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Kinetics and Mechanism of Oxidation of Dimethyl Sulfoxide with Benzoyl Peroxide in Superbasic Media

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Abstract—Oxidation of dimethyl sulfoxide with benzoyl peroxide in some dipolar aprotic solvents and superbasic media was studied. The kinetic parameters were correlated with the main physicochemical characteristics of solvents. The oxidation rate grows with increasing donor number and polarizability of the solvent. A two-step scheme of dimethyl sulfoxide oxidation with benzoyl peroxide in superbasic media was suggested, involving preliminary cleavage of the peroxide to perbenzoate with the base. In the reaction, sodium *tert*-butylate is preferable over sodium hydroxide.

Considerable interest in oxidation of organic sulfides to sulfoxides and of sulfoxides to sulfones is due to wide applications of these compounds. Sulfoxides and sulfones are used as extractants and surfactants; some of them exhibit a physiological effect [1–5]. A number of effective antioxidant systems were suggested on the basis of data on liquid-phase oxidation of sulfides and sulfoxides with molecular oxygen [6–8]. The most effective oxidants of sulfides and sulfoxides are peroxy compounds, among which the most widely used are per acids, hydroperoxides, and hydrogen peroxide.

The kinetics of oxidation of sulfides and sulfoxides largely depends on the reaction medium [1]. However, correlations between the effect of the solvent and its main physicochemical parameters were considered only in a few papers. For example, Dutka *et al*. [9, 10] showed that the rate of oxidation of sulfoxides with per acids is largely determined by the solvent electrophilicity. In the presence of an alkali, the rate of dimethyl sulfoxide (DMSO) oxidation with cumene hydroperoxide strongly depends on the presence of other solvents whose effect is determined by their ionizing and dissociating power with respect to the alkaline salt of the hydroperoxide and by the competing solvation of the alkali metal ion [11].

Oxidation of organic sulfides with peroxides was studied most thoroughly and comprehensively. Oxidation of sulfoxides was studied much more scarcely, and virtually no data are available on oxidation of sulfoxides with acyl peroxides. This possibility is not discussed in papers concerning thermolysis of acyl peroxides in sulfoxides as solvents [12, 13]. At the same time, acyl peroxides (in particular, benzoyl peroxide), owing to their readier availability (compared to per acids and hydroperoxides) and higher stability (compared to per acids), may be more effective oxidants of organic sulfides and sulfoxides. Oxidation of the solvent was detected in our experiments on thermolysis of benzoyl peroxide **I** in DMSO [14]. Therefore, in this work we studied in more detail the kinetics and mechanism of DMSO oxidation with **I** and the effect exerted on this reaction by some dipolar aprotic solvents and superbasic systems containing them. As solvents we used hexamethylphosphoramide (HMPA), dimethylformamide (DMF), and dioxane, and as bases, sodium hydroxide and sodium *tert*-butylate.

In all the solvents used, the consumption of available oxygen is satisfactorily described by a first-order kinetic equation: $W = k_{app}[(PhCOO)_2]$. The apparent rate constant depends on the solvent and decreases in the order HMPA > DMF > dioxane (Table 1). From the temperature dependence of k_{app} in the range 298–338 K, we calculated the activation energies and preexponential factors (Table 1). The factors A_0 are low, suggesting an intricate reaction mechanism. The activation energy of DMSO oxidation with **I** grows in the series of solvents HMPA < DMF < dioxane.

The dependences of the apparent rate constant of consumption of available oxygen on the DMSO concentration also suggest an intricate reaction mechanism (Fig. 1). In all the solvents used, the initial linear ascending portion is followed by a saturation portion (plateau). This means that the reaction order with respect to DMSO is initially 1 and then changes to 0 with increasing DMSO concentration. In the DMSO concentration range from 0 to 0.1–0.15 M (depending

Table 1. Kinetic parameters of oxidation of dimethyl sulfoxide with benzoyl peroxide and physicochemical characteristics of solvents ([**I**] 0.05, [DMSO] 0.05 M)

