Kinetics and Catalysis, Vol. 43, No. 4, 2002, pp. 459–464. Translated from Kinetika i Kataliz, Vol. 43, No. 4, 2002, pp. 499–504.
Original Russian Text Copyright © 2002 by Nazarov, Khursan, Kalinichenko, Ziganshina, Komissarov.

Determination of the Absolute Rate Constants of Reactions between Diphenyl Carbonyl Oxide and Alcohols by Flash Photolysis

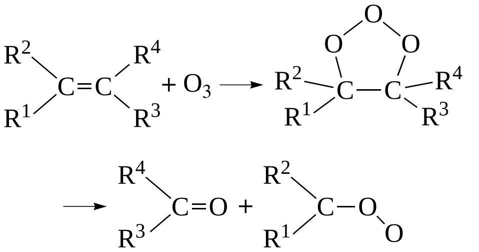
A. M. Nazarov*, S. L. Khursan, I. A. Kalinichenko*,**
S. Kh. Ziganshina*, and V. D. Komissarov**
** Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, Ufa, 450054 Bashkortostan, Russia*
*** Bashkortostan State University, Ufa, 450074 Bashkortostan, Russia*

Received August 6, 2001

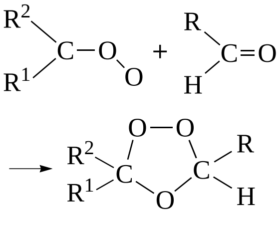
Abstract—The rate constants of the reactions of diphenyl carbonyl oxide Ph_2COO with a number of alcohols and water in acetonitrile, benzene, and *n*-decane solutions (295 K) were measured by flash photolysis. The rate constants vary over a range from 400 (triphenylmethanol in a MeCN solution) to 2.5×10^5 l mol^{-1} s^{-1} (adamantanol in a benzene solution). α-Methoxydiphenylmethyl hydroperoxide is the reaction product of Ph_2COO and MeOH. The absence of a kinetic isotope effect and the dependence of the logarithms of the rate constants on the first ionization potentials of alcohols are indicative of the formation of a C–O bond at the rate-limiting step of the reaction.

INTRODUCTION

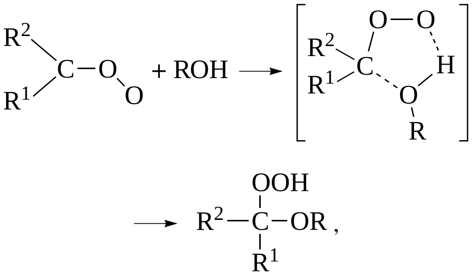
Carbonyl oxides R^1R^2COO are key intermediates in the ozonolysis of unsaturated organic compounds [1–3]



The subsequent reactions of carbonyl oxides depend on the nature of the solvent in which ozonolysis is performed. With the use of inert solvents, such as CH_2Cl_2 and CCl_4, or aldehydes, the main reaction product of ozonolysis is a 1,2,4-trioxolane:



Ozonation in protic solvents, such as alcohols, water, and carboxylic acids, results in the formation of α-alkoxy hydroperoxides. As a rule, the yield of these hydroperoxides is considerably higher than that of 1,2,4-trioxolanes [1]. The α-alkoxy hydroperoxides result from the insertion of a carbonyl oxide into the O–H bond of the solvent



where R = H, HO, alkyl, aryl, or acyl.

In the ozonolysis of tetramethylethylene in the presence of alcohols, the highest yields of α-alkoxyalkyl hydroperoxides were found with the use of methanol and ethanol ($R^1 = R^2 =$ Me; R = Me or Et) [4]. The kinetics of reactions between carbonyl oxides and hydroxyl-containing compounds is not completely understood. Previously [4–6], data on the relative reactivities of alcohols in the reactions with structurally different carbonyl oxides were obtained. Therefore, in this work, we studied the kinetics of diphenyl carbonyl oxide reactions with a number of alcohols (methanol, ethanol, isopropanol, *n*-butanol, isobutanol, isopentanol, cyclohexanol, menthol, triphenylmethanol, phenylmethanol, and adamantanol) and water in acetonitrile and benzene solutions using flash photolysis and kinetic spectrophotometry.

