Reactivity of aromatic compounds toward diphenylcarbonyl oxide

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The reactivity of organic compounds (PhH, PhMe, PhF, PhCl, PhOH, PhOEt, PhCHO, Ph_2CO, PhCN, Ph_2S, Ph_2SO, Ph_2SO_2, and p-$Me_2C_6H_4$) toward diphenylcarbonyl oxide Ph_2COO was characterized by the k_{33}/k_{31} ratio, where k_{33} and k_{31} are the rate constants for the reactions of Ph_2COO with the arene and diphenyldiazomethane Ph_2CN_2, respectively. The values of k_{33}/k_{31} vary from $2.6 \cdot 10^{-3}$ (PhCN) to 0.65 (Ph_2S) (70 °C, MeCN). The reaction is preceded by formation of a complex with charge transfer from a substrate to Ph_2COO. In the reactions with aromatic substances (except for Ph_2SO, PhCHO, and Ph_2CO), carbonyl oxide behaves as an electrophile.

Key words: aromatic compounds, carbonyl oxides, reactivity, chemiluminescence.

Thermal decomposition of diphenyldiazomethane RN_2 ($R = Ph_2C$) in the presence of oxygen is accompanied by chemiluminescence (CL) in the visible region, emitted by triplet excited benzophenone $^3R{=}O$.[1] This compound was shown[2] to result from the reaction of diphenylcarbonyl oxide ROO formed intermediately with the initial RN_2 molecule. In the present work, quenching of the CL of this light step was used to study the relative reactivities of ROO toward a number of substituted arenes: PhH, PhMe, PhF, PhCl, PhOH, PhOEt, PhCHO, Ph_2CO, PhCN, PhSPh, Ph_2SO, Ph_2SO_2, and p-$Me_2C_6H_4$.

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 were $(0.55-1.7) \cdot 10^{-3}$ and $(0.7-3.5) \cdot 10^{-3}$ mol L^{-1}, respectively.

Acetonitrile and aromatic compounds were purified by standard procedures.[3,4] RN_2 were synthesized and purified by known procedures.[5]

The CL setup consisted of a lightproof chamber containing a glass reactor maintained at a constant temperature and equipped with a thermocouple, a bubbler for the supply of a gas mixture (air, oxygen, or Ar : O_2 = 50 : 50% v/v), a reflux condenser, and a system for quick introduction of solutions of aromatic substrates. An FEU-39 or FEU-148 photoelectric multiplier was used as the emission detector.

Results and Discussion

The mechanism of thermal decomposition of diphenyldiazomethane in the RN_2—O_2—MeCN system without active additives includes the following main reactions:[2]

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

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

$${}^3R + RN_2 \longrightarrow R{=}N{-}N{=}R \tag{2.1}$$

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

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

$${}^3R{=}O \xrightarrow[-h\nu]{} R{=}O \tag{4.0}$$

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

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

From here on, P_i is the product of a chemical reaction or physical quenching in step (i).

In accordance with this scheme, the intensity of CL in a steady-state regime is described by the following equation:

$$\begin{aligned} I_0 = \varphi_{31}\varphi_{40} \frac{k_{22}[O_2]}{k_{21}[RN_2] + k_{22}[O_2]} \times \\ \times \frac{k_{40}}{k_{40} + k_{41}[RN_2] + k_{42}[O_2]} \cdot k_0[RN_2] \end{aligned} \tag{1}$$

After introduction of aromatic substrate Q into the RN_2—O_2—MeCN system, the intensity of CL rapidly decreases to reach a new steady-state value I (see Fig. 1). In the case of benzaldehyde, fast quenching of CL is first observed, and then the emission intensity slowly

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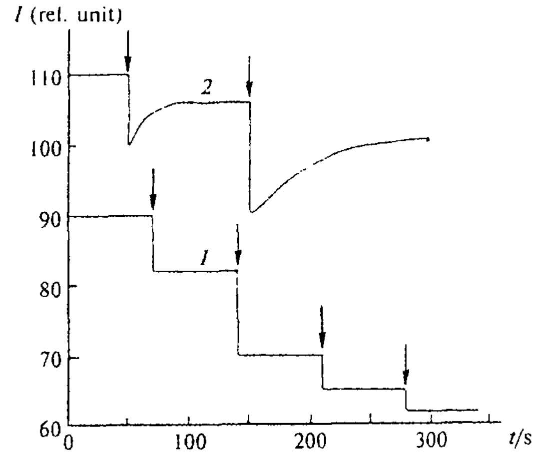


Fig. 1. Quenching of chemiluminescence in the RN_2—O_2—MeCN system (70 °C) after addition of solutions of PhF (*1*) and PhCHO (*2*). The arrows mark the instances of the introduction of a substrate.

increases. For other arenes, kinetic curves for the variation of intensity I are similar to curve *1* shown in Fig. 1 as an example.

