BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 3363—3366 (1971)

The Solvent Effect on the Electron-Transfer Reactions of Cobalt(III) Complexes. The Reduction of the *cis*-Chloro-2-aminoethanolbis(ethylenediamine)cobalt(III) Ion by Iron(II) in Aqueous Solutions of Organic Solvents

Kousaburo OHASHI, Katsumi YAMAMOTO, Toshio SUZUKI, and Yoshimi KURIMURA*
Department of Chemistry, Ibaraki University, Mito, Ibaraki
**College of General Education, Ibaraki University, Mito, Ibaraki*

(Received April 7, 1971)

The solvent effect on the reduction of the *cis*-chloro-2-aminoethanolbis(ethylenediamine)cobalt(III) ion by iron(II) was investigated in aqueous solutions of dimethylsulfoxide (DMSO), dimethylformamide (DMF), ethanol, and acetone. The second-order rate constants for the reduction are 4.4×10^{-5} $\text{M}^{-1}\text{sec}^{-1}$ in the absence of an organic solvent, 1.4×10^{-3} $\text{M}^{-1}\text{sec}^{-1}$ in 0.20 M_f DMSO, 7.3×10^{-4} $\text{M}^{-1}\text{sec}^{-1}$ in 0.20 M_f DMF, 1.1×10^{-4} $\text{M}^{-1}\text{sec}^{-1}$ in 0.20 M_f ethanol, and 1.0×10^{-4} $\text{M}^{-1}\text{sec}^{-1}$ in 0.20 M_f acetone, at 25°C and at 0.16 M $HClO_4$ and $\sum[ClO_4^-]=0.60$ M (M_f=mol fraction of organic solvent). From the kinetic and spectral data, it is suggested that the increase in the rate upon the addition of an organic solvent may be mainly due to a change in the solvation sphere of the reductant by replacing the water molecules by the organic molecules.

Systematic kinetic investigations of the reductions of the cobalt(III) complexes in the organic solvents and in the organic solvent-water mixtures would provide important information regarding the mechanism of the electron-transfer reactions. Relatively few papers have been reported, however, on the effect of a solvent on the electron-transfer reactions of the metal complexes.

The exchange reactions between Co(phen)$_3^{2+}$ and Co(phen)$_3^{3+}$ in acetone-water[1] and that between iron(II) and iron(III) in isopropanol-water,[2] acetone-water,[3] methanol-water,[3] ethanol-water,[3] 1-propanol-water,[3] and dimethylsulfoxide-water[4] have been investigated. The rates of all these reactions decrease with an increase in the concentrations of the organic solvents.

In some organic solvent-water mixtures, it was found by the present authors that the rates of the reductions of some Co(III)-chloro complexes by iron(II) increase with an increase in the concentration of the nonaqueous solvent, such as dimethylsulfoxide (DMSO), dimethylformamide (DMF), ethanol, and acetone.

In this connection, a rate study of the reduction of the *cis*-chloro-2-aminoethanolbis(ethylenediamine)-cobalt(III) ion by iron(II) was done in organic solvent-water mixtures so as to obtain some information about the effect of the solvent on the electron-transfer reactions.

Experimental

Preparation of Complex. The *cis*-chloro-2-aminoethanolbis(ethylenediamine)cobalt(III) chloride used as the oxidant was prepared in a manner previously reported.[5] The identity and purity of the complex were confirmed analytically and spectrophotometrically. Found: C, 20.68; H, 6.51; N, 20.91. Calcd for $[Co(en)_2(NH_2CH_2CH_2OH)Cl]Cl_2$: C, 20.79; H, 6.68; N, 20.21.

Materials. Dimethylsulfoxide and dimethylformamide of a spectroscopic grade (Tokyo Kasei) were distilled under reduced pressure. Ethanol and acetone of G. R. grade (Tokyo Kasei) were distilled two times before use.

The preparation of the iron(II) solution and the determinations of the concentrations of hydrogen and perchlorate ions in this solution were carried out by a method similar to that described previously.[6] All the other chemicals used were of a G. R. grade and were used without further purification. The ionic strengths of the solutions were adjusted by the addition of sodium perchlorate solution.

