Solvent effects on the absorption spectrum and recombination kinetics of diphenylcarbonyl oxide

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

[a]Bashkir State University,
32 ul. Frunze, 450074 Ufa, Russian Federation.
Tel: (347 2) 23 6727
[b]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

The absorption spectra and rate constants of diphenylcarbonyl oxide recombination in a series of solvents and their binary mixtures were determined by flash photolysis. An increase in the solvent polarity causes hypsochromic shift of the maximum in the absorption spectrum of Ph_2COO. The analysis of the solvent effect on the recombination rate constant in terms of the four-parameter Koppel—Palm equation shows that the reactivity of carbonyl oxide depends on both specific and non-specific solvations. Quantum chemical B3LYP/6-31G(d) calculations of H_2COO and PhHCOO carbonyl oxides as well as the complexes of H_2COO with acetonitrile and ethylene in different media were performed using a polarized continuum model.

Key words: carbonyl oxides, reaction kinetics, absorption spectra, solvent effect, quantum chemical calculations.

A study of the solvent effects on the reactivity and other physicochemical parameters of reactants[1] is important for elucidating the mechanisms of chemical reactions, especially in the case of ionic or highly polar reactants. Carbonyl oxides R′R″COO are highly reactive intermediates in the ozonolysis of unsaturated organic compounds and in photosensitized or thermal decomposition of diazo compounds. The delocalized three-center π–system of carbonyl oxides provides the high dipole moments and high polarizability by the molecular environment. Because of these properties the chemical behavior of carbonyl oxides depends on the solvent nature. Earlier, we reported the medium effect on the kinetics of the reaction of diphenylcarbonyl oxide Ph_2COO with sulfoxides[2] and alkenes.[3]

In this work, the kinetics of Ph_2COO recombination in different solvents (previous communication, see Ref. 4) was studied and the theoretical and experimental investigations of the medium effect on the electronic structure of carbonyl oxides was carried out.

Experimental

Solvents (acetonitrile, *n*-pentane, *n*-decane, AcOEt, benzene, chlorobenzene, and 1,4-dioxane (Russia)) were purified according to the known procedure.[5] Diphenyldiazomethane Ph_2CN_2 was synthesized and purified by a known protocol.[6]

Kinetic runs were carried out on an FP setup described in work[7]. An IFP 5000-2 lamp was the light source; the maximal pulse energy was 400 J, and ~90% of light energy was irradiated during 50 μs. A quartz cell with $l = 10$ cm and ~1 cm diameter was used as a reactor. The setup whose parameters were reported in work[7], was supplemented with a device for computer processing a pulse signal. A UFS-2 light filter (transmission range is 240—380 nm) was used for the flash photolysis of the Ph_2CN_2—solvent—O_2 (air) system. To keep Ph_2CN_2 from photochemical decay, the light intensity was weakened with an SS-15 filter (transmission range is 300—520 nm). The initial concentration $[Ph_2CN_2]_0$ was $(1.5—2) \cdot 10^{-4}$ mol dm^{-3}. The reaction kinetics was monitored by the decrease in the optical density A in the maximum of the absorption band for diphenylcarbonyl oxide.

Results and Discussion

The flash photolysis of diphenyldiazomethane in all the solvents studied produces the short-lived optical absorption in the range of wave lengths λ = 370—470 nm (Fig. 1). The photolytic decomposition of Ph_2CN_2 is a well studied process.[8—11] The photolysis under ultraviolet radiation and visible light initially produces triplet carbene Ph_2C whose reaction with O_2 is characterized by a great (likely diffusional) rate constant (Scheme 1).

Scheme 1

$$Ph_2CN_2 \xrightarrow{h\nu,\ \lambda\,=\,280—370\ \text{nm}} {}^1(Ph_2C:) + N_2,$$

$${}^1(Ph_2C:) \rightleftharpoons {}^3(Ph_2C:),$$

(K_{eq} = 321, see Ref. 12)

$${}^3(Ph_2C:) + O_2 \longrightarrow Ph_2COO$$

($k = 5 \cdot 10^9$ L mol^{-1} s^{-1}, see Ref. 8)

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 759—763, May, 2001.

