The influence of substituents on the kinetics of the reaction of carbonyl oxides with benzaldehyde

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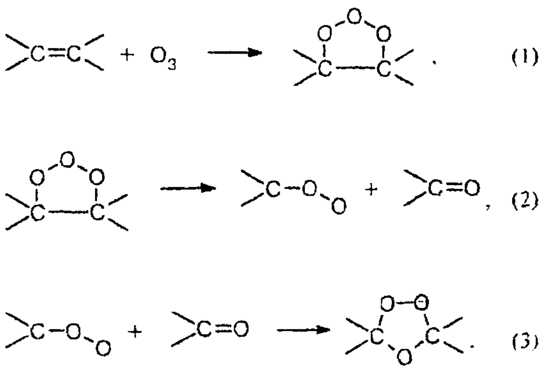
The reactivity of carbonyl oxides toward benzaldehyde was characterized by the k_{33}/k_{31} ratio, where k_{33} and k_{31} are the rate constants of the reactions of RCOO with PhCHO and diphenyldiazomethane Ph_2CN_2, respectively. The k_{33}/k_{31} ratios obtained at 60 °C in acetonitrile range from $0.61 \cdot 10^{-2}$ (m-$BrPh_2CN_2$) to $20 \cdot 10^{-2}$ (Ph_2MeCHO). The reactions are probably preceded by the formation of a charge-transfer complex (CTC) with charge transfer from aldehyde to RCOO. The carbonyl oxide reacts with aldehydes by both the nucleophilic pathway (at the C atom of the —CHO group to form 1,2,4-trioxolane) and electrophilic pathway (by the attack at the aromatic ring with the intermediate formation of CTC). In the latter case, either 1,2,4-trioxolane or oxidation products of the phenyl ring are formed.

Key words: carbonyl oxides, benzaldehyde, diazomethanes, reactivity, chemiluminescence, kinetics, quenching constant, reaction mechanism.

Carbonyl oxides (COx) are the key intermediates of ozonolysis of unsaturated organic compounds (Scheme 1).[1] They are formed by the decomposition of primary ozonide, 1,2,3-trioxolane (reaction (2)). In inert solvents and in the absence of active additives, reaction (3) (the interaction of the carbonyl group of aldehyde resulting in 1,2,4-trioxolane) is the main channel of COx decomposition.

Scheme 1



Stages (1) and (2) have been studied in detail.[1] The ozonolysis of aryl-substituted olefins predominantly affords carbonyl oxides (ROO) in which the substituents stabilize the positive charge on the C atom of the carbonyl oxide group.[2,3]

Stage (3) was studied to a lesser extent; the available facts indicate that the reaction of COx with a carbonyl compound proceeds in two or more stages rather than by synchronic 1,3-cycloaddition. This is reasoned, in particular, by involvment of ROO in side reactions.[4—6]

Aldehydes (RCHO) are the most reactive compounds containing the carbonyl group. Therefore, the electron effects of substituents in reaction (3) were studied mainly for the interaction of COx with RCHO. In particular, it has been found[7] that in terms of the Hammett correlation equations the reaction is characterized by the reaction series constant $\rho = +1.4$, which indicates a nucleophilic nature of the attack of COx on aldehyde.

We have previously shown[8] that diphenylcarbonyl oxide Ph_2COO reacts with several aromatic aldehydes as an electrophile rather than a nucleophile. The last process proceeds, most likely, through the intermediate formation of a charge transfer complex (CTC).

It has previously been found[9] that the thermal decomposition of diazomethanes RN_2 in the presence of O_2 is accompanied by chemiluminescence (CL) in the visible spectral region. The mechanism of this process has been studied[10]; kinetic analysis has been performed, and the chemiexcitation stage has been substantiated. The CL quenching by additives of an organic substrate is a convenient method for studying the reactivity of organic compounds with COx.[11] In this work, this approach was applied to study the influence of the COx structure on the kinetics of the reaction with benzaldehyde.

