April, 1984] *Bull. Chem. Soc. Jpn.*, *57*, *1021—1025 (1984)* 1021

Kinetics and Equilibrium Studies on the Anation Reactions in Pentakis(dimethyl sulfoxide)dioxouranium(VI) and Tetrakis-(hexamethylphosphoric triamide)dioxouranium(VI) Ions in Nonaqueous Media

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(Received October 26, 1983)

The anation reactions in $[UO_2(dmso)_5]^{2+}$ (dmso=dimethyl sulfoxide) and $[UO_2(hmpa)_4]^{2+}$ (hmpa=hexamethylphosphoric triamide) ions by SCN^- and N_3^- have been studied by the stopped-flow method in DMSO and acetonitrile. For the anation reactions of $[UO_2(dmso)_5]^{2+}$ in DMSO as a medium, the pseudo-first order rate constant(k_{obsd}) is expressed by $k_{obsd}=\{k_{-1}+(k_1+k_{-1})\times K_{os}[X]\}/(1+K_{os}[X])$, where X=$SCN^-$ and $[UO_2(dmso)_5]^{2+}$ for the anation reactions by SCN^- and N_3^-, respectively. The values of k_1, k_{-1}, and K_{os} at 25 °C are 2.06×10^2 s^{-1}, 62 s^{-1}, 35 M^{-1} ($M=mol\ dm^{-3}$), and 7.60×10^2 s^{-1}, 0.0 s^{-1}, and 41 M^{-1} for the SCN^- and N_3^- anation reactions in $[UO_2(dmso)_5]^{2+}$, respectively. For the anation reaction in $[UO_2(hmpa)_4]^{2+}$ by SCN^-, the pseudo-first order rate constant was found to be proportional to the concentrations of $[UO_2(hmpa)_4]^{2+}$ and free HMPA: $k_{obsd}=k_f[UO_2(hmpa)_4{}^{2+}]+k_b[HMPA]_{free}$. The values of k_f and k_b at 25 °C are 9.70×10^3 $M^{-1}\,s^{-1}$ and 9.05×10^2 $M^{-1}\,s^{-1}$, respectively. The equilibrium constants for the titled reactions were also measured at 25 °C: $K=85$ $M^{-1}$for the anation reaction of $[UO_2(dmso)_5]^{2+}$ by SCN^- in DMSO and $K'=42.7$ for the SCN^- anation reaction in $[UO_2(hmpa)_4]^{2+}$ in acetonitrile. The kinetic results suggest that the anation reactions in uranyl complexes proceed through an associative or an associative interchange mechanism.

For ligand exchange reactions in the equatorial position of uranyl complexes, it is proposed that most of the reactions proceed through the dissociation (D) or the dissociative interchange (I_d) mechanism.[1-8]

The authors have reported that the ligand substitution reactions in $[UO_2(dmf)_5]^{2+}$ (dmf=*N,N*-dimethylformamide) ion proceeded *via* an associative interchange (I_a) mechanism and the anation rate constant depended on the basicity of entering ligands.[9] Few other studies on the anation reactions of uranyl complexes have been reported.

A detailed kinetic and equilibrium study on the anation reactions in $[UO_2(dmso)_5]^{2+}$ and $[UO_2(hmpa)_4]^{2+}$ ions was performed for the following reactions:

$$[UO_2(dmso)_5]^{2+} + SCN^- \rightleftharpoons [UO_2(dmso)_4NCS]^+ + DMSO,$$

$$[UO_2(dmso)_5]^{2+} + N_3^- \rightleftharpoons [UO_2(dmso)_4N_3]^+ + DMSO,$$

$$[UO_2(hmpa)_4]^{2+} + SCN^- \rightleftharpoons [UO_2(hmpa)_3NCS]^+ + HMPA.$$

The reaction mechanism is discussed by comparing the results of kinetic study of these reactions with the previous results for the anation rcactions in $[UO_2(dmf)_5]^{2+}$.