Solvent	$k_{app} \times 10^2$, s^{-1} (T 338 K)	$A_0 \times 10^{-3}$, s^{-1}	E_a, kJ mol^{-1}	*AN*	*DN*	*Y*	*P*
HMPA	7.58	6.80	44.8	10.6	38.8	0.4751	0.3606
DMF	2.22	5.48	47.8	16.0	26.6	0.4798	0.3435
Dioxane	0.72	4.78	51.1	10.8	14.8	0.2232	0.3385

Table 2. Rate constants of oxidation of dimethyl sulfoxide with benzoyl peroxide in various solvents ([**I**] 0.05, [DMSO] 0.05 M)

Solvent	*T*, K	$k \times 10^3$, l $mol^{-1} s^{-1}$
HMPA	318	2.80
DMF	338	1.67
Dioxane	338	0.65

on solvent), the reaction kinetics is described by the equation

$$W = k[(PhCOO)_2][DMSO].$$

The rate constants *k* are listed in Table 2.

The kinetic parameters of the reaction were correlated with certain physicochemical characteristics of the solvents: donor (*DN*) and acceptor (*AN*) numbers, polarity (*Y*), and polarizability (*P*) (Table 1). Correlation analysis shows that oxidation is affected most significantly by the donor number and polarizability of the solvent. As these quantities grow, the activation energy decreases, and the constants k_{app} and *k* and, correspondingly, the rate of DMSO oxidation with **I** increase.

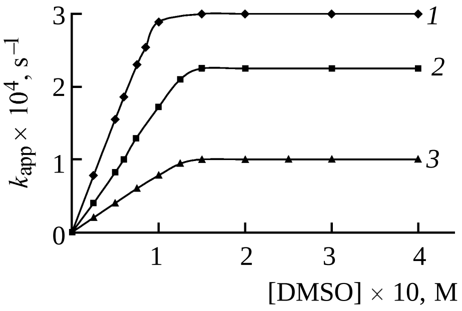


Fig. 1. Apparent rate constant of consumption of available oxygen in reaction of **I** with DMSO in (*1*) HMPA, (*2*) DMF, and (*3*) dioxane as a function of DMSO concentration. [**I**] 0.05 M; *T*, K: (*1*) 318 and (*2, 3*) 338.

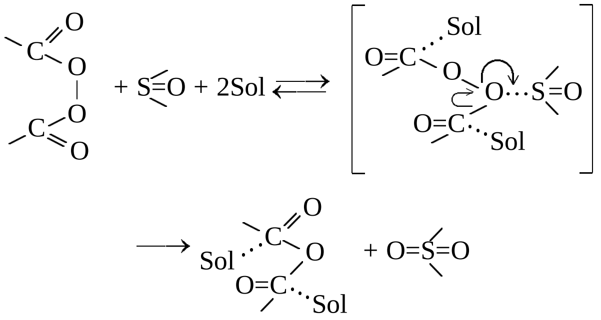
According to GLC analysis, the main reaction products are dimethyl sulfone and benzoic anhydride. Hence, the reaction follows the equation

$$PhC(O)OOC(O)Ph + (CH_3)_2SO \longrightarrow PhC(O)OC(O)Ph + (CH_3)_2SO_2.$$

The fact that the dependence of k_{app} on DMSO concentration flattens out (Fig. 1) suggests that the reaction may occur via an intermediate labile compound or complex. As the concentration of one of the reactants is increased, with that of the other component left unchanged, the reaction rate grows, which is followed by saturation due to complete binding of the second component (whose concentration was left unchanged) in an intermediate complex. In this case, the concentration of this complex, determining the overall reaction rate, does not further change on adding further amounts of the first component. There are indications in the literature on formation of intermediates and labile complexes in oxidation of sulfides and sulfoxides with peroxides [1, 9, 10, 15, 16].

A specific feature of HMPA, DMF, and dioxane as dipolar aprotic solvents is their capability to solvate predominantly cations, without solvation of anions. The affinity for the cation is determined by the basicity of these solvents. The role of the solvents in the reaction consists, apparently, in solvation of the starting peroxide at the carbonyl carbon atom, weakening the O–O bond and enhancing its reactivity.