EXPERIMENTAL

The solvents (acetonitrile, benzene, and *n*-decane) were purified in accordance with a standard procedure [7]. Diphenyldiazomethane was synthesized and purified according to a published procedure [8].

A flash-photolysis assembly (the photolytic source was an IFP 5000-2 lamp with a maximum pulse energy of 400 J at $U = 5$ kV and $C = 32$ μF; ~90% light energy was emitted in 50 μs) was used for kinetic experiments. The reactor was a quartz cell with an optical path length (l) of 10 cm and an internal diameter of ~1 cm. The assembly, whose parameters were reported previously [9], was supplemented with a device for the computer processing of pulse signals [10].

The flash photolysis of the Ph_2CN_2–alcohol–solvent–O_2 system (in air) was performed using filtered light (a UFS-2 light filter with a transmission range of 240–380 nm). In all experiments, to prevent the photochemical degradation of Ph_2CN_2, the intensity of the probing light beam was attenuated using an SS-15 light filter (transmission range of 300–520 nm). The initial concentration $[Ph_2CN_2]_0$ was $(1.5–2) \times 10^{-4}$ mol/l. The minimal initial alcohol concentration $[ROH]_0$ was varied over a range of 0.0002–0.01 mol/l depending on the reactivity of the alcohol; the concentration of ROH in solution was changed by a factor of 10–100. The reaction kinetics was followed by measuring a decrease in the absorbance A of diphenyl carbonyl oxide at its absorption band maximum (λ_{max} = 410 (MeCN), 415 (PhH), or 420 nm (n-$C_{10}H_{22}$), $\varepsilon_{max} = 1.9 \times 10^3$ l mol^{-1}cm^{-1} [11]).

The yield of α-methoxydiphenylmethyl hydroperoxide (the product of the reaction of Ph_2COO with methanol) was determined under conditions of steady-state diphenyldiazomethane oxidation photosensitized with methylene blue. Methylene blue was excited with light at $\lambda > 560$ nm (a 500-W nitrogen incandescent lamp; an OS-13 light filter). The distance from the light source to the reactor was 15 cm. Acetonitrile (15 ml), methylene blue (1×10^{-5} mol/l), and methanol in a required concentration were placed in the cylindrical reactor, which was thermostatted at 298 K. To prevent the consumption of Ph_2COO in a reaction with diphenyldiazomethane, the latter was added as it was consumed, so that the current concentration of Ph_2CN_2 in solution was no higher than 2×10^{-4} mol/l; the total diphenyldiazomethane concentration was 2×10^{-3} mol/l. Air was bubbled through the solution in the course of photolysis. After completion of the reaction (20–40 min), the reaction mixture was analyzed for peroxide products by iodometry.

The ^1H and ^{13}C NMR spectra were measured on a Bruker AM-300 instrument (300 MHz). Before the analysis of a reaction mass, the solvent was distilled off, and the residue was dissolved in $CDCl_3$.

RESULTS AND DISCUSSION

Diphenyl carbonyl oxide (Ph_2COO) was obtained by the flash photolysis of diphenyldiazomethane solutions saturated with atmospheric oxygen [11]:

$$Ph_2CN_2 \longrightarrow {}^1Ph_2C: + N_2, \qquad \text{(I)}$$

$${}^1Ph_2C: \rightleftarrows {}^3Ph_2C:, \qquad \text{(ST, TS)}$$

$${}^3Ph_2C: + O_2 \longrightarrow Ph_2COO, \qquad \text{(II)}$$

$$Ph_2COO + Ph_2CN_2 \longrightarrow 2Ph_2C{=}O + N_2, \qquad \text{(III)}$$

$$Ph_2COO + Ph_2COO \longrightarrow 2Ph_2C{=}O + O_2. \qquad \text{(IV)}$$

In all cases, the initial concentration of Ph_2CN_2 was $\sim 1.8 \times 10^{-4}$ mol/l. All experiments were performed at room temperature. As found previously [11, 12], the quadratic decay rate of Ph_2COO in reaction (II) under these conditions is much higher than the rate of reaction (III). The kinetic curve, that is, the time dependence of the absorbance of diphenyl carbonyl oxide, is described by the second-order equation

$$-\frac{dA}{dt} = \frac{2k_4}{\varepsilon l}A^2, \qquad (1)$$

where $\varepsilon = 1.9 \times 10^3$ l mol^{-1} cm^{-1} [11] is the molar absorption coefficient, $l = 10$ cm is the cell length, A is the absorbance of diphenyl carbonyl oxide, and k_4 is the reaction rate constant of Ph_2COO combination.

