## Kinetic Features of Decomposition of Benzoyl Peroxide in Superbasic Media

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**Abstract**—Kinetics of decomposition of benzoyl peroxide in superbasic media comprising mixtures of a dipolar aprotic solvent and a strong ionic base is studied. The process occurs in two steps through formation of intermediate perbenzoate anion. The contribution of ionic reactions is controlled by the polarity and dielectric constant of the solvent. The decomposition products are molecular oxygen and an alkali metal benzoate or perbenzoate. These products can be alkylated with butyl bromide in superbasic media.

Diacyl peroxides are widely used in many processes as a source of free radicals, so that their radical decomposition is studied in detail [1-5], including the mechanism and effects of various factors [6-10]. In polar solvents, decomposition of diacyl peroxides can proceed via the ionic mechanism [5, 11, 12]. However, the contribution of ionic reactions is insignificant.

Nucleophilic (ionic and ion-radical) reactions of diacyl peroxides are investigated to a considerably lesser extent. For example, reactions with amines, sulfides, and phosphates were studied [13]. It was suggested that they proceed via a polar transition state formed by nucleophilic attack by the oxygen atom of the peroxy group. In base-induced decomposition of benzoyl peroxide (I), nucleophilic attack of the OH<sup>-</sup> ions at the carbonyl carbon can occur with formation of an intermediate per acid anion [14]. To our knowledge, the effect of superbasic medium on the nucleophilic reactions of diacyl peroxides has not been studied yet.

Here we studied the kinetics and products of decomposition of peroxide I in some superbasic systems consisting of a dipolar aprotic solvent and a base. As a solvent we used hexamethylphosphoramide (HMPA), dimethylformamide (DMF), trimethyl phosphate, and dioxane; and as a base, sodium *tert*-butylate, NaOH, and KOH.

We studied the temperature dependence of the initial decomposition rate of **I** in the systems dipolar aprotic solvent-base and estimated the activation energy and preexponential factor (Table 1). In contrast to thermal decomposition [12], base-induced decomposition of **I** is characterized by lower activation energy. Analysis of data on the activation energies (Table 1) and characteristics of the solvents (Table 2) reveals no direct correlation. At the same time, in thermal decomposition, the activation energy decreases and the reaction rate increases with increasing basicity (donor number DN) of a solvent [12].

Table 1. Kin	netic parameters	of decomposition of	of I in the system	1 dipolar aprotic	c solvent-base	e ([ <b>I</b> ] 0.1, [t	-BuONa] 0.15,
and [KOH]	0.1 M)						
			$(10^5, \text{ mol } 1^{-1} \text{ s}^{-1})$				1

Base	Solvent	$v_0 \times 10^5$ , mol $l^{-1} s^{-1}$			$A_0$ ,	$E_{a}$ ,	$k \times 10^3$ ,	
		298 K	308 K	318 K	328 K	mol $l^{-1} s^{-1}$	kJ mol <sup>-1</sup>	1 mol <sup>-1</sup> s <sup>-1a</sup>
t-BuONa	HMPA	5.3	11.5	22.3	43.5	$5.9 \times 10^{5}$	57.0	9.02
t-BuONa	DMF	2.1	4.2	7.4	13.5	$9.4 \times 10^{3}$	49.0	2.93
t-BuONa	Dioxane	4.4	8.4	15.2	26.7	$1.8 \times 10^4$	49.0	7.20
KOH	HMPA	0.9	1.8	3.8	7.4	$2.7  imes 10^5$	60.0	4.28
KOH	DMF	2.8	5.2	8.5	15.2	$3.9  imes 10^3$	47.0	5.81
KOH	Dioxane	0.6	1.1	2.2	4.1	$2.0 \times 10^4$	55.0	0.90

<sup>a</sup> At 308 K.

Solvent	AN	DN	в	Y	Р
HMPA DMF Dioxane Trimethyl phosphate	10.6 16.0 10.8 16.3	38.8 26.6 14.8 23.0	30.0 36.1 2.21 20.6	0.4751 0.4798 0.2232 0.4645	0.3606 0.3435 0.3385 0.3220

Table 2. Characteristics of solvents used<sup>a</sup>

a (AN) Acceptor number, (DN) donor number, (ε) dielectric constant, (Y) polarity, and (P) polarizability.

The effect of the base depends to a considerable extent on the solvent (Table 1). For example, in the presence of sodium *tert*-butylate, the decomposition rate decreases in the order HMPA > dioxane > DMF. In the case of KOH, the order changes to DMF > HMPA > dioxane, suggesting that both the base and solvent are directly involved in the process.