Based on the experimental data, we suggest the following scheme of DMSO oxidation with **I**:



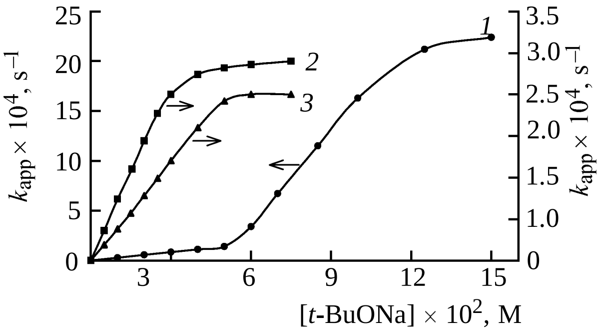


Fig. 2. Apparent rate constant of DMSO oxidation with **I** in (*1*) HMPA, (*2*) DMF, and (*3*) dioxane as a function of t-BuONa concentration. [**I**] 0.05 and [DMSO] 0.2 M; T 298 K.

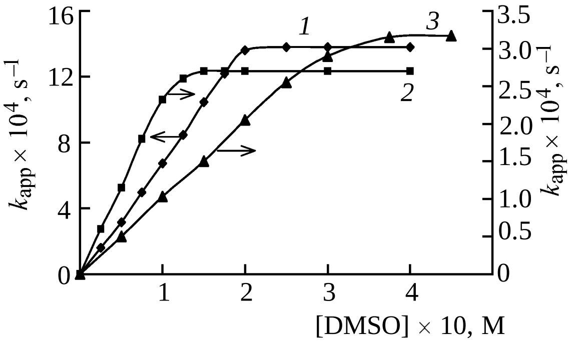


Fig. 3. Apparent rate constant of DMSO oxidation with **I** in (*1*) HMPA, (*2*) DMF, and (*3*) dioxane as a function of DMSO concentration. [**I**] 0.05 and [t-BuONa] 0.05 M; T 298 K.

Solvation of DMSO decreases the rate of its oxidation [10]. Therefore, in acetic acid capable of solvating DMSO, oxidation does not occur at all.

The next step of our studies involved experiments on oxidation of DMSO with **I** in superbasic media using the above-mentioned dipolar aprotic solvents. Because of the high reaction rates, these experiments were performed at 298 K. In the presence of t-BuONa, the consumption of available oxygen is also described by a first-order kinetic equation. To determine the kinetic orders with respect to DMSO and sodium *tert*-butylate, we studied the corresponding concentration dependences of the apparent rate constant of consumption of available oxygen (Figs. 2, 3). The dependences (except that on [t-BuONa] in HMPA) consist of the initial linear ascending portion followed by a plateau. As in the previous case, such a trend is apparently due to formation of an intermediate complex or compound. In HMPA, the dependence passes through an inflection and then also tends to saturation (Fig. 2, curve *1*). The inflection is observed at [t-BuONa] 0.05 M. At higher and lower [t-BuONa], the dependence of k_{app} on [t-BuONa] is virtually linear, i.e., the first reaction order with respect to the base is preserved, but the rate constant increases jumpwise. This may be due to a change in the relative contributions of particular reaction pathways differing in quantitative parameters only. To calculate the kinetic parameters, we used the initial portion of the curve in Fig. 2.

The linearity of the ascending portions in Figs. 2 and 3 suggests that, within this concentration range, oxidation of DMSO with **I** is a first-order reaction with respect to each reaction participant:

$$W = k[(\mathrm{PhCOO})_2][\mathrm{DMSO}][t\text{-}\mathrm{BuONa}].$$

The rate constants k are given below.

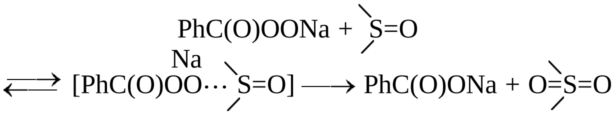
Solvent	HMPA	DMF	Dioxane
$k_{app} \times 10^2$, $l^2\ mol^{-2}\ s^{-1}$	13.2	3.90	2.00

Comparison of these data with those in Table 1 shows that the rate constants of DMSO oxidation with **I** in superbasic media also decrease with decreasing donor number and polarizability of the solvent. There is no correlation with the other solvent parameters.

