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Kinetic Studies of the Electron Transfer Reaction in Iron(II) and Iron(III) Systems. VIII. The Effect of Hexamethylphosphoric Triamide on the Electron Transfer Reaction in Aqueous Solution

Goro WADA,* Sayuri NAKAGO, and Yuriko ABE

Department of Chemistry, Nara Women's University, Nara 630

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The kinetics and mechanism of the electron transfer reaction between Fe(II) and Fe(III) in mixed solvents of water and hexamethylphosphoric triamide (HMPA) were studied. The apparent rate constant k varies depending upon [HMPA] and $[H^+]$; k exhibits a minimum value at [HMPA]$=1.5$ M at constant $[H^+]$ and increases linearly with respect to $[H^+]^{-1}$ at constant [HMPA]. Judging from the basicity constant of HMPA, the complex formation constant of $Fe(hmpa)^{3+}$, and the absorption spectra of aqueous solutions containing Fe(II), Fe(III), HMPA, and $HClO_4$, the existing species in the reaction systems are mostly $Fe^{2+}{}_{aq}$, $Fe^{3+}{}_{aq}$, $Fe(OH)^{2+}$, $Fe(hmpa)^{3+}$, and $Fe(hmpa)(OH)^{2+}$ at low concentrations of HMPA. Therefore, the probable reaction paths are Fe^{2+}–Fe^{3+}, (k_0); Fe^{2+}–$Fe(OH)^{2+}$, (k_H); Fe^{2+}–$Fe(hmpa)^{3+}$, (k_L); and Fe^{2+}–$Fe(hmpa)(OH)^{2+}$, (k_{HL}) at the concentration range of [HMPA]$=0$—1 M and $[HClO_4]=0.03$—0.2 M. The occurrence of a minimum value of k *vs.* [HMPA] is reasonably understood by taking the complex formation between Fe(III) and HMPA into account in reaction rate equation. If the hydrolysis constants of both $Fe(OH)^{2+}$ and $Fe(hmpa)(OH)^{2+}$ are considered to be nearly of the same order, the value of k_H are approximately ten times larger than that of k_{HL}. At higher concentrations of HMPA, the higher Fe(III)-complexes with HMPA might take part in the electron transfer reaction.

The electron transfer reaction between iron(II) and iron(III) in aqueous media, Fe(II)+*Fe(III)→Fe(III)+*Fe(II), has been studied since the radioactive tracer method by use of ^{59}Fe was first established by Silvermann and Dodson,[1] and it is now well-known that, in case that no catalytic ligand exists, the reaction in aqueous media proceeds predominantly through a hydrogen atom transfer mechanism along the extended chains of the hydrogen bonds between a certain number of water molecules connecting the two reacting species.[2,3] Therefore, in aqueous solvents mixed with aprotic organic substances, such as acetone,[4] nitromethane,[5] and dimethyl sulfoxide,[6] the rate of the electron transfer reaction *via* the hydrogen atom transfer mechanism is made smaller than that in pure water, because of the partial breakdown of the hydrogen bondings by such aprotic molecules.

In this investigation, hexamethylphosphoric triamide (abbreviated HMPA) is adopted as another aprotic substance, since HMPA has come into notice on account of a recent finding that the life time of solvated electrons in this medium is surprisingly long, as compared with those of hydrated electrons or other usual solvated ones.[7] In this connection, it looks to be very interesting to study how the effect of HMPA appears on the electron transfer reaction mechanism of iron(II) and iron(III) system.

Experimental

Materials. The commercially obtained HMPA of guaranteed reagent grade was refined as follows: after it was refluxed over barium oxide at 85—90 °C under a reduced pressure of nitrogen of 5 mmHg for 2 h and the first portion of the distillate was taken out, the rest of the liquid was distilled with iron(II) chloride at 80 °C under reduced pressure of nitrogen, and then the middle portion of the distillate was collected and immediately used for the experiments. Since HMPA had a slight tendency to form a kind of peroxide with time which would perturb our present experiments, iron(II) chloride was adopted for reducing it under nitrogen atmosphere.

The purification of other materials such as $Fe(ClO_4)_2$, $Fe(ClO_4)_3$, $NaClO_4$, and water and the preparation of iron(III) tracer labeled by radioisotope ^{59}Fe were already described elsewhere.[8,9] $NaClO_4$ was used for maintaining the ionic strength of the reaction media at $\mu=0.2$ M.

