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Kinetics, mechanism, and products of the reaction of diphenylcarbonyl oxide with carboxylic acids

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

[a]*Institute of Organic Chemistry, Ufa Scientific Center of the Russian Academy of Sciences,*
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: (347 2) 35 6066
[b]*Bashkir State University,*
32 ul. Frunze, 450074 Ufa, Russian Federation.
Tel: (347 2) 23 6727. E-mail: KhursanSL@bsu.bashedu.ru

The kinetics of the reactions of acetic, benzoic, formic, oxalic, malic, tartaric, trifluoroacetic, and hydrochloric acids with diphenylcarbonyl oxide Ph_2COO was studied. The carbonyl oxide Ph_2COO was generated by flash photolysis of diphenyldiazomethane Ph_2CN_2 in solutions of acetonitrile and benzene at 295 K. The apparent rate constants of the reaction range from $4.6 \cdot 10^8$ for $(COOH)_2$ in MeCN to $7.5 \cdot 10^9$ L mol^{-1} s^{-1} for acetic acid in a benzene solution. The reaction mechanism was proposed, according to which at the first stage the carbonyl oxide is reversibly solvated by the solvent. Then the solvated carbonyl oxide reacts with the acid molecule by the mechanism of insertion at the O—H bond.

Key words: carbonyl oxides, flash photolysis, carboxylic acids, kinetics of reactions.

Carbonyl oxides R_2COO are intermediates in several oxidation processes, such as ozonolysis of unsaturated compounds and thermo- and photoxidation of diazo compounds.[1—3] Unique electronic properties and high reactivity of these intermediates attract permanent attention to the chemistry of carbonyl oxides. We have previously studied the kinetics of diphenylcarbonyl oxide recombination in various solvents[4—7] and the kinetics of its reactions with organic substrates, *viz.*, olefins, sulfoxides, phenols, and amines.[8—11]

In this work we studied by the combined flash photolysis and time-resolved spectrophotometry method (FP—TS) the regularities of Ph_2COO decay in the presence of acetic (**1**), benzoic (**2**), formic (**3**), oxalic (**4**), malic (**5**), tartaric (**6**), trifluoroacetic (**7**), and hydrochloric (**8**) acids.

Experimental

Kinetic studies were performed on an FP—TS setup with a known design.[12] The reactor was a quartz cell with the optical length l = 10 cm and an inner diameter of ~1 cm. Photolysis of diphenyldiazomethane Ph_2CN_2 was carried out by the separated light (UFS-2 light filter, transmission region 270—380 nm). To prevent Ph_2CN_2 from decomposition under the light beam, the absorption region of the diazo compound was attenuated by an SS-15 light filter (transmission region 300—520 nm).

Acetic, trifluoroacetic, and formic acids (reagent grade) were used as received. Benzoic and oxalic acids were purified by sublimation. Malic and tartaric (racemate) acids were recrystallized from isopropyl alcohol. Acetonitrile was purified according to a known procedure.[13] Synthesis and purification of Ph_2CN_2 were conducted according to a previously published method.[14]

Experiments were carried out at ~20 °C. A solution of Ph_2CN_2 with a known concentration was subjected to flash photolysis (FP) in a cell, and the kinetic curve of the absorbance (A) decay of diphenylcarbonyl oxide at the maximum of its absorption band was monitored (λ_{max} = 410 nm, ε_{max} = $1.9 \cdot 10^3$ L mol^{-1} cm^{-1}).[6] Then a specified amount of an acid was introduced into the solution, and the kinetics of carbonyl oxide decay was monitored again. The procedure was repeated several times varying the acid concentration. The obtained kinetic curves were processed by nonlinear regression analysis.

The formation of the peroxide products of the reaction of Ph_2COO with AcOH was studied under the conditions of steady-state diphenyldiazomethane oxidation photosensitized by methylene blue (MB). The MB dye was excited by the light with $\lambda > 560$ nm (nitrogen incandescent lamp, power 500 W, OS-13 light filter). The distance from the light source to the reactor was 15 cm. A cylindrical reactor, whose temperature was maintained at 298 K, was charged with MeCN (15 mL), MB ($1 \cdot 10^{-5}$ mol L^{-1}), and AcOH with a specified concentration. To prevent Ph_2COO consumption through the reaction with diphenyldiazomethane, the latter was gradually added as it was consumed so that the Ph_2CN_2 concentration in the solution was at most $2 \cdot 10^{-4}$ mol L^{-1}. Air was bubbled through the solution during photolysis. At the end of the reaction (20—40 min) the reaction mixture was analyzed iodometrically for the content of peroxide products.