Kinetic Runs. Erlenmeyer flasks containing appropriate amounts of redistilled water, the iron(II) solution, an organic solvent, and a dry complex respectively were kept in a thermostat. The desired volumes of redistilled water and organic solvent were added to the flask containing the dry complex, and the resulting solution was kept in a thermostat for about 30 min. Then, appropriate amounts of the iron(II) solution were added to this solution. A por-

---

1) B. R. Baker, F. Basolo, and H. M. Neuman, *J. Phys. Chem.*, **63**, 371 (1959).

2) N. Sutin, *ibid.*, **64**, 1766 (1960).

3) R. A. Horne, Ph. D. Thesis, Columbia University, New York, 1955.

4) J. Menashi, W. L. Reynolds, and G. Van Auken, *Inorg. Chem.*, **4**, 299 (1965).

5) S. C. Chan and F. Leh, *J. Chem. Soc.*, *A*, **1967**, 1730.

6) Y. Kurimura, K. Ohashi, T. Ohtsuki, and K. Yamamoto, This Bulletin, **44**, 1293 (1971).

tion of the reaction mixture was transferred rapidly into a 1-cm optical cell placed in a thermostated cell compartment of a Hitachi Model 124 spectrophotometer. The variation in the absorbance of the reaction mixture was recorded automatically in the vicinity of the first absorption maximum of the cobalt(III) complex. The wavelength used for the rate determination was 534 nm.

In all the experiments, the reactions were followed under pseudo-first-order conditions, in which the iron(II) concentration was in great excess with respect to that of the cobalt(III) complex. The pseudo-first-order rate constants, k_p, were calculated from the slope of the log (A_t-A_∞) *vs.* time plots, where A_t and A_∞ are the absorbances at time t and after all the cobalt(III) is reduced to cobalt(II) respectively.

Results

Reduction of cis-*$Co(en)_2(NH_2CH_2CH_2OH)Cl^{2+}$ in an Aqueous Solution.* The pseudo-first-order plots for the iron(II) reduction are shown in Fig. 1. The second-order rate constant, k, for the reaction can be obtained from the slope of the log (A_t-A_∞) *vs.* time plot and a known value of the iron(II) concentration, which is essentially constant under the conditions employed.

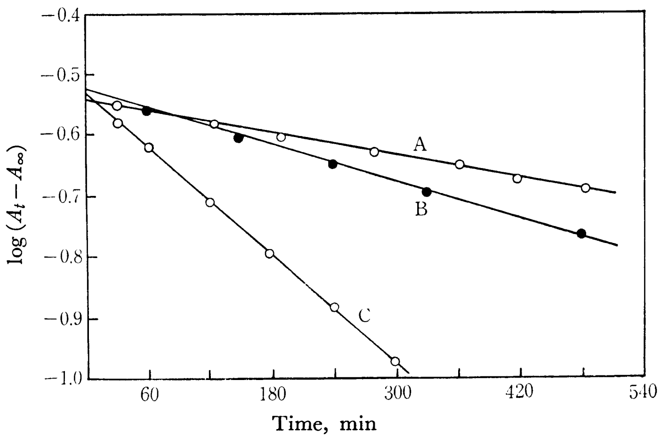

Fig. 1. The pseudo-first-order plots for the reactions of *cis*-$Co(en)_2(NH_2CH_2CH_2OH)Cl^{2+}$ with iron(II) in ethanol-water mixtures.
[Fe(II)]=0.210 M, $\sum$[ClO_4^-]=0.60 M, [$HClO_4$]=0.16 M, 25±0.1°C.
A : aqueous solution, [Co(III)]=4.30×10^{-3} M.
B : 0.20 mol fraction of ethanol, [Co(III)]=4.62×10^{-3} M.
C : 0.56 mol fraction of ethanol, [Co(III)]=4.48×10^{-3} M.

