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Reactions of O_2^--Containing Supramolecules with Alkyl Halides

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Abstract—Formation of O_2^--containing supramolecules generated from the system 18-crown-6–KO_2 and electrochemically (tetraethylammonium superoxide) and the kinetics of the reactions of the generated O_2^- with alkyl halides in acetonitrile were studied conductometrically and UV-spectrophotometrically; the kinetic parameters of the processes were determined. The *E*2 mechanism was suggested for the reaction.

Reactions of O_2^- with various substrates receive much attention in view of participation of superoxide anions in chemical and biochemical processes [1–5]. However, many important details of the mechanisms of reactions involving O_2^- are still poorly understood, in particular, the influence of the countercation. As investigation object we chose the reactions of O_2^--containing supramolecules [counterions (K-18-crown-6)$^+$ (Kcrown) and tetraethylammonium (TEA)] with such substrates as propyl bromide (PrBr) and butyl bromide (BuBr) in acetonitrile.

To generate O_2^- with the (Kcrown)$^+$ counterion, we used the complexation reaction of KO_2 with 18-crown-6 [6]:

$$KO_{2(\mathrm{solid})} + \mathrm{Crown} \longrightarrow (\mathrm{Kcrown})^+ + O_2^-. \qquad (1)$$

In this work we monitored the complexation kinetics by two methods: UV spectroscopy (direct monitoring of the O_2^- concentration) and conductometry.

It is known [2] that in CH_3CN solution electrochemically generated O_2^- shows a well-defined absorption maximum at 249 nm, corresponding to the free radical anion, with the extinction coefficient of 1760 $\mathrm{l\,mol^{-1}\,cm^{-1}}$. Under the conditions of electrochemical reduction of oxygen (electrolyte tetraethylammonium perchlorate in CH_3CN), following the procedure described in [2], we obtained O_2^- whose spectral characteristics were consistent with published data (solvent CH_3CN) [2]. In generation of O_2^- by reaction (1), we also detected a band with a well-defined maximum at the above wavelength (Fig. 1). The kinetics of O_2^- generation and its consumption in the reaction with RBr was monitored by variation of the optical density *D* at 249 nm and electrical conductivity of two different O_2^--containing supramolecules: those with the (Kcrown)$^+$ and (TEA)$^+$ counterions.

Variation of the spectra of the reaction mixture with time after mixing of KO_2 with 18-crown-6 in acetonitrile is shown in Fig. 1a, and variation of the optical density in the absorption maximum with time, in Fig. 1b. The latter curve flattens out. The time in which the *D* values corresponding to a definite conversion (99.0% in our case) are attained strongly depends on the initial concentrations of the reactants [6]. The UV monitoring of the kinetics of the ion formation in the system containing KO_2 and 18-crown-6 in CH_3CN proved the possibility of describing the complexation kinetics by a first-order equation of type (2), as in [6] (for the reaction in DMSO).

$$D = D_\infty - (D_\infty - D_0)e^{-at}. \qquad (2)$$

Here *D* is the optical density corresponding to time *t*, and *a* is the apparent rate constant of the complex formation (k_{app}). Figure 1b shows that the experimental data (points) are well fitted by Eq. (2) (solid line). The parameters of Eq. (2) (Table 1) were determined by the nonlinear least-squares method. The kinetic equations obtained allow us to estimate the time required for attaining 99% conversion and to compare the complex formation rates in different solvents. In particular, the rate of complex formation of KO_2 with 18-crown-6 in DMSO [6] (*a* 0.04) is by an order of magnitude higher than in CH_3CN (*a* 0.003). Such comparison of the data for different solvents, obtained by different methods (UV spectroscopy and conductometry), is possible because both methods give the same results (Table 1, run nos. 2 and 7).

The time required to attain 99% conversion, estimated from data in Table 1 (24 h), was used in preparation of equilibrium O_2^- solutions for kinetic studies of the reaction with RBr. Figure 2 shows typical time dependences of the (a) optical density and (b) electrical conductivity of the solution in the reaction of RBr with O_2^-.

The results obtained by monitoring the optical density (run nos. 1–4, Table 2) show that the reaction kinetics in the chosen range of reactant concentrations obeys a first-order kinetic equation:

$$D = D_0 + D_1\exp(-k_t t). \qquad (3)$$

Here D_0, D_1, and k_i are the empirical parameters. This could be expected from the presumed reaction mechanism provided that [RBr] ≫ [O_2^-].

$$RBr + O_2^- \longrightarrow RO_2^{\bullet} + Br^-, \qquad (4)$$

$$O_2^{\bullet} + O_2^- \longrightarrow RO_2^- + BO_2, \qquad (5)$$

$$RO_2^{\bullet} + RO_2^{\bullet} \longrightarrow \text{Inactive products.}$$

As for similar analysis of the results obtained by measuring the electrical conductivity (Table 2), equation of type (3) is not obeyed in this case, but a more complex equation of type (7) can be used:

$$\chi = \chi_0 - \chi_1\exp(-k_1 t) - \chi_2\exp(-k_2 t). \qquad (7)$$

Here χ_0, χ_1, χ_2, k_1, and k_2 are empirical parameters.

