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Contributions from Monomolecular and Bimolecular Reactions to the Disappearance of Diphenylcarbonyl Oxide in Solution

R. L. Safiullin[a], S. L. Khursan[b], E. M. Chainikova[a], and E. G. Galkin[a]

[a] *Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, Ufa, 450054 Bashkortostan, Russia*
[b] *Bashkortostan State University, Ufa, 450074 Bashkortostan, Russia*
e-mail: kinetic@anrb.ru

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Abstract—It was found by flash photolysis that the overall kinetics of diphenylcarbonyl oxide disappearance in acetonitrile, benzene, and *n*-hexane has both a bimolecular and a monomolecular component. The monomolecular route is the isomerization of diphenylcarbonyl oxide into dioxirane. The activation parameters of this process were measured. The activation energy of the bimolecular decay of diphenylcarbonyl oxide is slightly positive for acetonitrile, is close to zero for benzene, and is negative for *n*-hexane. This dependence of the activation energy on the nature of the solvent is due to the fact that the reaction includes the equilibrium formation of an intermediate species.

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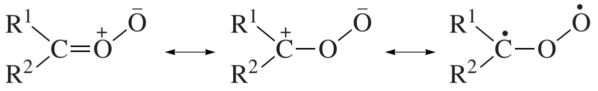
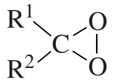
Carbonyl oxides (**I**), which are intermediates in olefin ozonolysis [1], have attracted researchers' rapt attention in recent decades. They have a unique electronic structure, which is conventionally represented as the superposition of the following resonance structures:



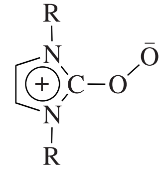
I



II

Although there have been numerous publications concerning the structure, physicochemical properties, and reactivity of these species, we think that the mechanism of their conversion in solution in the absence of oxidizable substrates has not been elucidated completely.

It has been established that the conversion of aromatic carbonyl oxides ($R^1 = R^2 = Ar$) obeys a second-order rate equation and yields the corresponding ketones [2–6]. An alternative carbonyl oxide disappearance route is isomerization into a dioxirane (**II**). However, the calculated activation energy of the cyclization of the simplest carbonyl oxide ($R^1 = R^2 = H$) into the corresponding dioxirane ranges between 75 and 100 kJ/mol, depending on the complexity level of the computational method [7–9]. With these energy demands, this reaction must be hampered in solution, but it does take place upon the photochemical activation of the carbonyl oxide [10]. According to the literature, substituents at the carbonyl oxide group can reduce the activation energy of isomerization to an extent sufficient for the reaction to occur in solution at low or moderate temperatures. For example, dioxirane formation from phenylmethoxycarbonyl oxide (R^1 = Ph, $R^2 = CH_3O$) was observed at –20°C in CD_2Cl_2 using ^{13}C NMR spectroscopy [11]. The occurrence of a similar reaction for phenyltrifluoromethylcarbonyl oxide (R^1 = Ph, $R^2 = CF_3$) in acetonitrile at 20°C was proved by indirect methods [12]. The rate constant of the isomerization of 4,4'-dimethoxyphenylcarbonyl oxide ($R^1 = R^2 = 4\text{-}CH_3O\text{–}C_6H_4$) into the corresponding dioxirane in acetonitrile and benzene at 25°C has recently been measured using flash photolysis [13]. It turned out to have a surprisingly large value of the order of 10^7 s^{-1} for both solvents. Carbonyl oxide **III** yields a dioxirane in deuterated benzene under thermal activation [14].



III

These works, as well as studies carried out in our laboratory, prompted us to reinvestigate the kinetics of diphenylcarbonyl oxide ($R^1 = R^2$ = Ph) disappearance in acetonitrile, benzene, and *n*-hexane solutions.

Using flash photolysis in combination with UV–vis spectrophotometric kinetic measurements, we demonstrated that the overall kinetics of diphenylcarbonyl oxide disappearance in solution always has a monomolecular component. The activation parameters of the rate constant were determined for the monomolecular and bimolecular Ph_2COO disappearance reactions.

EXPERIMENTAL

Acetonitrile, benzene, and *n*-hexane were purified using standard procedures [15]. Diphenyldiazomethane (Ph_2CN_2) was synthesized and purified by a standard method [16].