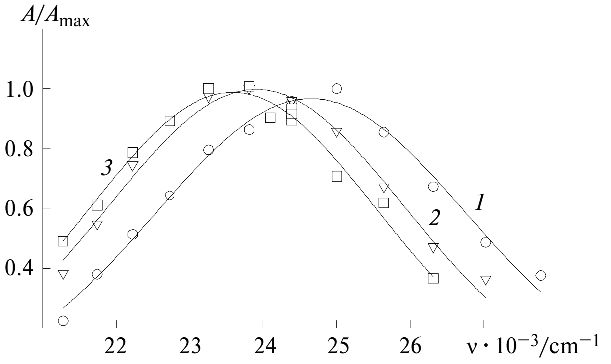
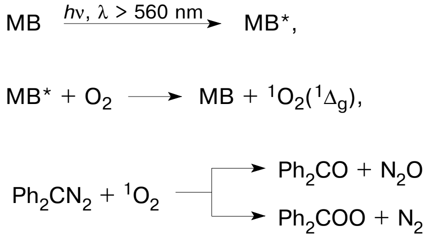


Fig. 1. Gaussian shape of the optical spectra of diphenylcarbonyl oxide at 295 K in different solvents: *1*, acetonitrile; *2*, chlorobenzene, and *3*, *n*-pentane.

The product of this reaction is diphenylcarbonyl oxide Ph_2COO, which absorbs light with λ = 370—470 nm and is further consumed through the reaction with an appropriate substrate or *via* a bimolecular reaction. Under the conditions of sensitized photolysis (Scheme 2), the interaction of singlet dioxygen ($^1\Delta_g$) with a diazo compound is a source of carbonyl oxides. For Ph_2CN_2, the efficiency of Ph_2COO formation is 60% ($CH_3CN : CH_2Cl_2$ = 2 : 3; 294 K).[13]

Scheme 2



$$MB \xrightarrow{h\nu,\ \lambda > 560\ nm} MB^*,$$

$$MB^* + O_2 \longrightarrow MB + {}^1O_2({}^1\Delta_g),$$

$$Ph_2CN_2 + {}^1O_2 \longrightarrow \begin{cases} Ph_2CO + N_2O \\ Ph_2COO + N_2 \end{cases}$$

($k = 1 \cdot 10^9$ L mol^{-1} s^{-1}, see Ref. 11).

Here MB is methylene blue, acetonitrile is the solvent.

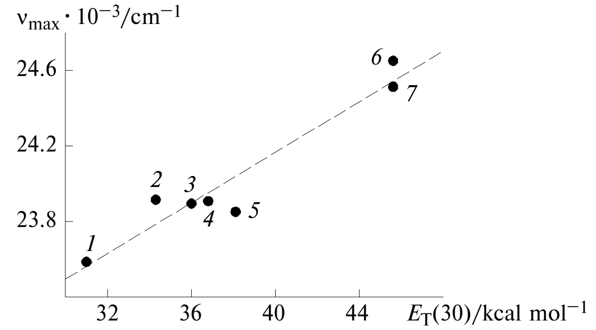


Fig. 2. Effect of solvating ability of a solvent $E_T(30)$ on the position of maximum of the absorption band for diphenylcarbonyl oxide: *1* , *n*-pentane; *2*, benzene; *3*, 1,4-dioxane; *4*, chlorobenzene; *5*, AcOEt; *6*, acetonitrile; *7*, acetonitrile with photosensitizer (methylene blue).

The signal recorded can be assigned to the Ph_2COO absorption because of coincidence of the absorption spectra and characteristic life time $\tau = 10^{-4}$—10^{-2} s.[14,15] In the absence of O_2, no optical absorption in the above spectral range was found.