Then we studied the concentration dependences of the base-induced decomposition of **I** in the indicated systems. In DMF, these dependences were studied in more detail. Figure 1 shows that, over the temperature range 292–318 K,  $v_0$  is a linear function of the peroxide and *t*-BuONa concentrations, suggesting the first order of the reaction with respect to both reactants [Eq. (1)].

$$v_0 = k[(PhCOO)_2][t-BuONa].$$
(1)

Below are given the corresponding constants.

T, K298308318 $k \times 10^3$ ,  $1 \mod^{-1} \text{s}^{-1}$ 1.62.96.0



**Fig. 1.** Initial decomposition rate of  $\mathbf{I} v_0$  in DMF as a function of (1-3) *t*-BuONa and (4) peroxide concentration at (1) 318, (2, 4) 308, and (3) 298 K. (1-3) [I] 0.082 M and (4) [*t*-BuONa] 0.15 M.

The temperature dependence of k is described by Eq. (2):

$$k = 7.4 \times 10^5 \exp(-49\,000/RT).$$
 (2)

Similar dependences were also obtained for the other systems dipolar aprotic solvent-base. The difference is that, in some cases, the concentration dependences of  $v_0$  flatten out (Figs. 2, 3). Furthermore, in the system HMPA-NaOH,  $v_0$  is independent of the reactant concentrations (Fig. 3), i.e., the reaction is zero-order with respect to both reactants. The rate constants are given in Table 1 and below (*T* 298 K; [NaOH] 0.1 and [I] 0.1 M).

SolventDMFTrimethyl phosphate
$$k \times 10^3$$
,  $1 \mod^{-1} \text{s}^{-1}$ 5.023.05

Comparison of the data given in Table 1 and above confirms our conclusion about complex effect of the base on the base-induced decomposition of I in dipolar aprotic solvents. In HMPA, the decomposition rate of I decreases in the order *t*-BuONa > KOH > NaOH. In DMF, the order changes to NaOH > KOH > *t*-BuONa. In dioxane, the order is like that in HMPA.

Previously we demonstrated that superbasic media facilitate ionic reactions of peroxy compounds [15–17]. In this study we confirmed this conclusion for base-induced decomposition of **I** in dipolar aprotic solvents. It was found that the investigated systems do not initiate polymerization of styrene, and introduction of an inhibitor of free-radical reactions ( $\alpha$ -naphthol) does not affect the reaction rate (no inhibitor consumption was observed). These facts suggest the lack of radical stages in the base-induced decomposition mechanism. The study of the reaction kinetics by measuring the electrolytic conductivity in the system



**Fig. 2.** Initial decomposition rate  $v_0$  of **I** in the system dipolar aprotic solvent–KOH as a function of (1-3) peroxide and (1'-3') KOH concentration at 308 K. (1) DMF, (2) HMPA, and (3) dioxane; (1-3) [KOH] 0.15 and (1'-3') [**I**] 0.1 M).



**Fig. 3.** Initial decomposition rate  $v_0$  of **I** in the system dipolar aprotic solvent–NaOH as a function of (1-3) peroxide and (1'-3') KOH concentration at 298 K. (1) DMF, (2) trimethyl phosphate, and (3) HMPA (1-3) [NaOH] 0.1 and (1'-3') [**I**] 0.1 M).

solvent-NaOH-benzoyl peroxide showed that, after introduction of the peroxide, the conductivity increased and then remained unchanged or slightly decreased, suggesting that the decomposition mechanism includes some ionic steps.

Below are given the initial rates and maximal conductivities in the system solvent–NaOH–benzoyl peroxide (T 298 K; [NaOH] 0.1 and [I] 0.1 M).

	$v_0 \times 10^5$ ,	mol l <sup>-1</sup> s <sup>-1</sup>	$\chi \times 10^5\text{,}$	$\Omega^{-1} \ \mathrm{cm}^{-1}$
DMF		4.90		89.0
Trimethyl	phosphate 3	3.10		4.1
HMPA	(	0.42		8.7

The results show no direct correlation between  $v_0$  and  $\chi$ . However, we observed the parallelism between the maximal conductivity and dielectric constant and polarity of the solvents (Table 2). Thus, as in thermal decomposition [12], in superbasic media, the contribution of the ionic steps to the process is controlled by the polarity and dielectric constant of the solvent.

