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Kinetic Studies of the Electron Transfer Reaction in Iron(II) and Iron(III) Systems. VII. The Electron Transfer Reaction in Solid Dimethyl Sulfoxide[1)]

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Synopsis. The electron transfer reaction between Fe(II) and Fe(III) in dimethyl sulfoxide (DMSO) was investigated in the solid phase, and compared with the case in the liquid. In the temperature range between the freezing point (T_M) and the eutectic point (T_E), the reaction actually proceeds in the liquid phase where the reactants are concentrated due to the partial separation of pure DMSO solid, while below T_E the reaction occurs in the solid phase at considerable reaction rates, with a lower activation energy, 4 kcal/mol, than that in the liquid. This indicates a different probable mechanism in solid DMSO.

It has been proved that the electron transfer reaction between iron(II) and iron(III), Fe(II)+*Fe(III)=Fe(III)+*Fe(II), in aqueous media in the absence of catalytic ligand proceeds *via* a hydrogen atom transfer mechanism through a Grotthuss type conduction along the extended chains of the hydrogen bonds between the oriented solvent molecules.[2—4)] As one proof of this mechanism, the occurrence of the reaction in solids of protic solvents was observed in the cases of ice[5—7)] and of very concentrated perchloric acid,[8)] although the reactants are frozen with no freedom of translational mass transfer in the solids of such media.

Dimethyl sulfoxide (DMSO) is typical of the aprotic solvents for which the hydrogen atom transfer mechanism is difficult. In fact, the reaction was shown to proceed not *via* the hydrogen atom transfer but rather *via* an inner-sphere mechanism in liquid DMSO.[9—11)] Consequently, it seems to be of interest to test whether the reaction can proceed in solid DMSO or not.

Experimental

The procedure of determination of the rate constant was similar to that already described,[9—11)] except for several points indicated below. Soon after the initiation of the reaction by mixing the two solutions of iron(II) and ^{59}Fe-labeled iron(III), equal amounts of the reaction solution were quickly delivered into eight glass tubes of the same shape and size in a thermostat at 20 °C, followed by simultaneous cooling to −78 °C. The solutions were solidified within several seconds at this temperature. Then the tubes were set in a bath at a fixed reaction temperature. The reaction temperatures adopted were −28, −48, −68, and −78 °C, which were attained by freezing mixtures of dry-ice with carbon tetrachloride, chloroform, or ethanol, according to the temperature adopted. At appropriate time intervals, one of the tubes was taken out of the bath and the quenching solution was quickly added. It took only about twenty seconds to complete dissolving the solid and quenching the reaction by using a vibrator. The concentration of perchloric acid was always 0.005 M.

For the sake of simplicity, the phase diagram of the binary system $Fe(ClO_4)_3$+DMSO was studied in the very low concentration range of $Fe(ClO_4)_3$.

Results and Discussion

As have been seen in the liquid system, McKay's plots of $\log(x_e - x)$ against time in the solid phase were also linear: here x and x_e stand for the specific radioactivities of iron(II) at reaction time t and at infinite time, respectively.[12)] Thus, the rate constant k of the electron transfer reaction can be obtained from the half period of the reaction $t_{1/2}$.

$$k = \frac{0.693}{([\mathrm{Fe(II)}]+[\mathrm{Fe(III)}])t_{1/2}} \qquad (1)$$

The Arrhenius plot of log k against reciprocal temperature is drawn in Fig. 1. The activation energy in the liquid phase is E_{liq}=9.2 kcal/mol, which is in agreement with the values in the literature.[9,11)] On the other hand, the activation energy obtained from the temperature range of the solid state appears to be approximately E_{solid}=4 kcal/mol, which is much smaller than E_{liq}.

The phase diagram of the $Fe(ClO_4)_3$–DMSO binary system in the low concentration range of $Fe(ClO_4)_3$ is shown in Fig. 2. When a liquid DMSO solution of $Fe(ClO_4)_3$ at low concentration is continuously cooled, it reaches its freezing point, T_M, below which an equilibrium between pure solid DMSO and concentrated liquid solution is established. As the cooling goes on, the liquid phase becomes more concentrated with $Fe(ClO_4)_3$ due to the progressive separation of solid DMSO, until the system arrives at the eutectic temperature, T_E, approximately −45±3 °C, where the concentrated solution itself freezes as a solid solution.