Procedure of Measurements. For the purpose of determining the basicity constant of HMPA in water, the spectrophotometric indicator method was adopted, using thymol blue as an indicator and a Hitachi-Perkin-Elmer UV-VIS spectrophotometer Model 139 for the observation. The detailed procedure is shown in the literature.[10]

For the determination of formation constant of $Fe(hmpa)^{3+}$, Job's continuous variation method was applied using the same spectrophotometer.[11]

The method to determine the rate constants of the electron transfer reaction was also the same as that described in the literature,[8,9] except that the concentration of iron(III) in the reaction solution was initially kept much lower than those in the cases in other media, because a small amount of iron(II) was inevitably oxidized to iron(III) by the peroxide in HMPA which happened to be formed even during the careful experimental procedure.

Results and Discussion

Basicity Constant of HMPA. Prior to the kinetic observations, the basicity constant of HMPA in water was needed to be known in order to make clear in what form HMPA exists in acidic media. The basicity constant of HMPA is defined as $K_a=[HMPA][H^+]/[HMPA\cdot H^+]$. Hence, the optical absorbance of a solution containing thymol blue and $HClO_4$ at a certain wavelength, A, is expressed as follows:[10]

$$A=\frac{\varepsilon_a[H^+]+\varepsilon_b K_{HIn}}{[H^+]+K_{HIn}}[HIn]_0 \tag{1}$$

where ε_a and ε_b stand for the molar absorptivities of thymol blue (HIn) in acid and base forms respectively, $[HIn]_0$ the total concentration of thymol blue, and K_{HIn} the dissociation constant of thymol blue as $K_{HIn}=[H^+][In^-]/[HIn]$. When HMPA is added at the total concentration $[HMPA]_0$ to the initial solution of thymol blue and $HClO_4$, the hydrogen ion concentration and the absorbance would alter as much as $\Delta[H^+]$ and ΔA respectively, in a relation expressed by the following equation.

$$\Delta A = \frac{(\varepsilon_a-\varepsilon_b)K_{HIn}\Delta[H^+]}{([H^+]+\Delta[H^+]+K_{HIn})([H^+]+K_{HIn})}[HIn]_0 \qquad (2)$$

Since $\Delta[H^+]$ is equal to $[HMPA.H^+]$, K_a can be calculated by using $\Delta[H^+]$ which is obtained from Eq. 2.[10]

$$K_a = \frac{([HMPA]_0-\Delta[H^+])([HClO_4]_0-\Delta[H^+])}{\Delta[H^+]} \qquad (3)$$

Thus, the value of K_a was given $K_a=0.71\pm0.16$ M as the mean value of thirty-one observations at $[HMPA]_0=0.23$—1.15 M, $[HClO_4]_0=0.01$—0.02 M and 25 °C at wavelengths 420, 440, 520, and 540 nm, where HMPA exhibits no absorption.[12] This value corresponds to $pK_a=0.15$, indicating that HMPA is a very weak base although it is a little more basic than *N,N*-dimethylformamide, $pK_a(DMF)=-0.19$[13] and dimethyl sulfoxide, $pK_a(DMSO)=-0.67$.[10] According to the Gutmann's donor numbers, D_{SbCl_5}, the sequence of the basic nature as Lewis bases agrees with the present results, HMPA>DMF>DMSO.[14]

Formation Constant of Fe(hmpa)$^{3+}$. In aqueous solution of iron(III) perchlorate, optical absorbance increases at the shorter wavelengths than 450 nm with decreasing concentration of perchloric acid from 1.0 M to 0.01 M due to the partial hydrolysis of Fe^{3+}_{aq} with the hydrolysis constant $K_H=[Fe(OH)^{2+}][H^+]/[Fe^{3+}]=2.2\times10^{-3}$ M at 25 °C.[15] In order to determine the formation constant of $Fe(hmpa)^{3+}$ defined as $K_L=[Fe(hmpa)^{3+}]/[Fe^{3+}][HMPA]$, it is desirable that the acid concentration is chosen to be high enough to be able to avoid the partial hydrolysis of Fe^{3+}, although too high acid concentration would give rise to the protonation of HMPA due to $K_a=0.71$ M, as described above.

