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Rate Constants for the Reaction of Diphenyl Carbonyl Oxide with Phenols

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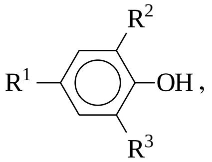
Abstract—The kinetics of the reaction of diphenyl carbonyl oxide Ph_2COO with *o*- and *p*-substituted phenols is studied by pulse photolysis and high-speed spectrophotometry. The rate constant strongly depends on the phenol structure and ranges from 1.3×10^3 for ionol to 2.1×10^8 l mol^{-1} s^{-1} for *o*-aminolphenol. A *U*-shaped curve illustrating how the logarithm of the rate constant changes with a change in the Hammett constants (σ^0) of the substituents in the aromatic ring is found for the studied compounds. Possible pathways for the reaction of Ph_2COO with phenols are discussed.

INTRODUCTION

Carbonyl oxides that are intermediates in olefin ozonolysis have been attracting researchers' attention for a rather long time. The spectral characteristics were studied quite comprehensively, and the coefficients of molar absorption and the rate constants for the recombination of several aromatic carbonyl oxides in various solvents were determined [1–6]. However, the reactivity of carbonyl oxides toward different organic substrates has been poorly studied so far [7].

In this work, we used pulse photolysis and high-speed spectrophotometry (PP–HSS) to determine the rate constants for the reaction of diphenyl carbonyl oxide Ph_2COO with a number of phenols



where $R^2 = R^3 = H$; $R^1 = H$ (**I**), Me (**II**), CMe_2Ph (**III**), OH (**IV**), MeCO (**V**), NH_2 (**VI**), NO_2 (**VII**), and NHCOMe (**VIII**); $R^1 = R^2 = H$; $R^3 = NH_2$ (**IX**), Cl (**X**); $R^1 = R^2 = Cl$, $R^3 = H$ (**XI**); $R^2 = R^3 = CMe_3$, and $R^1 =$ Me (**XII**) in acetonitrile.

EXPERIMENTAL

Kinetic studies were performed on a PP–HSS setup described earlier [8]. The reactor was a quartz cell with an optical length $l = 10$ cm and an inner diameter of ~1 cm. The pulse photolysis of diphenyldiazomethane Ph_2CN_2 was conducted using filtered light (a UFS-2 light filter; transmission region, 270–380 nm). To prevent Ph_2CN_2 decomposition under the action of the probe beam, the intensity of incident light in the absorption region of the diazo compound was reduced with an SS-15 light filter (transmission region, 300–520 nm).

Phenols were purified by sublimation at an atmospheric pressure or in a vacuum if necessary. 2-Chlorophenol was distilled at a low pressure. Acetonitrile was purified by the conventional procedure described in [9]. Ph_2CN_2 was synthesized and purified as described in [10].

The experiment was performed at 295 ± 2 K. Acetonitrile saturated with air was used as a solvent; $[O_2] = 1.5 \times 10^{-3}$ mol/l under these conditions [2]. An acetonitrile solution of Ph_2CN_2 (~2×10^{-4} mol/l) was poured into a cell and subjected to pulse photolysis to record the kinetic curve of decreasing optical density A for diphenyl carbonyl oxide at the maximum of its absorption band (at a wavelength λ_{max} of 410 nm and a coefficient of molar absorption $\varepsilon_{max} = 1.9 \times 10^3$ l mol^{-1}cm^{-1} [5]). Then, a certain amount of phenol was introduced into the solution, and the rate of carbonyl oxide consumption was measured again. The initial concentration of diphenyl carbonyl oxide generated under pulse photolysis conditions was ~10^{-6} mol/l. The procedure was repeated several times at various phenol concentrations. The kinetic curves were processed using nonlinear regression analysis.

The products of the reaction of Ph_2COO with phenols were examined for compound **I**, whose oxidation was performed under stationary photolysis conditions. Acetonitrile (5 ml), diphenyldiazomethane (2×10^{-3} mol/l), and the substrate (0.12 mol/l) were placed into a constant-temperature cylindrical reactor. Photolysis was carried out using light with $\lambda = 270$–380 nm (a UFS-2 light filter, a DRT-400 mercury lamp) at 298 K for 20 min until the pink color of the solution disappeared.

The air bubbled through the solution during photolysis. The products were analyzed by mass spectrometry coupled with chromatography. For analysis, the samples were concentrated 10–20 times.

