Electronic effects in the reaction of diphenylcarbonyl oxide with aldehydes

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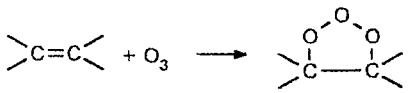
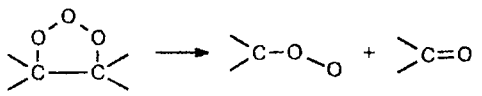
The reactivity of 14 aldehydes with diphenylcarbonyl oxide Ph_2COO was characterized by the k_{33}/k_{31} ratio. The values of k_{33}/k_{31} vary from $1.3 \cdot 10^{-2}$ (C_6F_5CHO) to 1.0 (*p*-Me_2N—PhCHO), 70 °C, acetonitrile as the solvent. A charge transfer complex (CTC) was suggested to be primarily formed during the reaction. The electronic effects of substituents in the reaction were analyzed using the published data. Carbonyl oxide reacts with aldehydes as a nucleophile (at the carbon atom of the —CHO fragment to form 1,2,4-trioxolane) and also as an electrophile (at the aromatic ring with the intermediate formation of CTC). The latter is transformed into either 1,2,4-trioxolane or the products of oxidation of the phenyl ring.

Key words: aldehydes, carbonyl oxides, reactivity, chemiluminescence.

Ozonolysis of olefins proceeds usually as a sequence of three main stages[1]: concerted attack of ozone on olefin (reaction (1)), decomposition of primary ozonide (1,2,3-trioxolane) to the carbonyl compound and carbonyl oxide (reaction (2)), and 1,3-addition of the latter to the C=O group resulting in secondary ozonide, 1,2,4-trioxolane (reaction (3a)). Other oxidation products (di-, tri-, polyperoxides, *etc.*) form in parallel in reaction (3b). The yield of ozonide also decreases due to recombination of carbonyl oxides and involvement of the solvent and active additives in the reaction.[1]


(1)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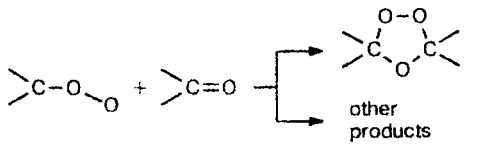
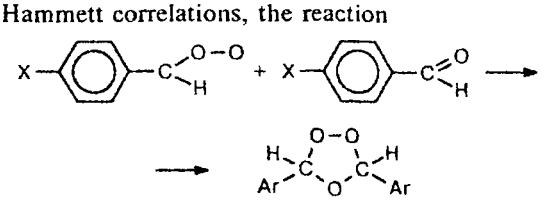


(3a)
(3b)

The first two stages have been studied in detail. The data available indicate that in reaction (1) ozone acts as an electrophilic agent, and the formation of 1,2,3-trioxolane occurs synchronously and with high rate constants even at low (~−100 °C) temperatures.[1] Ozonolysis of aryl-substituted olefins results in the predominant formation of carbonyl oxides (ROO), in which substituents stabilize the positive charge on the C atom of the carbonyl oxide group.[2,3] In the case of alkyl-substituted olefins, the formation of ROO is controlled by polar and steric factors.[4,5]

The third stage has been studied to a lesser extent, and the available facts indicate that the interaction of carbonyl oxide with the carbonyl compound is much more complicated than synchronous 1,3-cycloaddition *via* reaction (3a). A secondary kinetic isotope effect[6,7] is observed in this reaction, which agrees with the synchronous mechanism of recombination of carbonyl and carbonyl oxide. On the other hand, the interaction of these reactants does not always lead to 1,2,4-trioxolane because ROO is involved in side reactions.[8–10] These data indicate that reaction (3) can proceed as a successive two-stepped addition of the reactants to each other.

