Kinetics, products, and mechanism of the reaction of diphenylcarbonyl oxide with sulfoxides

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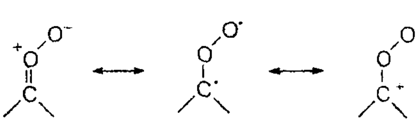
The kinetics of the reactions of diphenylcarbonyl oxide with dimethyl, di-*n*-hexyl, diphenyl, dibenzyl, and *n*-hexylbenzyl sulfoxides in acetonitrile was studied by flash photolysis at 295 K. The oxidation of sulfoxide affords the corresponding sulfone as the main reaction product, and diphenyl sulfide also forms in the case of Ph_2SO. Solvent effect on the reaction kinetics and the composition of the reaction products was studied. The reaction mechanism is discussed, which includes two parallel pathways: the nucleophilic attack of carbonyl oxide at the sulfur atom of sulfoxide and the formation of the cyclic sulfurane intermediate *via* the electrophilic 1,3-cycloaddition of Ph_2COO at the S=O bond. The sulfurane undergoes fragmentation *via* parallel channels to form sulfone or sulfide.

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

It is known[1] that the oxidation of substituted diphenyl sulfoxides by fluorenone oxide to sulfones proceeds *via* the nucleophilic mechanism ($\rho = +0.26$). At the same time, α,α,α-trifluoroacetophenone oxide reacts with these substrates *via* the electrophilic mechanism ($\rho = -0.74$), and the corresponding sulfide forms along with the main product.[2,3]

The ambiphilic nature of carbonyl oxides (COx) is due to the specific features of their electronic structure. Carbonyl oxides are described in the framework of the concepts on strongly polar intermediates with pronounced biradical properties, for example, in the form of resonance structures, zwitterionic (**A**, **C**) and biradical (**B**).



A **B** **C**

The substantial mixing of states **A**—**C** indicates that the energies of the resonance forms are close, which assumes the strong influence of various factors (the nature of the substituent, solvent, and co-reactant) on the chemical properties of COx.

We may conclude that the structures with the negatively charged terminal oxygen atom prevail in the reactions of fluorenone oxide[1] with sulfoxides, because the planar structure of the fluorenone oxide molecule favors the conjugation of electrons of the aromatic ring and carbonyl oxide fragment and the additional stabilization of the polar resonance structures.[4] In the case of $Ph(CF_3)COO$, the strong electron-withdrawing capability of the CF_3 group favors a lower polarization of the COO fragment of carbonyl oxide,[2,3] due to which it has more pronounced biradical properties and the capability of electrophilic attack by the oxidant molecule.

In this work, we studied the kinetics of the reactions of diphenylcarbonyl oxide Ph_2COO with several sulfoxides R^1R^2SO ($R^1 = R^2 =$ Me (**1**), *n*-C_6H_{13} (**2**), Ph (**3**), CH_2Ph (**4**); $R^1 =$ *n*-C_6H_{13}, $R^2 = CH_2Ph$ (**5**)) at 295±2 K.

Experimental

Solvents (acetonitrile, benzene, *n*-pentane) were purified by standard procedures.[5] Dimethyl sulfoxide **1** was dried with NaOH and distilled *in vacuo*. Sulfoxides **2**—**5** were recrystallized from alcohol. Diphenyldiazomethane was synthesized and purified by the previously described procedure.[6]

The reaction products of Ph_2COO with sulfoxides **1** and **3** were studied under the conditions of steady-state photolysis. A DRT-1000 mercury-quartz lamp served as the photolytic source, the beam power in the wavelength interval of 270—380 nm was 95—110 W, and the reactor was remote from the source at 15 cm. Acetonitrile (5 mL), diphenyldiazomethane ($2 \cdot 10^{-3}$ mol L^{-1}), and the substrate of oxidation were placed in a thermostatting cylindrical reactor. Photolysis was carried out with λ = 270—380 nm (UFS-2 light filter) at 25 °C for 10—20 min until the pink color of the solution disappeared. In some experiments, the photosensitized photolysis of the diazo compound was performed in the presence of Methylene Blue (MB), which