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Results and Discussion

During flash photolysis the following reactions occur in a solution of Ph_2CN_2 according to the known scheme[4—6,15,16]:

$$Ph_2CN_2 \rightarrow {}^1Ph_2C: + N_2, \quad (1)$$

$${}^1Ph_2C: \leftrightarrow {}^3Ph_2C:, \quad (2)$$

$${}^3Ph_2C: + O_2 \rightarrow Ph_2COO, \quad (3)$$

$$Ph_2COO + Ph_2CN_2 \rightarrow 2\ Ph_2CO + N_2, \quad (4)$$

$$Ph_2COO + Ph_2COO \rightarrow 2\ Ph_2CO + O_2. \quad (5)$$

When $[Ph_2CN_2]_0 \le 5 \cdot 10^{-4}$ mol L^{-1}, reaction (4) can be neglected,[4,6] and the kinetics of the Ph_2COO absorbance decay obeys the second order equation up to at least 80%

$$-dA/dt = [2k_5/(\varepsilon l)]A^2, \quad (6)$$

where ε is the molar absorption coefficient, and l is the optical path length.

It is known that acids efficiently decompose diazo compounds.[14] In addition, photolysis of the Ph_2CN_2......HOC(O)R complex can likely produce the reaction products without the intermediate formation of carbonyl oxide. The initial reactant concentrations and the composition of the oxidation products can change due to the indicated reactions, which impedes the interpretation of kinetic experimental results. To estimate the contribution of these reactions to the process, we studied the kinetics of the reaction of diphenyldiazomethane with acetic acid (Table 1) in the dark and under irradiation of the solution with the light from a probing lamp. The short-wavelength region of the ultraviolet spectrum was attenuated by the BS-4 light filter, which is transparent in the region of the $n \rightarrow \pi^*$ transition of the diazo group.[14] The data in Table 1 indicate that in our experiments the reaction rate of Ph_2CN_2 with the acid is negligible. The irradiation of the solution with the probing lamp light substantially accelerates diphenyldiazomethane decomposition. However, its half-decay time remains rather long compared to the duration of the pulse experiment (Fig. 1). In the presence of the acid, Ph_2CN_2 photolysis somewhat slows down. It is most likely that during the photoexcitation of the diazo compound—acid complexes, Ph_2CN_2 can be deactivated by the excitation energy transfer to the acid molecule to the vibrational levels of the O—H oscillator, along with dissociation according to reaction (1).

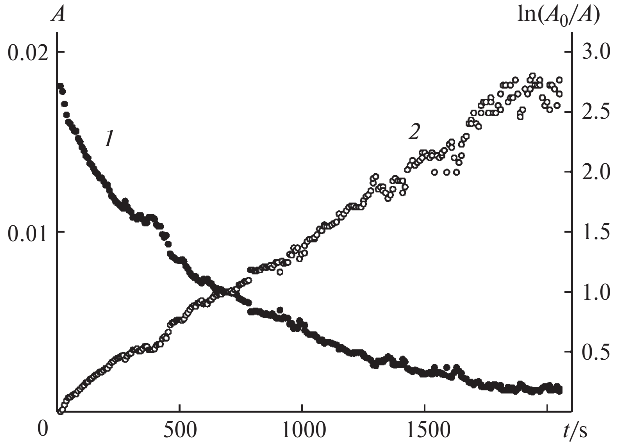


Fig. 1. Typical kinetic curve (*1*) for Ph_2CN_2 decomposition during its irradiation with the light from a probing lamp and the semilogarithmic anamorphosis of the kinetic curve (*2*). Solvent MeCN, $[Ph_2CN_2]_0 = 2 \cdot 10^{-4}$ mol L^{-1}, $[AcOH]_0 = 0$, 295 K, light filter BS-4, monitoring of the Ph_2CN_2 concentration at λ = 480 nm.

Table 1. Rate constants of diphenyldiazomethane decomposition ($[Ph_2CN_2]_0 = 2 \cdot 10^{-4}$ mol L^{-1}) in the presence of AcOH during irradiation with the light from a probing lamp (solvent MeCN, 295 K)

$[MeC(O)OH]_0$ /mol L^{-1}	Light filter	$k \cdot 10^3$/s^{-1}
$5.8 \cdot 10^{-3}$*	—	0.0055±0.0005
0**	—	1.20±0.02
$2.2 \cdot 10^{-4}$**	—	0.90±0.02
0	BS-4	1.34±0.02
0	BS-4	1.37±0.02
$2.2 \cdot 10^{-6}$	BS-4	1.50±0.02
$1.1 \cdot 10^{-5}$	BS-4	1.20±0.01
$2.2 \cdot 10^{-4}$	BS-4	1.10±0.01

* Without irradiation.