Kinetic studies were carried out using a flash photolysis setup, whose parameters are reported elsewhere [17]. The light source was an IFP 5000-2 lamp. The maximum pulse energy was 400 J at $U = 5$ kV and $C = 32$ μF. Approximately 90% of the light energy was emitted within 50 μs. The spectrophotometric part of the setup consisted of a source of continuous-wave probe radiation (DKSSh-150 xenon lamp with a system of quartz lenses and diaphragms for probe beam formation), an MDR-4 monochromator, an FEU-97 photomultiplier, and an S9-8 memory oscilloscope. This setup was fitted with a pulse signal processing device. The signal from the photomultiplier, after the compensation of its constant component, was amplified and was directed to the input of a digital oscilloscope operating in the standby mode. The oscilloscope was capable of saving the signal (2048 points) with a minimum time resolution of 50 ns and with 256-level voltage discreteness. The digitized signal was transferred into the computer through a GIPB interface (IEEE-488). The interface hardware on the computer side was made of standard parallel ports used in the bidirectional mode (EPP/ECP). All functions of the interface were realized in Pascal. The pulse processing program automatically determined the pulse onset and end points and the absorbance baseline and allowed manual correction. Using nonlinear regression analysis, it was possible to determine the effective order of the reaction, the initial absorbance, and the rate constant of any order and to fit kinetic profiles to an equation describing simultaneous first- and second-order reactions. The reactor was a temperature-controlled quartz cell with an optical path length of $l = 10$ cm and an inner diameter of ~1 cm. The flash photolysis of the diphenyldiazomethane–solvent–air system was carried out using filtered light (UFS-2 light filter, transmission range of $\lambda = 270$–380 nm). The initial diphenyldiazomethane concentration was $(1.0$–$15.8) \times 10^{-4}$ mol/l. The diphenylcarbonyl oxide disappearance kinetics was monitored as the decline of absorbance at the maximum-absorbance wavelength ($\lambda_{max} = 410$ nm for acetonitrile, 415 nm for benzene, and 420 nm for *n*-hexane; $\varepsilon_{max} = 1.9 \times 10^3$ l mol^{-1} s^{-1}) [5].

The products of diphenylcarbonyl oxide conversion were identified under steady-state photolysis conditions. A diphenylcarbonyl oxide solution in acetonitrile (1.34×10^{-4} mol/l, 15 ml) was placed in a temperature-controlled cylindrical quartz reactor. Photolysis was carried out using $\lambda = 270$–380 nm light (UFS-2 filter, DRT-400 mercury lamp) at 20°C under continuous air bubbling. The distance between the reactor and the light source was ~15 cm. Diphenyldiazomethane was added as it was consumed, so that its total amount after the experiment was 0.02 mmol. The reaction mixture was concentrated to ~0.3 ml. The products were analyzed by the GC-MS method using an AT-6890 chromatograph and an AT-5973 mass-selective detector. The data processing program was supplemented with a library containing 250000 spectra. The chromatographic conditions were as follows: Ultra-2 column (50 m × 0.2 mm); immobilized phase, 95% methyl silicone + 5% phenyl methyl silicone; initial temperature of 40°C; isotherm length of 3 min; final temperature of 250°C; heating rate of 10 K/min).

RESULTS AND DISCUSSION

A few years ago, we published a study devoted to the disappearance kinetics of diphenylcarbonyl oxide in solvents differing in polarity [5]. We measured the extinction coefficient and the rate constants of the bimolecular conversion of this species in acetonitrile, benzene, *n*-pentane, and *n*-decane. Our experimental facilities at that time did not allow us to analyze kinetic curves of complex orders or to separate the monomolecular route (whose contribution is small) from the dominant bimolecular route. In the work reported here, we reinvestigated the Ph_2COO disappearance kinetics, thoroughly processed the kinetic data using nonlinear regression analysis, and discovered that the overall Ph_2COO disappearance kinetics in acetonitrile, benzene, and *n*-hexane has both bimolecular and monomolecular components.