Thus, the formation constant K_L was determined under a carefully considered condition of $[HClO_4]_0=1.0$ M by Job's continuous variation method.[11] In Fig. 1, are drawn two Job's curves of $[Fe^{3+}]_0+[HMPA]_0=0.1$ and 0.08 M at 350 nm, where Y is defined by the following relation, in which ε_0 and ε_1 are the molar absorptivities of Fe^{3+} and $Fe(hmpa)^{3+}$ respectively.

$$\begin{aligned} Y &= \varepsilon_0[Fe^{3+}] + \varepsilon_1[Fe(hmpa)^{3+}] - \varepsilon_0[Fe^{3+}]_0 \\ &= (\varepsilon_1-\varepsilon_0)[Fe(hmpa)^{3+}] \qquad (4) \end{aligned}$$

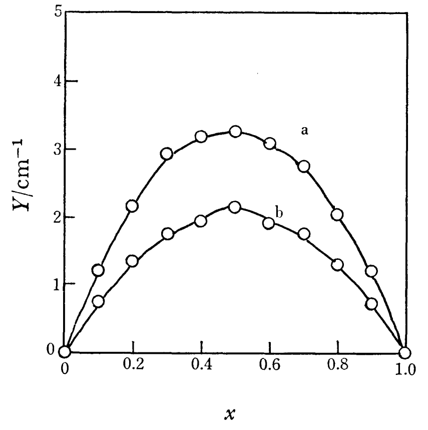

Fig. 1. Job's plot of continuous variation at 350 nm. $Y=(\varepsilon_1-\varepsilon_0)[Fe(hmpa)^{3+}]$ and $x=[Fe^{3+}]_0/([Fe^{3+}]_0+[HMPA]_0)$.
a: $[Fe^{3+}]_0+[HMPA]_0=0.1$ M, b: $[Fe^{3+}]_0+[HMPA]_0=0.08$ M.

The curves exhibit maxima both at $x=[Fe^{3+}]_0/([Fe^{3+}]_0+[HMPA]_0)=0.5$ indicating that the predominant species is a 1 : 1 complex between Fe^{3+} and HMPA at these concentration ranges, and give $K_L=1.46\pm0.22$ M^{-1} as a result.[11]

At higher concentrations of HMPA than 0.1 M, higher complexes such as $Fe(hmpa)_n{}^{3+}$ ($n\geqq2$) might be formed.

Effect of Concentration of HMPA on Rates of the Electron Transfer Reaction. The process of the electron transfer reaction between iron(II) and iron(III) obeys the following McKay's relationship, as has been commonly recognized in any exchange reactions;

$$\ln\left(1-\frac{x}{x_\infty}\right) = -([Fe(II)]+[Fe(III)])kt \qquad (5)$$

in which x and x_∞ represent the specific radioactivity of Fe(II) species at reaction time t and at equilibrium, respectively. Therefore, the apparent second-order rate constant, k, is expressed by use of half-time period of the reaction, $t_{1/2}$, which is obtained from the linear plot of $\ln(x_\infty-x)$ *vs.* t.

$$k = \frac{0.693}{([Fe(II)]+[Fe(III)])t_{1/2}} \qquad (6)$$

When $[H^+]$ is maintained constant, k is affected by addition of HMPA; at a low concentration range of HMPA, k is lowered by HMPA and after passing the minimum point at about $[HMPA]_0=1.5$ M, k increases with increasing $[HMPA]_0$. The variation of k with $[HMPA]_0$ are shown in Fig. 2. Similar

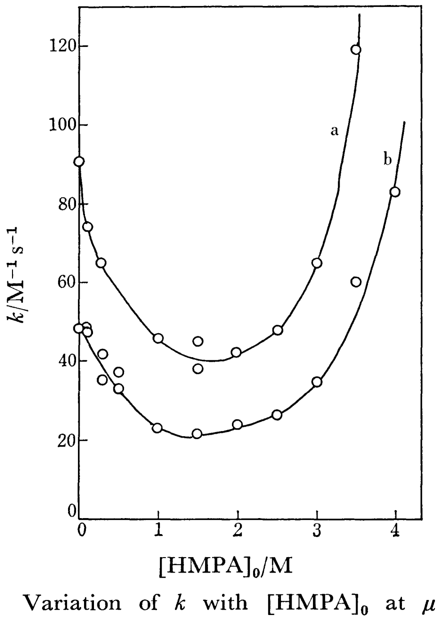

Fig. 2. Variation of k with $[HMPA]_0$ at $\mu=0.2$ M and 25 °C.
a: $[HClO_4]_0=0.05$ M, b: $[HClO_4]_0=0.1$ M.