** Irradiation without light filters.

Carbene Ph_2C formed by diphenyldiazomethane decomposition is either oxidized to the corresponding carbonyl oxide (reaction (3)) or inserts at the O—H bond of the acid molecule. The kinetic consequence of these reactions is a decrease in the initial Ph_2COO concentration as the acid concentration increases (Fig. 2). The reaction product, diphenylmethyl ester of the corresponding acid, is inert under experimental conditions. Thus, side reactions initiated by the addition of the acid to a solution of the diazo compound have no substantial effect on the kinetics and mechanism of the reactions of diphenylcarbonyl oxide with acids.

In the presence of even small amounts of the acid (~10^{-5} mol L^{-1}) the rate of Ph_2COO consumption increases sharply. At least three channels of interaction can be proposed: the very fast, diffusion-controlled reaction of carbonyl oxide with acid (*A*) and the reactions

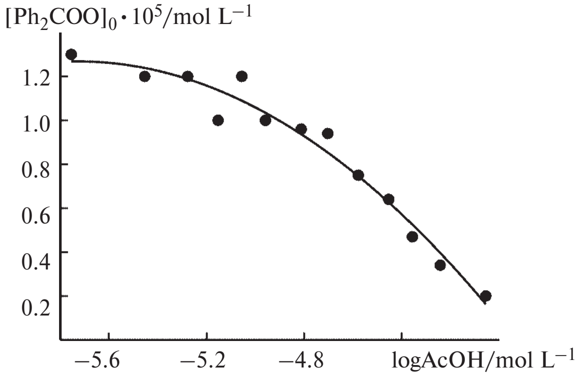


Fig. 2. Initial absorbance of diphenylcarbonyl oxide as a function of the concentration of acetic acid in MeCN.

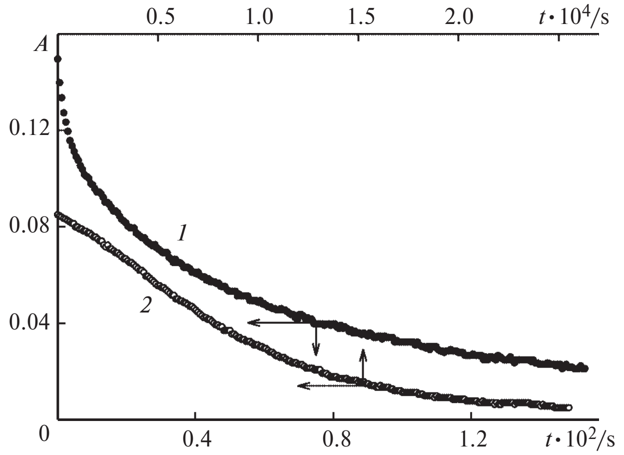
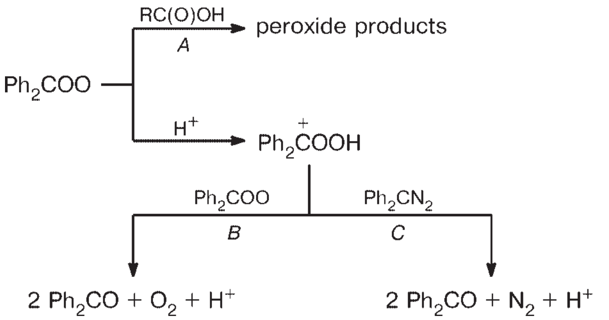


Fig. 3. Kinetic curves for the Ph_2COO decay absorbance in the presence of benzoic acid in MeCN ($[Ph_2CN_2]_0$ = $1 \cdot 10^{-4}$ mol L^{-1}): *1*, $[PhC(O)OH]_0 = 6.25 \cdot 10^{-7}$ mol L^{-1}; and *2*, $[PhC(O)OH]_0 = 1.4 \cdot 10^{-5}$ mol L^{-1}.

of the protonated Ph_2COO molecules with another carbonyl oxide molecule (*B*) or with the initial diazo compound (*C*).