The calculation results show that the suggested equations (3) and (7) quite adequately describe the kinetics of the reaction of O_2^- with RBr (Table 2). Comparison of the parameters k_2 determined by the two different methods shows that they are virtually equal at comparable initial concentrations and experimental conditions (run nos. 2 and 7, Table 2). Therefore, the apparent rate constant in this case is $k_{app} = k_2 = kc_0$(PrBr), which allows determination of the first-order rate constant k. As for the initial, very fast reaction step (parameter k_1), here we, apparently, see the difference in the possibilities of the two monitoring methods: Conductometry, probably, detects more efficiently formation of some additional ionic species in the initial reaction step, yielding a more complex kinetic equation.

Table 2 shows that, at similar initial concentrations and conditions [c_0(BuBr) 7 × 10^{-2}, c_0(PrBr) 8.3 × 10^{-2} and 9 × 10^{-2} M] (run nos. 2, 3, 7, 8, Table 2), the k_{app} (and hence k) values for BuBr (3 × 10^{-1} l mol^{-1} min^{-1}) are unexpectedly high compared to PrBr (k 4 × 10^{-2} l mol^{-1} min^{-1}). That is, O_2^- shows increased selectivity in reactions with these two very similar halohydrocarbonds.

The difference is also large when the reaction is performed in an oxygen atmosphere (run nos. 5, 6, Table 2). The parameters obtained by the two methods, conductometry and UV spectroscopy, are quite comparable. It is also evident from Table 2 (run nos. 2, 5) that, in going from one generation procedure

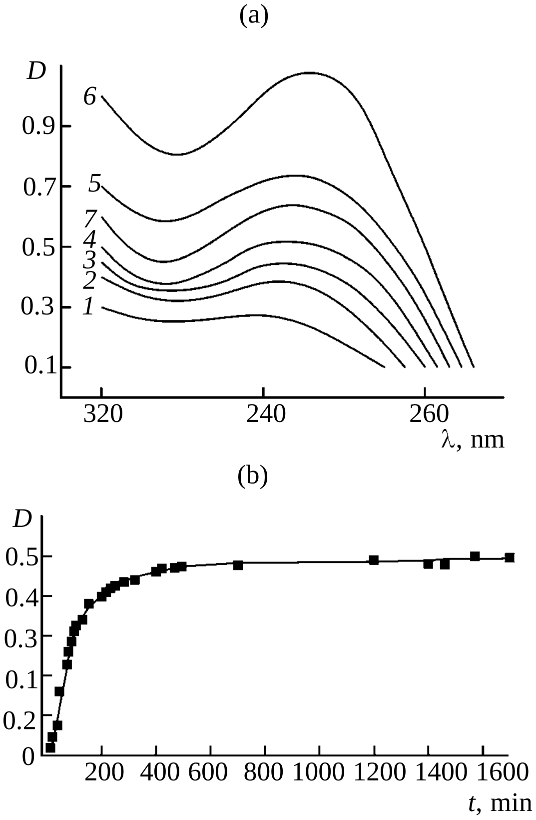

Fig. 1. Reaction of KO_2 with 18-crown-6 in CH_3CN, 25°C. (a) Spectra of the reaction mixture, recorded (*1*) 4, (*2*) 16, (*3*) 22, (*4*) 33, (*5*) 56, and (*6*) 86 min after mixing; $c_0(KO_2)$ 8.8 × 10^{-3}, c_0(crown) 6.4 × 10^{-3} M; (*7*) spectrum of electrolytically generated O_2^-. (b) Plot of the solution optical density D (λ 249 nm) vs. time t; $c_0(KO_2)$ 2.6 × 10^{-3}, c_0(crown) 4.2 × 10^{-3}.

Table 1. Parameters of Eq. (2) for reaction (1) (CH_3CN, 25°C)

Run no.	$c_0(KO_2)$ × 10^3, M	c_0(crown) × 10^3, M	b	c	a × 10^3, min^{-1}	r
1	8.8	6.4	1.78	1.61	4.8	0.991
2	6.0	7.0	1.47	1.44	3.2	0.999
3	5.8	7.2	1.44	1.18	2.7	0.988
4	4.2	2.6	0.88	0.88	2.0	0.971
5	2.6	4.2	0.48	0.52	1.7	0.994
6	2.5	2.7	0.67	0.50	1.5	0.991
7	6.0[a]	12.0	0.57 × 10^{-3}	1.7 × 10^{-3}	2.9	0.996

[a] Conductometric method (measuring χ), $b = \chi_0$, Ω^{-1} cm^{-1}, $c = \chi_\infty - \chi_0$, Ω^{-1} cm^{-1}; in other cases, UV spectroscopy (measuring D), $b = D_\infty$, $c = D_\infty - D_0$.

