Kinetics and Catalysis, Vol. 42, No. 6, 2001, pp. 746–750. Translated from Kinetika i Kataliz, Vol. 42, No. 6, 2001, pp. 823–827.
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The Reactivity of Diphenyl Carbonyl Oxide in Reactions with Alcohols

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Received August 25, 2000

Abstract—The reactivities of ten alcohols in the reactions with diphenyl carbonyl oxide Ph_2COO is characterized by the ratio k_{33}^{OH}/k_{31}, where k_{33}^{OH} and k_{31} are the rate constants of Ph_2COO reactions with an alcohol and diphenyldiazomethane PH_2CN_2, respectively. The values of k_{33}^{OH}/k_{31} range between 0.6×10^{-2} for MeOH to 6.0 for *iso*-PrOH at 70°C in acetonitrile. The donation of electron density to the alcohol hydroxyl group favors the attack of Ph_2COO; that is, Ph_2COO reacts as an electrophile.

INTRODUCTION

Carbonyl oxides are intermediates in olefin ozonolysis and have been attracting attention for a rather long period [1]. The reactivity of carbonyl oxide toward aromatic substrates and aldehydes has been studied in detail [2, 3]. However, their reactivity toward alcohols has been well studied only for Me_2COO [4].

Several methods are known for generating carbonyl oxide in solutions [1]. One method is the thermal decomposition of diazomethanes in solutions containing oxygen. Carbonyl oxide is formed via the following sequence of reactions:

$$Ph_2CN_2 \xrightarrow{\Delta} Ph_2C\colon \xrightarrow{O_2} Ph_2COO. \qquad (I)$$

Serenko *et al*. [5] have found that the thermal decomposition of diphenyldiazomethane Ph_2CN_2 in the presence of oxygen is accompanied by chemiluminescence in the visible region of spectrum. The mechanism of this process, its kinetic analysis, and the explanation for chemiluminescence are given in [6]. It has been shown that chemiluminescence quenching by the additives of an organic substrate is a convenient method for the study of the reactivities of organic compounds in reactions with carbonyl oxide [2, 3]. We use this method in this work, which deals with the study of the effect of alcohol structure on the kinetics of the reaction between Ph_2COO and a number of alcohols: methanol, ethanol, *iso*-propanol, *iso*-butanol, *tert*-butanol, 2-butanol, *cyclo*-hexanol, allyl alcohol, benzyl alcohol, and ethylene glycol.

EXPERIMENTAL

The thermolysis of RN_2 was carried out at 70°C in MeCN. The initial concentrations of $[RN_2]_0$ and $[O_2]_0$ in the solution were $(0.5–2.0) \times 10^{-3}$ and $(0.7–3.5) \times 10^{-3}$ mol/l, respectively. Acetonitrile, benzene, and alcohols were purified according to the standard procedures [7]. The synthesis and purification of RN_2 were carried out as described in [8].

The chemiluminescence setup consisted of a lightproof chamber with a constant-temperature glass reactor mounted inside. The reactor was equipped with a thermocouple, a bubbler for supplying the gaseous mixture (air, oxygen, or an Ar : O_2 = 50 : 50 vol % mixture), a reflux condenser, and a device for the fast injection of solutions. FEU-39 and FEU-148 were used as radiation detectors.

DISCUSSION

The mechanism of the thermal decomposition of diphenyldiazomethane in the RN_2–O_2–MeCN system in the absence of active additives involves the following steps [6]:

$$RN_2 \longrightarrow {}^1R + N_2, \qquad (0)$$

$${}^1R \rightleftarrows {}^3R, \qquad (ST, TS)$$

$${}^3R + O_2 \longrightarrow ROO, \qquad (2.2)$$

$$ROO + RN_2 \longrightarrow R{=}O,\ {}^3R{=}O,\ N_2, \qquad (3.1)$$

$${}^3R{=}O \longrightarrow R{=}O,\ h\nu, \qquad (4.0)$$

$${}^3R{=}O + RN_2 \longrightarrow P_{41}, \qquad (4.1)$$

$${}^3R{=}O + O_2 \longrightarrow P_{42}. \qquad (4.2)$$

Henceforth, P_i stands for the products of the corresponding *i*th step. Numbering is the same as in [6]. Other reactions (e.g., the interaction of singlet carbene with the initial diazo compound, the quadratic decay of carbonyl oxide, etc.) did not occur under the conditions of our experiments [6]. In the absence of active addi-