Experimental

Synthesis of Complexes. The $[UO_2(dmso)_5](ClO_4)_2$ and $[UO_2(hmpa)_4](ClO_4)_2$ complexes were prepared under an atmosphere of nitrogen by refluxing hydrated uranyl perchlorate with triethyl orthoformate at 60°C for 1 h, followed by the addition of dimethyl sulfoxide and hexamethylphosphoramide at room temperature, respectively. The resulting light yellow crystals of these complexes were recrystallized from dichloromethane and washed with dried diethyl ether, and freed of the diethyl ether *in vacuo* for 2 d. Calcd for $[UO_2(dmso)_5](ClO_4)_2$: C, 13.97; H, 3.52%. Found: C, 13.45; H, 3.41%. Calcd for $[UO_2(hmpa)_4](ClO_4)_2$: C, 24.3; H, 6.12; N, 14.18%. Found: C, 24.6; H, 6.10; N, 14.50%. Elemental analysis of the complexes was carried out by using a Shimadzu CHN-1A analyzer.

Other Materials. Hexamethylphosphoric triamide (Wako Pure Chemical Ind. Ltd.) was distilled twice under reduced pressure and stored over 4A molecular sieves (Wako). Dimethyl sulfoxide (Wako) was kept in contact with barium oxide for 2 d, distilled twice under reduced pressure and stored over 4A molecular sieves. Acetonitrile (MeCN) (Wako) was dehydrated with calcium oxide and diphosphorus pentaoxide, and distilled. Triethyl orthoformate(Wako) was of guaranteed grade and used without further purification. Sodium thiocyanate (Wako) was dried at 100°C for 2 h and stored *in vacuo*. The concentration of azide ion in DMSO solution was determined by measuring sodium ion concentration with a Varian-Techtron 1100 flame-spectrophotometer. The amount of water contained in DMSO and MeCN solvents was measured by a Mitsubishi CA-02 moisture-meter and the maximum concentration was found to be less than 0.03 M. Anhydrous sodium perchlorate (Wako) was used to adjust the ionic strength of solutions to 0.2 M.

Measurement of NMR Spectra. ^1H NMR spectra were measured at 100 Hz on a JEOL JNM-FX 100 FT-NMR spectrometer equipped with a JNM-VT-3B temperature controller.

Measurement of Equilibrium Constants. The equilibrium constants between uranyl complexes and thiocyanate or azide ions were measured spectrophotometrically by using a Shimadzu UV-210A double-beam spectrophotometer with a cell compartment thermostated at 25°C. The ionic strength of sample solutions was adjusted to 0.2 M by using sodium perchlorate.

Kinetic Measurements. The anation rates were measured by using a specially designed double-beam stopped-flow apparatus with a nitrogen-pressurized flow system. The temperature of the sample solutions was adjusted by a conventional temperature controller. The memorized stopped-flow signals were introduced to a Sord microcomputer (M223 Mk III), accumulated and curve-fitted. At least ten runs were performed for each measurement.

Results and Discussion

Equilibrium of $[UO_2(dmso)_5]^{2+}$ *Ion with* SCN^- *and* N_3^-. The ^1H NMR spectra of solutions containing $[UO_2(dmso)_5]^{2+}$, DMSO, CD_3CN, and $(CD_3)_2CO$ were observed at −65 °C. It was shown that the structure of $[UO_2(dmso)_5]^{2+}$ was consistent with that reported by Fukutomi *et al.*, *i.e.*, a pentagonal bipyramidal structure.[2] In the case of N_3^- anation, the area of the dmso methyl proton signal varied according to the concentration of added N_3^-. It was suggested that this reaction proceeded stoichiometrically as given by Eq. 1 with a fairly large equilibrium constant. It was impossible, in fact, to determine the equilibrium constant of this reaction by measuring the spectral change. Kinetic measurements also proved that the backward reaction rate constant is zero and the equilibrium constant is fairly large.

$$[UO_2(dmso)_5]^{2+} + N_3^- \rightleftharpoons [UO_2(dmso)_4N_3]^+ + DMSO \qquad (1)$$

Figure 1 shows the spectral change of $[UO_2(dmso)_5]^{2+}$ with varying the concentration of $[UO_2(dmso)_5]^{2+}$ from 0.002 to 0.006 M at a constant concentration of SCN^- (2.0×10^{-4} M). Although an isosbestic point is not observed, the most probable reaction corresponding to the spectral change seems to be

$$[UO_2(dmso)_5]^{2+} + SCN^- \overset{K}{\rightleftharpoons} [UO_2(dmso)_4NCS]^+ + DMSO. \qquad (2)$$