Table 2. Kinetic parameters of Eqs. (3) and (7) for the reaction of O_2^- with RBr (CH_3CN, 25°C)

Run no.	RBr, determination method, atmosphere	c_0(RBr) × 10^2, M	c_0(KO_2) × 10^3, M	c_0(crown) × 10^3, M	$\chi_0 \times 10^4$,[a] Ω^{-1} cm^{-1}	$\chi_1 \times 10^4$,[b] Ω^{-1} cm^{-1}	$\chi_2 \times 10^4$, Ω^{-1} cm^{-1}	$k_1 \times 10^2$, min^{-1}	$k_2 \times 10^3$, min^{-1}	*r*
1	PrBr, *D*, Ar	1.4	2.5	2.7	0.42	0.23	–	–	0.91	0.998
2	BuBr, *D*, Ar	7.0	4.2	2.6	0.77	0.56	–	–	20.0	0.999
3	PrBr, *D*, Ar	9.0	4.2	2.6	0.27	0.00	–	–	4.00	0.987
4[c]	PrBr, *D*, Ar	2.0	–	–	0.70	0.39	–	–	2.00	0.996
5	PrBr, χ, O_2	8.3	4.2	2.6	2.22	0.10	0.10	15.3	4.00	0.998
6	BuBr, χ, O_2	3.5	4.2	2.6	2.21	0.09	0.20	32.6	11.4	0.995
7	PrBr, χ, Ar	8.3	4.2	2.6	2.33	0.12	0.21	16.32	4.50	0.999
8	BuBr, χ, Ar	7.0	4.2	2.6	2.85	0.53	0.74	70.77	20.3	0.998

[a] For run nos. 1–4, D_0 (dimensionless). [b] For run nos. 1–4, D_1 (dimensionless). [c] O_2^- generated electrochemically, $c_0(O_2^-)$ 6×10^{-4} M.

[with $(Kcrown)^+$ counterion] to the other [with $(TEA)^+$ counterion], the activity of the radical anion toward alkyl halide slightly grows ($k = 1 \times 10^{-1}$ l mol^{-1} min^{-1}, run no. 4).

To evaluate the possible influence exerted on the overall reaction rate by the reaction product and by variation of the solution ionic strength (through participation in the corresponding equilibrium steps), we added KBr to the reaction mixture at the start of the reaction (Fig. 3). As seen from Fig. 3, the solution conductivity slightly increases [compared to the experiment with c_0(KBr) 0 M], but the kinetic relationships remain unchanged; hence, the forming products exert no effect.

Afanas'ev *et al.* [2] suggested for the reactions of O_2^- with RX the S_N2 mechanism. The rate of such transformations decreases in the following series of substituents R: benzyl, allyl > tertiary alkyl > secondary alkyl > primary alkyl; with respect to halogens X, the reactivity order is iodide > chloride > bromide [5]. In S_N2 reactions, methyl halides react by a factor of 20 faster than ethyl halides; in going to higher homologs, the variation of the reaction rate is less significant.

The increased selectivity of the reaction with O_2^- can be explained in terms of the *E*2 mechanism. In the presumed base-catalyzed elimination of hydrogen halide from RHlg, O_2^- will act as an electron pair donor, and the proton elimination will become preferable in a substrate in which the carbon atom adjacent to the reaction center bears a substituent, because of significant hyperconjugation effect.

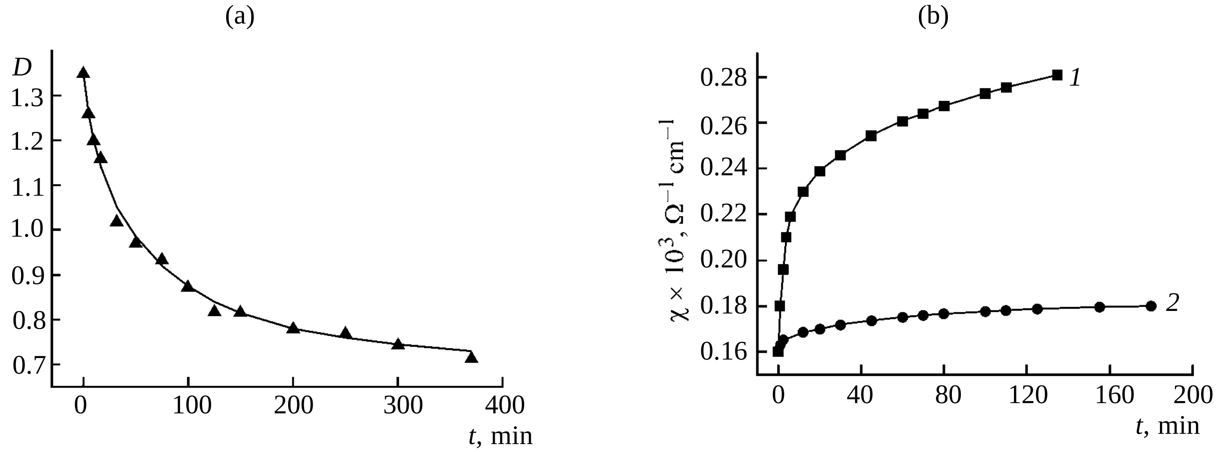
(a)
(b)

