay of CbO corresponds satisfactorily to second-order kinetic in the whole range of the RN_2 concentrations. However, for the concentrations of diazo compounds higher than 10^{-3} mol L^{-1}, the effective rate constant depends on the initial concentration of diazo compound $[RN_2]_0$. This indicates a noticeable contribution of the

Table 2. Spectral parameters and recombination rate constants of Ph(X)COO

X	Sol- vent	λ_{max} /nm	ε_{ROO} /L mol cm^{-1}	$2k_6$ /L mol^{-1} s^{-1}	$2k_6/\varepsilon_{ROO}$ /cm s^{-1}
Ph*	MeCN	410	1900±100	$1.8 \cdot 10^7$	$9.4 \cdot 10^3$
	C_6H_6	415		$7.4 \cdot 10^7$	$3.9 \cdot 10^4$
	C_5H_{12}	425		$2.0 \cdot 10^9$	$1.05 \cdot 10^6$
	$C_{10}H_{22}$	420		$1.5 \cdot 10^9$	$7.9 \cdot 10^5$
4-MePh	MeCN	410		$(2.9\pm0.2) \cdot 10^7$	$(3.1\pm0.1) \cdot 10^4$
	C_6H_6	420	950±100	$(4.5\pm0.9) \cdot 10^7$	$(4.8\pm0.4) \cdot 10^4$
	$C_{10}H_{22}$	430		$(2.5\pm0.3) \cdot 10^8$	$(2.7\pm0.1) \cdot 10^5$
4-ClPh	MeCN	410		$(3.5\pm0.2) \cdot 10^7$	$(1.8\pm0.1) \cdot 10^4$
	C_6H_6	430	1880±430	$(1.4\pm0.2) \cdot 10^8$	$(7.6\pm0.1) \cdot 10^4$
	C_5H_{12}	430		$(2.6\pm0.3) \cdot 10^9$	$(1.6\pm0.1) \cdot 10^6$
2-BrPh	MeCN	400		$(6.4\pm0.7) \cdot 10^5$	$(4.6\pm0.5) \cdot 10^2$
	C_6H_6	410	1370±140	$(2.0\pm0.3) \cdot 10^6$	$(1.5\pm0.2) \cdot 10^3$
	$C_{10}H_{22}$	410		$(2.3\pm0.2) \cdot 10^7$	$(1.7\pm0.1) \cdot 10^4$
Me	MeCN	385		$(2.9\pm0.2) \cdot 10^9$	$(3.1\pm0.2) \cdot 10^6$
	C_6H_6	400	920±80	$(1.6\pm0.4) \cdot 10^9$	$(1.8\pm0.4) \cdot 10^6$
	$C_{10}H_{22}$	410		$(2.8\pm0.2) \cdot 10^9$	$(3.1\pm0.2) \cdot 10^6$
2,5-Me_2Ph	MeCN	410			$(2.2\pm0.3) \cdot 10^5$
	$C_{10}H_{22}$	410			$(9.0\pm0.9) \cdot 10^4$

* Published data.[7]

monomolecular consumption of CbO (reactions (5) and (7), and the latter, most likely, has a minimum effect in the case of the solvents used in our work). To determine the ratio of the two channels of decay of the CbO studied, we investigated the dependence of the reaction rate constant on the initial concentration of the reagents. If reaction (7) is neglected, the rate of CbO consumption is the following:

$$-d[ROO]_0/dt = k_5 \cdot [ROO]_0[RN_2] + 2k_6 \cdot [ROO]_0^2. \quad (I)$$

On going to the optical absorption values, we can easily obtain

$$W_0/A_0[RN_2] = k_5 + (2k_6/\varepsilon_{ROO} \cdot l) \cdot A_0/[RN_2]. \quad (II)$$

Here $W_0 = -dA_0/dt$, ε_{ROO} is the absorption coefficient of CbO, and l is the optical path length (10 cm).