Aldehydes (R′CHO) are the most reactive compounds containing the carbonyl group; therefore, electronic effects in reaction (3) were mainly studied for the interaction of carbonyl oxides with R′CHO. It has been established,[11] in particular, that according to the Hammett correlations, the reaction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is characterized by the constant of the reaction series $\rho = +1.4$. This indicates the nucleophilic nature of the attack of carbonyl oxide on aldehyde. These data agree qualitatively with the results of Ref. 12, in which the positive slope in the Hammett equation coordinates was found for the reaction of diphenylcarbonyl oxide (R = Ph_2C) with the series of *para*-substituted benzaldehydes. However, the replacement of Ph_2COO by propanal oxide (R = EtCH) results in a more complex dependence[13]: both electron-donating and electron-withdrawing substituents in the aromatic ring of benzaldehyde accelerate the formation of 1,2,4-trioxolane. The effect of electron-donating substituents is explained by the stabilization of the quinoid resonance form R′CHO:

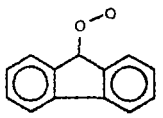
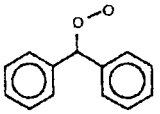
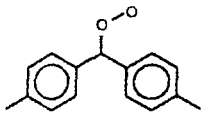
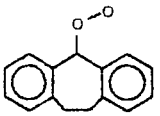
Then carbonyl oxide attacks aldehyde at the positively charged carbon atom. However, it is not clear why this stabilization is not manifested in the reaction of R′CHO with Ph_2COO.

However, linear correlations of free energies in the reaction of ROO with aldehydes were studied by analysis of the amount of ozonide formed.[11–13] Since the formation of 1,2,4-trioxolane does not exhaust all variants of interaction, this approach makes it possible to study electronic effects only in one of the possible parallel reactions of ROO with aldehydes.

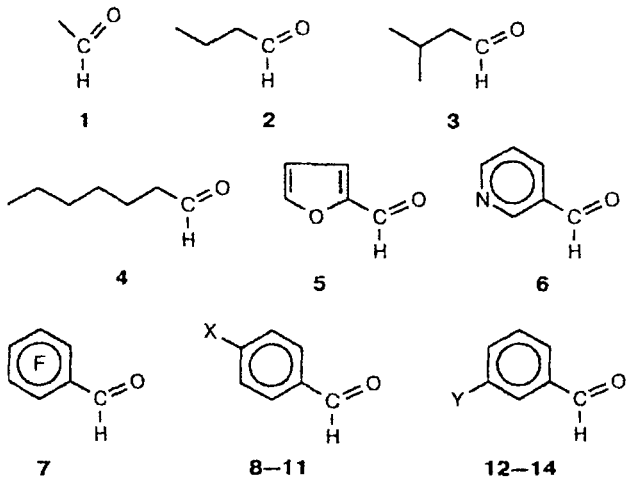
Absolute rate constants of reaction (3) were determined spectrophotometrically by the laser pulse photolysis technique[14–16] and optical modulation.[17] The scarcity of available data (Table 1) do not allow us to draw substantiated conclusions on the influence of the nature of reactants on the kinetics and mechanism of reaction (3).

It has previously been found[18] that thermal decomposition of diphenyldiazomethane RN_2 (R = Ph_2C) in the presence of oxygen is accompanied by chemiluminescence (CL) in the visible spectral region. The mechanism of this process, its kinetic analysis, and substantiation of the light stage are presented in Ref. 19. We have shown[20] that quenching of CL by additives of an organic substrate is a convenient method for studying the reactivity of organic compounds in the reaction with carbonyl oxides. This approach was used in this work to study the effect of the aldehyde structure on the kinetics of the reaction of Ph_2COO with several alkyl- and aryl-substituted R′CHO.