In the absence of active additives, the following values of k_4 were found: 1.8×10^7 (solvent: MeCN), 7×10^7 (C_6H_6), and 1.5×10^9 l mol^{-1} s^{-1} (n-$C_{10}H_{22}$). These values are consistent with published data [11].

The introduction of an alcohol into the test system resulted in a decrease in the initial absorbance of Ph_2COO because of the reaction

$$Ph_2C: + ROH \longrightarrow Ph_2CHOR, \qquad \text{(V)}$$

which resulted in the consumption of diphenyl carbene, the carbonyl oxide precursor. Nevertheless, the major portion of the carbene was consumed in reaction (II) with oxygen. Indeed, according to previous data [13], the ratio between the specific rates of the reactions of carbenes with an alcohol and oxygen under conditions of our experiments is $\frac{k_{TS}k_5}{k_{ST}k_2} = (2–9) \times 10^{-3}$. Consequently, even at an alcohol concentration of ~1 mol/l, the consumption in reaction (V) is no greater than half the total consumption of diphenyl carbene. Moreover, a decrease in the lifetime of Ph_2COO in proportion to an increase in the alcohol concentration was observed. The rate law of Ph_2COO consumption was changed: the apparent order of reaction with respect to the carbonyl oxide became lower than second, whereas it approached unity at high alcohol concentrations. This fact is indicative of the occurrence of the reaction

$$Ph_2COO + ROH \longrightarrow Ph_2C(OOH)OR. \qquad \text{(VI)}$$

In this case, the consumption of diphenyl carbonyl oxide is described by the equation

$$-\frac{\mathrm{d}A}{\mathrm{d}t} = k_6[\mathrm{ROH}]A + \frac{3k_4}{\varepsilon l}A^2 = k_{\mathrm{I}}A + k_{\mathrm{II}}A^2. \qquad (2)$$

The analytical solution to Eq. (2) takes the form

$$\ln\frac{(k_{\mathrm{I}} + k_{\mathrm{II}}A)A_0}{(k_{\mathrm{I}} + k_{\mathrm{II}}A_0)A} = k_{\mathrm{I}}t. \qquad (3)$$

The apparent rate constants k_I were found by nonlinear regression analysis with the use of Eq. (3) and the known values of k_{II}. The absolute rate constants k_6 of the reactions of Ph_2COO with alcohols (Table 1) were calculated from the slope of k_I as a function of ROH concentration (Fig. 1).

The yield of α-alkoxydiphenylmethyl hydroperoxide, the main product of reaction (VI), was determined using the interaction of diphenyl carbonyl oxide with methanol as an example. The hydroperoxide was determined by iodometry (Table 2 summarizes the concentrations) and NMR spectroscopy. ^{1}H NMR (δ, ppm): 3.15 (s, 3H, OCH_3), 9.95 (s, 1H, OOH). ^{13}C NMR (δ, ppm): 56.89 (OCH_3), 126.88, 127.40, 128.22, 129.08, 142.00 ($2 \times C_6H_5$). To prevent side reaction (V), which decreases the peroxide yield, the carbonyl oxide was generated using the methylene blue–photosensitized decomposition of Ph_2CN_2 ($\lambda > 560$ nm) [14, 15].