Dependence (II) was verified by the variation of the initial concentrations of the starting diazo compound and CbO (the light pulse energy was changed for this purpose). Equation (II), shown for compounds **1d** and **1e** in Fig. 2, is well fulfilled for all CbO studied. This justifies the neglect of reaction (7) and makes it possible to determine the conditions under which reaction (6) is virtually the only channel of CbO consumption:

$$\frac{W_5}{W_6} = \frac{k_5 \cdot [RN_2]}{2k_6 \cdot [ROO]_0} = \frac{a \cdot [RN_2]}{b \cdot A_0} \le 0.1. \quad (III)$$

Coefficients a and b are the interception and the angular coefficient of Eq. (II), respectively. Taking into account that the typical value of the initial optical absorption is 0.2 under conditions of our experiments, inequality (III) is fulfilled at concentrations $[RN_2]$ lower than $3 \cdot 10^{-4}$ mol L^{-1} for all the compounds studied. In fact, under these conditions, the kinetic curves of changing the optical absorption of CbO are well linearized in coordinates of the second-order equation, and the slope is independent of the initial concentration of the diazo compound (the typical range $(0.3-3) \cdot 10^{-4}$ mol L^{-1}):

$$1/A = 1/A_0 + (2k_6/\varepsilon_{ROO} \cdot l) \cdot t, \quad (IV)$$

which indicates an insignificant effect of monomolecular channels on the reaction rates.

The absorption coefficients were determined by recording the overall initial optical absorption of CbO per several (usually 10) light pulses and the corresponding change in the concentration of RN_2:

$$\Sigma[ROO]_0 = \Sigma A_0/\varepsilon_{ROO} \cdot l = \Delta[RN_2], \quad (V)$$

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

The equations presented are valid when the photodecomposition of RN_2 is the only channel of its consumption, and the RN_2 decomposed is quantitatively transformed into CbO. Therefore, the experiments were carried out under conditions that allow the contribution of reaction (5) to be reduced to a minimum: benzene as the solvent, $[RN_2] < 3 \cdot 10^{-4}$ mol L^{-1}.

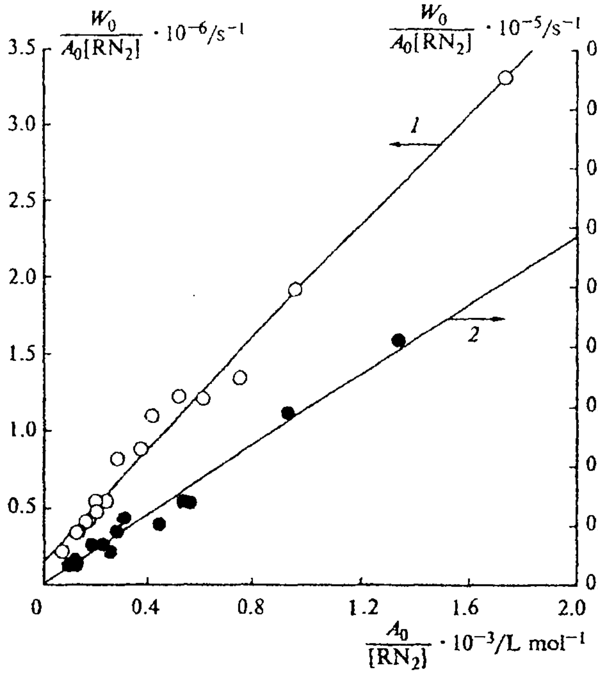


Fig. 2. Dependences of the rates of the optical absorption decay detected under pulse photolysis conditions (295 K, MeCN) on the concentration of diazo compounds **2d** and **2e** and initial optical absorption of carbonyl oxides **1d** (*1*) and **1e** (*2*).

Reaction (3) is one more possible channel of the consumption of RN_2. A change in the concentration of diazo compound in a wide range has a complex effect on the optical absorption observed due to superposition of several factors. As $[RN_2]$ increases, the number of active species formed by light pulses increases, which results in an increase in the optical absorption A. At the same time, due to reactions (3) and (5), the optical absorption decreases. Finally, at high $[RN_2]$, the effect of an "internal filter" is observed, which also results in a decrease in the A value. Therefore, to estimate the contribution of reaction (3), a trap of singlet carbenes (n-butyl alcohol)[11] was added to the system:

$$^1R{:} + R'OH \longrightarrow RHOR'. \quad (8)$$

According to the kinetic scheme, the yields of the products of transformation of triplet (reaction (4), CbO) and singlet (reaction (8), ether) carbenes are related by the correlation

$$\frac{[RHOR']}{[ROO]_0} = \frac{A_0 - A}{A_0} = \frac{k^{TS}k_8[R'OH]}{k^{ST}k_4[O_2]}, \quad (VII)$$

where k^{TS} and k^{ST} are the rate constants of intersystem crossing of carbene *via* reaction (2); k_4 and k_8 are the