Diphenylcarbonyl oxide was obtained by the flash photolysis of solutions of the diazo compound in the presence of atmospheric oxygen via the following consecutive reactions [18]:

$$Ph_2CN_2 \xrightarrow[-N_2]{h\nu} {}^1Ph_2C \rightleftharpoons {}^3Ph_2C \xrightarrow{O_2} Ph_2COO.$$

These reactions were complete within the flash time plus the recording system readiness time (~100 μs). Thereafter, the absorbance of the solution, which was determined by the diphenylcarbonyl oxide concentration, was recorded in the wavelength range of 360–460 nm.

It turned out that Ph_2COO absorbance decline to an extent of ~95% is poorly described by the second-order rate equation (Fig. 1) and the effective order of the reaction with respect to the Ph_2COO concentration is intermediate between 1 and 2. Therefore, diphenylcarbonyl oxide undergoes some monomolecular conversion, and we will attempt to understand the nature of this conversion.

Let us consider all the diphenylcarbonyl oxide conversions possible in the system examined:

$$Ph_2COO + Ph_2CN_2 \longrightarrow 2Ph_2CO + N_2, \quad \text{(I)}$$

$$Ph_2COO + S \longrightarrow \text{products} \quad \text{(II)}$$

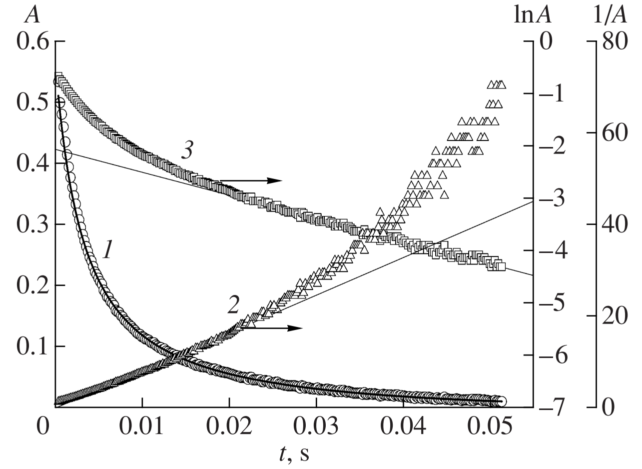
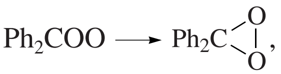


Fig. 1. (*1*) Diphenylcarbonyl oxide absorbance decline curve ($T = 20°C$, $\lambda = 410$ nm) and its fit to Eq. (1); the same curve fitted to (*2*) a second-order and (*3*) a first-order kinetic equation. $[Ph_2CN_2] = 1.0 \times 10^{-4}$ mol/l.

(S is a solvent molecule),

 (III)

$$Ph_2COO + Ph_2COO \longrightarrow 2Ph_2CO + O_2. \qquad (IV)$$

Under our experimental conditions, the initial Ph_2COO concentration is ~$(2–3) \times 10^{-5}$ mol/l for acetonitrile and benzene and ~$(1.0–1.5) \times 10^{-5}$ mol/l for *n*-hexane. Thus, the condition $[Ph_2COO] \ll [Ph_2CN_2]$ is fulfilled for reaction (I) and, obviously, the condition $[Ph_2COO] \ll [S]$ is fulfilled for reaction (II) as early as the initial point in time, ensuring pseudomonomolecular Ph_2COO disappearance. As follows from the above scheme, the Ph_2COO absorbance decline equation,

$$-dA/dt = k^{I}A + k^{II}A^2,$$

describes monomolecular carbonyl oxide consumption with a rate constant of $k^I = k_1[Ph_2CN_2] + k_2[S] + k_3$ and bimolecular Ph_2COO consumption with an effective rate constant of $k^{II} = 2k_4/\varepsilon l$. The integral form of the kinetic equation appears as

$$\ln\frac{(k^I + k^{II}A)A_0}{(k^I + k^{II}A_0)A} = k^I t. \qquad (1)$$

Using this equation and nonlinear regression analysis, we derived, from the absorbancer decline curves, the rate constants of monomolecular and bimolecular Ph_2COO conversions (Fig. 1).