phenomena have been recognized in water–DMSO systems, with the minimum value of k appearing at the mole fraction of DMSO 0.2—0.3 ([DMSO] =6.5—8.0 M) when $[HClO_4]=5\times10^{-2}$ M,[8] and in water–DMF systems, with the minimum value of k appearing at $[H_2O]=2$ M (namely [DMF]=12.5 M) when $[HClO_4]=1\times10^{-2}$ M.[16]

Dependence of Rate Constants upon Acid Concentration. The apparent rate constant k is also dependent upon $[H^+]$ at constant [HMPA], becoming smaller as $[H^+]$ becomes larger. When k is plotted against the reciprocal $[H^+]$, straight lines are obtained at respectively constant concentration of HMPA, as is reproduced in Fig. 3, at the concentration range of $[HMPA]_0=0$—3 M and $[H^+]=0.03$—0.2 M. Therefore, k is apparently expressed by the following equation at constant [HMPA];

$$k = k_A + \frac{k_B}{[H^+]} \tag{7}$$

where k_A and k_B are the intercept and the slope of an empirically observed straight line respectively in Fig. 3; k_A's are very small at every $[HMPA]_0$, while k_B varies with $[HMPA]_0$ and exhibits a minimum again at $[HMPA]_0=1.5$ M, as is shown in Fig. 4.

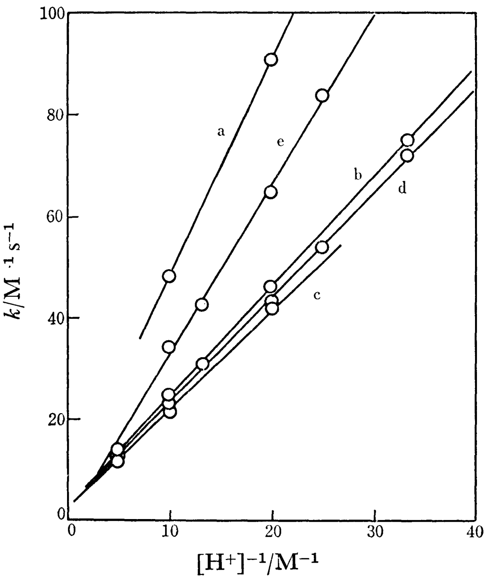

Fig. 3. Linear relationships of k with $[H^+]^{-1}$ at μ= 0.2 M and 25 °C.
a:$[HMPA]_0=0$ M, b: $[HMPA]_0=1.0$ M, c: $[HMPA]_0=1.5$ M, d: $[HMPA]_0=2.0$ M, e: $[HMPA]_0=3.0$ M.

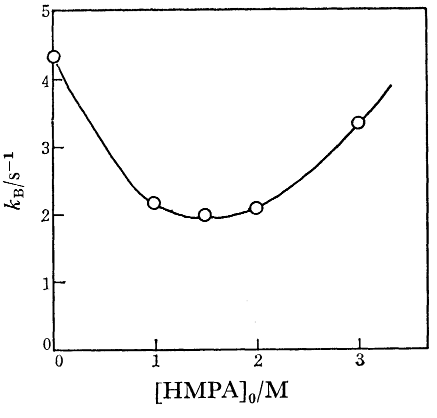

Fig. 4. Variation of k_B with $[HMPA]_0$ at μ=0.2 M and 25 °C.

Mechanism. According to the absorption spectra of aqueous solutions containing Fe^{3+}, HMPA, and $HClO_4$ at various concentrations at a wavelength range of 270—500 nm, the following results are observed : in the ultraviolet region, the absorbance increases with increasing [HMPA] and decreasing $[HClO_4]$, whereas in the visible region, it increases with increasing both [HMPA] and $[HClO_4]$, and approximate isosbestic phenomena occur in the vicinity of 340—350 nm among spectra of different $[HClO_4]$ at individually constant [HMPA]. These observed facts are caused by the hydrolysis of iron(III) species and the complex formation between iron(III) and HMPA. Consequently, it can be deduced that in the mixed solvents of water and HMPA, predominant part of iron(III) exists in the forms such as Fe^{3+}, $Fe(OH)^{2+}$, $Fe(hmpa)^{3+}$, and $Fe(OH)(hmpa)^{2+}$, and the rest part is in the forms of some higher complexes of HMPA. Since the pK_a value of HMPA is comparatively small, the occurrence of the protonated species of $Fe(hmpa)^{3+}$ is not probable. In regard to iron(II) species, both the hydrolysis and the complex formation with HMPA would be weak.