The absorption spectrum for Ph_2COO (see Fig. 1) can be described by the Gaussian function and does not depend on the signal intensity. This indicates that carbonyl oxide is the single intermediate species that absorbs light in the above range. The absorption band for Ph_2COO corresponds to the allowed π—π^* transition.[16] On going from acetonitrile to *n*-pentane, the maximum of the absorption band λ_{max} shifts to the long-wave region by 20 nm (Table 1). This solvatochromic effect correlates with the solvent parameter $E_T(30)$ (Fig. 2).[1]

In the absence of active additives, the main channel of Ph_2COO consumption in the solvents under study is bimolecular decay with the formation of two molecules of benzophenone and O_2 molecule:

$$Ph_2COO + Ph_2COO \longrightarrow Ph_2CO + Ph_2CO + O_2. \quad (1)$$

On going from acetonitrile to *n*-pentane, the rate constant for this reaction (2*k*) changes from $1.8 \cdot 10^7$ to

Table 1. Maxima of absorption bands (λ_{max}), rate constants (2*k*) of diphenylcarbonyl oxide recombination in different solvents, and parameters of the Koppel—Palm equation (*Y*, *P*, *E*, *B*)[17]

Solvent	λ_{max}[a] /nm	2*k* /L mol^{-1} s^{-1}	*Y*	*P*	*E*	*B*
Acetonitrile	406	$1.8 \cdot 10^7$	0.4803	0.2119	5.2	160
Acetonitrile (MB)[b]	408					
Benzene	418	$1.0 \cdot 10^8$	0.2306	0.2947	2.1	48
Chlorobenzene	418	$6.3 \cdot 10^7$	0.3775	0.3064	0	38
1,4-Dioxane	418	$3.0 \cdot 10^7$	0.2231	0.2543	4.2	237
AcOEt	419	$1.4 \cdot 10^8$	0.3850	0.2275	0	181
n-Decane	420	$1.2 \cdot 10^9$	0.1989	0.2488	0	0
n-Pentane	424	$2.0 \cdot 10^9$	0.1800	0.2193	0	0

[a] Calculated from experimental spectra for the Gaussian shape of bands.

[b] Methylene blue was used as photosensitizer ([MB] = $4 \cdot 10^{-7}$ mol L^{-1}).

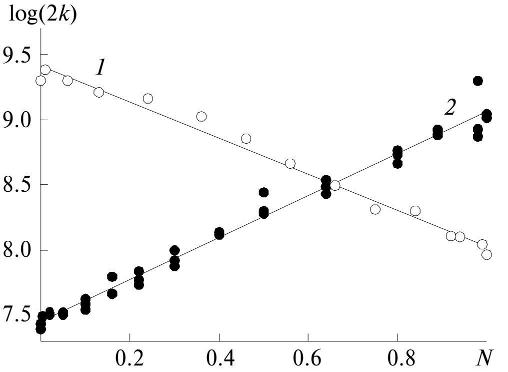


Fig. 3. Rate constant of the bimolecular decay (2*k*) of diphenylcarbonyl oxide as a function of the composition of a binary mixture (*N*) at 295 K in different solvents: *1*, *n*-pentane—benzene mixture; *2*, dioxane—*n*-decane mixture.

$2.0 \cdot 10^9$ L mol^{-1} s^{-1} (see Table 1). A study of Ph_2COO recombination in the benzene—*n*-pentane and 1,4-dioxane—*n*-decane systems showed that the molar fraction of a solvent affects the $2k$ value (Fig. 3)

$$\log 2k_{AB} = N_A \log 2k_{AB} + N_B \log 2k_B,$$

where N_A, N_B are the molar fractions of the components of a binary mixture; $2k_A$, $2k_B$, $2k_{AB}$ are the rate constants for reaction (1) in the pure and mixed solvents.

