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INVESTIGATION OF THE REACTION OF Br_2^- AND Fe(II) USING LASER PULSED PHOTOLYSIS

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In aqueous solutions reactions of X_2^- (X = Cl, Br, I) with the metal ions Co^{2+} and Fe^{2+} occur according to an intrasphere mechanism and are limited by the process of replacement of water molecules in the first coordination sphere of the ion [1]. It is well known that for solvated complexes of these ions methanol molecules are exchanged with a rate one to two orders less [2, 3] than molecules of water in aqua-complexes [1, 4]. As a result the reaction of the ion with Br_2^- may become extra-sphere or not be limited by the exchange rate. In this paper to clarify realization of these possibilities the mechanism of reaction of Br_2^- with the Fe²⁺ ion in a mixture of methanol with diethyl ether is studied.

EXPERIMENTAL

In this work a laser pulsed photolysis setup with an XeCl excimer laser was used (308 nm). The resolving time (50 nsec) was determined by the system of digital signal recording (1024 channel, 8 discharge ATsP), connected to the "Elektronika D3-28 Kamak" complex.

To generate Br_2^- pulsed photolysis of solutions of the FeBr₄ complex, CBr₄ or the $Br_3^$ ion, which was obtained by adding to a solution of the Br⁻ ion molecular bromine, were used. All these particles have a rather intense absorption at 308 nm and are sources either of the bromine atom (CBr₄ and Br_3^-) or Br_2^- (FeBr₄ and Br_3^-). The Br atom in reaction with the Br⁻ ion also leads to formation of Br_2^- .

The Fe²⁺ solvated complex was obtained by stationary photolysis of solutions either of $\operatorname{Fe_{SOlv}_{3}}^{2+}$ [Fe₂(SO₄)₃ solution] with subsequent addition of LiBr, or of the FeBr₄ complex (FeBr₃). The fact that Fe²⁺ exists in solvated form in the presence of Br⁻ is seen in Fig. 1, from which it follows that stationary photolysis of FeBr₄ solution in a mixture of methanol with diethyl ether (1:1 by volume) leads to the appearance of the absorption band of free Br⁻ with preservation of the isobestic point. This shows that after photoreduction of the FeBr₄ complex four free Br⁻ ions are formed. Kinetic measurements were performed at the 365 nm wavelength, at the maximum of the Br₂⁻ absorption band. In the calculations a value of the extinction coefficient of this band equal to $8.5 \cdot 10^3 \text{ dm}^3/\text{mole} \cdot \text{cm}$ was used [5].

DISCUSSION

In water solutions for the disproportionation reaction

$$Br_2^{-\bullet} + Br_2^{-\bullet} \rightarrow Br_3^{-} + Br^{-}$$
(1)

the rate constant is close to the diffusional $(5 \cdot 10^9 \text{ dm}^3/\text{mole} \cdot \text{sec} \text{ at } 298 \text{ K } [6])$. Reaction (1) limits the possibilities of studying the reactions of Br_2^- with other particles, and therefore it is desirable to reduce its rate constant. With this goal we used a mixture of

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Fig. 1. Stationary photolysis of the FeBr₄ complex in MDE at 296 K: 1) initial spectrum; 2-4) irradiation for 5, 20, and 80 sec, respectively; 5) spectrum of solution of Br⁻ in MDE with $[Br⁻] = [FeBr₄]_0$.

methanol with diethyl ether having a reduced dielectric constant (ϵ 18.4 [7]), which reduces the rate constant of the reaction of the two identical charged particles [8]. In this solvent the Fe²⁺ ion is solvated by mechanol molecules.

On pulsed photolysis of CBr_4 and Br_3^- solutions the linear dependence of the effective rate constant on the initial Br_2^- concentration was tested; from these data the bimolecular rate constant of reaction (1) at different temperatures was determined (Fig. 2). At 298 K it is equal to $5.4 \cdot 10^8 \text{ dm}^3/\text{mole} \cdot \text{sec}$, which is smaller by an order than its values in water. The activation energy, 11 kJ/mole, is close to the values of the activation energies of diffusion in these solvents.

The value of the rate constant obtained agrees well with the value of the permittivity, charges, particle sizes and solvent viscosity. Reaction with the solvent plays a role at low Br_2^- concentrations, and its rate constant (k_2) coincides with the rate constant of the reaction Br_2^- with methanol $(k_2 = 4 \cdot 10^3 \text{ dm}^3/\text{mole} \cdot \text{sec [5]})$.

In the presence of Fe_{SOLV}^{2+} the effective rate constant of destruction of Br_2^{-1} in the initial region of the kinetic curve

$$k_{\text{eff}} = -(d \ [\text{Br}_2^{-*}]/dt)/[\text{Br}_2^{-*}]_0 = 2k_1 \ [\text{Br}_2^{-*}]_0 + k_2 \ [M] + k_3 \ [\text{Fe}_{\text{solv}}^{2+}]$$
(2)

linearly depends on the concentration of Fe_{solv}^{2+} (Fig. 3). The temperature dependence of k_3 (Fig. 2) was measured at $[Fe_{solv}^{2+}] = 1.3 \cdot 10^{-2} \text{ moles/dm}^3$, where the initial rate of reaction (1) is considerably less than the rate of the reaction of Br_2^- with Fe_{solv}^{2+} . At 298 K $k_3 = (5.9 \pm 0.5) \cdot 10^7 \text{ dm}^3/\text{mole·sec}$, and the activation energy comprises (28 ± 1) kJ/mole.