Figure 2 shows the dependence of the k_p value on the concentration of iron(II) in aqueous solutions. The linear behavior shown in Figs. 1 and 2 indicates that the rate equation can be expressed by:

$$-\frac{d[Co(III)]}{dt}=k[Co(III)][Fe(II)] \qquad (1)$$

The effect of the hydrogen-ion concentration on the rate was examined at a given ionic strength of 0.60 in aqueous solutions. The results indicate that the second-order rate constant is independent of the hydrogen-ion in the concentration region between 0.14 M to 0.43 M.

The effect of the ionic strength on the rate was also examined at a given hydrogen-ion concentration.

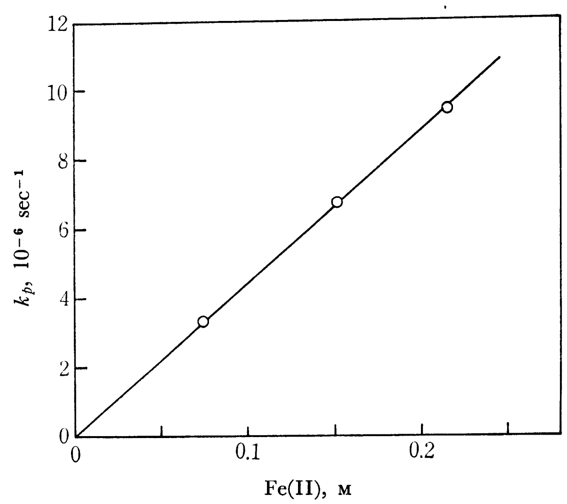

Fig. 2. The dependence of the pseudo-first-order rate constant for the reduction of *cis*-$Co(en)_2(NH_2CH_2CH_2OH)Cl^{2+}$ in aqueous solutions upon iron(II) concentration.
[Co(III)]=4.30×10^{-3} M, $\sum$[ClO_4^-]=0.60 M, [$HClO_4$]=0.16 M, 25±0.1°C.

TABLE 1. EFFECT OF IONIC STRENGTH ON THE SECOND-ORDER RATE CONSTANTS FOR THE REDUCTION OF *cis*-$Co(en)_2(NH_2CH_2CH_2OH)Cl^{2+}$ BY IRON(II) IN AQUEOUS SOLUTIONS

$\sum$[ClO_4^-]	Rate constant[a] M^{-1} sec^{-1}
0.60	4.38×10^{-5}
1.0	5.07×10^{-5}
2.0	5.78×10^{-5}

a) [Co(III)]=5.40×10^{-3} M, [Fe(II)]=0.18 M, [$HClO_4$]=0.20 M, 25±0.1°C.

A relatively small increase in the rate with an increase in the ionic strength was observed in the hydrogen-ion concentration region investigated. The results are shown in Table 1.

The rate constants and activation parameters for the reduction in an aqueous solution are represented in Table 2, along with the values obtained in an ethanol-water mixture.

Reduction of cis-*$Co(en)_2(NH_2CH_2CH_2OH)Cl^{2+}$ in Some Organic Solvent-Water Mixtures.* The reduction of the Co(III) complex in DMSO-water, DMF-water, ethanol-water, and acetone-water mixtures also obeys the rate expression (1) under the experimental conditions employed.

The second-order rate constants and activation parameters for the reduction at various mol fractions of ethanol are listed in Table 2. With the addition of ethanol to an aqueous solution, the values of the rate constants, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ increase gradually. Such a trend in the rate constants and activation parameters was also observed in the other organic solvent-water mixtures investigated.

The variations in the rate constants with the mol fraction of the organic solvent are illustrated in Fig. 3. In all cases, especially in the cases of DMSO-water and DMF-water, a marked increase in the rates with an increase in the mol fraction of organic

TABLE 2. THE RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE REDUCTION OF *cis*-$Co(en)_2(NH_2CH_2CH_2OH)Cl^{2+}$ IN ETHANOL-WATER MIXTURES AT 25±0.1°C

Mol fraction of ethanol	Rate constant[a] M^{-1} sec^{-1}	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta F^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ e.u.
0	4.38×10^{-5}	13.2	23.4	−36.4
0.074	7.19×10^{-5}	14.6	23.2	−33.8
0.20	1.12×10^{-4}	15.5	22.8	−30.6
0.32	1.65×10^{-4}	17.8	22.6	−25.6
0.56	3.72×10^{-4}	21.2	22.1	−17.8

a) [Co(III)]$=4.01\times10^{-3}$ M, [Fe(II)]$=0.21$ M, $\sum[ClO_4^-]=0.60$ M, [$HClO_4$]$=0.16$ M.