In the last two cases, the participation of a proton in several steps of the reaction can explain the strong influence of the low acid concentration on the rate of carbonyl oxide consumption. However, our finding that the apparent rate constant of carbonyl oxide consumption does not increase with an increase in the diazo compound concentration (see below) indicates a negligible contribution of channel *C* to the reaction rate. The predominant occurrence of channel *A* is indicated by the following experimental facts:

(1) analysis of the products showed the accumulation of peroxides in the reaction mixture, whereas both Ph_2COO recombination and its reaction with Ph_2CN_2 barely produce peroxides;

(2) when the acid (~10^{-7}—10^{-6} mol L^{-1}) is introduced into the system, an initial fast region at the curve for the Ph_2COO absorbance decay appears (Fig. 3, curve *1*), and it disappears upon the next light pulse, indicating acid consumption;

(3) as the acid concentration increases, the degree of Ph_2COO conversion corresponding to the fast region of the kinetic curve increases.

Thus, Ph_2COO is consumed in two processes with noticeably different rates. At the final, slow region of the kinetic curve Ph_2COO recombination predominates, and the presence of the fast region is caused by the reaction of Ph_2COO with the acid characterized by the first order with respect to the carbonyl oxide concentration

$$d[Ph_2COO]/dt = \\ = k_b[RC(O)OH][Ph_2COO] + 2k_5[Ph_2COO], \qquad (7)$$

where [RC(O)OH] is the acid concentration, and k_b is the rate constant of the bimolecular reaction of Ph_2COO with the acid. Going to absorbance, we obtain

$$(-dA/dt)k_b[RC(O)OH]A + [2k_5/(\varepsilon l)]A^2 = \\ = k^I A + k^{II} A^2, \qquad (8)$$

where $k^I = k_b[RC(O)OH]$, $k^{II} = 2k_5/(\varepsilon l)$.

The analytical solution of Eq. (8) has the form

$$\ln\{(k^I + k^{II}A)A_0/[(k^I + k^{II}A_0)A]\} = k^I t. \qquad (9)$$

The k^I rate constant was calculated by Eq. (8) from the initial fast region of the kinetic curve using k^{II} = $2k_5/(\varepsilon l) = 940$ s^{-1}.[4,6]

At rather high acid concentrations Ph_2COO is consumed according to a kinetic law of the first order (see Fig. 3, curve *2*), and k^I can be determined by the linearization of the kinetic curve in the coordinates of a first-order equation

$$\ln A = \ln A_0 - k^I t. \qquad (10)$$

Influence of experimental conditions on the reaction kinetics. The apparent rate constant for the reaction of diphenylcarbonyl oxide with acids **1—6** depends variously on the experimental conditions. In solutions of acetonitrile and benzene, when the initial acid concentration increases, the apparent k^I rate constant increases according to a nonlinear law, approaching to a limiting

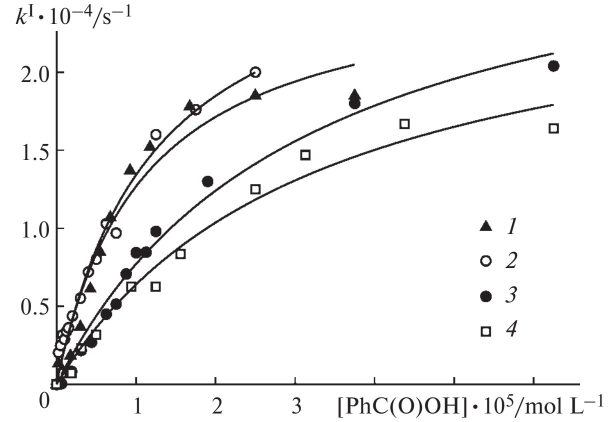


Fig. 4. Apparent rate constant of Ph_2COO decay as a function of the benzoic acid content at different concentrations of Ph_2CN_2 in MeCN; $[Ph_2CN_2]$/mol L^{-1}: *1*, $1.6 \cdot 10^{-1}$; *2*, $5.0 \cdot 10^{-1}$; *3*, $2.0 \cdot 10^{-4}$; and *4*, $5.0 \cdot 10^{-4}$.

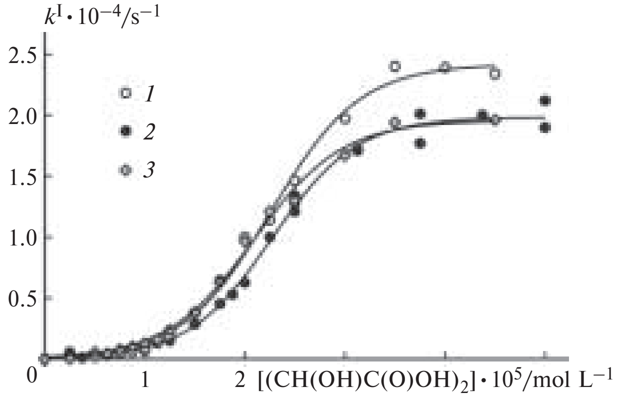


Fig. 5. Apparent rate constant of Ph_2COO decay as a function of the of tartaric acid content at different concentrations of Ph_2CN_2 in MeCN; $[Ph_2CN_2]$/mol L^{-1}: *1*, $5.0 \cdot 10^{-5}$; *2*, $2.0 \cdot 10^{-4}$; and *3*, $5.0 \cdot 10^{-4}$.

