

SHORT
COMMUNICATIONS

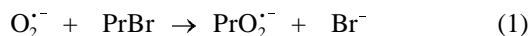
Kinetics of Reaction between Superoxide Anion and Propyl Bromide

I. A. Opeida, I. V. Efimova, and A. I. Pomeshchenko

Litvinenko Institute of Physical Organic and Coal Chemistry, Ukrainian Academy of Sciences, Donetsk, 83114, Ukraine

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Investigating complexation in a system salt (KX)–ether 18-crown-6 (cr) ($X = \text{OH}^-$, O_2^- , Br^- , Γ^-) in DMSO we established that the kinetics of equilibrium attainment was well described by equation of Erofeev–Avrami type that permitted calculation of the time required for coming to equilibrium in each case [1]. Investigations of similar systems were described with the use of other solvents [2–5]. The goal of this study was investigation of reaction kinetics of superoxide anion O_2^- arising at equilibrium in the system $\text{KO}_2 + \text{cr}$ with propyl bromide in DMSO.



The kinetics was measured by change in the electrical conductance of solution χ . The reaction was carried out at large excess of PrBr, i.e. under pseudofirst order conditions with respect to O_2^- .

Treating the data by the least-squares method for nonlinear functions revealed that the change in the conductance of solution whose value is proportional to O_2^- content [1] was described by first order kinetic equation with respect to this reagent:

$$\chi = \chi_\infty - \chi_0 \exp(-k_{\text{app}} t) \quad (2)$$

Besides the first order rate constant does not change at variation of superoxide anion concentration at constant concentration of propyl bromide. The parameters of equation (2) are given in table.

In propyl bromide concentration range from 0.1 to 0.9 mol l⁻¹ the reaction is also of first order in propyl bromide as shows equation

$$k_{\text{app}} = (0.113 \pm 0.004) [\text{PrBr}] + (21 \pm 2) 10^{-5} \quad (3)$$

r 0.994, s 0.004, n 5

These facts and taking into account the data of [1] on χ dependence on salt concentrations for Br^- and O_2^- permit a conclusion that KO_2 is completely converted into KBr, and the side reactions, e.g., peroxides formation, are excluded. The comparison of the slope of equation (3) with the known rate constant of the same reaction in acrylonitrile, $\approx 1.10^3$ l mol⁻¹ s⁻¹ [5], shows that the reactivity of O_2^- in DMSO is by several orders of magnitude greater.

The replacement of 18-crown-6 by dibenzo-24-crown-8 virtually does not affect the reactivity of O_2^- toward propyl bromide.

Reaction kinetics for propyl bromide and OH^- anion obtained by complexation of KOH with 18-crown-6 is also described by equation (2) whereas the reactivity of O_2^- is significantly higher than that of OH^- (see table).

Parameters of equation (2) for reaction of anions KX with PrBr in the presence of 18-crown-6, DMSO, 25°C, $[\text{PrBr}]_0$ 0.22 mol l⁻¹

$[\text{KX}]_0$, mmol l ⁻¹	$[\text{cr}]_0$, mmol l ⁻¹	$k_{\text{app}} \times 10^3$, s ⁻¹	$\chi_0 \times 10^4$, Ohm cm ⁻¹	χ_∞ , Ohm cm ⁻¹	r
7.0 ^{a,b}	9.0	5.6	2.74	1.86	0.986
7.0 ^a	9.8	2.6	2.94	1.88	0.990
10.0 ^a	17.0	2.9	5.50	3.21	0.990
6.1 ^a	7.3	2.0	6.35	2.90	0.999
10.0 ^{a,c}	13.0	3.2	0.28	9.60	0.999
6.6 ^d	7.0	0.7	1.32	0.26	0.999

^a Reactions with superoxide anion.

^b $[\text{PrBr}]_0 = 0.44$ mol l⁻¹.

^c In the presence of dibenzo-24-crown-8.

^d Reaction with hydroxide anion.

The electrical conductance was measured on Tesla BM559 RLCG Mostvoltmetr instrument. The cell by water flow from a thermostat. The salts KBr and KO_2 used in the study were of "pure for analysis" grade. Preparation of reagents and details of kinetic measurements were described in [1]. The resistance of each solution was measured in a cell with a constant of 0.31 cm^{-1} , operating volume 5 ml. The solution KX-cr was kept till establishment of stationary concentration of ions and then it was used for kinetic measurements: PrBr was added thereto. The moment of reagents mixing was taken as the time of the reaction start.

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