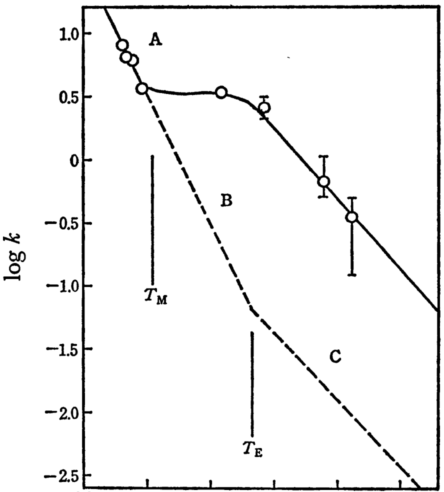

Fig. 1. Arrhenius plot for liquid and solid phase reaction.

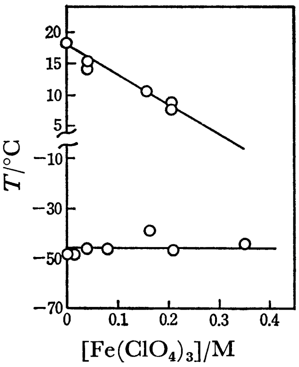

Fig. 2. Phase diagram of $Fe(ClO_4)_3$-DMSO binary system.

In the present reaction system, the phase diagram must be more complicated than this, but the fundamental tendency appearing in this simple system would be similarly valid: the concentration phenomenon of the dissolved species in the liquid phase and the eutectic freezing of the concentrated liquid would also occur.

At temperatures between T_M and T_E, the reaction system is a heterogeneous mixture of liquid solution and solid DMSO, and the reaction takes place only in the liquid phase, where the reactants are concentrated according to the reaction temperature. This results in an apparent increase in k, because the true [Fe(II)] and [Fe(III)] in the concentrated liquid phase must be larger than those used in Eq. (1). When the apparent and the true rate constants are denoted by k and k_0 respectively, k is apparently enlarged by a factor of p.

$$k = p\, k_0 \tag{2}$$

The lower the temperature, the larger the p value. In Fig. 1, the straight line above T_M (A) is extrapolated into the T_M-T_E range, where the liquid phase reaction still continues to occur with an unchanged activation energy E_{liq}. Consequently, this extended straight line (B) gives the corrected true rate constant k_0 at the respective temperatures.

At temperatures below T_E, the reaction occurs truely in the solid phase, where p no longer varies with temperature but is a constant. Thus, another straight line (C) can be drawn in parallel with the observed one with an equal slope corresponding to E_{solid}, as is done by the broken line in Fig. 1. From the vertical shift of the straight line C from the apparent one, the p value below T_E could be roughly estimated as $p=40$.

Since the glass tubes containing the reaction solution were cooled far below the eutectic point as quickly as possible, the geometric sizes of the crystalline particles of both pure DMSO and solid solution might be very small, and it is likely that there remains some local heterogeneity of concentration of the reactants and that heterogeneous catalysis on the mosaic interfaces between the solid particles may affect the reaction rate. However, if the probabilities of these heterogeneous effects are small and the reaction is simply supposed to occur homogeneously in the solid phase, the averaged distance between iron(II) and iron(III) is calculated to be about 50 Å in our present case. Since in the solid phase the medium is too viscous for the reactants to diffuse so that the electron transfer reaction may proceed not through the migration of the reactants carrying electrons but through the tunnelling of electrons for long distances over several medium molecules. The extension of wave functions of the electrons is suitable for such a transfer.[13] In such a case, the low activation energy observed as E_{solid} to be 4 kcal/mol would seem to be reasonable.

In the case of aqueous media, the reaction mechanism is the same indifferent to whether in the liquid or in ice: *via* the hydrogen atom transfer along the bridges of the hydrogen bonds between water molecules. Therefore, the activation energy is also the same for both phases.[5,6] On the other hand, in the case of DMSO, the reaction mechanism must differ in going from liquid to solid, with a consequent variation in the activation energies.

According to our present study, the true rate constant of the reaction in solid DMSO at −78 °C is approximately of the order of $10^{-2}\,M^{-1}\,s^{-1}$, which roughly coincides with $7\times10^{-3}\,M^{-1}\,s^{-1}$ in a liquid mixed solvent of water : DMSO=3 : 2,[14] although the reaction mechanisms might be completely different from each other. At any rate, looking at the cases of aqueous, aqueous-DMSO, and pure DMSO media together, one problem yet remains unsolved: whether electrons can be transferred not only *via* the hydrogen atom transfer mechanism but also *via* an alternative mechanism, probably *via* electron tunneling over a considerably long distance.

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