Diazomethane derivatives (aromatic (**1—6**) and aliphatic (**7**)) were used as sources of COx, and PhCHO was the aldehyde.

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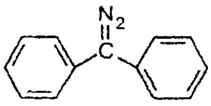

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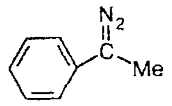

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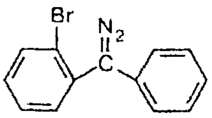

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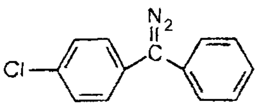

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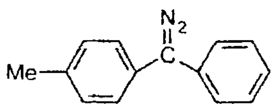

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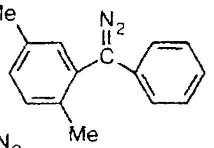

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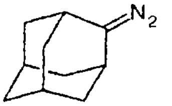

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Experimental

Thermolysis of diazomethanes RN_2 was carried out at 60 °C in MeCN, the initial concentrations $[RN_2]_0$ and $[O_2]_0$ in the solution being $(1.5—20) \cdot 10^{-3}$ and $(0.7—3.5) \cdot 10^{-3}$ mol L^{-1}, respectively. Acetonitrile and benzaldehyde were purified by standard procedures.[12] RN_2 was synthesized and purified as described previously.[13]

The CL setup consisted of a lightproof chamber containing a glass thermostatted reactor supplied with a thermocouple, bubbler for feeding of a gas mixture (air, oxygen, or Ar—O_2 (50 : 50, vol.%) mixture), reflux condenser, and device for fast introduction of solutions. FEU-39 or FEU-148 photoamplifiers were used as detectors of radiation.

Results and Discussion

The CL intensity (I) changes as a solution of aldehyde is added to the reactor containing a solution of RN_2 in MeCN. For all diazomethanes except **4**, a sharp decrease in the intensity from I_0 to I was observed first, and then the CL intensity began to increase (Fig. 1). When new portions of PhCHO were introduced, the intensity of the secondary luminescence became lower, and then only CL quenching occurred. In the case of **4**, the addition of PhCHO resulted only in increasing glow, which decreased almost to the initial level after the achievement of a maximum (see Fig. 1). NMR analysis of the products in the RN_2—PhCHO—MeCN—O_2 system showed the absence of 1,2,4-trioxolane after the end of the reaction. However, the formation of ozonide was distinctly detected in the same system with the photochemical generation of ROO.

Table 1. Parameters of quenching of CL in the RN_2—O_2—MeCN system by benzaldehyde (60 °C; air bubbling)

RN_2	$[RN_2]$ /mol L^{-1}	k_Q /L mol^{-1}	$k_{33}/k_{31} \cdot 10^2$	$\Sigma\sigma^*$
1	$1.5 \cdot 10^{-3}$	42±3	6.3	0.650
2	$1.9 \cdot 10^{-3}$	110±3	20	0.257
3	$2.3 \cdot 10^{-3}$	2.7±0.3	0.61	2.140
5	$8.9 \cdot 10^{-2}$	1.38±0.04	12.3	0.775
6	$2 \cdot 10^{-2}$	1.61±0.04	3.2	1.180
7	$1 \cdot 10^{-2}$	1.4±0.2	1.4	—