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was photoexcited with $\lambda > 560$ nm (nitrogen incandescent lamp, power 500 W, OS-14 light filter). Air was passed through the solution during photolysis. The sample for analysis was concentrated to a volume of ~0.2 mL. The products were analyzed by GC-MS on a Finnigan 4021 instrument (EI, 70 eV; gas chromatograph, quartz capillary column 50 m × 0.2 mm, SE-30, carrier gas He, linear temperature programming from 50 to 300 °C, heating rate 6 °C min^{-1}). The absolute calibration of the instrument was performed by benzophenone—sulfoxide and benzophenone—sulfone calibrating systems with relative sensitivities of 1.0 : 1.1 and 1.0 : 1.2 and absolute sensitivity at a level of 1% (~$4 \cdot 10^{-8}$ g).

An impulse photolysis (IP) setup was used for kinetic experiments (an IFP 5000-2 lamp as the photolytic source, maximum energy of the pulse 400 J at U = 5 kV, C = 32 μF, ~90% photoenergy was emitted per 50 μs). A quartz cell with an optical length (l) of 10 cm and an inner diameter of ~1 cm was used as the reactor. The setup, whose parameters have been presented previously,[7] was supplemented by a device of computer simulation of the pulse signal. The program of signal processing determined automatically (with the possibility of manual correction) the beginning and end of the photopulse and the zero optical density. Nonlinear regression analysis makes it possible to determine the effective reaction order, initial optical density, and rate constants of any order and to process the kinetic curve in the coordinates of the equation that describes the simultaneous first- and second-order reactions.*

Flash photolysis (FP) of the Ph_2CN_2—sulfoxide—solvent—O_2 system (in air) was performed with filtered light (UFS-2 light filter, transmission region 240—380 nm). In all experiments, to prevent the photochemical decomposition of Ph_2CN_2 the photointensity of the probing beam was attenuated by an SS-15 light filter (transmission region 300—520 nm). The initial concentration of diphenyldiazomethane ($[Ph_2CN_2]_0$) was (1.5—2) $\cdot 10^{-4}$ mol L^{-1}, and the concentration of sulfoxides ($[R^1R^2SO]_0$) was varied in the range of 0.001—0.1 mol L^{-1}. The reaction kinetics was monitored by a decrease in the absorbance (A) of diphenylcarbonyl oxide at the maximum of its absorption band (λ_{max} = 410 nm, $\varepsilon_{max} = 1.9 \cdot 10^3$ L mol^{-1} cm^{-1}).[8]

Results and Discussion

Reaction kinetics. The flash photolysis of a solution of diphenyldiazomethane in the presence of oxygen results in the formation of the corresponding carbonyl oxide[8]:

$$Ph_2CN_2 \xrightarrow{h\nu} {}^1Ph_2C\colon + N_2, \quad (1)$$

$${}^1Ph_2C\colon \rightleftharpoons {}^3Ph_2C\colon, \quad (2)$$

$${}^3Ph_2C\colon + O_2 \longrightarrow Ph_2COO, \quad (3)$$

which then is consumed in the reactions

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

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

As shown previously,[8,9] at $[Ph_2CN_2]_0 \le 3 \cdot 10^{-4}$ mol L^{-1} the consumption of Ph_2COO in reaction (4) can be neglected. Under these conditions, the curve of a decrease in diphenylcarbonyl oxide optical density (A) is described by the second-order equation

$$-\frac{dA}{dt} = \frac{2k_5}{\varepsilon l}A^2.$$

In the presence of sulfoxides, the half-time of diphenylcarbonyl oxide consumption decreases and the formal reaction order (n) changes: when the concentration $[R^1R^2SO]_0$ increases, n decreases from 2 to 1.1. This indicates that Ph_2COO reacts with sulfoxides in parallel with reaction (5):

$$Ph_2COO + R^1R^2SO \longrightarrow \text{Products}, \quad (6)$$

and, hence,

$$-\frac{d[Ph_2COO]}{dt} = k_6[R^1R^2SO][Ph_2COO] + 2k_5[Ph_2COO]^2$$

or, going to the optical absorption values,

$$-\frac{dA}{dt} = k_6[R^1R^2SO]A + \frac{2k_5}{\varepsilon l}A^2 = \kappa_1 A + \kappa_2 A^2,$$

where $\kappa_1 = k_6[R_1R_2SO]$, $\kappa_2 = 2k_5/(\varepsilon l)$ ($2k_5 = 1.8 \cdot 10^7$, $7.4 \cdot 10^7$, and $2.0 \cdot 10^9$ L mol^{-1} s^{-1} for solutions in acetonitrile, benzene, and n-pentane, respectively[8]; ε and l are indicated above).