The dependence of the reaction rate constant on the solvent nature is described by the Koppel—Palm equation (correlation coefficient, $r = 0.999$, confidence level is 0.95):

$$\log(2k) = \log(2k)_0 + yY + pP + eE + bB,$$

$$\log(2k)_0 = 11.89\pm0.78,\ y = -2.74\pm0.92,\ p = -9.3\pm2.8,$$

$$e = -0.161\pm0.057,\ b = -(3.1\pm1.4)\cdot10^{-3}.$$

Here $Y = (\varepsilon - 1)/(2\varepsilon + 1)$; $P = (n^2 - 1)/(n^2 + 2)$; E and B are the parameters of electrophilicity and nucleophilicity of a solvent, respectively; y, p, e, and b are coefficients characterizing the sensitivity of the reaction to the effects of non-specific (polarity, polarizability) and specific (electrophilicity, nucleophilicity) solvations.

One can conclude that different properties of a solvent (yY, pP, eE, bB) affect the kinetics of Ph_2COO decay. All coefficients of the Koppel—Palm equation are negative, *i.e.*, the enhancement of any interaction results in a decrease in the $2k$ value. This can be connected with an increase in the fraction of the zwitterionic state of carbonyl oxide due to its stabilization by a solvent. In nonpolar solvents (*n*-alkanes), in the absence of specific solvation, the biradical state of Ph_2COO is more probable, increasing the rate constant.

To elucidate in more detail the solvent effects on the properties and reactivity of carbonyl oxides, we performed *ab initio* quantum chemical calculations of the equilibrium structure, electronic structure, and electronic absorption spectra for the simplest carbonyl oxide H_2COO and phenylcarbonyl oxide PhHCOO in *n*-heptane, benzene, and acetonitrile, as well as in the gas phase. Since the electron correction should be taken into account to describe correctly the structure and distribution of electron density of 1,3-dipoles, calculations were performed in the framework of density functional theory using the valent-splitted basis set, including the polarization d-functions for non-hydrogen atoms, B3LYP/6-31G(d). It has been shown[18] that this approach provides high accuracy of the calculation of the geometric and electronic parameters of carbonyl oxides, which is comparable with the accuracy of other methods taking into account the correlation energy, for example, CCSD(T)/TZ+2P.[19,20]

The geometry of the carbonyl oxide moiety changes regularly with increasing medium polarity (Table 2) in the sequence gas phase ($\varepsilon = 1$)—*n*-heptane ($\varepsilon = 1.924$)—benzene ($\varepsilon = 2.284$)—acetonitrile ($\varepsilon = 37.5$). The length of the O—O bond in this sequence increases, whereas the length of the C—O bond slightly decreases, *i.e.*, the

Table 2. Parameters of equilibrium structure (bond lengths (*d*), angle C—O—O), distribution of electron density (*q*), dipole moment (μ), and energy characteristics (total energies (E_{tot}) and solvation energies (ΔG_{solv})) calculated by the B3LYP/6-31G(d) method for carbonyl oxides R_2C—O(1)—O(2) in different media

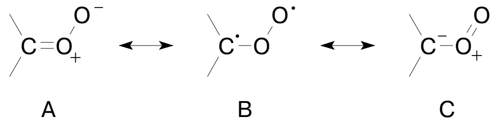
Medium	*d*/Å		C—O—O /deg	*q*(C)	*q*(O(1))	*q*(O(2))	μ /D	E_{tot} /a.u.	ΔG_{solv} /kcal mol^{-1}
	O(1)—O(2)	C—O(1)		el.u.					
				H_2COO					
Gas phase	1.3433	1.2653	119.47	−0.024	−0.025	−0.338	3.921	−189.576821	0.00
Heptane	1.3461	1.2635	119.41	−0.019	−0.027	−0.358	4.216	−189.579010	−1.37
Benzene	1.3466	1.2631	119.40	−0.018	−0.027	−0.362	4.274	−189.577675	−0.53
Acetonitrile	1.3534	1.2612	119.24	−0.011	−0.032	−0.391	4.703	−189.578957	−1.34
				PhHCOO					
Gas phase	1.3582	1.2763	118.21	0.149	−0.122	−0.353	5.662	−420.651465	—
Heptane	1.3638	1.2749	118.01	0.151	−0.125	−0.354	5.708	−420.651445	—
Benzene	1.3650	1.2747	117.98	0.151	−0.126	−0.354	5.718	−420.651434	—
Acetonitrile	1.3746	1.2740	117.76	0.151	−0.130	−0.355	5.796	−420.651311	—