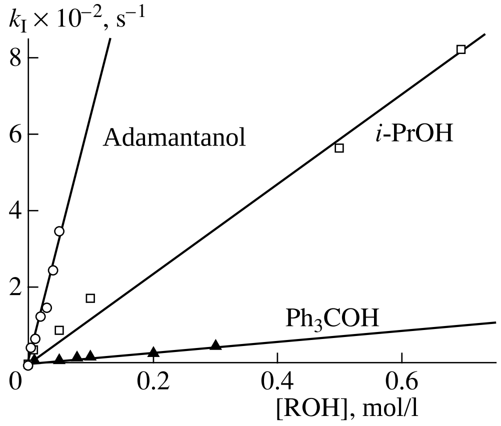


Fig. 1. Apparent rate constant of diphenyl carbonyl oxide consumption as a function of alcohol concentration; solvent, acetonitrile; 295 K.

The amount of the resulting hydroperoxide was almost independent of methanol concentration within a range of 0.75–7.0 mol/l (Table 2). This fact suggests that the carbonyl oxide (the intermediate of the photosensitized decomposition of Ph_2CN_2) was completely scavenged by the alcohol. In the calculation of the hydroperoxide yield (γ), we took into account that the reaction of Ph_2CN_2 with singlet oxygen affords diphenyl carbonyl oxide with the probability $\alpha = 0.6$ [16]. We found that $\gamma = 1.1 \pm 0.2$; this value is consistent with known data on the mechanism and products of the reaction of Ph_2COO with ROH.

Table 1. Absolute rate constants of the reactions of Ph_2COO with ROH at 293 K

ROH	[ROH], mol	$k_6 \times 10^{-3}$, $l\ mol^{-1}\ s^{-1}$		*IP* [20]
		MeCN	C_6H_6	
H_2O	0.01–0.7	0.47 ± 0.09		12.17
MeOH	0.01–0.7	1.0 ± 0.1	13 ± 2	10.82
EtOH	0.01–1.0	1.8 ± 0.4	10 ± 1	10.41
iso-PrOH	0.005–1.0	1.2 ± 0.1	5.3 ± 0.5	10.10
iso-BuOH	0.01–1.0	1.8 ± 0.1	14 ± 2	10.02
n-BuOH*	0.01–0.5	2.2 ± 0.2	10 ± 2	9.99
n-C_4D_9OD	0.001–0.1	2.2 ± 0.4	9 ± 1	
iso-$C_5H_{11}OH$**	0.005–0.3	2.3 ± 0.4	7 ± 1	9.78
cyclo-$C_6H_{13}OH$	0.005–0.04	4.8 ± 0.7	30 ± 10	9.75
Menthol	0.006–0.4	2.9 ± 0.5	20 ± 3	
tert-Adamantanol	0.004–0.05	7 ± 1	250 ± 60	9.09
Ph_3COH	0.01–0.3	0.4 ± 0.1	–	
$PhCH_2OH$	2×10^{-4}–0.01		24 ± 4	8.26

* In *n*-decane, $k_6 = (5 \pm 1) \times 10^4$ $l\ mol^{-1}\ s^{-1}$.

** In *n*-decane, $k_6 = (1.1 \pm 0.2) \times 10^5$ $l\ mol^{-1}\ s^{-1}$.

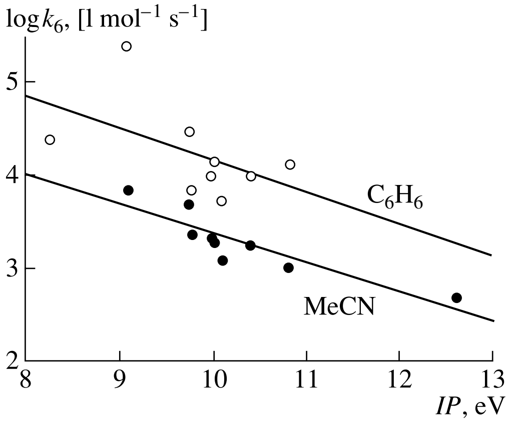


Fig. 2. Rate constants of the reactions of Ph_2COO with ROH in acetonitrile and benzene as functions of the first ionization potentials of alcohols, 295 K.