The products of DMSO oxidation with **I** in the presence of t-BuONa contain *tert*-butyl benzoate, dimethyl sulfone, and sodium benzoate. Data on the composition of the forming products and the observed kinetic dependences suggest that oxidation of DMSO with **I** in superbasic media occurs in two steps. The first step is formation of *tert*-butyl benzoate and sodium perbenzoate by cleavage of the peroxide under the action of t-BuONa.

$$\mathrm{PhC(O)OOC(O)Ph} + t\text{-}\mathrm{BuONa} \longrightarrow \mathrm{PhC(O)OBu}\text{-}t + \mathrm{PhC(O)OONa}.$$

The second step is DMSO oxidation proper with the arising sodium perbenzoate, which may also occur via an intermediate labile complex or compound:



$$\mathrm{PhC(O)OONa} + \,\rangle\mathrm{S{=}O} \rightleftarrows [\mathrm{PhC(O)}\overset{\mathrm{Na}}{\mathrm{OO}}\cdots\rangle\mathrm{S{=}O}] \longrightarrow \mathrm{PhC(O)ONa} + \mathrm{O{=}}\rangle\mathrm{S{=}O}$$

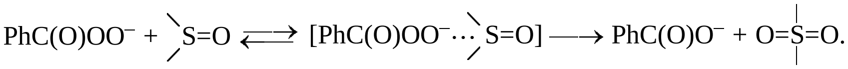
This assumption is indirectly confirmed by the fact that the plot of the apparent rate constant of consumption of available oxygen vs. DMSO concentration (Fig. 3) flattens out.

The dipolar aprotic solvents used to obtain superbasic media exhibit high ionizing and dissociating power with respect to the dissolved substances [17, 18], in particular, to the introduced sodium *tert*-butylate and forming sodium perbenzoate. Therefore, oxidation of DMSO with **I** in superbasic media occurs also by a pathway involving free ions:

$$t\text{-BuONa} + \text{Sol} \rightleftarrows \text{BuO}^- + \text{Na}^+\cdots\text{Sol},$$

$$\text{PhC(O)OOC(O)Ph} + t\text{-BuO}^- \longrightarrow \text{PhC(O)OBu-}t + \text{PhC(O)OO}^-,$$

$$\text{PhC(O)OONa} + \text{Sol} \rightleftarrows \text{PhC(O)OO}^- + \text{Na}^+\cdots\text{Sol},$$



$$\text{PhC(O)OO}^- + {>}\text{S=O} \rightleftarrows [\text{PhC(O)OO}^-\cdots{>}\text{S=O}] \longrightarrow \text{PhC(O)O}^- + \text{O=S=O}.$$

The rates of steps involving free ions are, as a rule, considerably higher than those of steps involving associated ions. The contribution of the pathway involving free ions to the overall reaction balance is determined by the degree of ionization and dissociation of, primarily, *t*-BuONa [and also PhC(O)OONa], which, in turn, is determined by the dielectric permittivity and basicity of the solvent (characterized semiquantitatively by the donor number [17]). Therefore, the rate of DMSO oxidation with **I** grows with increasing donor number of the solvent. Among the solvents used in this work, HMPA has the highest donor number [17, 18]; as a result, the contributions of ionic steps in systems with HMPA is the largest. The change in the ratio of the steps involving free and associated ions may be specifically responsible for the inflection in the curve of k_{app} vs. [*t*-BuONa] in HMPA (Fig. 2).