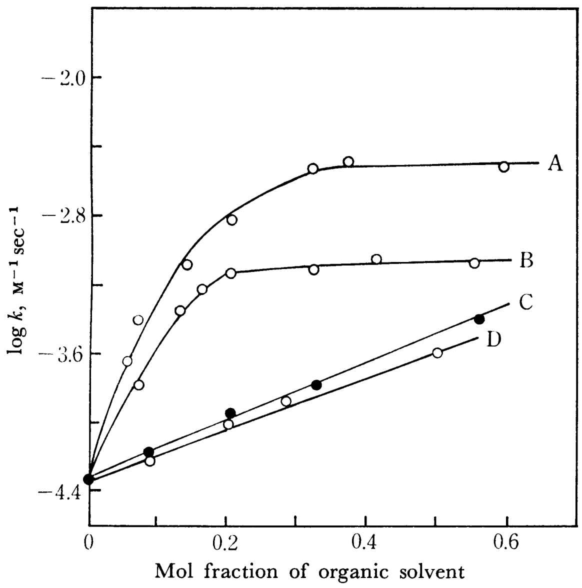

Fig. 3. The plots of logarithmic second-order rate constant *vs.* mol fraction of organic solvent.
[Co(III)]$=4.30\times10^{-3}$ M, [Fe(II)]$=0.086$—0.210 M, $\sum[ClO_4^-]=0.60$ M, [$HClO_4$]$=0.16$ M, 25±0.1°C
A : dimethylsulfoxide—water
B : dimethylformamide—water
C : ethanol—water
D : acetone—water

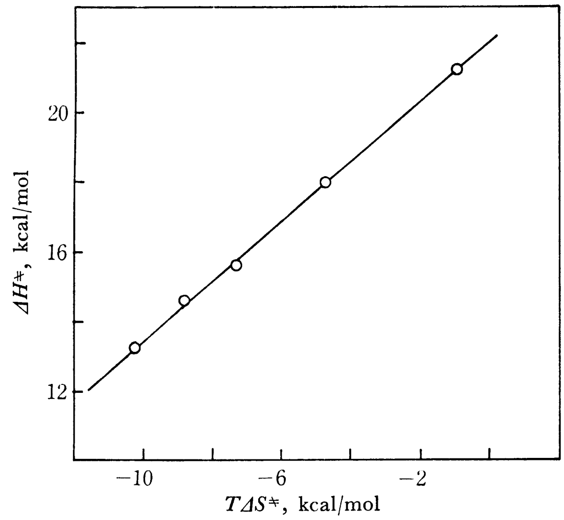

Fig. 4. A plot of $\Delta H^{\ddagger}$ *vs.* $T\Delta S^{\ddagger}$ for the iron(II) reduction of *cis*-$Co(en)_2(NH_2CH_2CH_2OH)Cl^{2+}$ in aqueous solution of ethanol.
$\sum[ClO_4^-]=0.60$ M, [$HClO_4$]$=0.16$ M, 25°C.

solvent is to be seen in this figure. A plot of $\Delta H^{\ddagger}$ *vs.* $T\Delta S^{\ddagger}$ at 25°C for the reaction in the ethanol-water mixture gives a straight line with a slope of about 0.85 (Fig. 4). This seems to indicate that there is a certain degree of compensation effect between $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$.

