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Influence of Substituents on Kinetics of the Reaction of Carbonyl Oxides with Ethanol

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Abstract—The reactivity toward EtOH of nine carbonyl oxides (ROO) obtained by the thermolysis of the corresponding diazo compounds (RN_2) is studied by the chemiluminescence method. The reactivity is characterized by the ratio of constants $k_{33}^{\mathrm{EtOH}}/k_{31}$, where k_{33}^{EtOH} and k_{31} are the rate constants of the reactions of ROO with EtOH and RN_2, respectively. The negative slope of the Taft correlations ($\rho < 0$) indicates the electrophilic character of the reaction of ROO with EtOH. The substituents, electron density acceptors, increase the relative reactivity of the carbonyl oxides.

INTRODUCTION

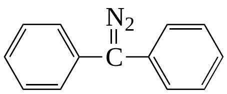
Carbonyl oxides ROO are labile intermediates in the ozonolysis of alkenes and alkynes, aerobic photolysis and thermolysis of diazo compounds RN_2, and reactions of the latter with singlet oxygen [1]

$$RN_2 \longrightarrow {}^1R \longrightarrow {}^3R \xrightarrow{O_2} \text{ROO (“triplet pathway”)},$$

$$RN_2 + {}^1O_2 \longrightarrow \text{ROO (“singlet pathway”)}.$$

The chemistry of carbonyl oxides has seen intensive growth in recent years. Their interaction with each other, olefins, aromatic compounds, and aldehydes intensively studied [2–6]. At the same time, quantitative data characterizing the reactivity of carbonyl oxides toward organic substrates and the influence of the ROO structure on the reactivity are very limited [3]. The reactions of carbonyl oxides with arenes [5] and aldehydes [6] were studied in detail. Quantitative data on the kinetics of the reaction of carbonyl oxides with alcohols are scarce. The work by Yamamoto *et al.* [7] is worth mentioning in which the reaction of dimethylcarbonyl oxide with several hydroxyl-containing reactants was studied.

The thermal decomposition of diphenyldiazomethane RN_2 ($R = Ph_2C$) in the presence of oxygen is accompanied by chemiluminescence (CL) in the visible spectral range [8]. The mechanism of this process, its kinetic analysis, and evidence for the photostep are reported in [9]. Using this approach, we have previously studied the regularities of the reaction of diphenylcarbonyl oxide with arenes [5] and aldehydes [6]. In this work, we used the CL method to study the influence of the structure of carbonyl oxides formed in the thermal decomposition of diazo compounds **1**–**9** in the presence of oxygen on the reactivity toward ethanol.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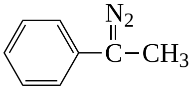
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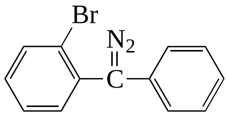
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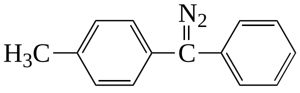
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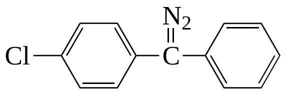
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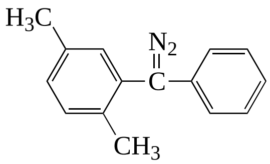
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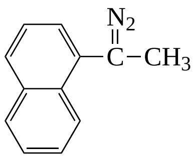
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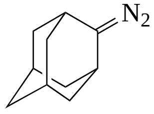
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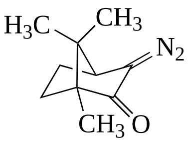
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EXPERIMENTAL

RN_2 thermolysis was carried out at 60°C in MeCN. The initial concentrations $[RN_2]_0$ 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 ethanol were purified using standard procedures [10]. RN_2 was synthesized and purified according to [11].

Chemiluminescence in the visible spectrum was measured on a photometric setup, which consisted of a photoimpermeable chamber. A glass reactor with a thermocouple for temperature control, a bubbler for feeding a gaseous mixture containing oxygen in a specified ratio with an inert gas, a reflux condenser, and a device for fast injection of solutions was placed in the chamber. A FEU-39 or FEU-148 photoelectric amplifier was used as a photodetector.