To clarify the mechanism of the reaction we investigated the composition of the initial products. In the case of extra-sphere electron transfer the $\operatorname{Fe}_{SO1V}^{3+}$ complex must arise, and in the case of intrasphere the FeBr^{2+} complex (or $\operatorname{FeBr}^{+}_{2}$). All these complexes have different optical spectra given in Fig. 4. There the spectrum arising at the moment of total disappearance of $\operatorname{Br}^{-}_{2}$ is also given. The extinction coefficient for the experimental points was calculated from the value of this quantity for $\operatorname{Br}^{-}_{2}$. The $\operatorname{Fe}_{SO1V}^{2+}$ concentration was 2.15·10⁻² mole/dm³, which excluded reaction (1). To generate $\operatorname{Br}^{-}_{2}$ a solution of CBr₄ with a small concentration of Br⁻ (1.5·10⁻³ moles/dm³) was used. The closeness of the spectrum obtained to the spectrum of FeBr^{2+} complex is the primary product, since processes of substitution in the coordination sphere of Fe^{3+} are several orders slower than for Fe^{2+} , and lie in the region 10⁻³⁻¹ sec [2]. We note that the rate constant in MDE is greater by a factor of 15-20 than in water solutions, despite the considerably lower rate of exchange of methanol molecules in the coordination sphere of doubly charged ions of metals of the iron group [2, 3] in comparison with the rate of exchange of water molecules [1, 4].

In the framework of a model with formation of a diffusion pair [8]

$$\operatorname{Br}_{2^{-+}} + \operatorname{Fe}^{2^{+}} \underset{k_{-+}}{\overset{k_{1}}{\longrightarrow}} (\operatorname{Br}_{2^{-+}} \dots \operatorname{Fe}^{2^{+}}) \xrightarrow{k_{p}} \operatorname{Fe}\operatorname{Br}^{2^{+}} + \operatorname{Br}^{-}$$
(3)



Fig. 2. Temperature dependence of the rate constant of reactions: 1) reaction (1) in MDE and water (A) [6]; 2) reaction of Br_2^- and Fe_{solv}^{2+} ; 3) reaction of Br_2^- and Fe_{solv}^{2+} ; 6]. Pulsed photolysis of solutions: a) Br_3^- ; b) CBr_4 ; c) $FeBr_4^-$.

Fig. 3. Dependence of the effective rate constant of destruction of Br_2^- on $[Fe_{SOlv}^{2+}]$ at 260 K (pulsed photolysis of FeBr₄ solution).

Fig. 4. Optical spectrum of complexes: 1) $\text{Fe}_{\text{SOlv}}^{3+}$; 2) FeBr^{2+} in water [9]; 3) FeBr^{2+} in MDE; 4) spectrum 30 µsec after laser pulse at the instant of total disappearance of Br_2^- on photolysis of CBr_4 (1.7·10⁻² mole/dm³) at 280 K, $[\text{Fe}_{\text{SOlv}}^{2+}]$ and [LiBr], 2.15·10⁻² and 1.5·10⁻³ mole/dm³, respectively.

the experimental value of the rate constant is equal to $k_{exp} = k_p K_{eq}$, where $K_{eq} = k_1/k_{-1}$. Taking into account the charges, particle radii and permittivity of the solvent $k_{eq} \approx 1.3$ and $\approx 460 \text{ dm}^3/\text{mole}$ for water and MDE, rspectively. Consequently, for water $k_{exp} \approx k_p$ and coincides with the exchange rate of H₂O molecules [1, 4]. For MDE $k_{exp} \approx 460 k_p$ and exceeds the exchange rate in value by almost three orders of magnitude. Thus, the reduced permittivity leads to an increase in the lifetime of the diffusion pair [Eq. (3)] and despite the reduced exchange rate, partners more effectively survive to the moment when space for Br₂⁻ is freed in the coordination sphere. From the data obtained it follows that for exchange of methanol molecules in the coordination sphere of Fe²⁺ in MDE solution at 298 K $k_{exch} \approx k_p \approx 1.2 \cdot 10^5 \text{ sec}^{-1}$, while the activation energy comprises 49 kJ/mole.

CONCLUSIONS

The reaction of Br_2^- with Fe_{solv}^{2+} in a mixture of methanol with diethyl ether occurs according to a intrasphere mechanism with the primary product being the FeBr²⁺ complex. The rate constant $(5.9 \pm 0.5) \cdot 10^7 \text{ dm}^3/\text{mole} \cdot \text{sec}$ at 298 K is greater by a factor of 15-20 than in the reaction of Br_2^- with Fe_{aq}^{2+} , despite the slower rate of exchange of the solvent molecules for Fe_{solv}^{2+} . In the latter case the reduced permittivity considerably increases the lifetime of partners in the contact pair state.

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