RESULTS AND DISCUSSION

The pulse photolysis of diphenyldiazomethane involves the intermediate formation of triplet carbene, which reacts with molecular oxygen to form carbonyl oxide [1–5]:

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

$$^1Ph_2C\colon \rightleftharpoons {}^3Ph_2C\colon, \qquad \text{(II)}$$

$$^3Ph_2C\colon + O_2 \longrightarrow Ph_2COO. \qquad \text{(III)}$$

Carbonyl oxide is consumed in the reactions

$$Ph_2COO + Ph_2CN_2 \longrightarrow 2Ph_2CO + N_2, \qquad \text{(IV)}$$

$$Ph_2COO + Ph_2COO \longrightarrow 2Ph_2CO + O_2. \qquad \text{(V)}$$

It is difficult to process experimental data using this scheme, but it can substantially be simplified if the contribution of reaction (IV) into carbonyl oxide consumption is reduced. With this purpose, the pulse photolysis of diphenyldiazomethane was performed at $[Ph_2CN_2]_0 \le 3 \times 10^{-4}$ mol/l when reaction (IV) can be neglected [3, 5]. Indeed, the kinetic curve of a decrease in the optical density of Ph_2COO is described by the second-order equation up to high conversions (the carbonyl oxide conversion of ≥80%):

$$-\frac{dA}{dt} = \frac{k_5}{\varepsilon l}A^2, \qquad (1)$$

where ε is the coefficient of molar absorption of Ph_2COO, l is the optical path length, and k_5 is the rate constant for reaction (V).

The introduction of phenols (ArOH) **I**–**XII** into the system resulted in both a slight decrease in the initial optical density of diphenyl carbonyl oxide due to the reaction

$$^3Ph_2C\colon + ArOH \longrightarrow Ph_2CHOAr \qquad \text{(VI)}$$

and the shortening of its lifetime with an increase in the phenol concentration. The rate law of Ph_2COO consumption changes:

$$-\frac{dA}{dt} = k_{app}A^n. \qquad (2)$$

For phenols **IX**–**XI**, the kinetic curve illustrating a decrease in the optical density of Ph_2COO is well described by the first-order equation: $n = 1$. Therefore, Ph_2COO consumption largely occurs in the reaction

$$Ph_2COO + ArOH \longrightarrow \text{Products}. \qquad \text{(VII)}$$

For other phenols, the optimization of the reaction order gives n values ranging from 1.0 to 1.7, whereas the formal reaction order decreases as with an increase in the phenol concentration. This fact suggests that reactions (V) and (VII) occur in parallel, and the equation for the rate of Ph_2COO consumption is

$$-\frac{d[Ph_2COO]}{dt} = k_7[ArOH][Ph_2COO] + k_5[Ph_2COO]^2 \qquad (3)$$

or, in terms of the optical density,

$$-\frac{dA}{dt} = k_7[ArOH]A + \frac{k_5}{\varepsilon l}A^2 = k^{I}A + k^{II}A^2, \qquad (4)$$

where $k^{I} = k_7[ArOH]$, $k^{II} = k_5/\varepsilon l$, and k_7 is the rate constant for reaction (VII).

The analytical solution to Eq. (4) is

$$\ln\frac{(k^{I} + k^{II}A)A_0}{(k^{I} + k^{II}A_0)A} = k^{I}t, \qquad (5)$$

where A_0 is the initial optical density.

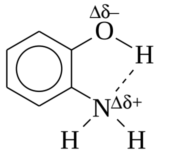
The k^{I} value was determined from Eq. (5) and the k^{II} value was taken from [5] as $k^{II} = k_5/\varepsilon l = 1880$ s^{-1}. As noted above, Ph_2COO consumption for phenols **IX**–**XI** follows the pseudomonomolecular law and the kinetic curves describing optical density variations are linearized in the coordinates of the first-order equation ($\ln A$–t). This allows the determination of the rate constant k^{I}. Figure 1a shows how the k^{I} value varies with the phenol concentration. The k_7 values were determined from the equation $k^{I} = k_7[ArOH]$ (see the table). Note that, for compounds **III**, **VI**, and **IX**, this relationship is linear only at relatively low phenol concentrations (Fig. 1b). Obviously, an increase in the [ArOH] value causes phenol association with either carbonyl oxide or another phenol molecule and reaction retardation. The k_7 value for phenols **III**, **VI**, and **IX** was calculated from the initial linear portion of the curve.