RESULTS AND DISCUSSION

According to our early works [8, 9], the mechanism of thermal decomposition of diphenyldiazomethane in the $RN_2–O_2–MeCN$ system in the absence of active additives capable of reacting with ${}^1R$, ROO, and ${}^3R{=}O$ includes the following steps:

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

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

$${}^3R + RN_2 \longrightarrow R{=}N{-}N{=}R; \qquad (II.1)$$

$${}^3R + O_2 \longrightarrow ROO; \qquad (II.2)$$

$$ROO + RN_2 \longrightarrow R{=}O,\ {}^3R{=}O,\ N_2; \qquad (III.1)$$

$${}^3R{=}O \longrightarrow R{=}O,\ h\nu; \qquad (IV.0)$$

$${}^3R{=}O + RN_2 \longrightarrow P_{41}; \qquad (IV.1)$$

$${}^3R{=}O + O_2 \longrightarrow P_{42}. \qquad (IV.2)$$

Scheme 1.

Here P_i is the product of the *i*th step. The reactions are numerated according to [9] (ST and TS are the singlet-triplet and triplet-singlet transitions, respectively). Other reactions, for example, the reaction of singlet carbene with the initial diazo compound, the recombination of carbonyl oxides, etc., do not occur to a noticeable degree under our conditions [9]. In the general case, in the absence of a quenching agent, it follows from Scheme 1 that

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

When ethanol is added, it reacts with all active intermediates of the process: singlet and triplet carbene, carbonyl oxide, and electron-excited ketone

$${}^1R\!: + EtOH \longrightarrow P_{13}, \qquad (I.3)$$

$${}^3R\!: + EtOH \longrightarrow P_{23}, \qquad (II.3)$$

$$ROO + EtOH \longrightarrow P_{33}, \qquad (III.3)$$

$${}^3R{=}O + EtOH \longrightarrow P_{43}, \qquad (IV.3)$$

where P_i is the product of the chemical reaction or physical quenching.

All these reactions decrease the stationary concentration of ${}^3R{=}O$ and, as a consequence, quench CL.

In the presence of alcohol, we have to take into account the k_{13} constant, which is close to the diffusion limit [12], and k_{23}.

In this system, the quenching reaction of ${}^3R{=}O$ (IV.3) is most likely insignificant because it cannot proceed through the energy transfer mechanism, since the energy of the triplet level E_T of alcohols studied in this work is higher than E_T of triplet ketones. On the other hand, due to a comparatively low rate constant, the radical abstraction of the H atom from the alcohol molecule by the ketone triplet ($10^5–10^6$ l mol^{-1} s^{-1} for benzophenone) occurs much more slowly than reaction (IV.2). Thus, the luminescence intensity in the steady-state regime is described by the following equation:

$$I_0 = \varphi_{31}\varphi_{40}\alpha_{ST}\alpha_{22}\alpha_{40} \times \frac{k_{31}[RN_2]}{k_{31}[RN_2]+k_{33}^{EtOH}[EtOH]}k_0[RN_2], \qquad (2)$$

where $\alpha_{40} = k_{40}/(k_{40} + k_{41}[RN_2]k_{42}[O_2])$, $\alpha_{ST} = k_{ST}/(k_{ST} + k_{13}[EtOH])$, $\alpha_{22} = k_{22}[O_2]/(k_2[RN_2] + k_{22}[O_2] + k_{23}[EtOH])$, and k_{33}^{EtOH} is the rate constant of reaction (III.3).