As can be seen in Table 1, the rate constants of diphenyl carbonyl oxide reactions with alcohols in benzene were higher than those in acetonitrile, on the average, by one order of magnitude for all ROH examined. The rate constant k_6 further increased on going to a nonpolar solvent, *n*-decane. This was demonstrated using *n*-butanol and isoamyl alcohol as examples (Table 1). Similar effects of solvents on the quadratic decay rate constants of Ph_2COO and on the kinetics of its reactions with olefins and sulfoxides were noted previously [10, 11, 13, 17]. The nature of the observed effect is due to the high polarizability of a carbonyl oxide moiety. The effective solvation of Ph_2COO by polar solvents increases the degree of charge separation in the carbonyl oxide and decreases its reactivity. The solvent effect on the kinetics of the test reaction can be quantitatively described by the Grunwald–Winstein equation [18]

$$\log k_6 = \log k_6^0 + mY, \tag{4}$$

where Y is the ionizing power of the solvent on an empirical scale [19], m is a constant that characterizes the reactivity of the reactant, and $\log k^0$ is the rate constant of the test reaction in a standard solvent (80% C_2H_5OH and 20% H_2O). Using *n*-butanol as an example, it was found that $\log k_6 = 5.52–0.167Y$ ($r = 0.998$).

Upon the complete replacement of hydrogen atoms by deuterium in the *n*-butanol molecule, the rate constant k_6 remained almost unchanged in both acetonitrile and benzene (Table 1). The absence of a kinetic isotope effect suggests that H-atom transfer from the alcohol molecule to the terminal oxygen atom of the carbonyl oxide does not control the rate of the reaction of Ph_2COO with ROH.

To explain the effect of the structure of an alcohol on the rate of its reaction with diphenyl carbonyl oxide, we studied the dependence of the reaction rate constant k_6 on the ionization potential (IP) of ROH (Fig. 2). Note that in the studied series of compounds the dependence of $\log k_6$ on other characteristics, which are frequently used in correlation analysis, such as the inductive Taft constants $\sigma^*(R)$ or the values of pK_a, is characterized by a low coefficient of correlation. Thus, reliable conclusions on the structure–reactivity relationship in the test reaction cannot be drawn.

Satisfactory correlation was observed between the rate constants of the reactions of Ph_2COO with ROH and the first ionization potentials of the corresponding alcohols. The rate constant k_6 decreased with IP in both of the solvents used. A higher coefficient of correlation ($r = 0.9$) characterizes the dependence of $\log k_6$ on IP in acetonitrile

$$\log k_6 = 6.5 - 0.31IP. \tag{5}$$

The results indicate that the carbonyl oxide exhibits electrophilic properties. They also suggest that, in the transition state of the test reaction, electron density is transferred from the molecular orbital that corresponds to the lone electron pair of alcohol oxygen to the π^*-antibonding orbital of the carbonyl oxide. This is accompanied by the formation of the C–O bond. This transfer controls the reaction rate and explains the absence of a kinetic isotope effect. A hydrogen bond between the hydrogen atom and the terminal oxygen atom of the carbonyl oxide is rapidly formed, and this is favorable for proton transfer to result in the formation of α-alkoxydiphenylmethyl hydroperoxide as a stable final compound. The scheme demonstrates the assumed reaction mechanism.

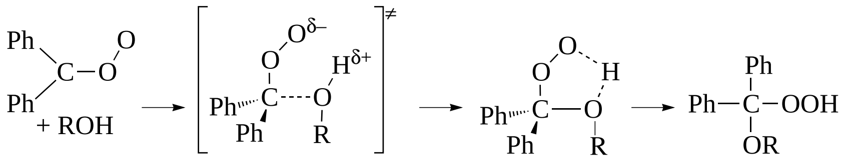
Table 2. Yields of α-methoxydiphenylmethyl hydroperoxide in the methylene blue–photosensitized decomposition of diphenyldiazomethane in the presence of methanol ($[Ph_2CN_2]_0 = 2.0 \times 10^{-3}$ mol/l*, [methylene blue] $= 1.0 \times 10^{-5}$ mol/l; solvent, MeCN; 298 K)

[MeOH], mol/l	0	0.75	3.0	5.0	6.0	7.0	
[ROOH] × 10^3, mol/l	0.18	1.1	1.3	1.4	1.1	1.6	1.3 ± 0.3
Yield**, %	15***	92	108	117	92	133	108 ± 20

* The total concentration; the diazomethane was added gradually to prevent its reaction with the carbonyl oxide (see Experimental).