The dependence of I (in relative units) on the content of an arene in the solution is presented in Table 1, whose analysis shows that in all the systems studied, the empirical equation

$$I_0/I = 1 + a_Q \cdot [Q], \quad \text{(II)}$$

where a_Q is a proportionality factor, holds with a high coefficient of correlation (≥0.99). The results of determination of the empirical parameter a_Q are summarized in Table 1.

In the presence of substrate Q, the above-presented mechanism should be supplemented by the following steps:

$$^1R + Q \longrightarrow P_{13} \quad (1.3)$$

$$^3R + Q \longrightarrow P_{23} \quad (2.3)$$

$$ROO + Q \longrightarrow P_{33} \quad (3.3)$$

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

According to a previous publication,[6] $k_{ST} = 3.2 \cdot 10^9$ s^{-1}; therefore, even when the k_{13} values are controlled by diffusion, the rate of reaction (1.3) under conditions of our experiments (low [Q]) is negligibly small compared to the rate of the virtually irreversible reaction (ST).

The rate constant $k_{22} = 5 \cdot 10^9$ L mol^{-1} s^{-1}.[7] For Ph_2S, which is among the most reactive substrates in the series studied here, $k_{23} = 1.7 \cdot 10^6$ L mol^{-1} s^{-1} [8] and the ratio of the rates of steps (2.2) and (2.3) amounts to $w_{22}/w_{23} = k_{22}[O_2]/k_{23}[Ph_2S] \approx 700$. For other aromatic compounds, this ratio is also fairly high, which makes it possible to neglect reaction (2.3) for all the substrates Q.

Let us estimate the w_{42}/w_{43} ratio. According to the data reported previously,[9—11] $k_{42} = (2—3) \cdot 10^9$ L mol^{-1} s^{-1}. It was found[12] that for aromatic compounds

$$\log k_{43} = (26.4 \pm 3.0) - (2.38 \pm 0.37) \cdot \mathrm{IP} \ (r = 0.988), \quad \text{(III)}$$

where IP is the first ionization potential of an arene.

Using the k_{42} value given above and the k_{43} values roughly estimated from Eq. (III) (see Table 2) we obtain $w_{42}/w_{43} = k_{42}[O_2]/k_{43}[Q] \approx 10—3 \cdot 10^4$, *i.e.*, reaction (4.3) also can be neglected.

Thus, of the reactions presented above, only reaction (3.3) is kinetically significant in the mechanism of thermal decomposition of RN_2 in the presence of Q. Taking account of this, we obtain the following expression for the steady-state intensity of CL:

$$I = \varphi_{31}\varphi_{40} \cdot ABC \cdot k_0[RN_2], \quad \text{(IV)}$$

$$A = \frac{k_{22}[O_2]}{k_{21}[RN_2] + k_{22}[O_2]},$$

$$B = \frac{k_{31}[RN_2]}{k_{31}[RN_2] + k_{33}[O_2]},$$

$$C = \frac{k_{40}}{k_{40} + k_{41}[RN_2] + k_{42}[O_2]},$$

φ_{31} and φ_{40} are quantum yields of excitation and emission of triplet benzophenone, respectively (the numbers of steps correspond to those accepted in Ref. 2).

When the concentrations of O_2 and RN_2 are constant under reaction conditions, it follows from Eqs. (I) and (IV) that

$$\frac{I_0}{I} = 1 + \frac{k_{33}[Q]}{k_{31}[RN_2]}. \quad \text{(V)}$$

For $a_Q = k_{33}/k_{31}[RN_2]$, the latter equation coincides with empirical formula (II), which makes it possible to determine the k_{33}/k_{31} ratio of rate constants (Table 2) and to calculate the k_{33}/k_{33}^0 value (the rate constant k_{33}^0 refers to the reaction of ROO with benzene).

The nature of the substituent in the aromatic ring has a substantial influence on the reactivity of the substrate (Table 2). Thus on going from PhCN to Ph_2S, the k_{33}/k_{31} ratio and, hence, the rate constant k_{33} increases 250-fold.