Since $[R_1R_2SO]$ exceeds $[Ph_2COO]$ by some orders of magnitude, then $[R_1R_2SO] = [R_1R_2SO]_0$ = const in each particular experiment, and the analytical solution of the equation presented above has the form:

$$\ln\frac{(\kappa_1 + \kappa_2 A)A_0}{(\kappa_1 + \kappa_2 A_0)A} = \kappa_1 t.$$

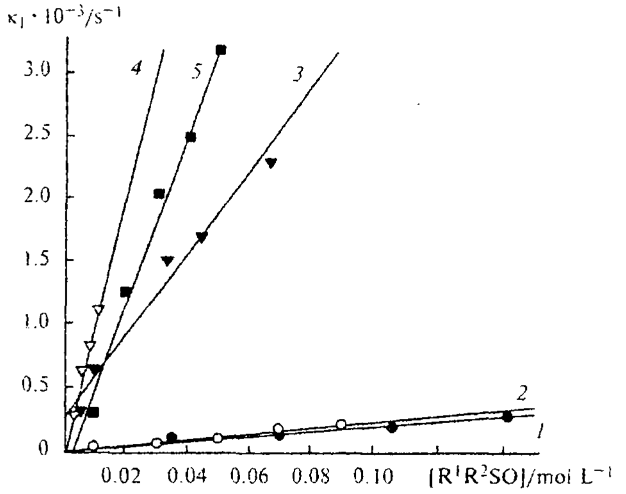

Fig. 1. Effective rate constant of the first order (κ_1) as a function of the concentration of sulfoxides (MeCN, 295 K). The numeration of the curves corresponds to the numbers of the sulfoxides.

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Table 1. Absolute rate constants of the reactions of Ph_2COO with sulfoxides (295 K)

Sulfoxide	Solvent	$\Delta[R^1R^2SO]$ /mol L^{-1}	k_6 /L mol^{-1} s^{-1}	π^*
1	MeCN	0.07—0.21	$(2.36\pm0.19)\cdot10^3$	—
1	PhH	0.04—0.21	$(3.21\pm0.06)\cdot10^3$	—
2	MeCN	0.01—0.09	$(2.58\pm0.17)\cdot10^3$	0.75
2	PhH	0.01—0.05	$(3.89\pm0.20)\cdot10^3$	0.59
2	n-C_5H_{12}	0.01—0.05	$(2.28\pm0.02)\cdot10^4$	−0.08
3	MeCN	0.0055—0.1100	$(3.47\pm0.25)\cdot10^4$	—
4	MeCN	0.001—0.01100	$(1.05\pm0.03)\cdot10^5$	—
5	MeCN	0.01—0.05	$(6.67\pm0.39)\cdot10^4$	—

Using this equation, we determined the effective rate constants κ_1 by nonlinear regression analysis from the kinetic curves of A decrease. The κ_1 value was measured at least five times for each sulfoxide concentration. The rate constant κ_2 for all sulfoxides remains almost unchanged under different experimental conditions. The effective rate constant κ_1 depends linearly (correlation coefficient $r \geq 0.99$) on $[R_1R_2SO]_0$ (Fig. 1). The κ_1—$[R_1R_2SO]_0$ plots do not pass through the origin, which can be explained by an error of measurement of the effective rate constant. The absolute rate constants k_6 for the reactions of diphenylcarbonyl oxide with sulfoxides were determined from the slope (Table 1).