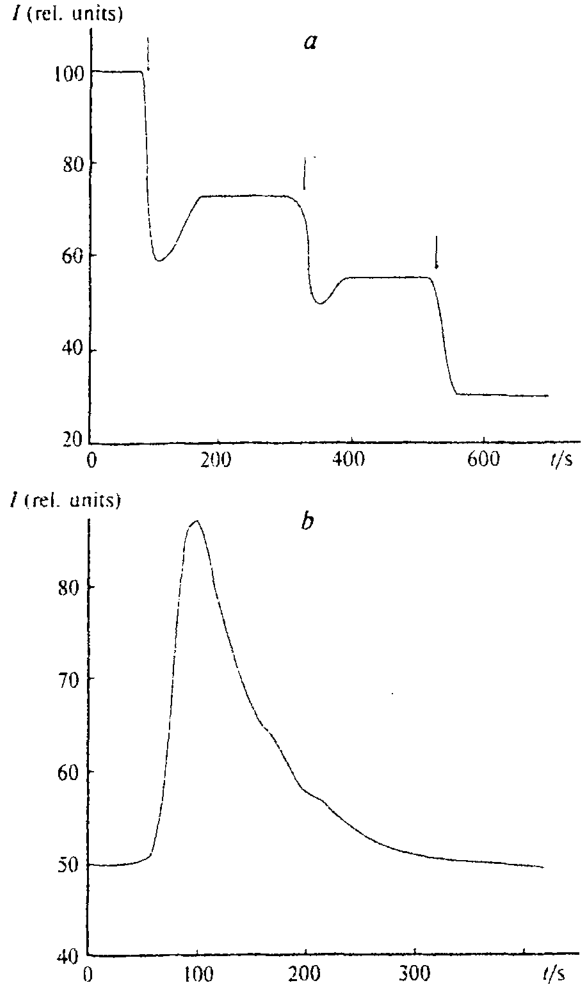


Fig. 1. Kinetics of CL quenching by additives of PhCHO during oxidative thermolysis of Ph_2CN_2 in a MeCN solution (*a*) and kinetics of changing the CL intensity after the addition of PhCHO to a solution of **4** in MeCN (*b*) at 70 °C. The moments of introduction of PhCHO are indicated by arrows.

To avoid the influence of the reaction products on the CL intensity, the dependence of I on the concentration of PhCHO was studied by adding the latter to a new solution of RN_2. The concentration of RN_2 was chosen in such a way as to provide the optimum CL intensity.

The quenching of CL of PhCHO for all RN_2 except **4** obeys the Stern—Volmer equation:

$$I_0/I = 1 + k_Q\,[\mathrm{PhCHO}]. \qquad (4)$$

The quenching rate constants (k_Q) are presented in Table 1.

The mechanism of thermal decomposition of RN_2 in the presence of oxygen includes the following stages[10]:

$$RN_2 \longrightarrow {}^1R + N_2, \tag{0}$$

$$^1R \rightleftharpoons {}^3R, \tag{ST, TS}$$

$$^3R + O_2 \longrightarrow ROO, \tag{2.2}$$

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

$$^3R{=}O \longrightarrow R{=}O + h\nu, \tag{4.0}$$

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

$$^3R{=}O + O_2 \longrightarrow P_{42}, \tag{4.2}$$

where P_i are the products of the corresponding stages (i). Numeration of the reactions here and below corresponds to that accepted previously.[10] Other reactions (for example, the interaction of singlet carbene with the starting diazo compound, the quadratic decay of COx, *etc.*) under the conditions of our experiment are virtually lacking.[10]

To elucidate the interrelation of k_Q and rate constants of the reactions involving COx, let us examine the kinetic scheme of thermal decomposition of RN_2.

As follows from the scheme, in the absence of active additives, the CL intensity in the steady-state regime is described by the equation

$$I_0 = \varphi_{31}\varphi_{40}\frac{k_{22}[O_2]}{k_{21}[RN_2] + k_{22}[O_2]}\times \\ \times\frac{k_{40}}{k_{40} + k_{41}[RN_2] + k_{42}[O_2]}\cdot k_0[RN_2], \tag{5}$$

where φ_{31} and φ_{40} are the quantum yields of excitation and luminescence of triplet benzophenone, respectively.

The addition of aldehyde results in its reactions with all reactive intermediates of the process: singlet and triplet carbene, COx, and electron-excited ketone.

$$^1R + PhCHO \longrightarrow P_{13}, \tag{1.3}$$

$$^3R + PhCHO \longrightarrow P_{23}, \tag{2.3}$$

$$ROO + PhCHO \longrightarrow P_{33}, \tag{3.3}$$

$$^3R{=}O + PhCHO \longrightarrow P_{43}. \tag{4.3}$$

However, only stage (3.3) is kinetically significant among the indicated reactions. As shown previously,[14] $k_{ST} = 3.2\cdot10^9\ s^{-1}$; therefore, even for diffusion-controlled values of k_{13}, under the conditions of our experiments ([PhCHO] = 0.1—70 mmol L^{-1}), the rate of reaction (1.3) is low as compared to that of the virtually irreversible reaction (ST).