The range of k_7 variations for phenols studied is rather wide: from 1.3×10^3 for ionol (**XII**) to 2.1×10^8 l mol^{-1} s^{-1} for aminophenol (**IX**). In this case, the rate constant k_7 depended on the phenol structure in a complex manner (Fig. 2) suggesting the effect of various factors on its reactivity. Note certain regularities in the k_7 variations.

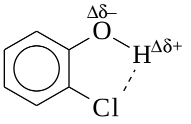
(1) The high activity of aminophenols **VI** and **IX** compared with other studied compounds indicates the participation of a NH_2 group in the reaction with carbonyl oxide. Aminophenols have three reaction centers: the amino and hydroxyl groups and the benzene ring. Note that the experimental rate constant for the reaction

of Ph_2COO with aniline is 1.7×10^5 l mol^{-1} s^{-1}. The high reactivities of aminophenols is obviously due to the cumulative effect of the "partial" rate constants for different reaction pathways and the synergistic effect of substituents.

(2) The *ortho*-effect of polar substituents is observed for the phenols. This manifests itself in a positive deviation from the curve presented in Fig. 2 for compounds **X** and **XI**, as well as in that the rate constants for compounds **IX–XI** with substituents in the *ortho* position are higher than those for *para*-substituted phenols (cf. the k_7 values for compounds **VI** and **IX** in the table). This effect may be attributed to the extra polarization of a phenol molecule, which favors the reaction with polar carbonyl oxide:

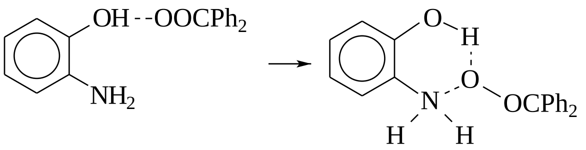


IX



X

Another possible explanation for an abrupt increase in the rate constant k_7 for *o*-aminophenol is the formation of a Ph_2COO complex with the OH group, which favors the formation of the transition state



Undoubtedly, the nature of the *ortho*-effect remains unclear and requires further study.

(3) The presence of bulky *tert*-butyl substituents in the *ortho*-position decreases the reactivity of phenol by nearly an order of magnitude (cf. the k_7 values for compounds **II** and **XII**). This is due to steric hindrances in the reaction of Ph_2COO with phenol with the efficiently shielded OH group.

(4) According to the table, the presence of both donor and acceptor substituents in the *ortho* and *para* positions in phenol, whose structures do not cause any steric hindrances, favors an increase in its reactivity compared with the simplest phenol **I**. When describing these reactions with the Hammett equation, we obtained a *U*-shaped curve describing the dependence of log $\log k_7$ on the Hammett constants of the substituents σ^0 (Fig. 2). The σ^0 values were taken from [11, 12]. This suggests the existence of several contradictory factors that determine the k_7 value. Note that such an unusual dependence of oxidation substrate reactivity in the reactions of phenols with carbonyl oxides on its structure was observed earlier for the reactions of diphenyl carbonyl oxide [13] and propionaldehyde oxide [14] with a number of aromatic aldehydes, as