Figure 2 presents the plot of $\log(k_{33}/k_{31})$ against ionization potentials of arenes; this plot suggests intermediate formation of a charge transfer complex (CTC) and, without consideration of Ph_2SO, Ph_2CHO, and PhOEt, it can be described by the following equation:

$$\log(k_{33}/k_{31}) = (8.9 \pm 2.1) - (1.19 \pm 0.24) \cdot \mathrm{IP},\ r = 0.966.$$

We checked the observance of one- and two-parameter Hammett equations in the series of compounds studied:

$$\log k = \log k_0 + \rho \cdot \sigma, \quad \text{(VI)}$$

$$\log k = \log k_0 + \rho_{ind} \cdot \sigma_{ind} + \rho_{res} \cdot \sigma_{res}. \quad \text{(VII)}$$

Table 1. Quenching of CL in the RN_2—O_2—MeCN system by aromatic compounds

Compound	$[RN_2]$	$[Q]\cdot 10^2$	I_0^s	a_Q	Compound	$[RN_2]$	$[Q]\cdot 10^2$	I_0^s	a_Q
PhH	$5.5\cdot 10^{-4}$	0	100	21.3±0.6	PhCl	$1.1\cdot 10^{-3}$	0	100	6.01±0.15
		2.3	69.6				2.0	89.6	
		4.5	50.6				5.9	73.6	
		6.8	41.1				9.8	62.4	
		9.0	34.8				11.8	58.4	
		11.3	29.1				13.8	55.2	
PhH[a]	$1.1\cdot 10^{-3}$	0	100	8.81±0.55	PhCN	$1.1\cdot 10^{-3}$	0	100	2.40±0.16
		2.3	86.4				2.0	96.5	
		4.5	72.8				3.9	91.8	
		6.8	64.1				5.9	87.6	
		9.0	55.4				7.8	83.5	
		11.3	49.5				9.8	80.0	
PhMe[a]	$1.1\cdot 10^{-3}$	0	100	38.1±3.9	Ph_2CO	$1.1\cdot 10^{-3}$	0	100	15.4±0.6
		1.9	60.0				0.9	86.1	
		3.8	43.8				2.0	77.8	
		5.6	32.5				2.7	70.9	
		7.5	25.0				4.0	62.0	
		—	—				4.5	58.9	
p-$Me_2C_6H_4$	$1.0\cdot 10^{-3}$	0	100	95.5±6.6	PhF[a]	$1.0\cdot 10^{-3}$	0	100	8.00±0.32
		1.6	40.9				2.1	84.0	
		3.3	24.7				4.3	73.7	
		4.9	18.3				6.4	65.4	
		6.5	13.4				8.5	59.6	
		—	—				10.7	54.5	
Ph_2S[a]	$5.5\cdot 10^{-4}$	0	100	1040±58	PhOH	$5.5\cdot 10^{-4}$	0	100	227±5
		0.06	64.1				0.21	69.6	
		0.12	45.3				0.41	51.9	
		0.18	35.2				0.60	42.2	
		0.24	28.1				0.79	36.3	
		0.30	21.9				0.96	31.1	
Ph_2S[a]	$1.1\cdot 10^{-3}$	0	100	668±22	PhOH	$1.1\cdot 10^{-3}$	0	100	132±15
		0.06	72.0				0.21	83.4	
		0.12	56.7				0.41	69.5	
		0.18	45.1				0.60	57.8	
		0.24	37.8				0.79	48.1	
		0.30	33.5				0.96	42.8	
Ph_2SO	$1.0\cdot 10^{-3}$	0	100	177±7	PhOEt	$1.0\cdot 10^{-3}$	0	100	51.9±2.3
		0.20	75.8				0.8	69.4	
		0.40	60.0				2.6	43.5	
		0.60	49.5				4.5	29.5	
		0.80	41.1				6.3	23.5	
		1.00	35.8				—	—	
Ph_2SO_2	$1.1\cdot 10^{-3}$	0	100	2.53±0.18	PhCHO[a]	$1.7\cdot 10^{-3}$	0	100	14.3±1.3
		1.1	96.6				0.39	92.6	
		2.2	94.6				0.78	89.3	
		4.4	89.3				1.18	85.5	
		11.0	78.5				1.57	82.0	
		—	—				1.96	78.7	
PhCl	$5.5\cdot 10^{-4}$	0	100	11.0±0.5	PhCHO[b]	$1.7\cdot 10^{-3}$	0	100	12.8±0.9
		2.0	81.7				0.39	94.3	
		3.9	71.2				0.78	90.9	
		5.9	62.0				1.18	87.0	
		7.9	52.9				1.57	83.3	
		9.8	48.1				—	—	

Note: 70 °C; the concentrations are expressed in mol L^{-1}; the intensities (I_0^s) are given in relative units; bubbling of an Ar : O_2 mixture (50 : 50% v/v).

