TUNNELING OF ELECTRON IN HS^- OXIDATION BY I_3^- COMPLEX IN AQUEOUS SOLUTION

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Recently a lot of papers on investigation of reactions proceeding through tunneling of electrons were published. Most of them relate to investigation of reactions at low temperature in glasses. There are several experiments at room temperature but the reactions in this experiments cannot be considered as "pure" chemical reactions. They are capture of solvated electrons by acceptors in non polar solvents [1].

The essential feature of our investigation is finding of the chemical reaction in which the large distances electron tunneling takes place at room temperature in solution. The contribution of the electron tunneling to reaction is so hogh that it permits an experimental observation of the features known for tunneling reactions as well as of peculiar features deschribed and explained in study for the first time.

We studied kinetics of hydrogen sulphide oxidation by iodine [2;3]. In our stop-flow experiments the reacting solution was obtained by mixing two jets, one of them containing H_2S solution and the other $I_2 + I^-$ solution. Both solutions contained also $HClO_4$ and $NaClO_4$ in order to maintain pH and ionic strength. Hydrogen sulphide exists in solution in protonated and deprotonated forms, and iodine gives a complex I_3^- with I^- ion. The ratio of species $[H_2S]/[HS^-]$ and of $[I_3^-]/[I_2]$ may be varied by varying pH and $[I^-]$.

In our experiments carried out at various starting concentrations of reactants and at various ratio of species given above, we showed that the reaction is bimolecular and that active forms are HS^- and I_3^- if $[I^-]$ is higher then 0.01 *M*.

Reaction proceeds through several stages, the first stage being

$$HS^- + I_3^- \rightarrow HSI + 2I^-$$

In this stage intermediate HSI is formed. The next stages are slow and at the experimental conditions do not contribute considerably to the observed kinetics of I_3^- decay. They are :$HSI + H_2S \rightarrow HSSH + HI$; $HSS^- + I_3^- \rightarrow HSSI + 2I^-$ and so on. The first stage is of the most interest. It's rate constants calculated formally are very high (up to $10^{14}\ M^{-1}s^{-1}$) this is several orders of magnitude higher than the rate constant of the diffusion controlled reaction. The next singularity is the dependence of the rate constant on $[\ I^-\ ]$ while I^- does not participate in the reaction. All this features cannot be explained in terms of classical reaction mechanisms.

We suggested the "flicker" model of the reaction [3]. According to this model the reaction begins when electron tunnels from HS^- to I_3^-.

Let us consider the I_3^- ion as the center of a reaction sphere of radius R_T, R_T being the largest distance at which tunneling takes place. In the volume of this sphere HS^- is generated in reaction (1). HS^- is decayed in reaction (2) and in the reaction opposite to reaction (1).

$$H_2S \underset{K-}{\overset{K+}{\rightleftarrows}} HS^- + H^+ \quad (1); \qquad HS^- + I_3^- \rightarrow HS + I_3^{2-} \quad (2)$$

HS^- may also be transported into the reaction sphere by diffusion from the surrounding medium. Taking into account these processes we have drawn out the equation for reaction rate constant.

$$k_{HS^-} = 4\pi(D_{HS^-} + D_{I_3^-}) \cdot R_T \cdot N_A + \frac{4\pi R_T^3 N_A K_-[\ H^+\ ]}{3(1 + K_-[\ H_+\ ]/P_T)}$$

Here D_{HS^-}, $D_{I_3^-}$ - diffusion coefficients, N_A - Avogadro number, P_T - probability of electron tunneling in a unity of time. The dependence of k_{HS^-} on $[\ H^+\ ]$ given by this equation is in agreement with the experimental data in figure.

Values of R_T calculated from this data are given in table.