The values of the rate constants k^I and k^{II} are listed in the table. The table also presents the calculated ratios of the bimolecular and monomolecular conversions of Ph_2COO (w^{II}/w^{I}) at the initial point in time. It is clear from these data that, at low temperatures, w^{II} exceeds w^{I} by a factor of 10–30. As the reaction temperature is raised, the contribution from the monomolecular component into the overall Ph_2COO disappearance kinetics increases systematically to reach 40–60% at $T \sim 323–333$ K. Since

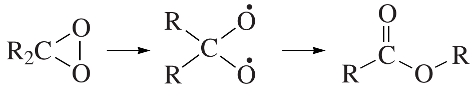
$$\frac{w^{II}}{w^{I}} = \frac{k^{II}A}{k^{I}} = \frac{2k_4[Ph_2COO]}{k^{I}},$$

the contribution from monomolecular conversion increases further as diphenylcarbonyl oxide is consumed.

Monomolecular reaction. The rate constant of the monomolecular disappearance of diphenylcarbonyl oxide in acetonitrile at 20°C is 35.7 s^{-1} for an initial Ph_2CN_2 concentration of 1.0×10^{-4} mol/l. First of all, it is necessary to see whether or not this reaction is the interaction between diphenylcarbonyl oxide and the diazo compound (reaction (I)). As the diphenyldiazomethane concentration is raised within the $(3.9–15.8) \times 10^{-4}$ mol/l range, the monomolecular Ph_2COO disappearance rate constant remains invariable (38.4 s^{-1} for $[Ph_2CN_2] = 3.9 \times 10^{-4}$ mol/l, 36.6 s^{-1} for $[Ph_2CN_2] = 6.6 \times 10^{-4}$ mol/l, 38.4 s^{-1} for $[Ph_2CN_2] = 9.2 \times 10^{-4}$ mol/l, 37.1 s^{-1} for $[Ph_2CN_2] = 11.8 \times 10^{-4}$ mol/l, and 35.6 s^{-1} for $[Ph_2CN_2] = 15.8 \times 10^{-4}$ mol/l). Raising the Ph_2CN_2 concentration by a factor of 16 does not increase the rate constant; that is, the contribution from reaction (I) to the monomolecular conversion of diphenylcarbonyl oxide can be neglected.

In order to answer the question as to the contribution from reaction (II) to the monomolecular conversion of Ph_2COO, we analyzed the products of the photooxidation of a diphenyldiazomethane solution. We carried out steady-state Ph_2CN_2 photolysis in acetonitrile so that the photolytic reactions of the resulting carbonyl oxide were ruled out and the Ph_2COO conversion products were the same as in the case of thermal activation (see Experimental). Reaction products were identified using the GC-MS method. The main reaction products were benzophenone (76.4%) and phenyl benzoate (17.3%). Mass spectra were interpreted using the HPChem Station program, which was supplied with the chromatograph–mass spectrometer–computer system. The goodness of fit between the observed spectrum and the corresponding library spectrum was 93 or higher. An analysis of the nine parameters determining the search strategy in the interpretation of a mass spectrum demonstrated that all the parameters have the best values for the compounds obtained. No Ph_2COO–solvent interaction products were detected. Therefore, reaction (II) is not responsible for the monomolecular disappearance of diphenylcarbonyl oxide.

The observation of ester among the reaction products is evidence in favor of reaction (III) taking place. Dioxiranes can rearrange into esters via the formation of an intermediate biradical [9, 19, 20]:



Rate constants of the monomolecular and bimolecular diphenylcarbonyl oxide decay reactions ($[Ph_2CN_2]_0 = 1 \times 10^{-4}$ mol/l)