value. The curves for the k^I—[RC(O)OH] plot are monotonic for acids **1—4** (Fig. 4), whereas hydroxy acids **5** and **6** exhibit a pronounced, well reproducible S-like shape of the plot of the apparent first-order rate constant on the acid concentration (Fig. 5). The limiting k^I value is independent of the nature of acid and is $(2.5 \pm 0.5) \cdot 10^4$ s^{-1} for acetonitrile. In a solution of *n*-pentane, the plot of k^I *vs.* acid concentration is almost linear and have no tendency to exceeding the limit in the studied concentration interval [MeC(O)OH] = $(0—1) \cdot 10^{-5}$ mol L^{-1}.

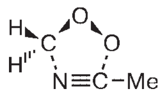
The influence of the solvent on the reaction kinetics was studied for the Ph_2COO—AcOH system. Unlike the regularity found earlier,[4—11] for the reactivity of diphenylcarbonyl oxide we found that the change in the medium polarity in the series MeCN—PhOH—pentane has no effect on the rate of Ph_2COO consumption. Taking into account the high value of the bimolecular rate constant (Table 2), this fact indicates, most likely, the diffusion-controlled regime of the reaction.

Assuming that carbonyl oxide interacts with the H^+ proton, an increase in the degree of acid dissociation should accelerate the reaction. However, it turned out that the addition of water (to $7 \cdot 10^{-2}$ mol L^{-1}) has almost no effect on the rate of the reaction of Ph_2COO with AcOH. An increase in the H_2O concentration over the indicated value results in diphenyldiazomethane precipitation on the cell walls and a sharp decrease in the concentration of the generated carbonyl oxide.

In the series of weak acids **1—6**, the nature of the acid has almost no effect on the apparent rate constants of their reaction with carbonyl oxide. It was difficult to study the reaction of Ph_2COO with trifluoroacetic and hydrochloric acid because of the fast acid-catalyzed decomposition of diphenyldiazomethane that is a precursor of diphenylcarbonyl oxide.

The influence of the initial concentration of the Ph_2CN_2 diazo compound on the apparent k^I rate constant is of interest. This influence is most pronounced for benzoic acid (see Fig. 4) and manifests itself as a decrease in the slope of the initial linear region of the k^I—$[RC(O)OH]_0$ curve with an increase in the Ph_2CN_2 concentration. The limiting k^I value is virtually independent of the initial concentration $[Ph_2CN_2]_0$. A similar, although less pronounced influence of the concentration of the diazo compound on the reaction kinetics is found in the case of acetic and tartaric acids. The slope of the k^I—$[\mathbf{5}]_0$ plot was determined in the inflection point of the S-like curve.

Kinetic scheme of the process. The found formal kinetic regularities indicate an important role of complex formation between the participants of the process: solvent, diphenylcarbonyl oxide, its precursor diazo compound, and, of course, acid RC(O)OH. The Ph_2COO formed under flash photolysis conditions can react with all components of the reaction mixture but, in our opinion, the most probable primary reaction of carbonyl oxide is its association with the solvent, in particular, acetonitrile. The concentration of the diazo compound is rather low, and in the absence of the acid Ph_2COO is consumed according to a kinetic law of the second order. This indicates a negligible contribution of reaction (4) to the overall process under experimental conditions. The concentrations of the solvent and acid differ by at least six orders, which enhances the probability of the solvation of Ph_2COO by the solvent molecule. In addition, quantum-chemical calculations[7] showed that carbonyl oxide H_2COO forms with ethylene and especially with acetonitrile rather stable intermolecular complexes of the type



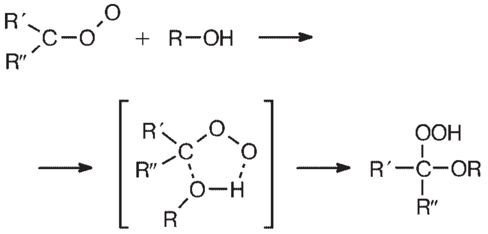
$\Delta H°_{298} = -5.6$ kcal mol^{-1}.