Fig. 2. Variation with time *t* of the (a) optical density *D* (λ 249 nm) [c_0(KO_2) 4.2×10^{-3}, c_0(crown) 2.6×10^{-3} M, R = Bu, c_0(BuBr) 7.5×10^{-2} M] and (b) electrical conductivity χ [R = Pr, c_0(PrBr) (*1*) 3.5×10^{-2} and (*2*) 8.3×10^{-2} M] of the solution in the course of the reaction of O_2^- with RBr in CH_3CN (25°C).

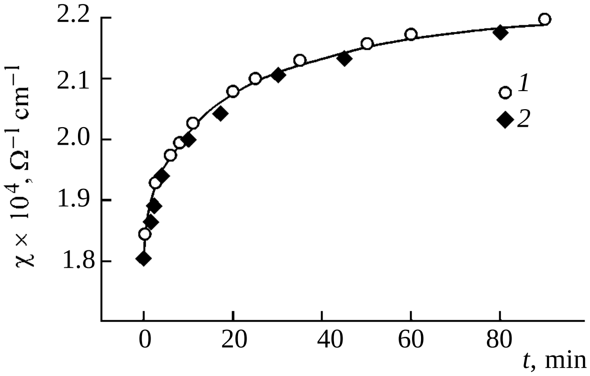

Fig. 3. Variation with time *t* of the specific electrical conductivity χ of the solution in the course of the reaction of O_2^- with RBr in CH_3CN. 25°C, c_0(PrBr) 8.3×10^{-2}, c_0(crown) 2.6×10^{-3} M. (*1*) $c_0(KO_2)$ 2.1×10^{-3} and c_0(KBr) 2.1×10^{-3} M; (*2*) $c_0(KO_2)$ 4.2×10^{-3} and c_0(KBr) 0 M.

EXPERIMENTAL

The solvents and reagents (PrBr, BuBr, 18-crown-6) were purified as described in [7]. KBr and KO_2 were of analytically pure grade. The procedure for the kinetic study of the reactions of the crown ether with KO_2 and of the resulting steady-state solution with alkyl halide (conductometry) was the same as in [6]. Conductometric measurements were performed with a Tesla BM-559 RLCG Most-Voltmetr device.

The resistance of each solution was measured in cells of constant volumes (0.23 and 0.31 cm^{-1}, working volume 5 ml). Similar experiments with optical density monitoring were performed in quartz cells (*l* 1 cm, V 4 ml) with ground-quartz stoppers of a Specord UV-Vis M-40 spectrophotometer. The reaction time was counted from the moment of adding the solvent or alkyl halide of appropriate concentration to the cell. In kinetic measurements with the alkyl halide, we used an equilibrium solution of KO_2 with crown ether in CH_3CN of the above-indicated volume, prepared in advance. The solution kept to attain the steady-state concentrations of the ions was diluted with the solvent to the required concentration. Also, in each case we measured the electrical conductivity (optical density) of the initial (steady-state) solution before adding alkyl halide. Such solutions preserve their properties for a week, as confirmed by measuring the electrical conductivity and optical density (λ_{max} 250–252 nm) of the steady-state solution. The presence of O_2^- was proved not only spectroscopically, but also by a qualitative reaction with Tetrazolium Blue [6]. Preliminary experiments performed with different stirring rates, similarly to [6], showed that the reaction is kinetically controlled.

The procedure for preparing solutions of O_2^- in CH_3CN by electrochemical reduction of oxygen was described in [2]. The electrochemical cell had a mercury cathode and a platinum anode. The supporting electrolyte was 0.1 M $(C_2H_5)_4NClO_4$ (prepared from tetraethylammonium bromide and $HClO_4$ [2]). After purging with Ar, solutions of O_2^- were transferred into a quartz cell and again purged with Ar. The concentration of the O_2^- solution thus prepared was determined spectrophotometrically and argentometrically (using an exchange reaction with butyl bromide [8]). To record the absorption spectra and study the reaction kinetics, the reference cell was filled with a solution of the supporting electrolyte in acetonitrile of the required concentration.

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