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^{1}H-NMR Spectroscopic Studies on the Ruthenocene and Its Salts

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Temperature dependence of ^{1}H-NMR spectra of a system containing ruthenocene and ruthenoceniumX$^+$Y$^-$ salts (X; Cl, Br, I and Y; PF_6, BF_4, I_3) in 1:1 molar ratio indicates the presence of intermolecular electron transfer between the ruthenocene and ruthenocenium species associated with an exchange of X atoms between the $Ru^{II}Cp_2$ molecules and $Ru^{IV}Cp_2X^+$ cations.

Mixed-valence biruthenoceniumX$^+$PF$_6^-$ (X; Cl, Br) salts expressed as $[Ru^{II}Cp(C_5H_4)(C_5H_4)CpRu^{IV}X]^+PF_6^-$ in a solid were prepared recently by oxidizing biruthenocene with FeX_3 in a solution of HX-NH_4PF_6 (X; Cl, Br, respectively).[1-3] Although no temperature dependence of the ^{1}H-NMR spectra is observed for ruthenocene and ruthenoceniumX$^+$PF$_6^-$ salts alone, remarkable temperature dependence of the ^{1}H-NMR spectra is found for the mixed-valence state of biruthenoceniumX$^+$PF$_6^-$ salts; i.e., a trapped valence state of biruthenoceniumX$^+$PF$_6^-$ salts, $[Ru^{II}Cp(C_5H_4)(C_5H_4)CpRu^{IV}X]^+$, is observed at lower temperature and an averaged-valence state of the salts, expressed as $[Ru^{II}Cp(C_5H_4)(C_5H_4)CpRu^{IV}X]^+ \rightleftharpoons [XRu^{IV}Cp(C_5H_4)(C_5H_4)CpRu^{II}]^+$ or $[Cp(C_5H_4)Ru^{III}\text{--}X\text{--}Ru^{III}(C_5H_4)Cp]^+$, is observed at higher temperature.[1,3] The fact suggests that there is some interaction between the $Ru^{II}(C_5H_4)Cp$ and $[XRu^{IV}(C_5H_4)Cp]^+$ moieties in the salts, while the question remains whether the interaction is ascribed to an intra- or intermolecular interaction. In order to clarify the question, the present studies were carried out on the mononuclear systems containing ruthenocene and ruthenoceniumX$^+$Y$^-$ salts (X; Cl, Br, I and Y; PF_6, BF_4, I_3) in 1:1 molar ratio with 0.0001-0.01 mol dm^{-3} for each component.

RuthenoceniumX$^+$PF$_6^-$ (X; Cl, Br) and related compounds were obtained by the method reported previously.[4] ^{1}H-NMR spectra were measured using a JEOL FX-200 spectrometer at 199.56 MHz, using TMS as a standard.

Figure 1 shows the temperature dependence of ^{1}H-NMR spectra of the ruthenocene/ruthenocenium$I^+I_3^-$ system in the mixed solvent of CD_3CN and $CDCl_3$ (1:1), and the chemical shift (δ_H) values are listed in Table 1. Sharp two lines at 4.53 and 6.10 ppm are observed at 183 K. Based on the data of ruthenocene and ruthenocenium$I^+I_3^-$, the former value (4.53 ppm) is ascribed to that of ruthenocene and the latter (6.10 ppm) to that of ruthenocenium-$I^+I_3^-$. The result suggests the absence of interaction between the ruthenocene and ruthenocenium$I^+I_3^-$ in the solution at 183 K.