Table 3. Medium effects on the maxima in the absorption spectra (λ_{max}) calculated by the B3LYP/6-31G(d) method and the oscillator strength of electron transitions (*f*) in carbonyl oxides

Medium	H_2COO				PhHCOO			
	n—π*		π—π*		n—π*		π—π*	
	λ_{max}/nm	*f*	λ_{max}/nm	*f*	λ_{max}/nm	*f*	λ_{max}/nm	*f*
Gas phase	602.3	0.0007	373.1	0.1778	593.5	0.0005	416.9	0.3913
Heptane	599.1	0.0007	373.9	0.1743	589.5	0.0005	418.6	0.3782
Benzene	598.6	0.0007	374.0	0.1737	588.7	0.0005	419.0	0.3756
Acetonitrile	593.7	0.0007	376.6	0.1665	582.9	0.0005	422.0	0.3566
Ethylene[a]	540.6	0.0002	342.5	0.1736	—	—	—	—
Acetonitrile[a]	499.6	0.0006	338.1	0.1556	—	—	—	—

[a] Complex of carbonyl oxide with a solvent molecule modeling the specific solvation of H_2COO.

contribution of the resonance structure A into the wave function of the carbonyl oxide molecule increases with increasing the dielectric permeability of a medium.



A decrease in the O—O bond order is accompanied by the increase in the electron density on the terminal O atom. This effect is most pronounced in the case of the simplest carbonyl oxide: Δq = 0.053 e.u. Conjugation with the phenyl group stabilizes the carbonyl oxide moiety resulting in a much less polarizability of the PhHCOO molecule. Correspondingly, the dipole moments of carbonyl oxides increase on going from the gas phase to acetonitrile and to a greater extent for H_2COO ($\Delta\mu$ = 0.782 D) than for PhHCOO ($\Delta\mu$ = 0.134 D).

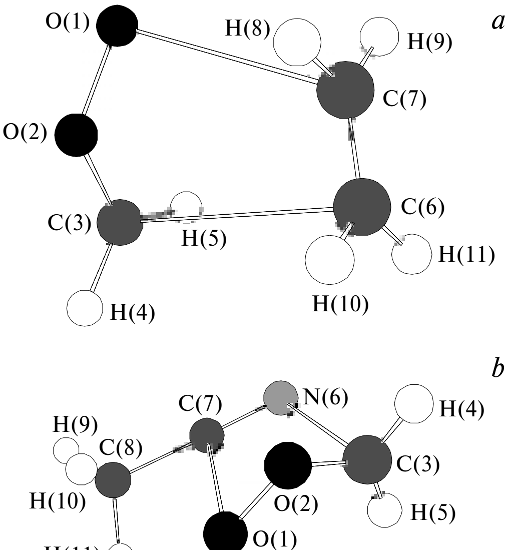


Fig. 4. Equilibrium geometry of complexes of carbonyl oxide with ethylene (*a*) and acetonitrile (*b*) calculated by the B3LYP/6-31G(d) method.