** The yield was calculated by the equation $\gamma = [ROOH]/\alpha[Ph_2CN_2]_0$, where α is the probability of carbonyl oxide formation in the photosensitized decomposition of diphenyldiazomethane; α = 0.6 [13].

*** Blank experiment; peroxide products were not identified.

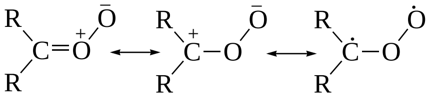


Scheme

The above experimental results are consistent with our data published recently [5, 6]. In these publications, the relative reactivities of a number of alcohols in reactions with Ph_2COO [6] and of a number of carbonyl oxides in reactions with ethanol [5] were studied by a chemiluminescence technique. It was found that the rate constant ratio $k(Ph_2COO + ROH)/k(Ph_2COO + Ph_2CN_2)$ increases as the ionization potential of ROH decreases [6]. The slope of this function is equal to –0.4 (70°C); this value agrees well with the slope of Eq. (5), taking into account the temperature difference. Previously [5], the reactivity of carbonyl oxides was characterized by the ratio $k(R^1R^2COO + EtOH)/k(R^1R^2COO + R^1R^2CN_2)$; this is less convenient for correlation analysis because the reference constant depends on the nature of the carbonyl oxide and its precursor (a diazo compound). Nevertheless, the reported results [5] are indicative of the electrophilic nature of a carbonyl oxide in the reaction with ethanol. Indeed, in the series of carbonyl oxides 4-X-Ph(Ph)COO, the relative rate constant increases as the electron-acceptor properties of substituent X increase: 2.3×10^{-3} (X = Me) < 1.9×10^{-2} (X = H) < 2.2 (X = Cl). Taking into account that these carbonyl oxides undergo recombination with similar rate constants [13], we may believe that they exhibit equal activities in the reactions with diazo compounds. Consequently, the above order of reactivity reflects the change in the electrophilic properties of *para*-substituted aromatic carbonyl oxides due to an increase (X = Me) or decrease (X = Cl) of electron density at the reaction site—the carbon atom of the carbonyl oxide group.

It is of interest to compare our data with the results obtained by Yamamoto *et al.* [4], who studied the relative reactivities of alcohols in the reactions with dimethyl carbonyl oxide Me_2COO. The relative rate constants were obtained from data on the amounts of the resulting hydroperoxides or on the conversion of alcohols under conditions of tetramethylethylene ozonolysis with the addition of two test alcohols. Yamamoto *et al.* [4] found that the reactivities of alcohols decreased in the order methanol, ethanol, *n*-propanol, isopropanol, water, *tert*-butanol, and acetic acid, that is, in the reversed order as compared to our data.

It is likely that differences in the electronic natures of carbonyl oxide intermediates are responsible for this inconsistency. It is well known that the structure of carbonyl oxides cannot be adequately represented by classical Lewis structures. Therefore, the electronic properties of carbonyl oxides are often illustrated as a combination of several resonance structures:



A **B** **C**

The contribution of a particular resonance structure to the molecular structure of a carbonyl oxide depends on the nature of substituent R and on the solvating ability of the solvent. Carbonyl oxides with alkyl substituents are characterized by a considerable contribution from resonance structure **C** and, hence, biradical properties, which are responsible for the high reactivity of the carbonyl oxides. The conjugation of the 4π-electron system of the carbonyl oxide with the aromatic system in Ph_2COO stabilizes the zwitterionic components **A** and **B** and decreases the activity of the carbonyl oxide in the reactions with itself and oxidation substrates. The polarization of the carbonyl oxide fragment explains the ambiphilic nature of Ph_2COO and makes the molecular mechanism of carbonyl oxide reactions more probable.