To exclude the unknown parameters φ_{31}, φ_{40}, α_{ST}, and α_{22}, benzene was added to the $RN_2–O_2–EtOH$–solvent system after measuring I_0 because its reactions with ${}^3R$ and ${}^3R{=}O$ can be neglected under these conditions, as shown previously [4]. When benzene and ethanol are simultaneously present, equation (2) takes the form

$$I = \varphi_{31}\varphi_{40}\alpha_{ST}\alpha_{22}\alpha_{40} \times \frac{k_{31}[RN_2]}{k_{31}[RN_2]+k_{33}^{ArH}[C_6H_6]+k_{33}^{EtOH}[EtOH]}k_0[RN_2], \qquad (3)$$

where k_{33}^{ArH} is the rate constant of the reaction of carbonyl oxide with benzene. Equations (2) and (3) give

$$\frac{I_0}{I} = 1 + \frac{k_{33}^{ArH}}{k_{31}[RN_2]+k_{33}^{EtOH}[EtOH]}[C_6H_6]. \qquad (4)$$

In all cases, at constant $[RN_2]$ and [EtOH], equation (4) is fulfilled. The CL quenching rate in the visible range was calculated from this function

$$k_Q = k_{33}^{ArH}(k_{31}[RN_2]+k_{33}^{EtOH}[EtOH])^{-1}. \qquad (5)$$

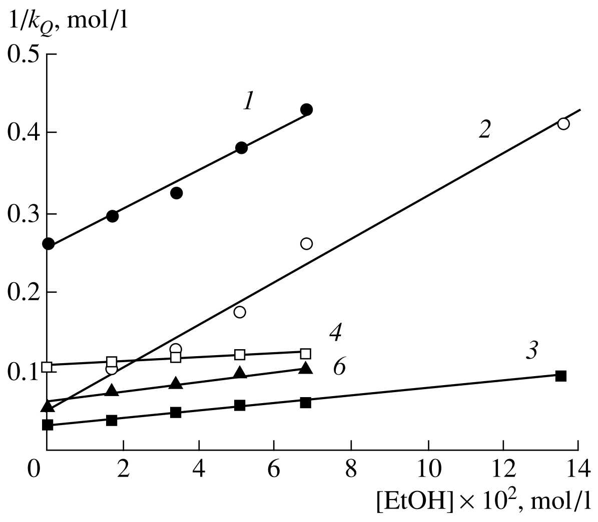


Fig. 1. Rate constant of chemiluminescence quenching by benzene in the RN_2–O_2–C_2H_5OH–MeCN system at 60°C as a function of the ethanol concentration in the coordinates of equation (6) for diazo compounds **1**, **2**, **3**, **4**, and **6**.

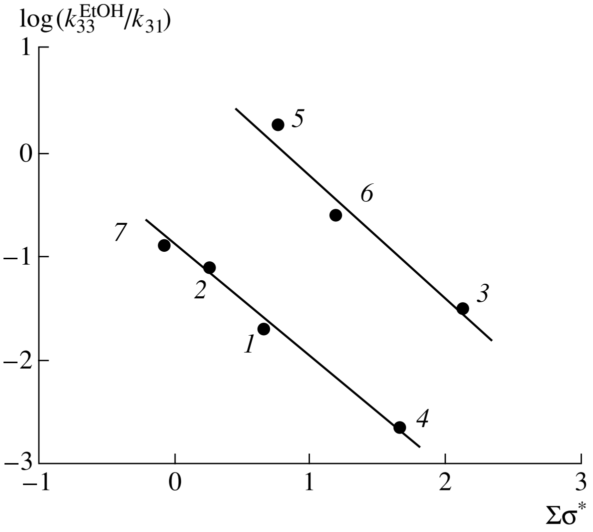


Fig. 2. Influence of the inductive properties of the substituents {Σσ*) on the relative reactivity of carbonyl oxides **1**–**7** in the reaction with ethanol ($k_{33}^{\mathrm{EtOH}}/k_{31}$). Solvent: MeCN; 60°C.