Data on the k_6 values are lacking in the literature. The relative rate constant of the reaction of diphenylcarbonyl oxide with sulfoxide **3** and the starting diazo compound was determined[10] by the chemiluminescence method: $k(Ph_2COO + Ph_2SO)/k(Ph_2COO + Ph_2CN_2) = 0.177$ (MeCN, 70 °C). Using the reference rate constant of $2.4\cdot10^5$ L mol^{-1} s^{-1} (MeCN, 22 °C),[8] we obtained the estimated value $k(Ph_2COO + Ph_2SO) = 4.2\cdot10^4$ L mol^{-1} s^{-1}, which well agrees with $k_6 = 3.4\cdot10^4$ L mol^{-1} s^{-1} calculated in this work.

Reaction products. To obtain additional information on the mechanism of the reactions of diphenylcarbonyl oxide with sulfoxides, we studied the products of the photolysis of Ph_2CN_2 ($2\cdot10^{-3}$ mol L^{-1}) in MeCN in the presence of sulfoxides **1** and **3**. The results of the analysis are presented in Table 2.

In all cases, benzophenone is the main product. The direct photolysis of diphenyldiazomethane with λ = 280—370 nm also gives diphenylmethanol and tetraphenylethylene. Unsaturated compounds appear, probably, during the following reaction[6]:

$$Ph_2CN_2 + HX \longrightarrow Ph_2CNN...H^+X^- \longrightarrow Ph_2CH^+ + N_2 + X^-, \qquad (7)$$

$$Ph_2CH^+ + Ph_2CN_2 \longrightarrow Ph_2C{=}CPh_2 + N_2 + H^+. \qquad (8)$$

Here HX is the acid formed by oxidation. The acid-catalyzed decomposition of the diazo compounds by the mechanism presented occurs under the action of strong acids.[6] Therefore, we may assume that HX is a sulfonic acid, in particular, $PhSO_3H$, whose formation is possible by the photooxidative destruction of sulfoxide **3** or the corresponding sulfone. Diphenylmethanol is either the product of diphenylcarbene insertion at the O—H bond of the H_2O molecule, or it appears due to the reaction of the diphenylmethyl cation with the H_2O molecule (acetonitrile contains some amount of water). Under the conditions of sensitized Ph_2CN_2 photolysis using MB, carbene is not formed and carbonyl oxide is generated in the following reactions[11,12]:

$$MB \xrightarrow{h\nu} MB^*, \qquad (9)$$

$$MB^* + O_2 \longrightarrow MB + {}^1O_2\,({}^1\Delta_g), \qquad (10)$$

$$Ph_2CN_2 + {}^1O_2 \xrightarrow{(\alpha)} Ph_2COO + N_2 \qquad (11)$$

$$Ph_2CN_2 + {}^1O_2 \xrightarrow{(1-\alpha)} Ph_2CO + N_2O. \qquad (12)$$

Under our experimental conditions, the fraction of the channel of the reaction of the diazo compound with singlet dioxygen that affords Ph_2COO is 0.6.[13] The products of diphenylcarbene transformation are absent from the oxidate, which agrees with the scheme presented. The high yield of benzophenone is due to the stoichiometry of the process. The reaction schemes for

Table 2. Relative yields of the products of the steady-state photolysis of diphenyldiazomethane in the presence of sulfoxides R_2SO (MeCN, 25 °C, $[Ph_2CN_2]_0 = 2\cdot10^{-3}$ mol L^{-1})

Entry	R	$[R_2SO]$	Yield (%)					Note
		/mol L^{-1}	R_2SO_2	R_2S	Ph_2CO	Ph_2CHOH	$Ph_2C{=}CPh_2$	
1	Ph	0.01	6.3	—	86.5	5.5	1.7	—
2	Ph	0.09	16.0	14.0	55.4	6.4	8.2	Average of two measurements
3	Ph	0.09	17.0	2.8	80.2	—	—	$[MB] = 1\cdot10^{-4}$ mol L^{-1}
4	Ph	0.01	31.2	3.3	61.8	1.9	1.3	Solvent — n-pentane, 0.5% PhCOOPh
5	Me	0.1	23.6	—	71.0	2.5	2.9	For the detection of Me_2S, see text
6	Me	0.1	18.0	—	82.0	—	—	$[MB] = 1\cdot10^{-4}$ mol L^{-1}