The rate constant of reaction (2.2) k_{22} is $5\cdot10^9$ L mol^{-1} s^{-1} (see Ref. 16). Comparison of the rate of this reaction with those of possible reactions of ^3R with the aldehyde, for example, the formation of oxonium ylide or the elimination of the H atom, shows that stage (2.2) must prevail. For example, taking into account the comparatively low rate constant for the H atom abstraction by diphenylmethylene ($k_{23} \approx 10^4$—10^5 L mol^{-1} s^{-1})[16,17] and the used concentration interval of PhCHO, we find the rate ratio for stages (2.2) and (2.3): $w_{22}/w_{23} = k_{22}[O_2]/k_{23}[PhCHO] \approx 10^2$—$10^4$. Therefore, reaction (2.2) is almost the single channel of consumption of triplet carbene.

Evidently, reaction (4.3) is also improbable because the energy of the triplet level (E_T) of PhCHO is higher than E_T of substituted benzophenones, acetophenones, and adamantanones.

Thus, the mechanism of thermal decomposition of RN_2 in the presence of PhCHO is supplemented only by stage (3.3). Taking into account this fact, we obtain the following expression for the CL intensity:

$$I = \varphi_{31}\varphi_{40}\frac{k_{22}[O_2]}{k_{21}[RN_2] + k_{22}[O_2]}\,\frac{k_{31}[RN_2]}{k_{31}[RN_2] + k_{33}[R'CHO]}\times \\ \times\frac{k_{40}}{k_{40} + k_{41}[RN_2] + k_{42}[O_2]}\cdot k_0[RN_2]. \tag{6}$$

For the unchanged (under the experimental conditions) concentrations of O_2 and RN_2, it follows from Eqs. (5) and (6) that

$$I_0/I = 1 + k_{33}[R'CHO]/(k_{31}[RN_2]). \tag{7}$$

When $k_Q = k_{33}/(k_{31}[RN_2])$, the last equation coincides with the empirical formula (4), which makes it possible to determine the ratio of rate constants k_{33}/k_{31} (see Table 1).

Note a strong influence of the nature of the substituent in COx on its reactivity: k_{33}/k_{31} varies from 0.61 (**3**) to 12.3 (**5**). The reactivity of COx in the reaction with PhCHO decreases when an electron-withdrawing substituent is introduced. This fact is rather unusual, because the nucleophilic character of the attack of R_2COO at the C atom of the aldehyde fragment has been suggested previously[7] for the reaction of COx with aldehydes.

The induction Taft constants σ^* [18,19] were used for the quantitative description of the effect of substituents on the reactivity of R_2COO. The linear correlation $\log(k_{33}/k_{31}) = -1.2 - 1.8\Sigma\sigma^*(R)$ is fulfilled, and the correlation coefficient is 0.94 (Fig. 2).

The negative slope in the coordinates of the Taft equation indicates that COx reacts with aldehyde by the electrophilic mechanism. All studied compounds, except **4** and **8**, which were not included in the correlation, satisfy the correlation found.