The latter can easily be transformed into

$$1/k_{\mathrm{Q}} = k_{31}[\mathrm{RN_2}]/k_{33}^{\mathrm{ArH}} + k_{33}^{\mathrm{EtOH}}/k_{33}^{\mathrm{ArH}}[\mathrm{EtOH}]. \qquad (6)$$

As can be seen from Fig. 1, equation (6) is fulfilled. The slope of the straight line and the intercept at the y axis was used to determine the parameters $a = k_{31}[\mathrm{RN_2}]/k_{33}^{\mathrm{ArH}}$ and $b = k_{33}^{\mathrm{EtOH}}/k_{33}^{\mathrm{ArH}}$ from which we calculated $k_{33}^{\mathrm{EtOH}}/k_{31} = b[\mathrm{RN_2}]/a$, the value that characterizes the relative reactivity of carbonyl oxides toward ethanol. The results obtained are presented in the table.

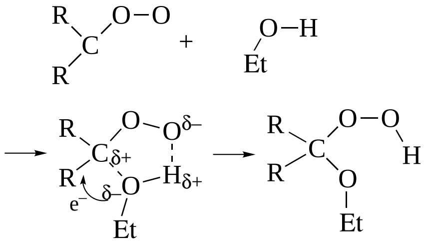
The inductive scale of Taft constants σ* [13, 14] was used to describe quantitatively the effect of substituents on the reactivity of ROO. The study of the plots of the reactivity of the carbonyl oxide vs. inductive properties of the R substituent (Fig. 2) shows the fulfillment of the linear correlations $\log(k_{33}^{\mathrm{EtOH}}/k_{31}) = -1.1–0.9\Sigma\sigma^*(\mathrm{R})$ with a correlation coefficient of 0.98 for **1**, **2**, **4**, and **7** and $\log(k_{33}^{\mathrm{EtOH}}/k_{31}) = 1.1–1.2\Sigma\sigma^*(\mathrm{R})$ with a correlation coefficient of 0.97 for **3**, **5**, and **6**. The negative slope ($\rho < 0$) in the coordinates of the Taft equation indicates that the carbonyl oxide reacts with EtOH via the nucleophilic mechanism.

Note that the obtained correlations indicate only a tendency because k_{33}/k_{31} is the relative constant. Perhaps, for compounds **3**, **5**, and **6** (which bear the Br(3) *ortho*-atoms, Me(6) creating steric effects, and electron acceptors Cl(5) and Br(3)), the substituents affect simultaneously k_{33}^{EtOH} and k_{31}, and this influence is not cymbate, which probably results in the situation where the $k_{33}^{\mathrm{EtOH}}/k_{31}$ value for carbonyl oxides prepared from diazo compounds **1**, **2**, **4**, **7** and **3**, **5**, **6** lie in different correlation lines. Nevertheless, these plots suggest that aryl-containing carbonyl oxides electrophilically attack the EtOH molecule, most likely, with the intermediate formation of a charge-transfer complex (CTC) (Scheme 2). A similar tendency has previously been found in the reaction of Ph_2COO with aldehydes [6].

Relative reactivity $k_{33}^{\mathrm{EtOH}}/k_{31}$ of carbonyl oxides ROO **1**–**9** toward ethanol in MeCN at 60°C

RN_2	$[RN_2] \times 10^3$, mol/l	Σσ*	a	b	$(k_{33}^{\mathrm{EtOH}}/k_{31}) \times 10^2$
1	2.0	0.650	0.26	2.5	1.9
2	2.3	0.257	0.11	2.3	4.8
3	2.3	2.140	0.034	0.45	3.03
4	10.9	1.670	0.11	0.27	0.23
5	158	0.775	2.56	35.6	220
6	20.0	1.180	0.06	0.7	23.3
7	22.8	−0.088	2.06	10.7	11.8
8	10.0	–	0.15	2.87	0.2
9	19.0	–	4.52	32.8	13.8

Note: The relative error in the determination of $k_{33}^{\mathrm{EtOH}}/k_{31}$ is ±17–20%.



Scheme 2.

The interaction of carbonyl oxide with ethanol most likely begins with the attack of the oxygen atom of the OH group and charge transfer. The charge-transfer complex undergoes further transformation into α-ethoxyperoxide. At the same time, it is evident that substituents that are electron density acceptors favor an increase in the reactivity of the carbonyl oxides toward alcohol.

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