Absorption spectra of Ferric Perchlorate in Several Organic Solvent-Water Mixtures. In Fig. 5, the absorption spectra of ferric perchlorate in DMSO-water mixtures are represented. The absorbances of the ferric perchlorate solutions in the mixtures of DMSO, DMF, ethanol, and acetone with water in 0.20 M perchloric acid solutions are plotted as a function of the mol fraction of the organic solvent (Fig. 6). It is apparent from these curves that the addition of DMSO, DMF, ethanol, or acetone to an aqueous solution of ferric perchlorate increases the absorbance of the solution

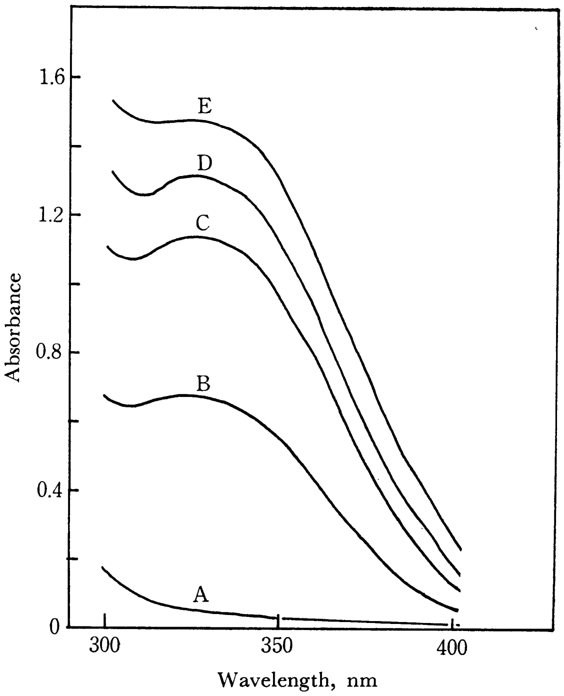

Fig. 5. Absorption spectra of ferric perchlorate in aqueous solution of dimethylsulfoxide.
[Fe(III)]$=1.60\times10^{-5}$ M, $\sum[ClO_4^-]=0.20$ M, [$HClO_4$]$=0.20$ M, 25°C.
A : aqueous solution.
B : 0.06 mol fraction of dimethylsulfoxide.
C : 0.20 mol fraction of dimethylsulfoxide.
D : 0.37 mol fraction of dimethylsulfoxide.
E : 0.70 mol fraction of dimethylsulfoxide.

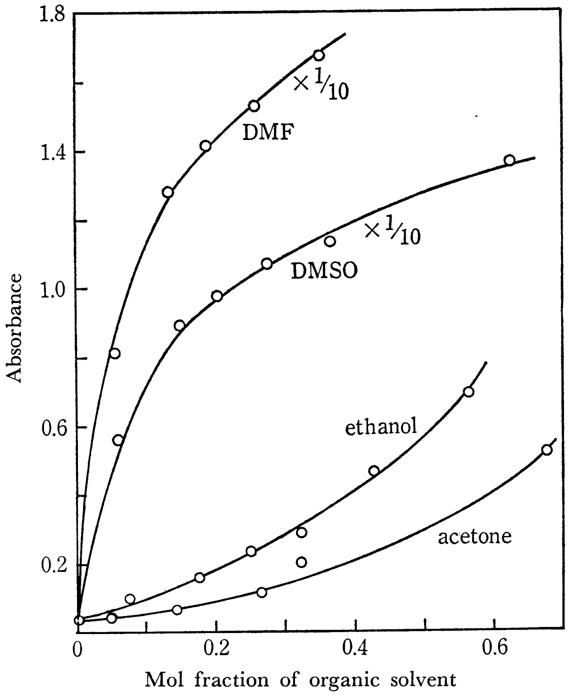

Fig. 6. The plots of absorbance *vs.* mol fraction of organic solvents.
[Fe(III)]=1.60×10⁻⁴ M, $\sum[ClO_4^-]=0.20$ M, $[HClO_4]=0.20$ M, at 350 nm, 25°C.

at wavelengths in the vicinity of 350 nm. Such increases in absorbance were also observed previously upon the addition of some alcohols to an aqueous solution of ferric perchlorate.[2,7]

Discussion

The facts that the rate of iron(II) reduction of the *cis*-$Co(en)_2(NH_2CH_2CH_2OH)Cl^{2+}$ is essentially independent of the hydrogen-ion concentration and that the rate is only slightly dependent upon the ionic strength of the solution seem to indicate that the marked increase in the rates with an increase in the concentration of the organic solvent in the organic solvent-water mixtures can not be due mainly to an alternation of the effective hydrogen ion concentration or that of the ionic strength in the media by the addition of organic solvents to aqueous solutions.