The content of decomposition products of I in superbasic media depends on the particular base. In the systems with *t*-BuONa, we found *tert*-butyl benzoate, sodium benzoate, and sodium perbenzoate. After complete decomposition of the peroxide in the systems with mineral bases, in the liquid phase we found sodium (or potassium) benzoate as the only product.

Based on the results obtained, we offered the following two-step mechanism for base-induced decomposition of  $\mathbf{I}$  in dipolar aprotic solvents. In the first step, peroxide  $\mathbf{I}$  reacts with the anion of the base with



**Fig. 4.** Kinetics of accumulation of *tert*-butyl benzoate in base-induced decomposition of I in (1) HMPA, (2) DMF, and (3) dioxane at 298 K ([I] 0.1 and [*t*-BuONa] 0.15 M).

formation of the perbenzoate anion **II** and *tert*-butyl benzoate **III** or benzoic acid (or its anion) **IV**.

$$\begin{array}{ccc} Ph(O)OOC(O)Ph + t \text{-}BuO^{-} \overleftarrow{\longleftarrow} Ph(O)OO^{-} + Ph(O)OBu \text{-}t, \\ \mathbf{I} & \mathbf{II} & \mathbf{III} \\ \mathbf{I} + 2^{-}OH \longrightarrow \mathbf{II} + PhCOO^{-} + H_{2}O. \\ \mathbf{IV} \end{array}$$

The second step involves decomposition of the perbenzoate anion.

$$\mathbf{II} \xrightarrow{k} \mathbf{IV} + 1/2\mathbf{O}_2.$$

Therefore, when studying the kinetics of decomposition of  $\mathbf{I}$  by the consumption of available oxygen using the iodometric method, in fact, we follow the kinetics of consumption of anion  $\mathbf{II}$  in the second step of the process.

In the systems dipolar aprotic solvent-mineral base, it is very difficult to fix the kinetics of the first stage, i.e., base-induced decomposition of peroxide I, since the products are an alkali metal benzoate and benzoic acid, the latter forming the corresponding salt with the excess alkali. On the contrary, in the systems with *t*-BuONa, the first stage produces ester III, which could be detected chromatographically. Therefore, in this case, we studied the kinetics of accumulation of Ph(O)OONa by the GC method, monitoring the accumulation of ester III.

The results are presented in Fig. 4. Analysis of the slopes of the kinetic curves shows that the rate of accumulation of III and, correspondingly, that of conversion of I into sodium perbenzoate depend on



**Fig. 5.** Kinetic curves of accumulation of butyl benzoate in decomposition of **I** in the presence of 1-bromobutane in the superbasic medium (dipolar aprotic solvent– NaOH) at 290 K: (1, 2) HMPA and (3) DMF. [ $v(\mathbf{I})$  1.5×  $10^{-3}$ ; v(1-BuBr)  $1.9 \times 10^{-3}$ ; v(NaOH) (1)  $3.0 \times 10^{-3}$  and (2, 3)  $1.5 \times 10^{-3}$  mol].

the solvent, decreasing in the order HMPA > DMF > dioxane in parallel with the donor numbers of the solvents (Table 2) [DN is a semiquantitative characteristic of the solvent basicity (affinity for cations)]. The lower the degree of solvation of the anions or the higher DN of the solvents, the higher will be the reactivity of the anions. Since the first step of the process involves nucleophilic attack of the peroxide molecule by the anion of the base, the decomposition rate of **I** increases with increasing DN of the solvent.

The experimental kinetic results could be explained by assuming that decomposition of **I** under the action of sodium *tert*-butylate is an equilibrium step. Such an assumption appears to be quite realistic, when analyzing the properties of dipolar aprotic solvents and superbasic media containing them. In systems with solvents having high DN, the reactivity of anions increases by virtue of their weak solvation. As a result, even weak nucleophiles, e.g., acetate, are transformed into strong ones [18].

In accordance with the suggested mechanism, the decomposition rate of I in the presence of sodium *tert*-butylate is written as

$$v = k'K \frac{[(PhCOO)_2][t-BuO^-]}{[PhC(O)OBu-t]}.$$
 (3)

Comparison of Eqs. (1) and (3) shows that the estimated rate constants of base-induced decomposition of  $\mathbf{I}$  (Table 1) depend on the conversion of  $\mathbf{I}$ . With increasing conversion of  $\mathbf{I}$ , *k* decreases according to Eq. (4).

$$k = k' K \frac{1}{[\text{PhC}(\text{O})\text{OBu-}t]} \,. \tag{4}$$

Evidently, it is this fact that causes the deceleration of decomposition of I.