Upon heating to 217 K the two peaks are broaden. The coalescence temperature (Tc) is found to be about 217 K. In a higher temperature than Tc, a sharp line at 5.35 ppm is observed (at 293 K). The value corresponds to the value (5.31 ppm) averaged for those of ruthenocene (4.52 ppm) and ruthenocenium$I^+I_3^-$ (6.10 ppm) at 298 K. The data suggest a rapid intermolecular electron transfer associated with an interchange in the bonding of I with Ru atoms between ruthenocene and ruthenocenium$I^+I_3^-$, to be expressed as $Cp_2Ru^* + Cp_2RuI^+I_3^- \rightleftharpoons Cp_2Ru^*I^+I_3^- + Cp_2Ru$. The formation of an intermediate dimer, such as $[Cp_2Ru^{III}\text{--}I\text{--}Ru^{III}Cp_2]^+I_3^-$ may not be ruled out either.

The life time (τ) at Tc is estimated to be 1.44 ms using the following equation $\tau = 2^{1/2}\pi^{-1}\sigma^{-1}$,5) where σ(Hz) is the difference in the chemical shifts of Cp-ring of the Cp_2Ru^{II} and $[Cp_2Ru^{IV}I]^+I_3^-$ (313.3 Hz). The value of $\Delta G^{\ddagger}$ at Tc is also estimated to be 40.8± 0.3 kJ mol^{-1} using the

Table 1. ^{1}H-Chemical shifts and activation parameters of ruthenocene/ruthenoceniumX^+Y^- systems and related compounds in mixed solvent of CD_3CN and $CDCl_3$ (1:1)

Compound	Temp K	Chem. shift δ_H	Tc K	δ(Tc) ms	$\Delta G^{\ddagger}$(Tc) kJ mol^{-1}	Ea kJ mol^{-1}
Ruthenocene	298	4.52				
Ruthenocenium$I^+I_3^-$	298	6.10				
Ruthenocenium$I^+PF_6^-$	298	6.08				
Ruthenocenium$I^+BF_4^-$	298	6.06				
Ruthenocenium$Br^+PF_6^-$	298	6.00				
Ruthenocenium$Cl^+PF_6^-$	298	5.95				
Ruthenocene/Ruthenocenium$I^+I_3^-$	183	4.53	217	1.44	40.8	30.6
		6.10				
	293	5.35				
Ruthenocene/Ruthenocenium$I^+PF_6^-$	183	4.52	228	1.43	42.9	31.5
		6.10				
	313	5.31				
Ruthenocene/Ruthenocenium$I^+BF_4^-$	183	4.53	227	1.43	42.7	31.1
		6.11				
	313	5.36				
Ruthenocene/Ruthenocenium$Br^+PF_6^-$	183	4.53	348	1.53	66.9	41.7
		6.01				
	273	4.54				
		6.01				
Ruthenocene/Ruthenocenium$Cl^+PF_6^-$	183	4.49	>>373	1.59	>>72.0	47.9
		5.91				
	373	4.55				
		5.97				

following equation, $\Delta G^{\ddagger}(Tc)=2.303RTc(10.319+\log\tau+\log Tc)$ where $R= 8.314$ J $mol^{-1}deg^{-1}$.[6)] Activation energy (Ea) is obtained in the usual way from plots of $\ln\kappa$ versus T^{-1}. Good linear plots are obtained and Ea value is found to be 30.6 kJ mol^{-1}. Similar remarkable temperature dependence of the spectra is observed for ruthenocene/ruthenoceniumI^{+}PF$_{6}^{-}$ and ruthenocene/ruthenoceniumI^{+}BF$_{4}^{-}$ systems. The Tc, $\Delta G^{\ddagger}$(Tc), and Ea values of the systems are, however, a little larger than those of ruthenocene/ruthenoceniumI^{+}I$_{3}^{-}$ system, as shown Table 1.

Figure 2 shows the temperature dependence of ^{1}H-NMR spectra of the ruthenocene/ruthenoceniumBr^{+}PF$_{6}^{-}$ system. Sharp two lines at 4.53 and 6.01 ppm are observed at 183-253 K, corresponding to ruthenocene and ruthenoceniumBr^{+}PF$_{6}^{-}$, respectively. Upon heating to 348 K (Tc) the peaks are broading. The Tc is much higher than that of ruthenocene/ruthenoceniumI^{+}Y^{-} (Y; PF$_{6}$, BF$_{4}$ and I$_{3}$) systems. The values of τ(Tc), $\Delta G^{\ddagger}$(Tc), and Ea are estimated to be 1.53 ms, 66.9, and 41.7 kJ mol^{-1}, respectively.