The non-specific solvation of carbonyl oxides does not affect in fact the calculated energies of the electron transitions and consequently the λ_{max} values (Table 3). This allows one to suggest that specific solvation mainly affects the spectral properties of carbonyl oxides. To simulate specific solvation, the geometric parameters of the H_2COO complexes with ethylene and acetonitrile were calculated. The equilibrium structures and geometric parameters of the complexes are presented in Fig. 4 and Table 4. The enthalpy of complex formation was calculated as a difference between the total energies of the complex and initial compounds, taking into account the correction by the zero potential energy (*ZPE*), as well

Table 4. Geometric parameters of complexes of carbonyl oxide with ethylene and acetonitrile

Parameter	$H_2COO...CH_2{=}CH_2$	$H_2COO...MeCN$
Bond	*d*/Å	
O(1)—O(2)	1.351	1.361
O(2)—O(3)	1.265	1.260
C(3)—C(6)	3.111	—
C(6)—C(7)	1.336	—
O(1)—C(7)	2.895	2.880
C(3)—N(6)	—	2.832
N(6)—C(7)	—	1.162
Valence angle	ω/deg	
O(1)—O(2)—C(3)	118.4	118.3
O(2)—C(3)—C(6)	94.1	—
C(3)—C(6)—C(7)	85.0	—
O(2)—O(1)—C(7)	89.9	89.3
O(1)—C(7)—C(6)	112.9	—
O(2)—C(3)—N(6)	—	92.0
C(3)—N(6)—C(7)	—	101.3
O(1)—C(7)—N(6)	—	100.6
Torsion angle	α/deg	
O(1)—O(2)—C(3)—C(6)	70.8	—
C(3)—O(2)—O(1)—C(7)	−65.6	−66.6
O(1)—O(2)—C(3)—H(4)	−179.2	−178.4
O(1)—O(2)—C(3)—H(5)	−3.2	−1.8
H(8)—C(7)—C(6)—H(10)	−1.5	—
H(8)—C(7)—C(6)—H(11)	−179.1	—
O(1)—O(2)—C(3)—N(6)	—	67.5

Table 5. Thermodynamic parameters of complex formation of H_2COO with acetonitrile and ethylene

Compound, complex	E_{tot} /a.u.	ZPE^a	$H°_{298} - H°_0{}^a$	$\Delta H°$	$\Delta G°^b$	$K_C{}^b$ /L mol^{-1}
		kcal mol^{-1}				
H_2COO	−189.576821	18.90	2.55	—	—	—
$CH_2{=}CH_2$	−78.587458	30.91	2.40	—	—	—
$H_2COO...CH_2{=}CH_2$	−268.168703	50.84	5.17	−1.53	3.54	0.06
MeCN	−132.754928	27.53	2.74	—	—	—
$H_2COO...MeCN$	−322.342812	47.50	5.56	−5.60	−0.53	60

[a] The values were corrected for anharmonicity of vibrations equal to 0.9614.[21]

[b] Changes in the Gibbs energy and concentration equilibrium constant were estimated using the value $\Delta S° = -17$ cal mol^{-1} K^{-1}.

as the change in temperature 0 → 298 K ($H°_{298} - H°_0$) (see Table 5). The complex of H_2COO with acetonitrile ($\Delta H° = -5.60$ kcal mol^{-1}) is stronger than the $H_2COO...CH_2{=}CH_2$ complex ($\Delta H° = -1.53$ kcal mol^{-1}). The calculation of the entropy variation upon the complex formation is less reliable due to the existence of low-frequency vibrations ($\lambda < 400$ cm^{-1}) in the complexes, which are the origin of significant errors in $\Delta S°$ determination. The $\Delta S°$ values for both complexes are within the range of −7—−27 cal mol^{-1} K^{-1}. The totality of the data indicates that nearly the whole carbonyl oxide in acetonitrile occurs in the form of the complex with the solvent (see Table 5), whereas the presence of free carbonyl oxide is more probable in benzene.

The calculation of the spectral properties of the H_2COO complexes with a solvent (see Table 3) revealed a strong hypsochromic shift (for acetonitrile $\Delta\lambda_{max} = 38.5$ (π—π*) and 94.1 (n—π*) nm). Since the phenyl ring in carbonyl oxide decreases polarizability of the molecule, one can expect a hypsochromic shift for the phenyl-substituted carbonyl oxides.