The ferrous-ferric exchange reaction proceed about 10^8 times slower in isopropyl alcohol than in water.[2] No specific explanation can be given for this results, however, it has been suggested that the predominant ferrous and ferric species may be quite different in the two solvents.[2] If the reactions have larger differences in configuration in isopropyl alcohol than in water, the reorganization energy may be much greater in alcohol.[2]

Because the coulombic repulsion free energy and outer-sphere reorganization free energy would be increased by a decrease in the macroscopic dielectric constant, and because the macroscopic dielectric constant is decreased with an increase in the organic solvent content, it may be supposed that the rate of the electron-transfer reaction between metal complexes is generally slower in organic solvents than in water, assuming that the same ionic species are present in the two solvents.[8]

In the present system, the anomalous increase in the rate upon the addition of an organic solvent to aqueous solution could not be explained by the effects of coulombic and outer-solvation-sphere reorganization free energy. The addition of an organic solvent to an aqueous solution of ferric perchlorate increases the absorbance of the solution. This increase is similar to that observed on the addition of other alcohols to aqueous solutions of ferric perchlorate.[7] This seems to suggest that some of the water molecules in the coordination-sphere of the ferric ion are replaced by organic solvent molecules. It may be supposed as was mentioned by Sutin,[2] that if the ionization potentials of the organic solvents used here are less than that of water, it would be easier to remove an electron from the solvation shell if the shell contains such organic molecules. This would shift the absorption band of the ferric perchlorate solution toward a longer wavelength and increase the absorbance in the vicinity of 350 nm.[2] Such a replacement of the water molecules by the organic molecules may also be expected in the case of the ferrous perchlorate solution by the addition of an organic solvent to the aqueous solution. In fact, it was suggested that, in a DMSO-water mixture at a higher water concentration, the mixed-ligand complexes, $Fe(DMSO)_{6-n}(H_2O)_n^{2+,3+}$,[4] and in pure DMSO, the DMSO complexes, $Fe(DMSO)_6^{2+,3+}$,[9] are important. On the other hand, the replacement of the ligands in the *cis*-$Co(en)_2(NH_2CH_2CH_2OH)Cl^{2+}$ by the organic molecules during the reaction may be ignored because of the inertness of this complex. The increase in the rate for the present reaction in the organic solvent-water mixtures seems to be contrary in trend to the cases of the electron-exchanges reactions between $Co(phen)_3^{2+}$ and $Co(phen)_3^{3+}$[1] and iron(II) and iron(III).[4] However, the change in the coordination sphere in the ferrous ions would be one of the most important reasons for the increase in the reactivity upon the addition of organic solvent to the aqueous solutions.

In acidified organic solvent-water mixtures, the main species of iron(II) may be present in the $Fe(OH_2)_{6-a}(OS)_a^{2+}$ form, where OS is the organic solvent molecule. The overall reaction may be given by:

$$cis\text{-}Co(en)_2(NH_2CH_2CH_2OH)Cl^{2+} + Fe(OH_2)_{6-a}(OS)_a^{2+}$$
$$Co^{2+} + 2en + NH_2CH_2CH_2OH + Cl^- + Fe(III)' \qquad (2)$$

Although the electron-transfer reaction between *cis*-$Co(en)_2(NH_2CH_2CH_2OH)Cl^{2+}$ and iron(II) would proceed *via* a chloride-bridged activated complex in aqueous solutions,[10] the mechanism for reaction (2) in the organic solvent-water mixtures would not necessarily be same as that for the reaction in aqueous solution.

---

[7] R. A. Horne, *J. Phys. Chem.*, **62**, 509 (1958).

[8] R. A. Marcus, *Discuss. Faraday. Soc.*, **29**, 21 (1960).

[9] G. Wada and W. Reynolds, *Inorg. Chem.*, **5**, 1354 (1966).

[10] Y. Kurimura and K. Ohashi, This Bulletin, **44**, 1797 (1971).