steady-state and flash photolyses are identical. However, reaction (5) of quadratic decay is the main channel of Ph_2COO consumption in the FP conditions and in the absence of sulfoxide, whereas in steady-state photolysis, reaction (4) prevails due to the low quasi-stationary concentration of carbonyl oxide. Thus, in the presence of sulfoxide, benzophenone is formed in parallel routes (4) and (6). It can easily be shown that, under our experimental conditions, these reactions proceed with comparable rates to provide a high yield of benzophenone. In addition, in sensitized Ph_2CN_2 photolysis, benzophenone is formed in side reaction (12), whose fraction is $1 - \alpha = 0.4$.[13]

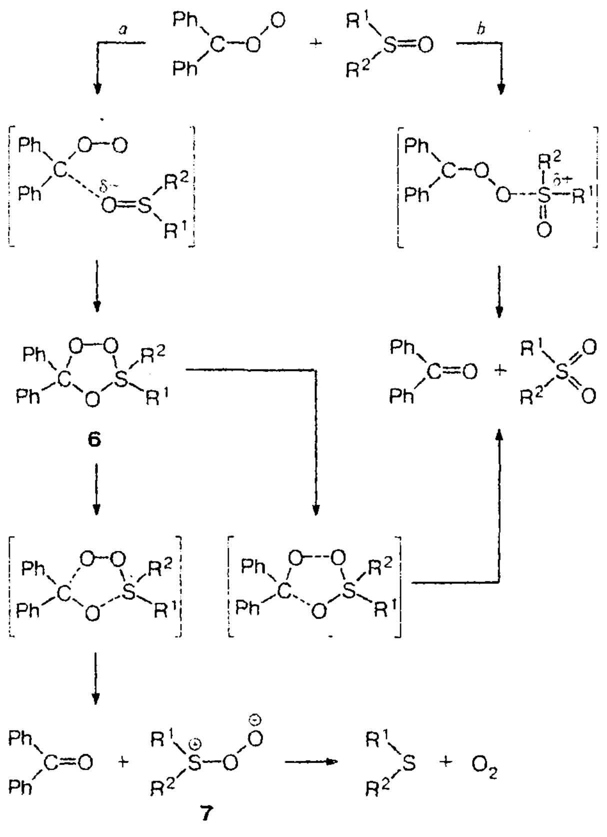
As expected, the oxidation of sulfoxides **1** and **3** affords the corresponding sulfone as the main product, whose yield increases when the reaction is carried out in nonpolar *n*-pentane (see Table 2, entries *1* and *4*) and the concentration of sulfoxide increases (entries *1* and *2*). In addition, diphenyl sulfide was detected in the reaction mixture (entries *2—4*). These findings agree with the published data,[2,3] according to which sulfides are the products of the reactions of sulfoxides with α,α,α-trifluoroacetophenone oxide. In the reaction of Ph_2COO with sulfoxide **1**, the product of deoxygenation, dimethyl sulfide, was detected only qualitatively. Due to its high volatility (b.p. 37.3 °C), Me_2S evaporated at the stage of reaction mixture concentrating preceding the analysis of the products. Therefore, dimethyl sulfide was captured in a trap cooled with liquid nitrogen at the initial stage of sample concentrating. Analysis showed the mass spectral peaks characteristic of Me_2S: 62 $[M]^+$, 47 $[MeS]^+$, 46 $[CH_2S]^+$, 45 $[CHS]^+$, 15 $[Me]^+$. We failed to estimate quantitatively the content of Me_2S against the background of acetonitrile.