Table 1. Absolute rate constants of the reactions of carbonyl oxides with aldehydes (MeCN as a solvent, 295–300 K)

Carbonyl oxide	Aldehyde	k /L mol^{-1} s^{-1}	References
	Me—CHO[a]	$1.21 \cdot 10^9$	15
	$PhCH_2$—CHO[a]	$5.0 \cdot 10^8$	15
	$Me(CH_2)_6$—CHO[a]	$4.5 \cdot 10^7$	15
	Nor—CHO[a,b]	$\sim 1.5 \cdot 10^7$	15
	Me—CHO	$3.1 \cdot 10^6$	14, 16
	$PhCH_2$—CHO	$2.1 \cdot 10^6$	14, 16
	Mes—CHO[c]	$\sim 1 \cdot 10^7$	16
	$Me(CH_2)_6$—CHO	$2 \cdot 10^4$	17
	Me—CHO	$4.5 \cdot 10^6$	16
	Me—CHO	$4.7 \cdot 10^5$	16
	$PhCH_2$—CHO	$2.9 \cdot 10^5$	16

[a] Freon-113 as a solvent.
[b] Nor is 5-norbornen-2-yl.
[c] Mes is mesityl.



X = H (**8**), Me_2N (**9**), MeO (**10**), Cl (**11**); Y = PhO (**12**), Br (**13**), NO_2 (**14**)

Aldehydes with the aliphatic radical R′ (**1**–**4**), aldehydes with the π-electron system adjacent to the CHO group (**5**–**14**), and benzaldehydes with substituents in the *para*- (**9**–**11**) and *meta*-positions (**12**–**14**) were used as the objects of the study.

Experimental

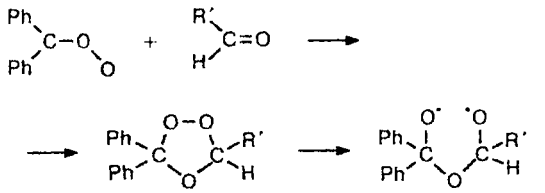
Thermolysis of RN_2 was carried out at 70 °C in MeCN, the initial concentrations $[RN_2]_0$ and $[O_2]_0$ in the solution being

$(0.5—1.7)\cdot10^{-3}$ and $(0.7—3.5)\cdot10^{-3}$ mol L^{-1}, respectively. Acetonitrile and aldehydes (**1—14**) were purified by standard procedures.[21,22] Synthesis and purification of RN_2 were carried out according to the known procedures.[23]

The CL installation used consists of a light-impermeable chamber in which a glass thermostatted reactor is placed. The reactor is provided with a thermocouple, a bubbler for supply of a gas (air, oxygen, or a mixture of $Ar:O_2 = 50:50$ vol.%), a reflux condenser, and a device for fast injection of solutions. An FEU-39 or FEU-148 amplifier was used as the radiation detector.

Results and Discussion

A solution of aldehyde, whose working concentration was varied depending on its reactivity, was introduced into a reactor thermostatted at 70 °C and containing ~10 mL of a solution of RN_2 in MeCN (0.5—1.7 mmol L^{-1}). This results in a change in the CL intensity (I) in the visible spectral region (Fig. 1). At first a sharp decrease in the intensity from I_0 to I is observed, then I begins to increase gradually and in some cases achieves or even exceeds the initial intensity of luminescence. When R'CHO was repeatedly added, the intensity of secondary luminescence became lower, and then only quenching of CL occurred. Analysis of the products in the "RN_2—R'CHO—MeCN—O_2" system by the NMR method showed that 1,2,4-trioxolane was absent at the end of the reaction. However, when ROO was photochemically generated in the same system, the formation of ozonide was distinctly observed, in agreement with the previous data.[12] It can be assumed that, under our experimental conditions, 1,2,4-trioxolane decomposes according to the scheme:



Monomolecular isomerization of the biradical on the triplet potential energy surface results in the formation of acid R'COOH and electron-excited benzophenone $^3(Ph_2C{=}O)$. The storage of this energy calculated by the additivity method[24] is at most 90—95 kcal mol^{-1}, which exceeds the energy of the triplet level of benzophenone (69 kcal mol^{-1}).[25] The elimination of the H atom from the aldehyde or solvent molecule is a possible reason for the appearance of secondary luminescence in the reaction under study. Thus, ozonide initiates the chain-radical oxidation that is accompanied in an oxygen atmosphere by the formation of triplet-excited carbonyl compounds.[26] Both processes lead to an increase in the CL intensity (see Fig. 1).