Table 2. Kinetic characteristics of the Ph_2COO decay rate in the presence of acids

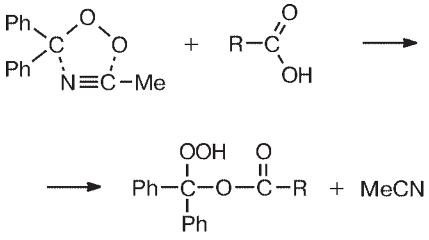
Acid	Medium	$[Ph_2CN_2] \cdot 10^5$ /mol L^{-1}	$k_b \cdot 10^{-8}$ /L mol^{-1} s^{-1}	$a \cdot 10^{-4}$ /s^{-1}	$b \cdot 10^5$ /L mol^{-1} s^{-2}	pK_a
Acetic	MeCN	1.6	48.8	2.5±0.2	0.5±0.1	4.75
		3.3	23.0	3.0±0.2	1.3±0.2	
		20	16.7	2.4±0.1	1.5±0.2	
		50	18.6	2.6±0.1	1.4±0.2	
		20	16.1[a]	3.0±0.2	2.0±0.3	
		20	14.5[b]	3.5±0.4	2.4±0.6	
		20	14.4[c]	3.9±0.5	5.2±1.2	
	C_6H_6	4.9	42.3	3.2±0.4	0.8±0.2	
		20	51.9	3.0±0.2	0.6±0.1	
		49	74.5	2.3±0.3	0.3±0.1	
	n-C_5H_{12}	20	29.6	—	—	
Benzoic	MeCN	1.6	24.9	2.6±0.2	1.0±0.2	4.18
		5.0	24.5	3.0±0.2	1.2±0.2	
		20	10.2	3.2±0.2	3.1±0.4	
		50	8.4	2.7±0.3	3.3±0.6	
Formic	MeCN	20	22.6	2.9±0.3	1.3±0.3	3.75
Oxalic	MeCN	20	4.6	3.7±0.3	8.1±1.5	1.27
Tartaric	MeCN	5	9.9[d]			2.98
		20	8.8[d]			
		50	8.5[d]			
Malic	MeCN	20	8.7[d]			3.40

[a] $[H_2O] = 6.9 \cdot 10^{-3}$ mol L^{-1};
[b] $[H_2O] = 6.9 \cdot 10^{-2}$ mol L^{-1};
[c] $[Ph_2COO]_0 \sim 2 \cdot 10^{-5}$ mol L^{-1}, which is by ~2 times higher than in all other cases;
[d] the rate constant was determined from the slope in the inflection point of the S-like plot of k^I *vs.* acid concentration.

Then solvated Ph_2COO reacts with the acid to produce molecular products. It is known[1,17,18] that the ozonolysis of alkenes in the presence of hydroxyl-containing compounds (*viz.*, H_2O, alcohols, hydroperoxides, acids) produces α-substituted hydroperoxides through the insertion of carbonyl oxide at the O—H bond.



By analogy to this reaction, we can assume that α-hydroperoxydiphenylmethyl carboxylate is the reaction product of solvated Ph_2COO with acids **1—6** under our experimental conditions (solvent molecule is released in the reaction).



This reaction explains the irreversible consumption of the acid found in experiments with low initial concentrations of RC(O)OH.

The formation of peroxides is confirmed by iodometric titration of the reaction mixture after the complete consumption of diphenyldiazomethane under the conditions of steady-state MB dye-photosensitized Ph_2CN_2 decomposition in the presence of AcOH. The photoexcitation of MB followed by its deactivation produces singlet dioxygen, whose reaction with diphenyldiazomethane affords Ph_2COO and N_2. Application of this method for generation of carbonyl oxide instead of Ph_2CN_2 photolysis by the near-UV irradiation (used in the kinetic experiments) is due to the fact that photolysis is accompanied by a side reaction of carbene Ph_2C:, the product of diazo compound photolysis, with the acid, decreasing the yield of peroxide.

The amount of the peroxide formed depends on the initial concentration of diphenyldiazomethane and is independent of the acid concentration in the 0.012—0.082 mol L^{-1} interval (Table 3). This indicates that the intermediate product of photosensitized Ph_2CN_2 decomposi-

Table 3. Relative yield of peroxide upon the decomposition of Ph_2CN_2 photosensitized by the MB dye in the presence of AcOH (solvent MeCN, 295 K)