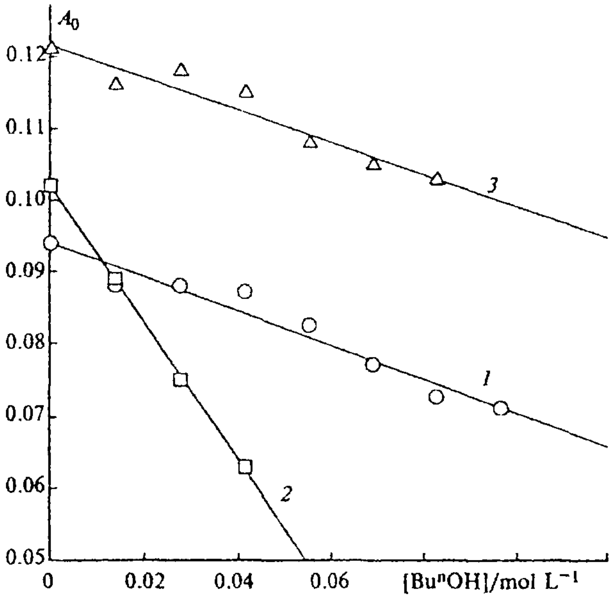
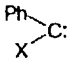


Fig. 3. Influence of additives of *n*-butyl alcohol on the initial optical absorption of carbonyl oxides **1a** (*1*), **1b** (*2*), and **1d** (*3*) (295 K, MeCN).

rate constants of reactions (4) and (8). It follows from the last equation that alcohol additives should result in a decrease in the initial optical absorption of CbO observed under pulse photolysis conditions. This dependence, shown in Fig. 3 for compounds **1a**, **1b**, and **1d**, is well fulfilled for all carbenes **3a—f** studied.



3a—f

X = Ph (**a**); 4-MePh (**b**);
2,5-Me$_2$Ph (**c**); 4-ClPh (**d**);
2-BrPh (**e**); Me (**f**)

The ratio of the specific rates of the reaction *via* the singlet and triplet routes was estimated from the angular coefficient of this dependence

$$\frac{k^{TS}k_8}{k^{ST}k_4} = \frac{A_0 - A}{A_0} \cdot \frac{[O_2]}{[ROH]} = (2—9) \cdot 10^{-3}. \qquad \text{(VIII)}$$

The rate constants of the reactions of singlet carbenes with alcohols are very high: k_8 = (1.5—6) · 10^9 L mol^{-1} s^{-1} (see Ref. 11). In this connection, taking into account the diffusion limit of the bimolecular rate constant, we can suggest that the rate constant of reaction (3) exceeds k_8 by at most an order of magnitude. At the same time, under our conditions, the concentration of RN$_2$ was (0.3—3) · 10^{-4} mol L^{-1}; therefore, taking into account Eq. (VIII), the ratio of the rates of the stages under question is the following:

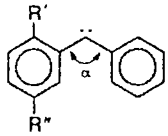
$$\frac{W_3}{W_4} = \frac{k^{TS}k_3[RN_2]}{k^{ST}k_4[O_2]} \le (2—9) \cdot 10^{-2} \cdot \frac{(0.3—3) \cdot 10^{-4}}{10^{-3}} \approx$$
$$\approx (0.6—27) \cdot 10^{-3}.$$