[a] Bubbling of air. [b] Bubbling of oxygen.

Two sets of inductive σ-contains were used: σ_I (in the two-parameter equation, the effect of conjugation was taken into account by σ_C^0 constants) and σ^0 (in combination with σ^+, to characterize the polar conjugation of the substituent in the aromatic ring). The σ_I-scale was constructed using the summaries presented in previous publications,[18,19] and the missing values were taken from a handbook.[20] The scale of the σ^0 constants was

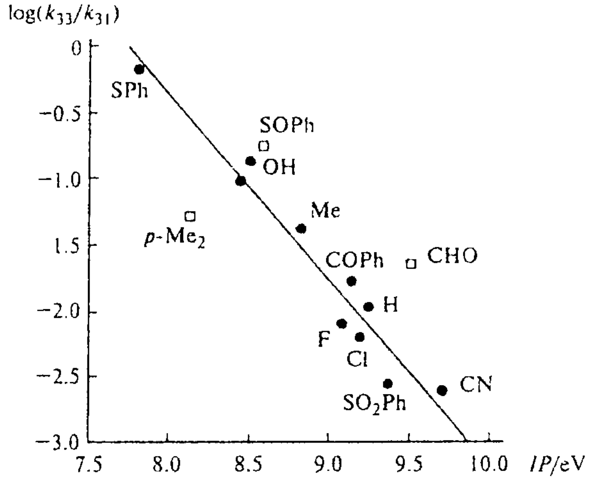


Fig. 2. The relationship between the relative rate constants k_{33}/k_{31} and the first ionization potentials (IP) for the substrate Q.

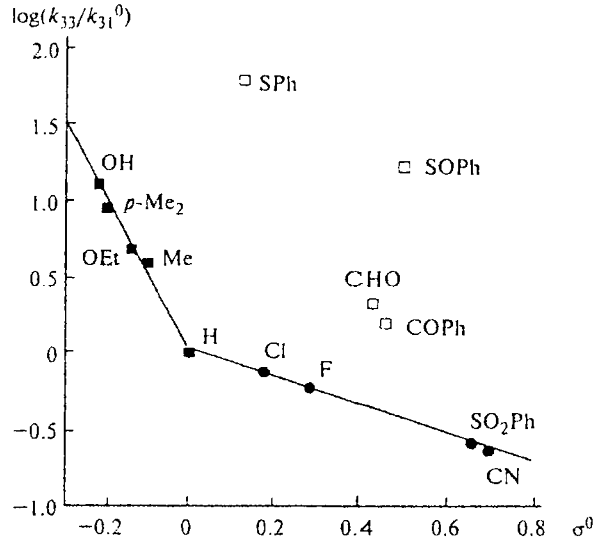


Fig. 3. Dependence of log($k_{33}/k_{31}{}^0$) for aromatic compounds on the inductive constants σ^0: for electron-withdrawing substituents (*1*) and for electron-donating substituents (*2*) in the aromatic ring.

based on published data.[17] For sulfur-containing substituents and for OH and CHO groups, the σ^0 values were taken from a previous study.[16]

Analysis of the experimental data in terms of Eqs. (VI) and (VII) showed that in the general case, no satisfactory correlation is actually observed; in our opinion, this means that the reaction follows several mechanisms depending on the structure of the substrate. In fact, attention is attracted to the dependence of log($k_{33}/k_{33}{}^0$) on the σ^0 constants of substituents X shown in Fig. 3 (constants for the *para*-position were used as σ^0, because these constants are not purely inductive[21] but contain a certain contribution (~57%) of the resonance constituent).

Table 2. Relative rate constants for the reaction of diphenylcarbonyl oxide with aromatic substrates (MeCN as the solvent, 70 °C)

Entry	Q	IP[a] /eV	σ^0 [b]	$k_{43} \cdot 10^{-5}$ [c] /L mol^{-1} s^{-1}	(k_{33}/k_{31}) · 10^2
1	PhCN	9.71	0.70	0.02	0.26±0.02
2	PhCHO	9.51	0.43	0.06	2.3±0.2
3	Ph_2SO_2	9.37	0.66	0.13	0.28±0.02
4	PhH	9.25	0.00	0.18	1.1±0.1
5	PhF	9.20	0.18	0.34	0.80±0.03
6	Ph_2CO	9.14	0.46	0.46	1.7±0.1
7	PhCl	9.08	0.29	0.64	0.63±0.03
8	PhMe	8.82	−0.10	5.20	4.2±0.4
9	Ph_2SO	8.58	0.50	10	17.7±1
10	PhOH	8.50	−0.22	15	13.5±1
11	p-$Me_2C_6H_4$	8.44	−0.20	21	9.6±0.7
12	PhOEt	8.13	−0.14	110	5.2±0.7
13	Ph_2S	7.80	0.13	700	65±8