In the system under study, the formation of carboxylic acids is possible due to the decomposition of ozonide, chain-radical oxidation of aldehyde, *etc.* When

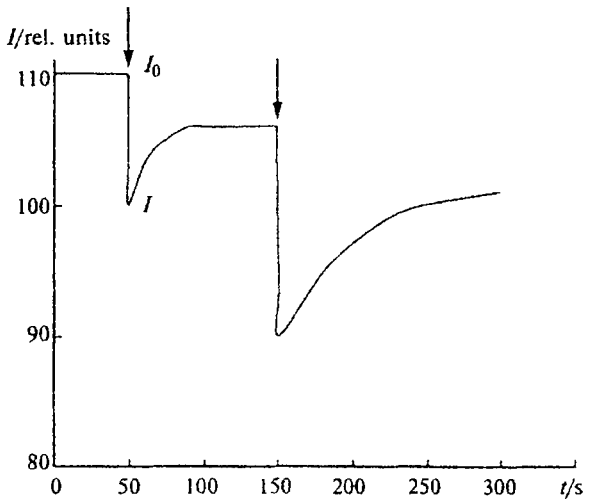


Fig. 1. Quenching of chemiluminescence in the RN_2—O_2—MeCN system (70 °C) by addition of a solution of PhCHO. Moments of introduction of the substrate are shown by arrows.

acid is accumulated, ozonide begins to decompose, predominantly catalytically[1] without formation of products in electron-excited states; therefore, the increase in luminescence ceases upon repeated addition of R'CHO.

To avoid the influence of the reaction products on the CL intensity, the dependence of I on the aldehyde concentration was studied by addition of R'CHO to a new solution of RN_2. The concentration of diphenyldiazomethane was chosen in such a manner that an optimum CL intensity was provided, because the effect of an "internal filter" decrease of I of CL appears at high RN_2 concentrations.

Analysis of the dependence of the I_0/I ratio on the aldehyde concentration shows that the efficiency of CL quenching obeys the Stern—Volmer equation for all substrates under consideration:

$$I_0/I = 1 + k_Q\cdot[R'CHO]. \qquad (5)$$

The rate constants of quenching k_Q are presented in Table 2.

To reveal a quantitative relation of this value to the rate constants of the reactions of carbonyl oxide, we performed kinetic analysis of the mechanism of thermal decomposition of RN_2 in the presence of oxygen and additives of aldehyde. The following reactions are the main stages in this mechanism[19]:

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

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

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

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

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

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

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

Scheme 1

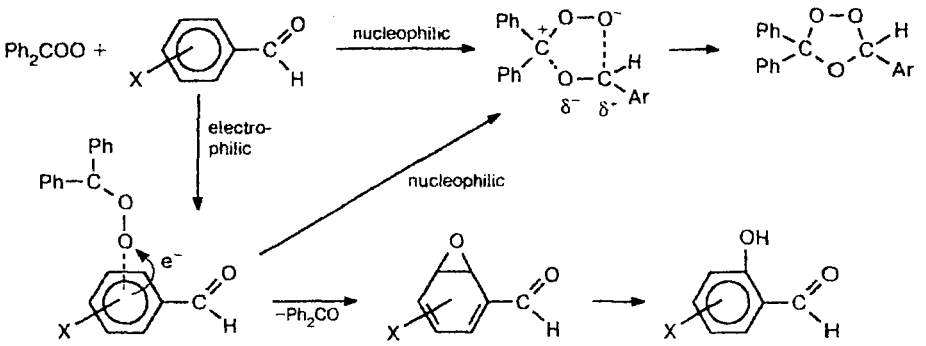


Table 2. Relative rate constants of the reactions of diphenylcarbonyl oxides with aldehydes R'CHO (MeCN as a solvent, 70 °C)