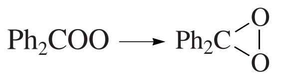
T, K	k^{I}, s^{-1}	$2k_4$, l mol^{-1} s^{-1}	$(w^{II}/w^{I})_{t=0}$
Acetonitrile solvent			
276	29 ± 6	$(7.6 \pm 0.7) \times 10^6$	8 ± 3
284	21 ± 3	$(8.4 \pm 0.3) \times 10^6$	7 ± 1
293	36 ± 4	$(9.0 \pm 0.3) \times 10^6$	8 ± 1
303	63 ± 6	$(9.4 \pm 0.6) \times 10^6$	3.3 ± 0.6
313	105 ± 8	$(9.0 \pm 0.6) \times 10^6$	2.0 ± 0.4
323	150 ± 20	$(1.2 \pm 0.2) \times 10^7$	1.7 ± 0.6
333	290 ± 30	$(1.3 \pm 0.3) \times 10^7$	0.7 ± 0.2
Benzene solvent			
279	61 ± 7	$(3.8 \pm 0.4) \times 10^7$	14 ± 3
287	86 ± 34	$(4.9 \pm 0.2) \times 10^7$	11 ± 2
296	150 ± 30	$(4.6 \pm 0.5) \times 10^7$	6.8 ± 1.6
306	170 ± 30	$(4.4 \pm 0.7) \times 10^7$	5.4 ± 1.5
316	200 ± 30	$(3.9 \pm 0.4) \times 10^7$	4.1 ± 0.8
326	460 ± 60	$(3.9 \pm 0.8) \times 10^7$	1.4 ± 0.5
336	490 ± 60	$(3.1 \pm 0.6) \times 10^7$	1.2 ± 0.4
n-Hexane solvent			
276	860 ± 570	$(1.7 \pm 0.1) \times 10^9$	32 ± 7
284	820 ± 440	$(1.6 \pm 0.2) \times 10^9$	34 ± 7
293	620 ± 190	$(9.0 \pm 0.9) \times 10^8$	22 ± 3
303	2000 ± 300	$(1.0 \pm 0.1) \times 10^9$	6.3 ± 0.8
313	1700 ± 200	$(4.9 \pm 0.8) \times 10^8$	3.1 ± 0.4
323	3200 ± 500	$(4.3 \pm 0.7) \times 10^8$	1.5 ± 0.2

It is known from the literature that esters can also form from a carbonyl oxide and a ketone via a reaction similar to the Bayer–Williger reaction [19]. However, benzophenone was initially absent in the system in which the Ph_2COO disappearance kinetics was studied by flash photolysis. Nevertheless, the overall disappearance kinetics of this species contains a monomolecular component. Therefore, the phenyl benzoate observed among the diphenyldiazomethane oxidation products forms from diphenyldioxirane, which is the product of diphenylcarbonyl oxide cyclization (reaction (III)); that is, $k^{I} = k_3$ (see the table).

We studied the temperature dependences of the monomolecular conversion of diphenylcarbonyl oxide in three solvents and obtained the following results: $\log k_3 = (8.9 \pm 0.2) - (41 \pm 2)/2.3RT$ for acetonitrile, $\log k_3 = (7.3 \pm 0.2) - (29 \pm 1)/2.3RT$ for benzene, and $\log k_3 = (7.6 \pm 0.8) - (27 \pm 5)/2.3RT$ for *n*-hexane (k_3, s^{-1}; E_a, kJ/mol).

Note the strong dependence of the rate constant k_3 on the nature of the solvent: at room temperature, k_3 = 36, 150, and 620 s^{-1} for acetonitrile, benzene, and *n*-hexane, respectively. For diphenylcarbonyl oxide, this dependence is not unique. Earlier [5], it was found that the bimolecular rate constant of diphenylcarbonyl oxide disappearance increases by two orders of magnitude on passing from the polar solvent acetonitrile to nonpolar *n*-alkanes. This trend was reproduced for the rate constant of reaction (IV) in this study (see below). A possible cause of the strong dependence of the rate constant on the nature of the solvent is that specific solvation in polar solvents reduces the reactivity of the zwitterionic intermediate Ph_2COO (μ = 4.0 D [21]). It was found using DFT calculations in the B3LYP/6-31G(d) approximation that the enthalpy of formation of the complex between H_2COO and an acetonitrile molecule is $\Delta H = -23$ kJ/mol [22]. The effect of solvation on the Ph_2COO isomerization kinetics can be explained in the framework of the following simple kinetic scheme:

$$Ph_2COO + S \rightleftharpoons Ph_2COO \cdot S, \qquad \text{(eq)}$$



(iso)

The solution contains carbonyl oxide as a complex with a solvent molecule ($Ph_2COO \cdot S$) and free carbonyl oxide (Ph_2COO). Only the latter can isomerize into a dioxirane. Therefore, the change of the total diphenylcarbo-