Thus, the interaction of singlet carbene with the starting diazo compound under our conditions can be neglected (the maximum contribution <3%). Our results agree well with the published data. It is known[12] that the ground state of carbenes (precursors of CbO studied in this work) is triplet. Diphenylcarbene **3a** formed during photolysis of compound **2a** is rapidly transformed from singlet into triplet (k^{ST} is 3.23 · 10^9 s^{-1} in acetonitrile and 1.05 · 10^{10} s^{-1} in isooctane at 298 K).[11] Under these conditions, the rate constant of the triplet—singlet transition is equal to (0.3—2.0) · 10^7 s^{-1}. Therefore, the quasi-equilibrium ^{1}R: $\rightleftarrows$ ^{3}R: characterized by the constant K^{ST} ≈ 300 and a fraction of singlet carbene <1% is observed in the nanosecond range. The triplet state of carbenes **3a**, **3b**, **3d**, and **3f** was established by the ESR method and characterized[12] by the zero field parameters *D* and *E*. The *D* and *E* values are virtually independent of the nature of the substituent in the *para*-position of one of the phenyl rings. This indicates that for compounds **3b** and **3d** (as well as for **3a**), the triplet state is predominant. The multiplicity of carbenes **3c** and **3e** is unknown; however, substituents in the *ortho*-position have been observed[13] to kinetically and thermodynamically stabilize triplet diarylcarbenes. The kinetic stabilization is the steric hindering of the reaction center of carbene by *ortho*-substituents. In addition, in these carbenes, the central bond angle increases, which destabilizes the singlet state to a higher extent. The change in the triplet energy with an increase in the central angle is insignificant, which results in an increase in the Gibbs free energy ΔG^{ST} and in the thermodynamic stabilization of the triplet state. Finally, the ground triplet state of all carbenes studied is confirmed by the results of calculations by the quantum-chemical semiempirical PM3-CI method.

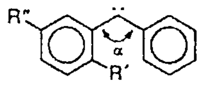
In an acetonitrile solution, the change in enthalpy on going from the singlet to triplet state of diphenyl carbene is equal[14] to −11 kJ mol^{-1}. A decrease in the solvent polarity results[14] in an increase in the difference in energies: in isooctane $\Delta H^{\circ} = \Delta E = E_T - E_S = -17$ kJ mol^{-1}. The ΔH° value calculated by the PM3-CI method as the difference between the enthalpies of formation of the corresponding states (−57.7 kJ mol^{-1}) differs noticeably from the experimental values. However, taking into account a strong dependence of the degree of singlet—triplet conversion on the solvent,[15] we can expect that the divergence of the calculated and experimental data is lower for the gas phase. In addition, the relative change in enthalpy is insignificant in the series of carbenes studied (Table 3). The geometric parameters of both singlet and triplet carbenes (except for sterically hindered isomers of **3c** and **3e**, see above) also remain almost unchanged. This agrees with a weak effect of the carbene structure on the *E*/*D* ratio (see Table 3), which is a measure of the opening of the central α angle in carbene. Thus, the semiempirical calculations indicate that the ground state of all the carbenes studied is triplet.

The estimations performed show that the use of Eqs. (V) and (VI) is quite valid for the determination of

Table 3. Results of quantum-chemical PM3-CI calculations of singlet (S) and triplet (T) carbenes Ph(X)C in conformations



(I) and



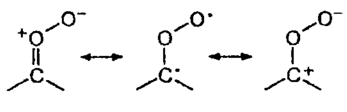
(II)

X	E/D [12]	ΔH_f°/kJ mol^{-1}			α/deg	
		T	S	T−S	T	S
Ph	0.0474	490.4	548.1	−57.7	147.1	125.3
4-MePh	0.0462	451.0	508.4	−57.4	147.1	124.7
2,5-Me_2Ph[a]		415.9	472.4	−56.5	147.5	126.2
4-ClPh	0.0482	462.8	520.5	−57.7	147.1	125.2
2-BrPh[b]		530.0	586.6	−56.6	146.8	125.0
Me	0.0547	356.9	406.3	−49.4	149.9	121.1
2,5-Me_2Ph[c]		422.6	474.0	−51.4	160.5	122.1
2-BrPh[d]		538.9	592.9	−54.0	165.5	121.2

[a] Conformation I, R′ = R″ = Me.
[b] Conformation II, R′ = R″ = Me.
[c] Conformation I, R′ = Br, R″ = H.
[d] Conformation II, R′ = Br, R″ = H.

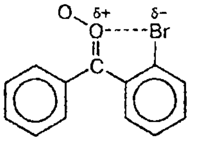
absorption coefficients of the CbOs studied. The ε_{ROO} values thus found are presented in Table 2. It has previously been shown[7] that the solvent nature has no noticeable effect on the ε_{ROO} value. Therefore, the absorption coefficients of carbonyl oxides **1b**, **1d**—**f** measured in benzene were used for calculation of the rate constants of reaction (6) in other solvents (see Table 2).