R'	$[R'CHO]_{max}$ / mmol L^{-1}	$[RN_2]$ / mmol L^{-1}	k_Q / L mol^{-1}	$(k_{33}/k_{31}) \cdot 10^2$	$(k_{33}/k_{31})_{av}^* \cdot 10^2$
Me (**1**)	15.7	0.6	23.9	1.43	1.7±0.3
	15.7	1.2	16.1	1.93	
n-Pr (**2**)	29.4	0.8	29.8	2.38	2.38
i-Bu (**3**)	36.3	0.8	40.5	3.24	3.24
n-Hx (**4**)	15.7	0.7	81.1	5.68	
	39.2	1.4	48.1	6.73	6.2±0.5
	15.7	1.4	45.2	6.33	
2-Furyl(**5**)	1.1	0.4	1120.0	45.00	50±5
	34.7	0.8	678.0	54.20	
3-Pyridyl (**6**)	38.8	0.4	48.5	1.94	1.7±0.2
	38.8	0.8	18.5	1.48	
C_6F_5 (**7**)	13.7	0.5	32.6	1.63	1.3±0.3
	27.5	1.0	9.8	0.98	
Ph (**8**)	23.4	0.5	56.7	2.84	
	23.4	0.5	73.1	3.66	
	19.6	1.0	19.3	1.93	
	39.2	1.0	23.1	2.31	2.6±0.6
	23.4	1.0	29.7	2.97	
	15.7	1.7	12.8	2.18	
	15.7	1.7	14.3	2.43	
p-Me_2N—Ph (**9**)	7.6	0.4	3150.0	126.00	100±30
	7.6	0.8	920.0	73.6	
p-MeO—Ph (**10**)	24.7	0.6	180.0	11.10	10±1
	24.7	1.2	70.2	8.63	
p-Cl—Ph (**11**)	8.6	0.5	48.3	2.42	2.6±0.2
	17.2	1.0	28.1	2.81	
m-PhO—Ph (**12**)	19.6	0.4	445.0	17.80	15±3
	19.6	0.8	157.0	12.60	
m-Br—Ph (**13**)	16.9	0.6	121.0	7.27	6.4±0.9
	16.9	1.2	45.7	5.48	
m-NO_2—Ph (**14**)	13.5	0.4	135.0	5.40	5.5±0.1
	13.5	0.8	70.3	5.62	

* Average values.

Here P_i are the products of the corresponding stages (*i*). The numeration of reactions is similar to that accepted in the previous work.[19] Other reactions (for example, the reaction of singlet carbene with the starting diazo compound, quadratic decay of carbonyl oxides, *etc.*) are not observed under our experimental conditions.[19]

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

$$I_0 = \varphi_{31}\varphi_{40} \frac{k_{22}[O_2]}{k_{21}[RN_2] + k_{22}[O_2]} \times \times \frac{k_{40}}{k_{40} + k_{41}[RN_2] + k_{42}[O_2]} \cdot k_0[RN_2], \quad (6)$$

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

The addition of aldehyde makes it possible to perform reactions with all active intermediates: singlet and triplet carbene, carbonyl oxide, and electron-excited benzophenone.

$$^1R + R'CHO \longrightarrow P_{13}, \quad (1.3)$$

$$^1R + R'CHO \longrightarrow P_{23}, \quad (2.3)$$

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

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

However, of the reactions presented above, only stage (3.3) is kinetically significant in the mechanism of thermal decomposition of RN_2 in the presence of aldehydes. In fact, according to the previously published data,[27] $k_{ST} = 3.2 \cdot 10^9$ s^{-1}; therefore, even at diffusion-controlled k_{13} values, the rate of reaction (1.3) under our experimental conditions ([R'CHO] = 0.1—10 mmol L^{-1}) is negligible as compared to that of the virtually irreversible reaction (ST).