Entry	$[Ph_2CN_2]_0 \cdot 10^3$	$[AcOH]_0 \cdot 10^2$	$[ROOH]_0 \cdot 10^3$	$[ROOH]/[Ph_2CN_2]_0$
		mol L^{-1}		
1	1.60	1.17	0.9±0.2	0.56
2	3.42	1.17	1.7±0.2	0.50
3	3.42	3.51	1.2±0.2	0.35
4	3.42	5.85	1.6±0.4	0.47
5	3.42	8.19	1.3±0.4	0.38
6	4.48	1.17	2.1±0.4	0.47

tion reacts completely with the acid, and the peroxide is formed from the diazo compound. The yield of peroxide based on the initial diphenyldiazomethane is 46±10%. Since the reaction of Ph_2CN_2 with singlet dioxygen produces diphenylcarbonyl oxide with 60% probability,[19] and the diazo compound decomposes partially by the acid, we can conclude that hydroperoxide formation in the reaction of Ph_2COO with RC(O)OH is the main reaction channel.

Finally, the complex formation between diphenyldiazomethane and carboxylic acid should be taken into account. In organic media the catalytic decomposition of diazo compounds by weak acid is rather slow. This is indicated by the virtual constancy of the Ph_2CN_2 concentration during the photolytic experiment (see above). In addition, the acid concentrations in our experiments are too low (~10^{-7}—10^{-5} mol L^{-1}) for the efficient decomposition of the diazo compound. However, the reaction of the acid with Ph_2CN_2 should be taken into account because the binding of RC(O)OH to a stable intermolecular complex decreases the concentration of free acid, which is active in reactions with solvated carbonyl oxide.

Thus, the kinetic scheme of the reaction of Ph_2COO with RC(O)OH under our experimental conditions has the form

$$Ph_2COO + Solv \rightleftharpoons Ph_2COO...Solv, \qquad (11, -11)$$

$$Ph_2COO...Solv + RC(O)OH \rightarrow \rightarrow Ph_2C(OOH)OC(O)R + Solv, \qquad (12)$$

$$RC(O)OH + Ph_2CN_2 \rightleftharpoons Ph_2CN_2...HO(O)CR. \qquad (13)$$

The concentration of free acid $[RC(O)OH]_a$ is related to the total acid concentration by the relationship

$$[RC(O)OH]_a = [RC(O)OH]/(1 + k_{13}[Ph_2CN_2]). \qquad (14)$$

In this expression, we neglected a change in the concentration of diazo compound due to complex formation because it is not substantial for qualitative analysis of the kinetic scheme.

The rate of diphenylcarbonyl oxide decay according to the first order kinetics is determined by the rate of reaction (12), so that

$$-d[PH_2COO]/dt = k^I[Ph_2COO] = k_{12}[Ph_2COO...Solv][RC(O)OH]. \qquad (15)$$

Using the expression for the quasi-equilibrium concentration of the Ph_2COO complex with the solvent and taking into account Eq. (14), we obtain the equation for the apparent rate constant k^I

$$k^I = \frac{k_{11}k_{12}[Solv][RC(O)OH]}{(k_{13}[Ph_2CN_2]+1)k_{-11}+k_{12}[RC(O)OH]}. \qquad (16)$$

Equation (16) corresponds to the found kinetic regularities of the process. It explains the hyperbolic dependence of the apparent rate constant k^I on the acid concentration. At low $[RC(O)OH]_0$ values, the first term of the denominator prevails, which agrees with the presence of the linear region in the curve for the plot of k^I *vs.* acid concentration

$$k^I = \{k_{11}k_{12}/(k_{13}[Ph_2CN_2] + 1)\}[RC(O)OH]. \qquad (17)$$

Equation (17) explains the decrease in the slope of the initial region in the k^I—[RC(O)OH] curve with an increase in the diphenyldiazomethane concentration (see Fig. 4). In this case, the diazo compound plays a role of the buffer decreasing the active concentration of the acid and the rate of reaction (12).

When the acid concentration increases, the rate of irreversible Ph_2COO decay by reaction (12) begins to exceed the rate of reverse reaction (−11), approaching to the limiting $k_{lim}{}^I$ value when $(k_{13}[Ph_2CN_2] + 1)k_{-11} \ll \ll k_{12}[Ph_2C(O)OH)]$

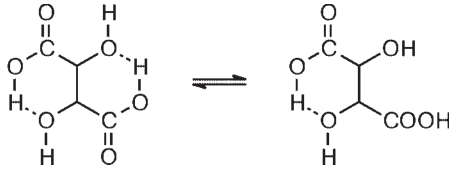
$$k^I{}_{lim} = k_{11}[Solv]. \qquad (18)$$