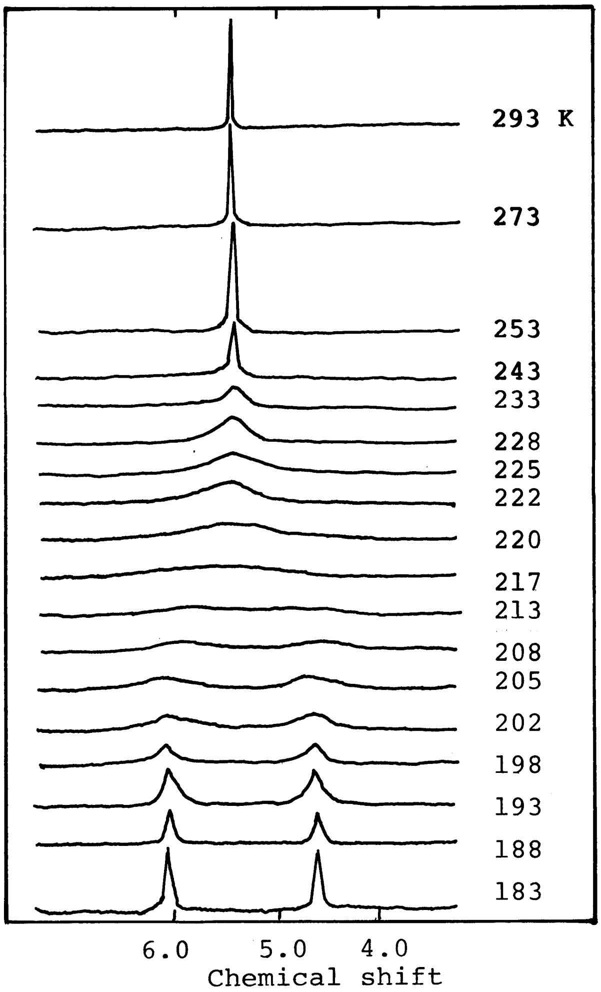

Fig. 1. ^{1}H-NMR spectra of ruthenocene/ruthenoceniumI^{+}I$_{3}^{-}$ at indicated temperatures.

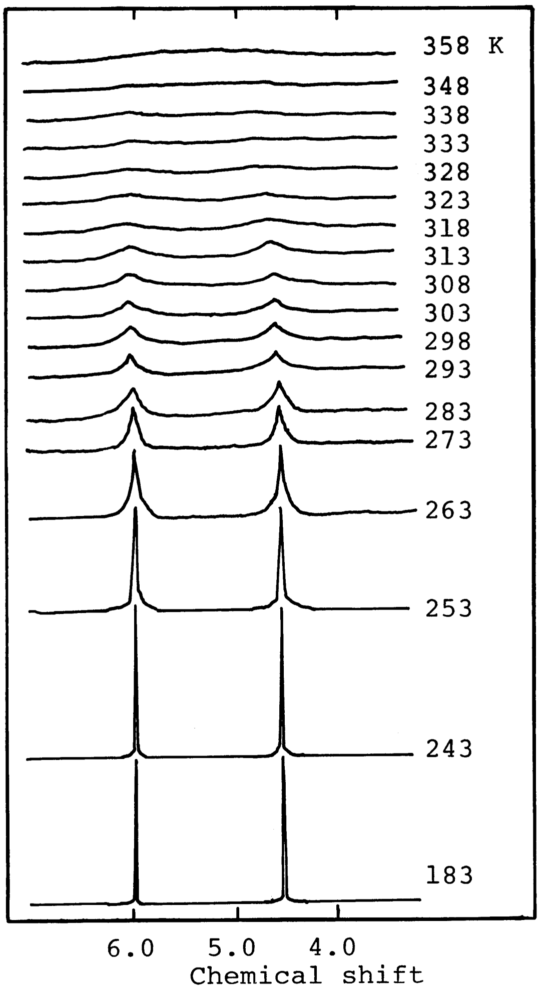

Fig. 2. ^{1}H-NMR spectra of ruthenocene/ruthenoceniumBr^{+}PF$_{6}^{-}$ at indicated temperatures.