The reaction rate is $k_{22} = 5 \cdot 10^9$ L mol^{-1} s^{-1}.[28] The reaction of ^3R with aldehyde does not result in the formation of oxonium ylide, because it is known[29] that only singlet carbenes thus react. The possible radical channel of the reaction

$$^3R + R'CHO \longrightarrow {}^{\cdot}RH + {}^{\cdot}R'CO$$

is also improbable if we take into account a comparatively low rate constant of elimination of the H atom by diphenylmethylene (k_{23} ~10^4—10^5 L mol^{-1} s^{-1},[30,31] *cyclo*-C_5H_{10}, *cyclo*-C_6H_{12}, PhMe, Et_2O, THF, 300 K) and the range of aldehyde concentrations used. The ratio of the rates of stages (2.2) and (2.3) is $w_{22}/w_{23} = k_{22}[O_2]/k_{23}[R'CHO]$ ~ 10^3—10^5 and, hence, reaction (2.2) is the only channel of consumption of triplet diphenylcarbene.

Reaction (4.3) is also improbable because the energy of the triplet level E_T of the aldehydes under study is higher than E_T of benzophenone. Competition between the radical elimination of the H atom by triplet benzophenone and reaction (4.2) favors the latter, because $k_{42} = (2—3) \cdot 10^9$ L mol^{-1} s^{-1},[25,32,33] and the reactivity of $^3R{=}O$ in reactions of homolytic elimination of the hydrogen atom ($k_{43} = 10^5$—10^6 L mol^{-1} s^{-1}) is close to that for the *tert*-butoxyl radical.

Thus, the mechanism of thermal decomposition of RN_2 in the presence of R'CHO is supplemented by reaction (3.3) only. Taking this into account, we obtain the following equation for the steady-state intensity of CL:

$$I_0 = \varphi_{31}\varphi_{40} \frac{k_{22}[O_2]}{k_{21}[RN_2] + k_{22}[O_2]} \cdot \frac{k_{31}[RN_2]}{k_{31}[RN_2] + k_{33}[R'CHO]} \times \times \frac{k_{40}}{k_{40} + k_{41}[RN_2] + k_{42}[O_2]} \cdot k_0[RN_2]. \quad (7)$$

It follows from Eqs. (6) and (7) at unchanged (under experimental conditions) concentrations of O_2 and RN_2 that

$$\frac{I_0}{I} = 1 + \frac{k_{33}[R'CHO]}{k_{31}[RN_2]}. \quad (8)$$

At $k_Q = k_{33}/k_{31}[RN_2]$, Eq. (8) coincides with empirical formula (5), which allows us to determine the ratio of the rate constants k_{33}/k_{31} (Table 2).

Note the strong effect of the nature of the substituent in aldehyde on its reactivity: the range of changing k_{33}/k_{31} from 0.013 for **7** to 1.0 for **9**. A distinct tendency toward decreasing the activity of aldehyde in the reaction with Ph_2COO is observed when electron-withdrawing substituents are introduced into the molecule. This is rather unusual because a nucleophilic character of the attack of ROO at the carbon atom of the aldehyde fragment has previously been suggested for the reactions of carbonyl oxides with aldehydes.[11,12]

The inductive scale of the Taft constants σ^*[34,35] that describes the polar effect of a substituent through space is usually used for the quantitative description of the influence of substituents on the reactivity of R'CHO. This scale was chosen because the aldehydes under study contain substituents that belong to different classes of organic compounds (alkanes, heteroorganic and aromatic compounds), which makes it impossible to use more specific scales (for example, σ^0, σ_p, *etc.*). The following linear correlation was found for the series of aldehydes under study:

$$\log (k_{33}/k_{31}) = 0.14 - 1.47 \cdot \sigma^* \ (r = 0.94, \ n = 18).$$

The negative value of the ρ coefficient indicates that the carbonyl oxide reacts with aldehyde *via* the electrophilic mechanism. Most of the compounds under study, except for **8** and aldehydes with hydrocarbon substituents **1**—**4**, satisfy the correlation found. Perhaps, aldehydes **1**—**4** fall out of the correlation because they have no π-electron system that participates directly in stage (3.3).