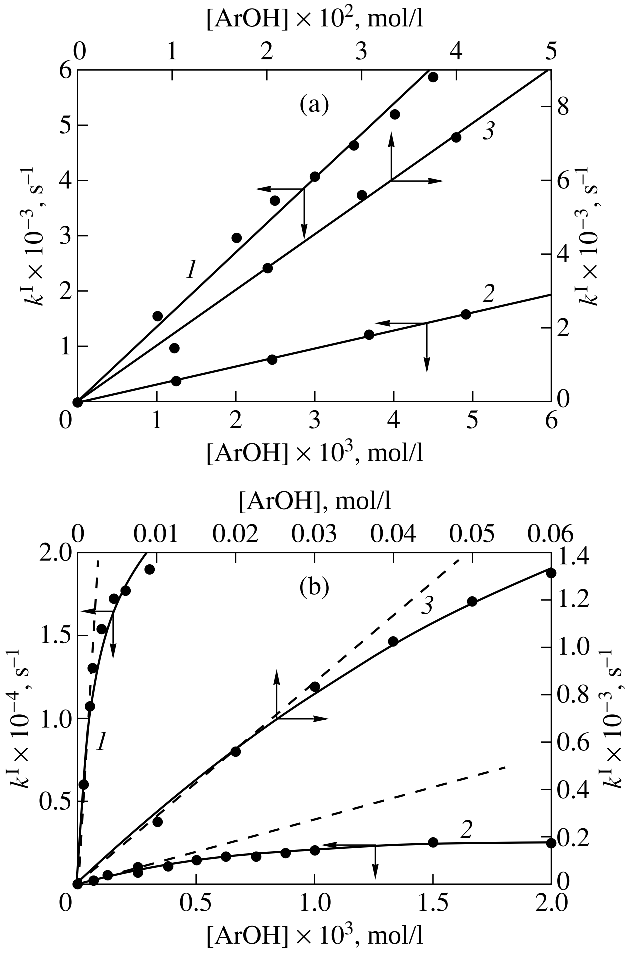


Fig. 1. Pseudomonomolecular rate constant $k^{\rm I}$ vs. phenol concentration in acetonitrile; $T = 295 \pm 2$ K: (a) (*1*) 2,4-dichlorophenol; (2) 2-chlorophenol; and (*3*) 4-acetylphenol; and (b) (*1*) 2-aminophenol; (*2*) 4-aminophenol; and (*3*) 4-cumylphenol.

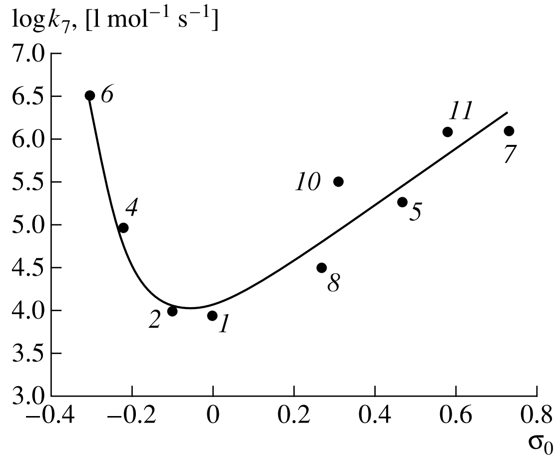


Fig. 2. Logarithm of the rate constant as a function of the Hammett constants σ^0 of the substituent for the reaction of diphenyl carbonyl oxide with phenols. The point numbering corresponds to the compound numbers used in the table.

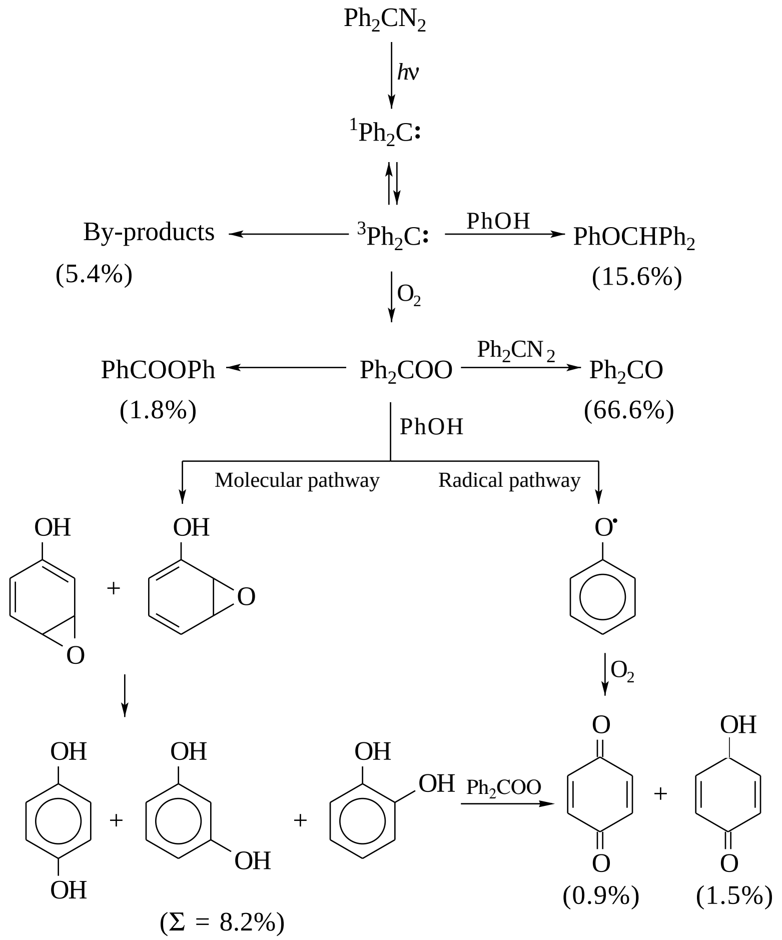
Rate constants for the reaction of diphenyl carbonyl oxide with phenols (acetonitrile, $T = 295 \pm 2$ K)