In accordance with these ideas, the reactions of Me_2COO with alcohols fully or at least partially occur by a homolytic mechanism. In this case, the rate of the reaction depends on the strength of the O–H bond to be cleaved; that is, in accordance with data [4], it decreases in the order alcohol > water > acetic acid. It is likely that the comparatively low reactivity of *tert*-butanol can be explained by steric hindrances. The insertion of diphenyl carbonyl oxide, which exhibits zwitterionic properties to a greater extent, into the O–H bond occurs by a nonradical mechanism. In this case, as mentioned above, the ability of an alcohol to transfer electron density to the carbonyl oxide is of first importance; this manifests itself in the dependence of the rate constant on ionization potential of ROH.

ACKNOWLEDGMENTS

We are grateful to A.F. Khalizov for his participation in discussions of the experimental results.

REFERENCES

1. Bailey, P.S., *Ozonation in Organic Chemistry,* New York: Academic, 1978, vol. 1.
2. Bailey, P.S., *Ozonation in Organic Chemistry,* New York: Academic, 1982, vol. 2.
3. Bunnelle, W.H., *Chem. Rev.,* 1991, vol. 91, no. 3, p. 335.

4. Yamamoto, Y., Niki, E., and Kamiya, Y., *Bull. Chem. Soc. Jpn.*, 1982, vol. 55, no. 8, p. 2677.
5. Nazarov, A.M., Yamilova, G.A., and Komissarov, V.D., *Kinet. Katal.*, 2001, vol. 42, no. 4, p. 508.
6. Nazarov, A.M., Yamilova, G.A., and Komissarov, V.D., *Kinet. Katal.*, 2001, vol. 42, no. 6, p. 823.
7. Weissberger, A., Proskauer, E.S., Riddick, J.A., and Toops, E.E., *Technics of Organic Chemistry.* Vol. 7. *Organic Solvents: Physical Properties and Methods of Purification*, New York: Wiley, 1955.
8. Regitz, M. and Maas, G., *Diazo Compounds: Properties and Synthesis*, Orlando: Academic, 1986.
9. Maslennikov, S.I., Nikolaev, A.I., and Komissarov, V.D., *Kinet. Katal.*, 1979, vol. 20, p. 326.
10. Nazarov, A.M., Chainikova, E.M., Krupin, P.V., *et al.*, *Izv. Akad. Nauk, Ser. Khim.*, 2000, no. 9, p. 1504.
11. Nazarov, A.M., Chainikova, E.M., Khursan, S.L., *et al.*, *Izv. Akad. Nauk, Ser. Khim.*, 1998, no. 7, p. 1329.
12. Nazarov, A.M., Chainikova, E.M., Safiullin, R.L., *et al.*, *React. Kinet. Catal. Lett.*, 1997, vol. 61, no. 1, p. 173.
13. Nazarov, A.M., Chainikova, E.M., Kalinichenko, I.A., *et al.*, *Izv. Akad. Nauk, Ser. Khim.*, 1999, no. 4, p. 677.
14. Casal, H.L., Sugamori, S.E., and Scaiano, J.C., *J. Am. Chem. Soc.*, 1984, vol. 106, no. 24, p. 7623.
15. Scaiano, J.C., McGimpsey, W.G., and Casal, H.L., *J. Org. Chem.*, 1989, vol. 54, no. 7, p. 1612.
16. Nojima, T., Ishiguro, K., and Sawaki, Y., *J. Org. Chem.*, 1997, vol. 62, no. 20, p. 6911.
17. Nazarov, A.M., Khursan, S.L., Krupin, P.V., and Komissarov, V.D., *Zh. Fiz. Khim.*, 2000, vol. 74, no. 11, p. 2043.
18. Denisov, E.T., *Kinetika gomogennykh khimicheskikh reaktsii* (Kinetics of Homogeneous Chemical Reactions), Moscow: Vysshaya Shkola, 1978.
19. Reichardt, C., *Solvents and Solvent Effects in Organic Chemistry*, Weinheim: VCH, 1988.
20. Lias, G.G., Liebman, J.F., Levin, R.D., and Kafafi, S.A., NIST Standard Reference Database 19A, Positive Ion Energetics, version 2.02, NIST: Gaithersburg, MD, 1994.