To examine the influence exerted by the kind of the base, we studied oxidation of DMSO with **I** in the superbasic system HMPA–NaOH. Under these conditions, the consumption of available oxygen also follows the first-order law, but the concentration dependences of k_{app} are somewhat different (Fig. 4). The process has the first order with respect to NaOH and a fractional order with respect to DMSO; it is described by the following kinetic equation:

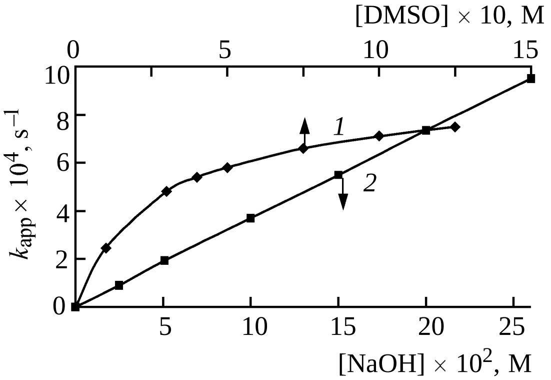


Fig. 4. Apparent rate constant of DMSO oxidation with **I** in the system HMPA–NaOH as a function of the concentrations of (*1*) base and (*2*) DMSO. [**I**] 0.10 M; *T* 298 K.

$$W = k[(\text{PhCOO})_2][\text{NaOH}][\text{DMSO}]^{0.4}.$$

The calculated rate constant k is $1.99 \times 10^{-2}\ \text{l}^{1.4}\ \text{mol}^{-1.4}\ \text{s}^{-1}$.

Comparison of the rates of DMSO oxidation with **I** under the same conditions (initial reactant concentrations, temperature) shows that in the superbasic medium HMPA–NaOH the oxidation is six times slower than in the system HMPA–*t*-BuONa.

The reaction mixture after the oxidation completion contained dimethyl sulfone and sodium benzoate. These data confirm the above-suggested two-step mechanism of DMSO oxidation with **I** in superbasic media. The arising benzoic acid binds sodium hydroxide; therefore, no less than a twofold excess of the alkali is required for complete decomposition of **I**.

Thus, compound **I** in dipolar aprotic solvents oxidizes DMSO to dimethyl sulfone. The reaction can be considerably accelerated by using superbasic media. The rate of DMSO oxidation with **I** grows with increasing donor number and polarizability of the solvent. *t*-BuONa as a component of superbasic media is preferable over alkalis.

EXPERIMENTAL

Experiments were performed in a temperature-controlled cell equipped with a magnetic stiirer at 298–338 K. Sodium hydroxide was preliminarily ground in a mortar under Ar. Solvents were dried over CaO, vacuum-distilled, and stored over 4 Å molecular sieves [19]. Compound **I** was prepared according to [20] and recrystallized three times from ethanol. The purity of **I** was 99.5–99.8%. To avoid induced decomposition of **I** and radical-chain oxidation of the solvent with atmospheric oxygen [21], experiments without superbasic media were performed under Ar in the presence of α-naphthol as radical reaction inhibitor. Special experiments [6, 22] showed that α-naphthol is consumed in the system under consideration only in reactions with free radicals. No additional consumption of **I** was detected. The α-naphthol concentration was 2×10^{-3} M, which is sufficient to suppress induced decomposition of **I** under our conditions.

The experimental procedure was as follows. The cell was charged with a weighed portion of the inhibitor or base (in experiments with superbasic media) and the required volume of the solvent; the mixture was brought to the required temperature over a period of 30 min, and compound **I** was added. The reaction progress was monitored by iodometric titration [23]. Liquid products were analyzed by gas chromatography (Chrom-5 chromatograph, flame ionization detector, stationary phase SE-30, carrier gas Ar, 3000 × 3-mm glass column, programmed heating from 323 to 523 K at a rate of 8 deg min^{-1}). Quantitative chromatographic analysis was performed with an internal reference.

Benzoic anhydride and *tert*-butyl benzoate (chromatographic references) were prepared by independent synthesis from sodium benzoate and benzoyl chloride in DMSO and from sodium *tert*-butylate and benzoyl chloride in HMPA, respectively [24].

To determine sodium benzoate, the reaction mixture was acidified with sulfuric acid and extracted with diethyl ether; the ether extract was analyzed by gas chromatography. The presence of benzoic acid in the ether extract was indicative of formation of sodium benzoate.

The reaction rate constants were determined by plotting the kinetic curves of consumption of available oxygen in semilog coordinates [22].

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