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tives, the chemiluminescence intensity in the stationary regime (I_0) is described by the equation

$$I_0 = \varphi_{31}\varphi_{40}\frac{k_{40}}{k_{40} + k_{41}[\mathrm{RN_2}] + k_{42}[\mathrm{O_2}]} \times \frac{k_{22}[\mathrm{O_2}]}{k_{21}[\mathrm{RN_2}] + k_{22}[\mathrm{O_2}]}k_0[\mathrm{RN_2}]. \quad (1)$$

In the presence of an alcohol R'OH, the following reactions may also occur:

$$^1\mathrm{R}\!: + \mathrm{R'OH} \longrightarrow P_{13}, \quad (1.3)$$

$$^3\mathrm{R}\!: + \mathrm{R'OH} \longrightarrow P_{23}, \quad (2.3)$$

$$\mathrm{ROO} + \mathrm{R'OH} \longrightarrow P_{33}, \quad (3.3)$$

$$^3\mathrm{R{=}O} + \mathrm{R'OH} \longrightarrow P_{43}. \quad (4.3)$$

Each of these reactions leads to a decrease in the steady-state concentration of ^{3}R=O and to chemiluminescence quenching. Let us consider these reactions using diphenyldiazomethane as an example (R = Ph_2C).

The rate constant k_{ST} is rather high: $k_{\mathrm{ST}} = 3.2 \times 10^9$ s^{-1} [9]. However, the rate constant of reaction (1.3) is also close to the diffusion limit: 5.6×10^9, 3.5×10^9, and 1.5×10^9 l mol^{-1} s^{-1} for MeOH, *iso*-PrOH, and *tert*-BuOH, respectively [9]. Therefore, in this case (at [R'OH] ≤ 0.1mol/l), the following inequality is true: $\frac{k_{\mathrm{ST}}}{k_{\mathrm{ST}} + k_{13}[\mathrm{R'OH}]} < 1$ and reactions (3.3), (1.3), and probably (2.3) lead to chemiluminescence quenching [10]. The reaction of ^{3}R=O quenching (4.3) cannot occur via the mechanism of energy transfer in this system because the energy of the triplet state E_{t} is higher for alcohols than for benzophenone. On the other hand, since the rate constant is rather low (10^5–10^6), the radical abstraction of a hydrogen atom from R'OH by triplet benzophenone is much slower than reaction (4.2), and we can neglect reaction (4.3). Taking the above notes into account, the chemiluminescence intensity in the stationary regime after adding alcohol is described by the equation

$$I_0 = \varphi_{31}\varphi_{40}\alpha_{\mathrm{ST}}\alpha_{22}\alpha_{40} \times \frac{k_{31}[\mathrm{RN_2}]}{k_{31}[\mathrm{RN_2}] + k_{33}^{\mathrm{OH}}[\mathrm{R'OH}]}k_0[\mathrm{RN_0}], \quad (2)$$

where $\alpha_{40} = k_{40}/(k_{40} + k_{41}[\mathrm{RN_2}]k_{42}[\mathrm{O_2}])$, $\alpha_{\mathrm{ST}} = k_{\mathrm{ST}}/(k_{\mathrm{ST}} + k_{13}[\mathrm{R'OH}])$, $\alpha_{22} = k_{22}[\mathrm{O_2}]/(k_{21}[\mathrm{RN_2}] + k_{22}[\mathrm{O_2}] + k_{23}[\mathrm{R'OH}])$, $\alpha_{40} = k_{40}/(k_{40} + k_{41}[\mathrm{RN_2}] + k_{42}[\mathrm{O_2}])$, and k_{33}^{OH} is the rate constant of the reaction between ROO and the alcohol.