Solvent effect. It is known,[8,9,15,16] that a solvent has a strong effect on the reactivity of carbonyl oxides in the recombination act (see reaction (5)). The solvent effect in the process under study was investigated for the reactions of Ph_2COO with sulfoxides **1** and **2** in acetonitrile, benzene, and *n*-pentane* (see Table 1). Parallel changes in the rate constant of the reaction of diphenylcarbonyl oxide with sulfoxide **2** and various solvent parameters were observed in the framework of the Winstein—Grünwald, Amis, Leidler—Eyring, Brownstein equations, *etc.* The k_6 values in Table 1 are compared to the polarity and polarizability parameters (π^*) in the Kamlet—Taft equation, reflecting the relative ability of the solvent to stabilize the charge or bipolar structure due to the dielectric constant of the solvent.[17] *n*-Pentane does not possess this stabilization, which increases sharply (ninefold) k_6. According to the effect found, for the oxidation of sulfoxide **3** in *n*-pentane, the yield of sulfone is much higher (see Table 2, entries *1* and *4*) due to an increase in the fraction of reaction (6) in the overall rate of carbonyl oxide consumption.

Reaction mechanism. The k_6 values range from $2.4 \cdot 10^3$ (sulfoxide **1**) to $1.1 \cdot 10^5$ L mol^{-1} s^{-1} (sulfoxide **4**). We failed to describe the reactivity of sulfoxides as a function of their structure in the framework of the conventional approaches (Hammett and similar correlation equations) perhaps because of the complex mechanism of the reaction of COx with R^1R^2SO.

The presented experimental data indicate an ambiphilic nature of carbonyl oxide. The character of its reaction with sulfoxide is determined, to a great extent, by the structures of COx itself (and, hence, of the prevailing resonance structure) and the co-reactant and the experimental conditions (temperature, solvent nature). The supposed mechanism of the reaction of COx with sulfoxides is presented in Scheme 1.

Scheme 1



(*a* — electrophilic, *b* — nucleophilic)

According to this scheme, the reaction can proceed *via* two routes. The first of them is the nucleophilic addition of the terminal oxygen atom to the sulfur atom of sulfoxide. This pathway, resulting in ketone and sulfone, is characteristic of the reactions of COx with more pronounced 1,3-bipolar properties, in particular, fluorenone oxide.[1] Another possible reaction route is the electrophilic attack of COx at the oxygen atom of sulfoxide (see Scheme 1), which is completed by the formation

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* Sulfoxide **1** is virtually insoluble in *n*-pentane.

of five-membered cyclic intermediate **6**.[3,18] This direction is more probable for α,α,α-trifluoroacetophenone oxide,[2,3] because the trifluoromethyl group decreases the electron density on the carbonyl oxide fragment to enhance the electrophilic properties of COx. Diphenylcarbonyl oxide is intermediate in properties between fluorenone oxide and α,α,α-trifluoroacetophenone oxide. This suggests that Ph_2COO can react with sulfoxide *via* both routes.

Cyclic sulfurane intermediate **6** is very labile and undergoes fragmentation *via* different directions. One of them affords products that can be obtained by the nucleophilic mechanism, ketone and sulfone. Another direction is completed by the formation of persulfoxide zwitterion **7**. The latter is unstable and rapidly decomposes to sulfide and molecular oxygen. This assumption agrees with the results of the analysis of the products. In fact, the use of *n*-pentane as a solvent accelerates the reaction (see Table 1) and increases the probability of sulfone formation, but the yield of sulfide is low in this system (see Table 2). It is most likely that polar acetonitrile efficiently stabilizes zwitterion **7**, thus facilitating the reaction *via* this direction. In *n*-pentane, the formation of bipolar ion **7** is thermodynamically unfavorable.

Note the high yield of diphenyl sulfide in the experiment where carbonyl oxide was generated by direct photolysis of the diazo compound with λ = 280—370 nm as compared to that in sensitized photolysis (λ > 560 nm) (see Table 2, entries *2* and *3*). Since the yield of the sulfide is low, we may assume that the fragmentation to benzophenone and diphenylsulfone is the main channel of the transformation of heterocycle **6**. Sulfurane photoexcitation, possible under the irradiation of the solution with the light in the wavelength interval of 280—370 nm, results in population of the triplet potential surface of the reaction. The subsequent decomposition of the triplet state of sulfurane **6** (with retention of the total multiplicity of the reaction products) to ketone, sulfide, and molecular oxygen in the ground state ($^3\Sigma_g$) is most energetically favorable.

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