Thence, the important reaction paths of the electron transfer would be expressed by the following equations, having the activated complexes composed of [Fe^{2+}, Fe^{3+}], [Fe^{2+}, OH^-, Fe^{3+}], [Fe^{2+}, HMPA, Fe^{3+}], and [Fe^{2+}, OH^-, HMPA, Fe^{3+}] respectively. The asterisked Fe in the equations stands for the labeled species by tracer radioisotope:

$$Fe^{2+} + {}^*Fe^{3+} \rightarrow Fe^{3+} + {}^*Fe^{2+} \qquad (k_0) \tag{8}$$

$$Fe^{2+} + {}^*Fe(OH)^{2+} \rightarrow Fe(OH)^{2+} + {}^*Fe^{2+} \qquad (k_H) \tag{9}$$

$$Fe^{2+} + {}^*Fe(hmpa)^{3+} \rightarrow Fe(hmpa)^{3+} + {}^*Fe^{2+} \qquad (k_L) \tag{10}$$

$$Fe^{2+} + {}^*Fe(OH)(hmpa)^{2+} \rightarrow Fe(OH)(hmpa)^{2+} + {}^*Fe^{2+} \qquad (k_{HL}) \tag{11}$$

When the respective rate constants of Reactions 8—11 are denoted by k_0, k_H, k_L, and k_{HL}, the formation constant of $Fe(hmpa)^{3+}$ by K_L, and the hydrolysis constants of $Fe(OH)^{2+}$ and $Fe(OH)(hmpa)^{2+}$ by K_H and K_{HL} respectively, the apparent rate constant k is given by the following equation.

$$k = \frac{k_0 + k_H K_H [H^+]^{-1} + k_L K_L [HMPA] + k_{HL} K_L K_{HL} [HMPA][H^+]^{-1}}{1 + K_H [H^+]^{-1} + K_L [HMPA] + K_L K_{HL} [HMPA][H^+]^{-1}} \tag{12}$$

Since HMPA is slightly basic in aqueous solutions, the concentration of free HMPA, [HMPA], appearing in Eq. 12, has to be strictly expressed by the following equation.

$$[HMPA] = \frac{[HMPA]_0}{1 + K_a^{-1}[H^+] + K_L[Fe^{3+}] + K_L K_{HL}[Fe^{3+}][H^+]^{-1}} \tag{13}$$

By using the values $K_a=0.71$ and $K_L=1.46$ and supposing that K_{HL} would be approximately as small as 10^{-3} of the same order as K_H, the value of the denominator of Eq. 13 can be regarded as unity at low but not extremely low acid concentrations, and therefore, $[\text{HMPA}]_0$ may be plausibly used in place of [HMPA] in Eq. 12.

On the other hand, among the three terms in the denominator of Eq. 12, only K_L[HMPA] is no longer negligible as compared with unity, according to the numerical consideration. Therefore, Eq. 12 can be simplified as follows:

$$k(1+K_L[\text{HMPA}]) = (k_0+k_LK_L[\text{HMPA}]) + (k_HK_H+k_{HL}K_LK_{HL}[\text{HMPA}])[\text{H}^+]^{-1} \tag{14}$$

Comparing Eq. 14 with Eq. 7, more accurate straight lines will be obtained when $k(1+K_L[\text{HMPA}])$, instead of the mere k, is plotted against $[\text{H}^+]^{-1}$, as are shown in Fig. 5, with the intercept k_A' and the slope k_B' of respective straight lines.

$$k_A' = k_0 + k_LK_L[\text{HMPA}] \tag{15}$$

$$k_B' = k_HK_H + k_{HL}K_LK_{HL}[\text{HMPA}] \tag{16}$$

The values of k_A' as obtained from the extrapolation of the straight lines are small and inaccurate to determine the value, while k_B' is accurately determined and found to increase with the increasing [HMPA], although it is not linear against the expectation from Eq. 16. The variation of k_B' with the function of [HMPA] is shown in Fig. 6, where any minimum phenomenon is no longer observed, which has been observed in the case of plotting k_B *vs.* [HMPA] in Fig. 4.