ArOH		$\sigma°$	[ArOH], mol/l	$k_7 \times 10^{-5}$, l mol^{-1} s^{-1}
2-Aminophenol	**IX**	–	$(0.1–3.0) \times 10^{-4}$	2100 ± 400
4-Aminophenol	**VI**	–0.30	$(0.06–2.0) \times 10^{-3}$	32 ± 4
Hydroquinone	**IV**	–0.22	0.002–0.02	0.93 ± 0.32
4-Cresol	**II**	–0.10	0.018–0.14	0.10 ± 0.01
Ionol	**XII**	–	0.01–0.05	0.013 ± 0.008
4-Cumylphenol	**III**	–	0.01–0.06	0.45 ± 0.37
Phenol	**I**	0.00	0.01–0.15	0.086 ± 0.017
4-Acetylaminophenol	**VIII**	0.27	0.01–0.02	0.31 ± 0.12
2-Chlorophenol	**X**	0.31	$(1.2–8.6) \times 10^{-3}$	3.2 ± 0.2
4-Acetylphenol	**V**	0.47	0.01–0.04	1.8 ± 0.1
2,4-Dichlorophenol	**XI**	0.58	$(1.0–4.5) \times 10^{-3}$	12 ± 1
4-Nitrophenol	**VII**	0.73	$(1.3–3.8) \times 10^{-4}$	12 ± 2

well as for alkene oxidation under the action of Ph_2COO [15]. The epoxide yield increases in the latter reaction upon the introduction of both electron-donor and electron-acceptor substituents into the molecule [16]. The curve illustrating how the logarithm of the rate constant for the oxidation of aromatic compounds by diphenyl carbonyl oxide changes with the σ^0 value exhibits an inflection point corresponding to the unsaturated compound (benzene) [7]. These regularities can be attributed to the fact that carbonyl oxide may act as both an electrophilic and nucleophilic species depending on the co-reactant and the distribution of electron density in the substrate.

By analogy with alkene epoxidation, these properties of carbonyl oxide can be due to the nature of the interaction of frontier molecular orbitals [17]. For phenols with a low electron density in the aromatic ring, the overlap of π-HOMO of carbonyl oxide with π^*-LUMO of phenol prevails. The electron-acceptor substituents that decrease the π^*-LUMO energy enhance this interaction. The transition state of the reaction may also be stabilized by the overlap of phenol π-HOMO with the low-lying σ^*-antibonding O–O molecular orbital of carbonyl oxide.

The products of the reaction of Ph_2COO with phenols were examined for phenol **I** under stationary photolysis conditions. The product of the reaction of Ph_2COO with the aromatic ring is the corresponding arene oxide, which rapidly transforms into a hydroxy derivative [16, 18–21]. Among the products of the photolysis of the acetonitrile solution containing Ph_2CN_2 (2×10^{-3} mol/l) and phenol I (0.12 mol/l) (see the scheme), we found hydroquinone, resorcin and pyrocatechol (the overall yield, 8.2%), semiquinone (1.5%), and quinone (0.9%). Diphenylmethylphenyl ether, the product of carbene insertion into the O–H bond of phenol via reaction (VI), is formed in noticeable amounts (15.6%). Using mass spectrometry, we detected a compound (5.1%) that was isomeric to ether and that could be the product of the reaction of carbene with the aromatic ring of phenol. We also registered trace amounts of phenyl benzoate formed via Ph_2COO isomerization



Scheme. Formation of the products of diphenyldiazomethane photooxidation in the presence of phenol.

(1.8%) and diphenyl methane (0.3%). The significant concentration of benzophenone (66.6%) in the reaction products is obviously due to the fact that reaction (IV) occurring in parallel with reaction (VII) prevails under stationary photolysis conditions.

Taking into account the pronounced biradical properties of carbonyl oxides, one should not rule out the radical mechanism of the reaction, which obviously implies H-atom abstraction from the hydroxyl group. In the presence of molecular oxygen, the resulting phenoxyl radical undergoes further oxidation via well-known reactions [22], the main products of which are quinone and semiquinone. The radical mechanism is favorable for phenols with weak O–H bond strengths containing electron-donor substituents [22].

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