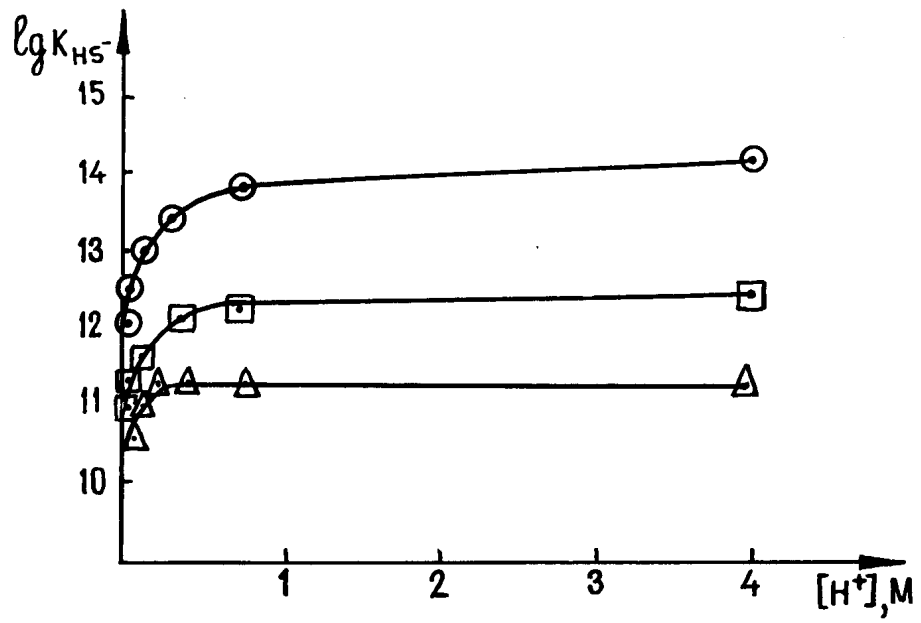

Fig. o - $[\ I^-\ ] = 0.01\ M$; - $[\ I^-\ ] = 0.1\ M$; - $[I^-] = 0.3M$

Table

Tunneling radii of electron at various [I^-]

[I^-],*M*	[H_2S],*M*	K_1, s^{-1}	R_T, Å	k_D, $M^{-1}s^{-1}$	R_T^D, Å
0.01	$8 \cdot 10^{-5}$	500	69	-	-
0.1	$6.8 \cdot 10^{-5}$	70	38	$1.5 \cdot 10^{10}$	9
0.3	$7 \cdot 10^{-5}$	20	25	$1.0 \cdot 10^{10}$	6
1.0	—	—	—	$6.0 \cdot 10^{9}$	3.6

In high pH region the rate constant is determined by diffusion into the reaction spheres. And in low pH region the rate constant is determined by generation of HS^- in the volume of the reaction spheres through reaction (1). In this "super diffusion" region the reaction rate exceeds the diffusion rate. The existence of diffusion and "super diffusion" regions was confirmed in our experimental series carried out at different solution viscosities. Our experiments also showed ionic strength of the solution to affect the rate constant only in "super diffusion" region. This is well explained as an influence of the ionic strength on diffusion of a negatively charged HS^- to negatively charged I_3^- , while generation of HS^- in the volume of reaction sphere is unaffected by the ionic strength. The effectiveness of tunneling decreases as the potential barrier increases. That is why the most effective is a short period of time just when the H_2S deprotonation occured and reorganization of surrounding medium is not completed. The reorganization of media in the neighborhood of HS^- increases potential barrier by the magnitude of ion hydration energy. This process becomes more rapid at higher solution temperature. This explains the temperature dependence of reaction rate constant. Another reason of rapid energy relaxation of formed HS^- is the influence of highly polarizable molecules.

Thus the effluence of I^- ions can be explaned. This assumption is confirmed by addition of other highly polarizable molecules such as maleic acid which shows the same effect on the reaction rate as addition of I^- does.

Our experiments with thioles instead of H_2S gave k_{RS^-} value close to the value of diffusion controlled reaction. E_A value $\approx$ 0. According to this electron tunneling occurs at short distances in the case of thioles.

REFERENCES

1. Goldanskii V.M., Trakhtenberg L.I., Flerov V.N. Tunneling Phenomena in Chemical Physics (Russian). Moskow. Nauka. 1986.

2. Gulin A.P., Klopov N.V., Patsekin V.P., Soroka N.V., Ufimtsev A.V. Preprint LNPI-1199. Leningrad. 1986. 14 p.

3. Ufimtsev A.V., Soroka N.V., Bagiyan G.A. //Izv. Akad. Nauk SSSR. Ser. Khim. 1992. N 3.