In both cases of mixed solvents of water–*N*-methylacetamide (NMA) and water–*N*,*N*-dimethylacetamide (DMA),[17] the linear relationship corresponding to Eq. 14 with the same physical meanings of k_A' and k_B' as the present case, was found to hold, and another linear relationship of k_B' with [NMA] or [DMA] as represented by Eq. 16 was also noticed, giving reasonable values of k_HK_H and $k_{HL}K_LK_{HL}$.

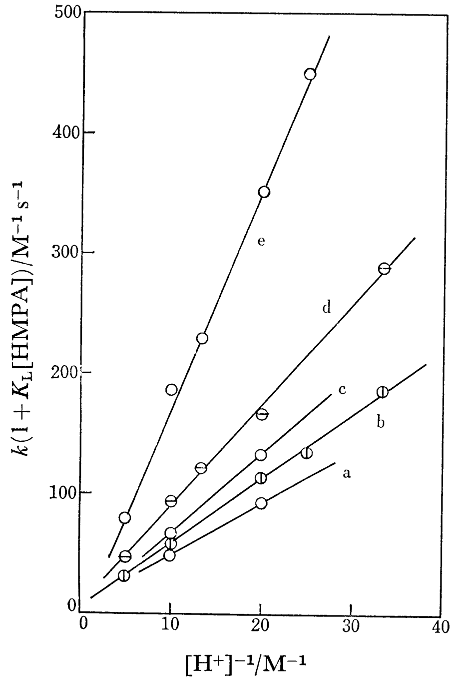

Fig. 5. Linear relationships of $k(1+K_L[\text{HMPA}])$ with $[\text{H}^+]^{-1}$ at $\mu=0.2$ M and 25 °C.
a, b, c, d, and e: Respectively the same as in Fig. 3.

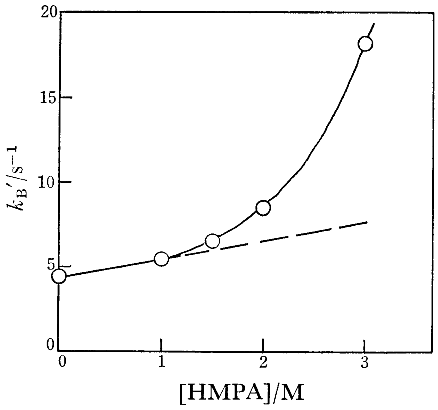

Fig. 6. Variation of k_B' with [HMPA] at $\mu=0.2$ M and 25 °C.

Both of the observed facts that k exhibits a minimum value as a function of $[\text{HMPA}]_0$ as in Fig. 2 and that k_B also shows a minimum at the same $[\text{HMPA}]_0$ as in Fig. 4 may result from a same cause and reflect on the failure of k_B' from the linearity with respect to [HMPA] as in Fig. 6.

The abrupt increment of k_B' failing from the linearity in Fig. 6 may indicate a probability that the higher complexes of $\text{Fe(hmpa)}_n{}^{3+}$ ($n \geqq 2$) participate in the total reaction at higher HMPA concentration. From the limiting slope of the curve at [HMPA]→0, the value of $k_{HL}K_LK_{HL}$ may be given to be $1.2\ \text{M}^{-1}\text{s}^{-1}$, which may lead to a further estimation of $k_{HL}=3.7\times10^2\ \text{M}^{-1}\ \text{s}^{-1}$. Since $k_H=2.7\times10^3\text{M}^{-1}\text{s}^{-1}$ at 25 °C,[15] the reaction path (11) is supposed to be about ten times slower than the reaction path (9). The existence of HMPA molecule in coordinate sphere of the iron(III) complex may interfere with the hydrogen atom transfer mechanism of the electron transfer, probably due to both the larger geometrical dimension of an HMPA molecule, and the poorer possibility of hydrogen bonding of an HMPA molecule which is surrounded with as many as six methyl groups towards the outside of the complex, than that of a water molecule.

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