On the other hand, little temperature dependence (183-373 K) is observed in the spectrum of ruthenocene/ruthenoceniumCl$^+$PF$_6^-$ system, as found in Fig. 3, although slightly broading lines are observed at higher temperatures (343-373 K). The value of Tc for the ruthenocene/ruthenoceniumCl$^+$PF$_6^-$ system is expected to be too high to be observed. The $\Delta G^{\ddagger}$(Tc) value are estimated to be much larger than 72.0 kJ mol^{-1}.

All the results obtained in the present studies lead us to the conclusion that there is some intermolecular electron transfer associated with an exchange of the X atoms between the ruthenocene and ruthenoceniumX$^+$ species as indicated in $^*Cp_2Ru^{II}+Cp_2Ru^{IV}X^+ \rightleftharpoons {}^*Cp_2Ru^{IV}X^+ + Cp_2Ru^{II}$. The exchange rate increases in the order of ruthenocene/ruthenoceniumI$^+$Y$^-$> ruthenocene/ruthenoceniumBr$^+$PF$_6^-$> ruthenocene/ruthenoceniumCl$^+$PF$_6^-$ systems. The order is quite different from that found for biruthenoceniumX$^+$Y$^-$ systems in which the rate decreases in the order of biruthenoceniumI$^+$> biruthenoceniumBr$^+$> biruthenoceniumCl$^+$ salts.[1,3] Moreover $\Delta G^{\ddagger}$(Tc) and Ea values are found to be 42.7 and 29.2 kJ mol^{-1} for the biruthenoceniumBr$^+$PF$_6^-$ system and to be 41.8 and 28.1 kJ mol^{-1} for the biruthenoceniumCl$^+$PF$_6^-$ system, respectively, which are much lower than the values of the ruthenocene/ruthenoceniumX$^+$PF$_6^-$ (X; Br, Cl) systems. The reason for the difference between the biruthenoceniumX$^+$PF$_6^-$ and the ruthenocene/ruthenoceniumX$^+$PF$_6^-$ systems may be ascribed to different mechanisms of the intra- and intermolecular electron transfer associated with the exchange of the X atom between ruthenocene- and ruthenoceniumX$^+$-type in solution, respectively.

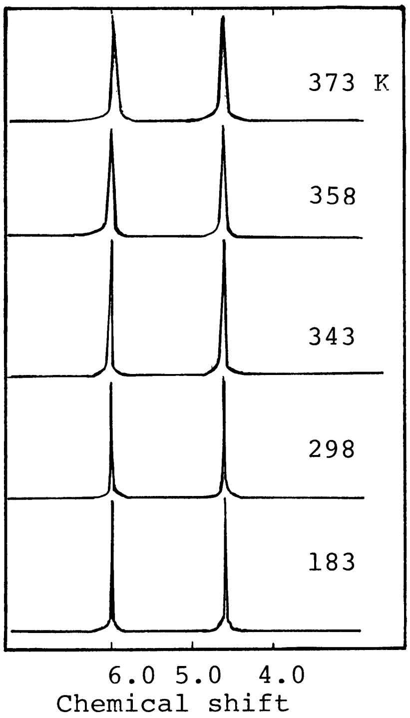

Fig. 3. ^{1}H-NMR spectra of ruthenocene/ruthenoceniumCl$^+$PF$_6^-$ at indicated temperatures.

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