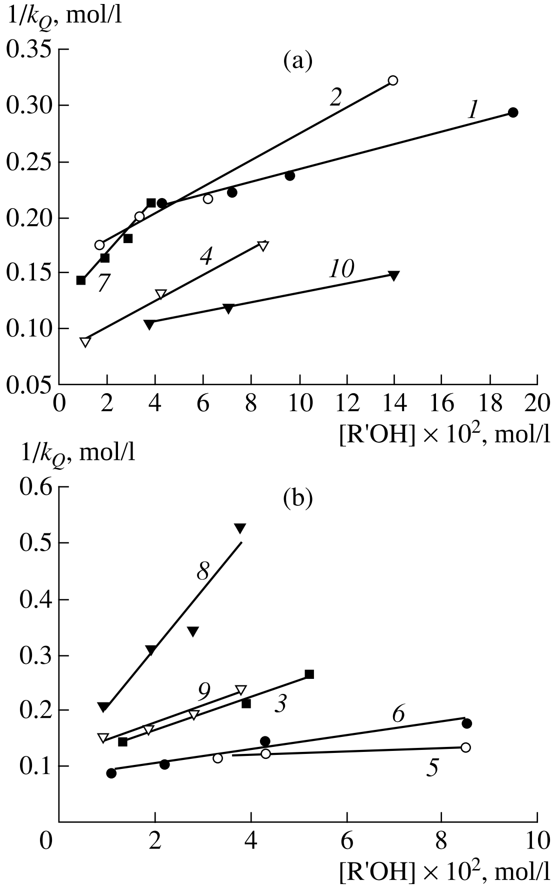


Fig. 1. Dependence of the rate constant of chemiluminescence quenching on the concentration of alcohol at [RN_2] = 2×10^{-3} mol/l and 70°C in MeCN: (a) (*1*) methanol, (*2*) ethanol, (*4*) *iso*-butanol, (*7*) *cyclo*-hexanol, (*10*) ethylene glycol; (b) (*3*) *iso*-propanol, (*5*) *tert*-butanol, (*6*) 2-butanol, (*8*) allyl alcohol, (*9*) benzyl alcohol.

To eliminate unknown parameters φ_{31}, φ_{40}, α_{ST}, α_{22}, and α_{40}, we injected benzene to the RN_2–O_2–R'OH–solvent system after measuring chemiluminescence I_0. As has been shown earlier [2], we can neglect the reactions of benzene with ^{1}R, ^{3}R, and ^{3}R=O under the conditions of our experiments. When both benzene and alcohol are present, the equation for the chemiluminescence intensity takes the following form:

$$k_{\mathrm{Q}} = k_{33}^{\mathrm{ArH}}(k_{31}[\mathrm{RN_2}] + k_{33}^{\mathrm{OH}}[\mathrm{R'OH}])^{-1}, \quad (3)$$

where k_{33}^{ArH} is the rate constant for the reaction of carbonyl oxide with benzene. It follows from Eqs. (2) and (3) that

$$\frac{I_0}{I} = 1 + \frac{k_{33}^{\mathrm{ArH}}}{k_{31}[\mathrm{RN_2}] + k_{33}^{\mathrm{OH}}[\mathrm{R'OH}]}[\mathrm{C_6H_6}]. \quad (4)$$

We found that Eq. (4) is fulfilled in all considered cases at constant values of [RN_2] and [R'OH] (Fig. 1). This dependence was used to calculate the constant of

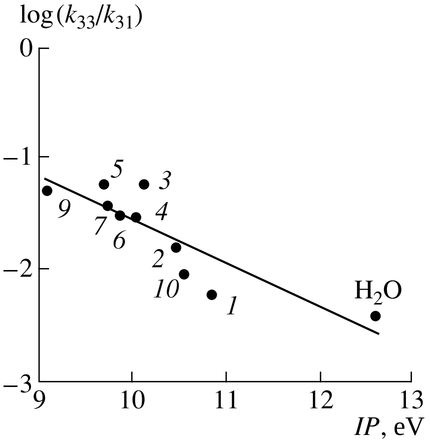


Fig. 2. Dependence of the relative rate constants k_{33}^{OH}/k_{31} on the first ionization potentials of alcohols. The numbering is the same as in the table and Fig. 1.

chemiluminescence quenching $k_Q = k_{33}^{ArH}(k_{31}[RN_2] + k_{33}^{OH}[R'OH])^{-1}$. Then the dependence

$$1/k_Q = a + b[R'OH] \tag{5}$$

was used to determine the parameters $a = k_{31}[RN_2]/k_{33}^{ArH}$ and $b = k_{33}^{OH}/k_{33}^{ArH}$, which are necessary for the calculation of the ratio $k_{33}^{OH}/k_{31} = b[RN_2]/a$ that characterizes the relative reactivity of carbonyl oxide toward alcohols. The results are summarized in the table.

The reactivity of the alcohols in the reaction with diphenyl carbonyl oxide increases in the series MeOH < $(CH_2OH)_2$ < $CH_2{=}CHCH_2OH$ < EtOH < *iso*-BuOH < 2-BuOH < *cyclo*-$C_6H_{11}OH$ < $C_6H_5CH_2OH$ < *tert*-BuOH < *iso*-PrOH. Although the reactivity of alcohols in the reaction with the diphenyl carbonyl oxide does not differ strongly (~10 times difference), we note that the donation of the electron density at the oxygen atom of the hydroxyl group favor the attack of the carbonyl oxide.

The dependence of $\log(k_{33}^{OH}/k_{31})$ on the first ionization potential of alcohols (Fig. 2) is suggestive of the formation of an intermediate with a charge-transfer complex. Without $CH_2{=}CHCH_2OH$, this dependence is described by the equation

$$\log(k_{33}^{OH}/k_{31}) = 2.4 - 0.4IP \quad (r = 0.75),$$

where *r* is the correlation coefficient.