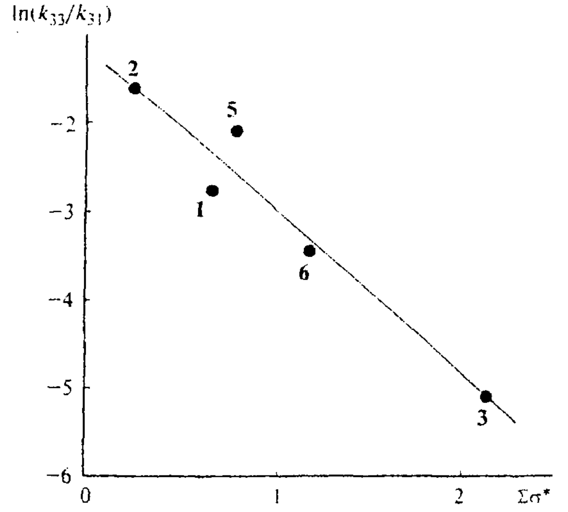


Fig. 2. Influence of the inductive properties of the substituents on the relative reactivity of COx, obtained from diazomethanes **1—3**, **5**, and **6**, in the reaction with benzaldehyde.

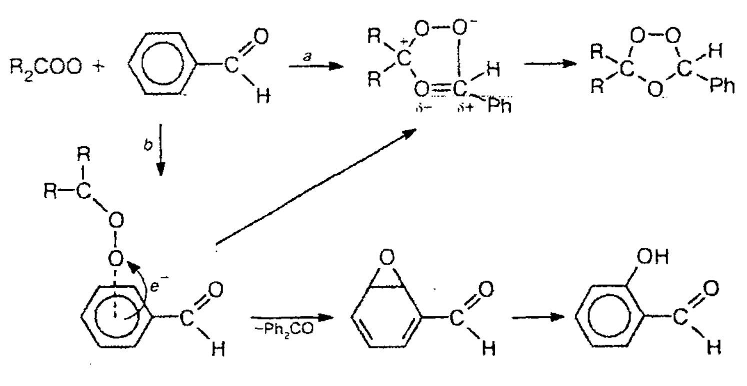
The obtained correlation indicates only a tendency, because the influence of the induction properties of the substituents on reaction (3.1) is not evident. Nevertheless, the found dependence suggests that interaction between the reagents involving the π-electronic system (Scheme 2) with the intermediate formation of CTC occurs along with the "classical" reaction of R_2COO with the carbonyl compound. The further transformation of the complex can result in both the standard products (1,2,4-trioxolane) and the products of oxidation at the ring. By analogy to the oxidation of aromatic compounds by carbonyl oxides,[20] we may assume that they can be oxiranes and the products of their further rearrangement.

Carbonyl oxide can attack the aldehyde molecule directly at the carbonyl group (pathway *a*). In this case, electron-withdrawing substituents increase the effective charge on the C atom and the rate of the nucleophilic attack. Since this process is ceased by the formation of 1,2,4-trioxolane, the yield of ozonide for these substituents regularly increases[7] ($\rho > 0$). Nevertheless, the experimentally measured yield of ozonide does not exceed 50%, which indicates the presence of other channels of formation of the products.

It is most likely that the interaction of COx with the π-electron system of aldehyde involving the intermediate formation of CTC (pathway *b*) is enhanced when electron donors are present at the reaction center of COx. Therefore, COx containing electron-donating substituents react with a high probability at both the aldehyde group and the benzene ring of the aldehyde. The CTC that formed has two possibilities of further transformations. If the oxidation of the aromatic ring is the main channel of the CTC consumption, this results, on the one hand, in a decrease in the yield of 1,2,4-trioxolane ($\rho > 0$ by the accumulation of ozonide) and, on the other hand, in an overall increase in the reaction rate ($\rho < 0$ by the overall kinetics). If the CTC is efficiently transformed into 1,2,4-trioxolane, both the electron-donating and electron-withdrawing substituents increase the yield of the product.

Thus, our experimental results along with the published data[7,21] indicate that both the donor and acceptor substituents facilitate the reaction $R_2COO + PhCHO$. Such an unusual influence of substituents on the rate of reaction (3.3) is observed due to two factors: (a) ambiphilicity of COx (it is known[20] that the latter exhibits both nucleophilic and electrophilic properties depending on the nature of the reagent interacting with it): (b) aromatic aldehydes contain centers of nucleophilic (the C atom of the aldehyde fragment) and electrophilic (π-electron system) addition.

Scheme 2



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