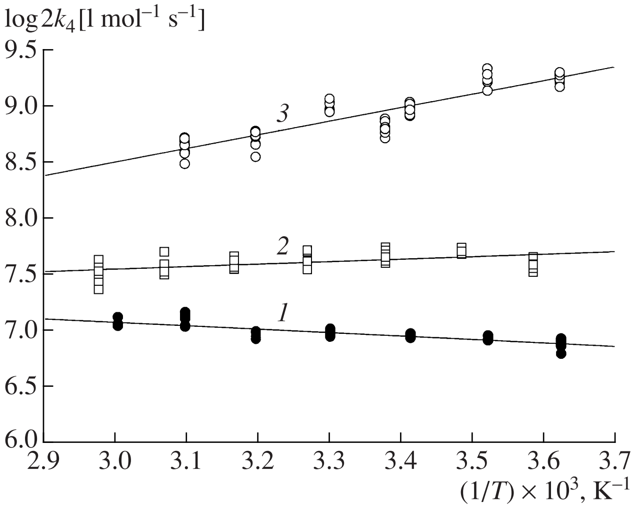


Fig. 2. Temperature dependence of the rate constant of the bimolecular decay of diphenylcarbonyl oxide in (*1*) acetonitrile, (*2*) benzene, and (*3*) *n*-hexane. $[Ph_2CN_2] = 1.0 \times 10^{-4}$ mol/l.

nyl oxide concentration ($[Ph_2COO]_\Sigma = [Ph_2COO \cdot S] + [Ph_2COO] = (1 + K_{eq}[S])[Ph_2COO]$), which is measurable experimentally, is equal to

$$-\frac{d[Ph_2COO]_\Sigma}{dt} = \frac{k_{iso}[Ph_2COO]_\Sigma}{1 + K_{eq}[S]} = k_3[Ph_2COO]_\Sigma.$$

According to quantum chemical estimates [22], the formation of the acetonitrile complex is energetically favorable; therefore, there is good reason to assume that $K_{eq}[S] \gg 1$. Hence, it readily follows that the experimentally measurable activation energy is $E_3 = E_{iso} - \Delta H$. It can be assumed that there is no specific solvation in *n*-hexane; that is, $K_{eq} = 0$, $k_3 = k_{iso}$, and $E_3 = E_{iso}$. Under the assumption that the effect of nonspecific solvation on the activation energy of diphenylcarbonyl oxide isomerization is weak (this assumption is substantiated by the similarity of the free energies of solvation of unsubstituted carbonyl oxide in acetonitrile and *n*-heptane [22]) and that the difference between the E_{iso} values for acetonitrile and *n*-hexane is negligible, the difference between the activation energies observed in these solvents characterizes the enthalpy of formation of the complex between diphenylcarbonyl oxide and acetonitrile: $\Delta E_3 = \Delta H = -14$ kJ/mol. Taking into account the error inherent in DFT calculations and the difference between the complex formation abilities of Ph_2COO and H_2COO, it can be stated that this enthalpy value is in good agreement with the theoretical estimate of ΔH [22].

Note, however, that the observed values of the activation energy of Ph_2COO isomerization are much lower than the values theoretically calculated for the simplest dioxiranes (R = H, CH_3) [7–9]. We have not understood the cause of this discrepancy as yet.

Bimolecular reaction. As would be expected, when we took into account the contribution from the monomolecular conversion of Ph_2COO to the overall disappearance kinetics of this species, the rate constant $2k_4$ for all the three solvents appeared to be 1.5–2 times smaller than the same constant obtained previously [5]: $(9.0 \pm 0.2) \times 10^6$ versus 1.8×10^7 l mol^{-1} s^{-1} for acetonitrile, $(4.6 \pm 0.5) \times 10^7$ versus 7.4×10^7 l mol^{-1} s^{-1} for benzene, and $(9.0 \pm 0.8) \times 10^8$ l mol^{-1} s^{-1} for *n*-hexane versus 1.5×10^9 l mol^{-1} s^{-1} for *n*-decane and 2.0×10^9 l mol^{-1} s^{-1} for *n*-pentane ($T = 20$°C). Nevertheless, the strong solvent effect on $2k_4$, which is likely due to the effective solvation of the carbonyl oxide and was noted in earlier works [5, 22], is confirmed by our data. Replacing acetonitrile with *n*-hexane causes a 100-fold increase of the rate constant of the bimolecular decay of Ph_2COO.