With a decrease in the value of the first ionization potential (*IP*) of alcohols, the rate constant of its reaction with Ph_2COO increases. That is, electron-donor substituents increase the reactivity of R'OH, and carbonyl oxide plays the role of an electrophile.

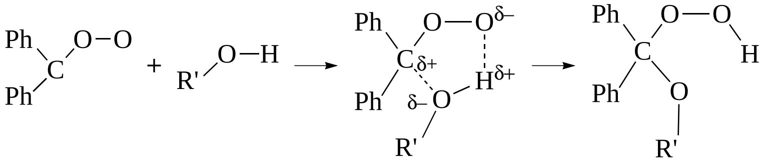
This result is unexpected since the following reactivity series was found for the reaction with dimethyl carbonyl oxide in CH_2Cl_2 at 0°C [4]: MeOH > EtOH, *n*-PrOH > *iso*-PrOH > H_2O > *tert*-BuOH. This discrepancy is probably associated with different effects of aliphatic and aromatic derivatives on the reactivity of carbonyl oxide. Aliphatic substituents in Me_2COO donate the electron density at the terminal oxygen atom of the carbonyl oxide and favor the nucleophilic attack on the hydrogen atom of the alcohol. In Ph_2COO, two aryl substituents may have a small positive mesomeric effect and a negative induction effect, which favors the electrophilic attack of the carbon atom (δ^+) from Ph_2COO onto the oxygen atom (δ^-) in R'OH.

These differences are also due to the solvent effect because the zwitter-ionic structure of carbonyl oxide is stabilized in polar solvents, such as MeCN [12]. The mechanism of the reaction of the zwitter ion with alcohols probably differs from the mechanism of the biradical reaction.

A relatively low reactivity of propenol is probably due to the double bond. The presence of the additional functional group in the alcohol probably changes the mechanism of the alcohol reaction with Ph_2COO. It has been shown [13] that this reaction involves the attack on the terminal oxygen of the carbonyl oxide by the double bond of the olefin to form radical products.

Earlier, when considering the mechanism of the Ph_2COO reaction with aromatic compounds and aldehydes, we assumed that the first stage of the reaction is the formation of a charge-transfer complex [2, 3]. It is likely that the formation of a charge-transfer complex also takes place in the reaction with alcohols.

The reaction probably occurs via the formation of the cyclic transition state



Thus, in this work, we used the chemiluminescence method to study the reactivity of alcohols in the reaction with diphenyl carbonyl oxide. We found that the rate constant of this reaction increases when an alcohol contains an electron-donor substituent and Ph_2COO reacts as an electrophile. The results obtained in this work together with published data point to an ambiphilic nature of carbonyl oxide, which has both nucleophilic and electrophilic properties depending on the second reactant and substituents at the carbonyloxy group.

Reactivity of diphenyl carbonyl oxide toward alcohols ($[RN_2] = 2 \times 10^{-3}$ mol/l, 70°C, MeCN)

	R'	$[R'OH] \times 10^2$, mol/l	k_Q, l/mol	a	b	$k_{33}^{OH}/k_{31} \times 10^2$
1	Me	4.3	4.7	0.19	0.56	0.60
		7.2	4.5			
		9.6	4.2			
		19	3.4			
2	Et	1.7	5.7	0.15	1.2	1.6
		3.4	5.0			
		6.3	4.6			
		14	3.1			
3	*iso*-Pr	1.3	7.0	0.10	3.0	6.0
		3.9	4.7			
		5.2	3.8			
4	*iso*-Bu	1.1	11.3	0.08	1.2	3.0
		4.25	7.6			
		8.5	5.7			
5	*tert*-Bu	3.3	8.8	0.11	0.31	5.8
		4.3	8.1			
		8.5	7.5			
6	2-Bu	1.1	11.4	0.08	1.24	3.1
		2.2	9.6			
		3.3	8.6			
		4.3	6.9			
		8.5	5.6			
7	*cyclo*-C_6H_{11}	0.94	6.9	0.12	2.3	3.8
		1.9	6.1			
		2.8	5.5			
		3.8	4.7			
8	$CH_2=CHCH_2$	0.94	4.8	0.2	1.1	1.1
		1.9	3.2			
		2.8	2.9			
		3.8	1.9			
9	$C_6H_5CH_2$	0.94	6.6	0.12	3.1	5.2
		1.9	6.0			
		2.8	5.2			
		3.8	4.2			
10	$HOCH_2CH_2$	3.75	9.45	0.09	0.41	0.9
		7.1	8.3			
		1.4	6.75			

Note: The relative error in determining k_Q is ±10–15% and those for k_{33}^{OH}/k_{31} is ±20–25%.

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