[a] Ionization potentials for Ph_2SO and Ph_2SO_2 were taken from Refs. 20 and 21, those for other compounds were taken from Ref. 22. [b] The σ^0 values for Ph_2CO, PhOH, and for sulfur-containing compounds were taken from Ref. 23, those for other compounds were taken from Ref. 24.

[c] Calculated from Eq. (III).

It can be seen from Fig. 3 that the plot consists of two linear sections intersecting at X = H. For electron-donating substituents (H, Me, p-Me$_2$, OH, OEt)

$$\log(k_{33}/k_{33}{}^0) = (-4.92\pm0.47)\cdot\sigma_p{}^0,\ r = 0.998.$$

For electron-withdrawing substituents (H, Cl, F, SO$_2$Ph, CN)

$$\log(k_{33}/k_{33}{}^0) = (-0.89\pm0.04)\cdot\sigma_p{}^0,\ r = 0.9995.$$

The negative values of the reaction constants ρ^0 point to an electrophilic nature of ROO in the reaction with these substrates.

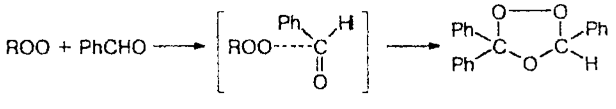
In the light of the obtained data, it can be suggested that the reaction of diphenylcarbonyl oxide with aromatic compounds starts with the formation of a CTC:

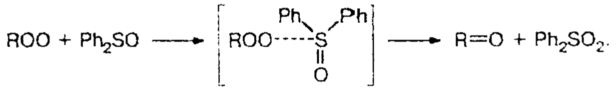
$$\mathrm{ROO + Q \longrightarrow [ROO^{-\cdot}...Q^{+\cdot}]}.$$

Note that CTCs formed by aromatic compounds and polyoxide species such as ozone[22] and oxygen[23] have been detected previously.

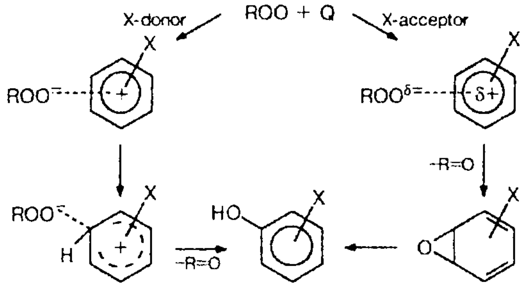
Then the process follows either a nucleophilic or an electrophilic mechanism depending on the nature of the substituent in the aromatic ring.

The former case is realized for PhCHO, Ph_2CO, and Ph_2SO as a nucleophilic attack by carbonyl oxide on the substituent,[24–28] for example





In the case where carbonyl oxide attacks the aromatic ring, the process occurs by an electrophilic mechanism.[29] These reactions are known[28] to give the corresponding phenols. The different types of influence of electron-donating and electron-withdrawing substituents on the magnitude of ρ^0 can be explained in terms of the following scheme:



Donors of electron density increase the degree of charge transfer in CTC (Fig. 2). The resulting peroxy anion is coordinated to a carbon atom in the aromatic ring; this is followed by a rearrangement to give a hydroxy derivative.

Electron-withdrawing substituents are responsible for low degrees of charge transfer in the ROO...Q complex. In this case, exchange electronic interactions prevail; this leads to the intermediate formation of arene oxide[28–32] and subsequent opening of the three-membered ring.

The point of intersection of straight lines *1* and *2* (Fig. 3), which falls on the unsubstituted compound, corresponds to transition from one pathway to phenol to another.

Thus, our study has shown that carbonyl oxides are similar in their chemical properties to other peroxide oxidative agents, namely, singlet oxygen and, first of all, ozone. They are efficient reagents for insertion of an oxygen atom into the substrate being oxidized. The presence of a π-electronic system in the substrate accounts for the possibility of a competing oxidation route involving the intermediate formation of a charge transfer complex. This is reflected in the complex character of influence of the electronic effects of substituents on the reaction rate.

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