It has previously been shown[20] that the π-aromatic system is involved in the interaction of diphenylcarbonyl oxide with a wide series of aromatic compounds. To verify the assumption on the participation of π-electrons in stage (3.3), we studied the relation of the reactivity of R'CHO to the first ionization potential (*IP*) of R'H, compounds in which the aldehyde group is replaced by

the H atom. The *IP* values were taken from the reference book.[36] Despite the fact that the R'H molecule contains no reaction center of reaction (3.3), the —CHO fragment, a satisfactory correlation between $\log(k_{33}/k_{31})$ and *IP*(R'H) is observed:

$$\log (k_{33}/k_{31}) = 4.87 - 0.70 \cdot IP(R'H) \ (r = 0.97, \ n = 21).$$

Aldehydes **5** and **14** fall out of the correlation. This dependence suggests that the interaction of the reactants *via* the π-electron system (Scheme 1) with intermediate formation of a charge transfer complex (CTC) occurs along with the "classical" reaction of Ph_2COO with carbonyl. Further transformation of the complex can result in both standard reaction products (1,2,4-trioxolane) and products of oxidation at the ring. It can be assumed by analogy to the oxidation of aromatic compounds by carbonyl oxides[37] that oxiranes and products of their subsequent rearrangement can be such products.

The scheme presented for the reaction of aldehydes with Ph_2COO explains the opposite electronic effects of substituents, determined by us using the CL method ($\rho < 0$) and from the accumulation of ozonide[11,12] ($\rho > 0$), as well as the break in the Hammett dependence (see Ref. 13).

Carbonyl oxide can attack the aldehyde molecule directly at the carbonyl group. In this case, electron-withdrawing substituents result in an increase in the effective charge on the carbon atom and an increase in the rate of nucleophilic attack of carbonyl oxide. Since this process is accomplished by the formation of 1,2,4-trioxolane, the yield of ozonide for these substituents increases regularly[11,12] ($\rho > 0$). Nevertheless, the yield of ozonide does not exceed 50%,[12] which indicates other channels of formation of the reaction products.

The interaction of carbonyl oxide with the π-electron system of organic compounds with intermediate formation of CTC is enhanced when electron density donors are present.[20] Therefore, aromatic aldehydes containing electron-donating substituents react with a high probability not at the aldehyde group, but at the ring. The CTC formed has two possibilities of further transformations. If the oxidation of the aromatic ring is the main channel of CTC consumption, this results, on the one hand, in a decrease in the yield of 1,2,4-trioxolane ($\rho >$ 0 by ozonide accumulation) and, on the other hand, in an overall increase in the reaction rate ($\rho < 0$ by overall kinetics). If CTC is actively transformed into 1,2,4-trioxolane, both electron-donating and electron-withdrawing substituents increase the yield of the product. This is reflected as a break in the Hammett relation,[13] observed by study of the yield of ozonide in the reaction of carbonyl oxide with propionaldehyde and *para*-substituted benzaldehydes.

Thus, the rate constant of the reaction of aldehydes with diphenylcarbonyl oxides increases on going from aldehydes containing electron-deficient π-aromatic systems to aldehydes with electron density donor substituents, in the benzene ring. The results of the work supplement the concepts on the interaction of aldehydes and carbonyl oxides (the third stage of the mechanism of ozonolysis of unsaturated compounds), in which, as has previously been considered, ROO exhibits nucleophilic character. The experimental and published[11–13] data indicate that both donor and acceptor substituents facilitate the reaction ROO + R'CHO. This unusual effect of substituents on the rate of reaction (3.3) is possible due to two factors: first, the ambiphilic character of carbonyl oxide (it is known[37] that the latter exhibits both nucleophilic and electrophilic properties depending on the nature of the co-reactant); second, the presence of centers of nucleophilic (the carbon atom of the aldehyde fragment) and electrophilic (π-electron system) addition in aromatic aldehydes.

This allows carbonyl oxide to vary the direction and electron mechanism of the attack depending on the nature of the substituent in the aromatic ring.

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