When studying the temperature dependence of the rate constant of the bimolecular decay of Ph_2COO, we observed a rather interesting fact. It was found that the activation energy of this reaction has a small positive value for acetonitrile, is close to zero for benzene, and is negative for *n*-hexane (Fig. 2: $\log 2k_4 = (8.1 \pm 0.1) - (6.5 \pm 0.7)/2.3RT$ for acetonitrile, $\log 2k_4 = (6.9 \pm 0.2) - (-4 \pm 1)/2.3RT$ for benzene, and $\log 2k_4 = (4.9 \pm 0.3) - (-23 \pm 2)/2.3RT$ for *n*-hexane ($2k_4$ is expressed in l mol^{-1} s^{-1}; E_a, in kJ/mol). The observed trend can be explained in the light of the above assumption that Ph_2COO undergoes effective specific solvation in acetonitrile. Under the assumptions that all of the diphenylcarbonyl oxide in *n*-hexane is free, all of the diphenylcarbonyl oxide in acetonitrile is bound into a complex, and the difference between the kinetic parameters of the bimolecular decay of Ph_2COO in these solvents is entirely due to this distinction, the following relationship can readily be established between the $2k_4$ values for acetonitrile and *n*-hexane:

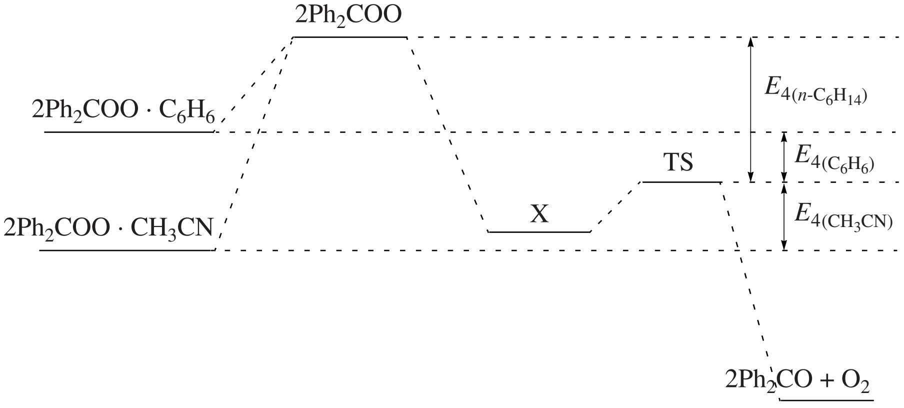
$$2k_{4(CH_3CN)} = \frac{2k_{4(n\text{-}C_6H_{14})}}{(1 + K_{eq}[S])^2} = \frac{2k_{4(n\text{-}C_6H_{14})}}{K_{eq}^2[S]^2}.$$

Hence, $E_{4(CH_3CN)} = E_{4(n\text{-}C_6H_{14})} - 2\Delta H$. Using the activation energies determined, we find that the enthalpy of formation of the complex between Ph_2COO and acetonitrile, $\Delta H = -14.8$ kJ/mol, coincides with the above estimate within the experimental error.

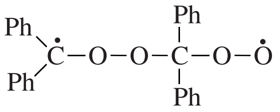
The negativity of the activation energy of the bimolecular Ph_2COO decay reaction is, obviously, a consequence of the complicated mechanism of this reaction, which includes the equilibrium formation of an intermediate:

$$Ph_2COO + Ph_2COO \rightleftarrows X \longrightarrow 2Ph_2CO + O_2.$$

The energy profile of the reaction taking into account diphenylcarbonyl oxide solvation can be represented as



It is assumed [18] that the intermediate X is the species resulting from the "head-to-tail" interaction between two diphenylcarbonyl oxide molecules:



The experimentally measurable apparent activation energy E_4 is determined by the enthalpy of the reversible formation of X, the height of the activation barrier of the irreversible decomposition of X, and the energy gain due to diphenylcarbonyl oxide solvation in the given solvent (see the above scheme). It is also possible that the solvent exerts an effect on E_4 by solvating the intermediate X and the transition state of the irreversible decomposition of X. These effects are not depicted in the scheme.

ACKNOWLEDGMENTS

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