A substantial dependence of the decay rate constant on the medium is observed for carbonyl oxides **1b**, **1d**, and **1e**. On going from polar acetonitrile to nonpolar *n*-decane or *n*-pentane, $2k_6$ increases by 10—100 times. Such a strong effect of the solvent agrees with the published data,[6,7] according to which a similar dependence is observed for **1a**. We believe that the polar solvent favors a more efficient charge separation and, as a consequence, the stabilization of a less reactive zwitterionic resonance form of CbO. In nonpolar solvents, CbOs exist predominantly as biradicals, whose recombination occurs with high, close to diffusional, rate constants.



As can be seen in Table 2, the presence of such substituents as methyl and chlorine in the *para*-position of one of the benzene rings has no substantial effect on the rate constant of recombination of diphenylcarbonyl oxides: the $2k_6$ values for **1b** and **1d** are close to those for **1a** in all solvents used (except for $2k_6$ for **1b** in decane, which an order of magnitude lower than the corresponding values for **1a** and **1d**).

The recombination rate constants for **1e** are remarkably low: they are almost 100 times lower than the corresponding constants for **1a**. Presently, the nature of this effect is not quite clear. It can be assumed as a working hypothesis that such a sharp decrease in the reactivity of **1e** is due to either the screening effect of the Br atom, which prevents the attack of the C atom of the COO group by another CbO molecule, or the stabilization of the zwitterionic state of the carbonyl oxide group due to the polar interaction of the Br atom in the *ortho*-position.



The conjugation of aromatic substituents with the 4π-electron system of the carbonyl oxide group also stabilizes the zwitterionic state of CbO. Therefore, the replacement of the phenyl group by the methyl group in molecule **1f** results in the shift of the equilibrium toward the biradical component. As a consequence, in the case of **1f**, the $2k_6$ value is independent of the nature of the medium and is high (~10^9 L mol^{-1} s^{-1}) in all solvents.

References

1. R. Criegee and G. Wenner, *Chem. Ber.*, 1949, **564**, 9.
2. N. H. Werstiuk, H. L. Casal, and J. C. Scaiano, *Can. J. Chem.*, 1984, **62**, 2391.
3. H. L. Casal, S. E. Sugamori, and J. C. Scaiano, *J. Am. Chem. Soc.*, 1984, **106**, 7623.
4. M. Girard and D. Griller, *J. Phys. Chem.*, 1986, **90**, 6801.
5. J. C. Scaiano, W. G. McGimpsey, and H. L. Casal, *J. Org. Chem.*, 1989, **54**, 1612.
6. A. M. Nazarov, E. M. Chainikova, R. L. Safiullin, S. L. Khursan, and V. D. Komissarov, *React. Kinet. Catal. Lett.*, 1997, **61**, 173.
7. A. M. Nazarov, E. M. Chainikova, S. L. Khursan, A. B. Ryzhkov, R. L. Safiullin, and V. D. Komissarov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1329 [*Russ. Chem. Bull.*, 1998, **47**, 1292 (Engl. Transl.)].
8. A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, *Technics of Organic Chemistry. 7. Organic Solvents. Physical Properties and Methods of Purification*, Interscience, New York, 1955.
9. M. Regitz and F. Menz, *Chem. Ber.*, 1968, **101**, 2622.
10. L. G. Galimova, S. I. Maslennikov, and A. I. Nikolaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 2464 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1980, **29**, 1731 (Engl. Transl.)].
11. K. B. Eisenthal, N. J. Turro, E. V. Sitzmann, I. R. Gould, G. Hefferon, J. Langan, and Y. Cha, *Tetrahedron*, 1985, **41**, 1543.
12. W. Sander, G. Bucher, and S. Wierlacher, *Chem. Rev.*, 1993, **93**, 1583.
13. H. Tomioka, M. Hattori, K. Hirai, and S. Murata, *J. Am. Chem. Soc.*, 1996, **118**, 8723.
14. K. B. Eisenthal, R. A. Moss, and N. J. Turro, *Science*, 1984, **225**, 25.
15. V. Sitzman, J. Langan, and K. B. Eisenthal, *J. Am. Chem. Soc.*, 1984, **106**, 1868.

Received April 24, 1998;
in revised form September 14, 1998