Therefore, decomposition of peroxide I in superbasic media is a complex multistep process. The solvent and base differently affect the kinetics of each step, so that the resultant kinetic trends are quite complicated.

To confirm the suggested mechanism, we examined the possibility of alkylation of intermediate sodium perbenzoate with alkyl halides. In these experiments, we used HMPA and DMF as solvents and 1-bromobutane as an alkylating agent.

In this case, the final products should be butyl perbenzoate V and butyl benzoate VI. The latter is formed by decomposition of the peroxy ester and also by alkylation of sodium benzoate.

$$\begin{array}{rcl} PhC(O)OONa \ + \ BuBr \ \longrightarrow \ PhC(O)OOBu \ + \ NaBr, \\ & \mathbf{V} \\ & \mathbf{V} \ \longrightarrow \ PhC(O)OBu \ + \ 1/2O_2, \\ & \mathbf{V} \\ & \mathbf{V} \\ PhC(O)ONa \ + \ BuBr \ \longrightarrow \ \mathbf{VI} \ + \ NaBr. \end{array}$$

The kinetics of accumulation of the esters, as studied chromatographically, reflects the total formation of esters V and VI. Figure 5 shows that the latter is accumulated in both systems, the accumulation rate being higher in HMPA.

$v(\text{NaOH}) \times 10^3$ , mol	$k_{\mathrm{ox}} \times 10^4,$ $\mathrm{s}^{-1}$	$k_{\rm b} \times \frac{10^4}{\rm s},$	Yield of ester III, %
HMPA 1.5	1.68	2.85	65
HMPA 3.5	7.26	6.38	85
DMF 1.5	0.39	1.00	47

It was demonstrated that the consumption of available oxygen and accumulation of the esters under the indicated conditions are first-order processes. The corresponding rate constants  $k_{ox}$  and  $k_b$  are given below [T 290 K; v(BuBr)  $1.9 \times 10^{-3}$  and v(I)  $1.5 \times 10^{-3}$  mol].

Comparison of  $k_{ox}$  and  $k_b$  shows that, in both solvents, at v(NaOH)  $1.5 \times 10^{-3}$  mol, the accumulation rate of ester **VI** is higher than that of decomposition of the peroxide, suggesting that, in HMPA and DMF, at the indicated reactant ratio, the peroxy ester is accumulated in the reaction mixture.

Finally, in superbasic media, the products of decomposition of  $\mathbf{I}$  could be alkylated with alkyl halides with formation of a peroxy ester and an ester. This

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result confirms the suggested twostep mechanism of

The experiments were carried out in a temperaturecontrolled cell equipped with a magnetic stirrer over the temperature range 298–328 K. NaOH and KOH were preliminarily crushed in a mortar in the Ar atmosphere. The solvents were dried over CaO, vacuum-distilled, and stored over 4 Å molecular sieves [19]. Benzoyl peroxide was synthesized as in [20] and then was recrystallized three times from ethanol. The purity of the product was 99.5– 99.8 wt%.

**Decomposition of benzoyl peroxide (I).** A weighed portion of the base was placed into the cell, a fixed volume of the solvent was added, the system was allowed to stand for 30 min at the desired temperature, and, finally, the peroxide was added. The process kinetics was monitored iodometrically. As a kinetic parameter we used the initial decomposition rate  $v_0$ . Liquid reaction products were determined by gas chromatography on a Chrom-5 instrument (flame-ionization detector;  $3000 \times 3$  mm glass column; stationary phase SE-30; carrier gas argon; temperature-programmed mode, 323-523 K; heating rate 8 deg min<sup>-1</sup>). The resulting chromatograms were processed using an internal reference.

The electrolytic conductivity of the reaction mixtures was measured by the compensation method using an R-577 ac bridge and an F-582 null indicator.

Alkylation of intermediate sodium perbenzoate was carried out at 290 K using the same procedure as in studying the decomposition kinetics. The alkylating agent was introduced 15 min after addition of the peroxide. The process was monitored by the consumption of available oxygen using the iodometric method and also by the accumulation of butyl benzoate using GC. Since peroxy compounds are unstable under GC conditions, they were reduced with triphenylphosphine prior to analysis. In so doing, butyl perbenzoate was reduced to butyl benzoate.

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