Thus, both specific and non-specific solvations change the properties of carbonyl oxide. Non-specific solvation manifests itself in the polarization of carbonyl oxide moiety and affects mainly the reactivity of Ph_2COO, decreasing it. Specific solvation determines the spectral properties of carbonyl oxide. The stronger the complex with a solvent, the greater the shift of λ_{max} to the short-wave region. The formation of strong complexes between carbonyl oxide and a solvent decreases its reactivity.

References

1. C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, VCH, Weinheim, 1988, 466 pp.
2. A. M. Nazarov, E. M. Chainikova, P. V. Krupin, S. L. Khursan, and V. D. Komissarov, *Izv. Akad. Nauk, Ser. Khim.*, 2000, 1504 [*Russ. Chem. Bull.*, 2000, **49**, 1496 (Engl. Transl.)].
3. A. M. Nazarov, S. L. Khursan, P. V. Krupin, and V. D. Komissarov, *Zh. Fiz. Khim.*, 2000, **74**, 2043 [*Russ. J. Phys. Chem.*, 2000, **74** (Engl. Transl.)].
4. A. M. Nazarov, E. M. Chainikova, S. L. Khursan, I. A. Kalinichenko, R. L. Safiullin, and V. D. Komissarov, *React. Kinet. Catal. Lett.*, 1998, **65**, 311.
5. *Technics of Organic Chemistry. Organic Solvents. Physical Properties and Methods of Purification*, Ed. A. Weissberger, Interscience Publishers, Inc., New York, 1955, **7**.
6. M. Regitz and G. Maas, *Diazo Compounds. Properties and Synthesis*, Academic Press, Orlando, 1986, 596 pp.
7. S. I. Maslennikov, A. I. Nikolaev, and V. D. Komissarov, *Kinet. Katal.*, 1979, **20**, 326 [*Kinet. Catal.*, 1979, **20** (Engl. Transl.)].
8. N. H. Werstiuk, H. L. Casal, and J. C. Scaiano, *Canad. J. Chem.*, 1984, **62**, 2391.
9. H. L. Casal, S. E. Sugamori, and J. C. Scaiano, *J. Am. Chem. Soc.*, 1984, **106**, 7623.
10. H. L. Casal, M. Tanner, N. H. Werstiuk, and J. C. Scaiano, *J. Am. Chem. Soc.*, 1985, **107**, 4616.
11. J. C. Scaiano, W. G. McGimpsey, and H. L. Casal, *J. Org. Chem.*, 1989, **54**, 1612.
12. K. B. Eisenthal, N. J. Turro, E. V. Sitzmann, I. R. Gould, G. Hefferon, J. Langan, and Y. Cha, *Tetrahedron*, 1985, **41**, 1543.
13. T. Nojima, K. Ishiguro, and Y. Sawaki, *J. Org. Chem.*, 1997, **62**, 6911.
14. A. M. Nazarov, E. M. Chainikova, R. L. Safiullin, S. L. Khursan, and V. D. Komissarov, *React. Kinet. Catal. Lett.*, 1997, **61**, 173.
15. 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.)].
16. D. Cremer, T. Schmidt, W. Sander, and P. Bischof, *J. Org. Chem.*, 1989, **54**, 2515.
17. S. G. Entelis and R. P. Tiger, *Kinetika reaktsii v zhidkoi faze. Kolichestvennyi uchet vliyaniya sredy* [*Reaction Kinetics in Liquid Phase. Quantitative Analysis of the Medium Effect*], Khimiya, Moscow, 1973, 416 pp. (in Russian).
18. C. Selcuki and V. Aviyente, *Chem. Phys. Lett.*, 1998, № 7, 669.
19. D. Cremer, J. Gauss, E. Kraka, J. F. Stanton, and R. J. Bartlett, *Chem. Phys. Lett.*, 1993, № 6, 547.
20. D. Cremer, E. Kraka, and P. G. Szalay, *Chem. Phys. Lett.*, 1998, № 1—2, 97.
21. A. P. Scott and L. Radom, *J. Phys. Chem.*, 1996, **100**, 16502.

Received March 18, 2000;
in revised form November 30, 2000