Equation (18) explains why the $k^I{}_{lim}$ value is independent of the acid nature and diphenyldiazomethane concentration. Equation (16) well reproduces the experimental plots. Presenting in the form

$$k^{\mathrm{I}} = ax/(b + x), \qquad (19)$$

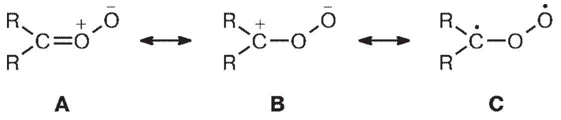
where x is the acid concentration, $a = k_{11}[\mathrm{Solv}] = k^{\mathrm{I}}_{\mathrm{lim}}$, $b = (k_{13}[\mathrm{Ph_2CN_2}] + 1)k_{-11}/k_{12}$, we can calculate the a and b coefficients (see Table 2). It is seen that the a value is independent of the experimental conditions because it is determined only by the solvent nature. Coefficient b and the concentration of diazo compound change in parallel according to Eq. (16).

The S-like shape of the plots of k^{I} *vs.* concentrations of tartaric and malic acids can be due to the fact that the concentration of active carboxylic groups in these acids is decreased by the formation of an intramolecular hydrogen bond.



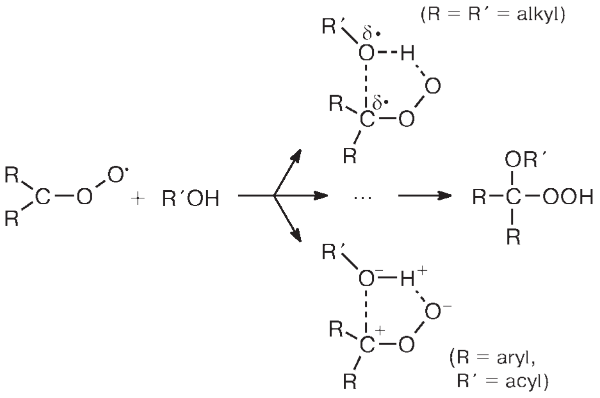
Since this equilibrium is shifted to the left, the reaction of carbonyl oxide with the acid is kinetically manifested at the tartaric acid concentrations $\geq 10^{-5}$ mol L^{-1} (see Fig. 5).

The ratio of coefficients a/b, which, as can easily be shown, represents the second order apparent rate constant k_{b}, can serve as a quantitative characteristic of the reactivity of acids in the reaction studied. The k_{b} values are presented in Table 2. It is seen that carbonyl oxide molecules are inserted at the O—H bond of the acids with almost diffusion constants. No relationship between the strength of organic acid (pK_{a}) and its reactivity was observed. The very high reactivity of acids in this reaction is in dramatic contrast with the results[18] demonstrating the low reactivity of AcOH in the reaction with dimethylcarbonyl oxide and $\mathrm{Me_2COO}$ reacts with MeOH most rapidly and with the highest yield of α-methoxyisopropyl hydroperoxide. The reason for this divergence, most likely, is a distinction in the electronic nature of carbonyl oxide intermediates. It is known that the structure of carbonyl oxide cannot correctly be presented in the framework of classical Lewis structures. Therefore, a combination of several resonance structures is often used to describe the electronic properties of carbonyl oxides.



The contribution of one or another resonance structure to the wave function of the carbonyl oxide molecule is determined by the nature of the R substituent and the solvating ability of the solvent. Carbonyl oxides with alkyl substituents are characterized by a substantial contribution of resonance structure **C** and, correspondingly, the biradical properties resulting in their high reactivity. The conjugation of the 4π-electronic system of the carbonyl oxide molecule with the aromatic system in $\mathrm{Ph_2COO}$ stabilizes the zwitterionic component **A** and **B** and decreases the reactivity of carbonyl oxide in the reaction with another carbonyl oxide molecule and oxidized substrates. The polarization of the carbonyl oxide fragment is responsible for the ambiphilic nature of $\mathrm{Ph_2COO}$ and facilitates the molecular mechanism of its reactions.

Thus, according to the above concepts, $\mathrm{Me_2COO}$ reacts with hydroxyl-containing compounds (*viz.*, alcohols, water, and acids) completely or at least partially *via* the homolytic mechanism. The reaction rate is determined by the strength of the O—H bond, *i.e.*, decreases in the series alcohol > water > acetic acid.[18] The insertion at the O—H bond of diphenylcarbonyl oxide, which exhibits zwitterionic properties to a greater extent, is facilitated when this bond is polarized (*viz.*, in reactions with acids). It is most likely that the reaction of carbonyl oxide with alcohols proceeds, in both cases, *via* the insertion mechanism through transition states with different polarities, which manifest in the limiting cases exclusively the homolytic or molecular nature.



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