The equilibrium constant (K) for this process was obtained from the following equation.

$$\frac{[SCN^-]}{Abs - \varepsilon_1[UO_2(dmso)_5^{2+}]} = \frac{1}{K(\varepsilon_2-\varepsilon_1)[UO_2(dmso)_5^{2+}]} + \frac{1}{\varepsilon_2-\varepsilon_1}, \qquad (3)$$

where Abs is the observed absorbance, and ε_1 and ε_2 are the molar extinction coefficients of $[UO_2(dmso)_5]^{2+}$ and $[UO_2(dmso)_4NCS]^+$, respectively. The plot of $[SCN^-]/(Abs-\varepsilon_1[UO_2(dmso)_5^{2+}])$ against $1/[UO_2(dmso)_5^{2+}]$ gave a straight line as shown in Fig. 2, which supports the validity of the reaction given by Eq. 2. From the slope and intercept, the value of K was calculated and listed in Table 1.

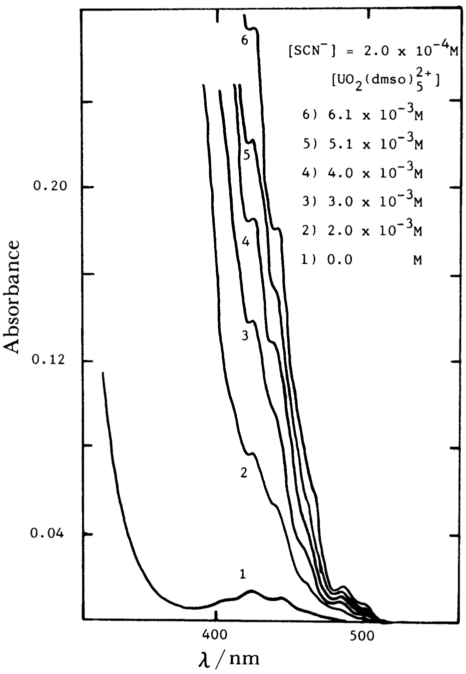

Fig. 1. The spectral change of $[UO_2(dmso)_5]^{2+}$ with varying the concentration of SCN^- in DMSO at 25 °C and ionic strength=0.2 M ($NaClO_4$).

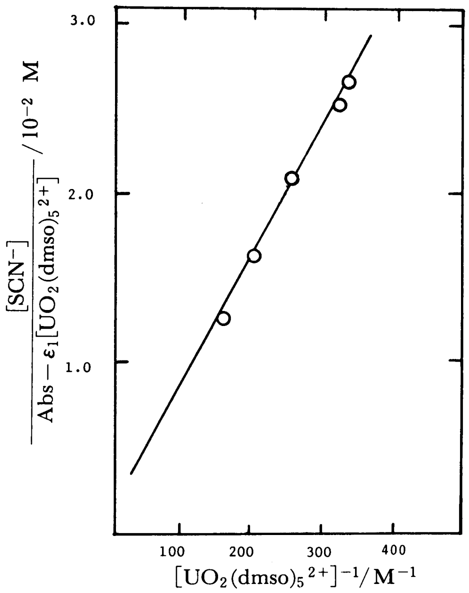

Fig. 2. The plot of $[SCN^-]/(Abs-\varepsilon_1[UO_2(dmso)_5^{2+}])$ *vs.* $1/[UO_2(dmso)_5^{2+}]$ for the anation reaction of $[UO_2(dmso)_5]^{2+}$ by SCN^- at 25 °C, 430 nm, and ionic strength=0.2 M ($NaClO_4$).

TABLE 1. EQULIBRIUM CONSTANTS OF LIGAND SUBSTITUTION REACTIONS IN URANYL COMPLEXES AT 25 °C[a)]

Reaction	Solvent	$K^{b)}$ / M^{-1}	$K'^{c)}$
$[UO_2(dmf)_5]^{2+}+SCN^-$	DMF	186±28	2400±210
	MeCN		2626±150
			2480±120[d]
$[UO_2(dmso)_5]^{2+}+SCN^-$	DMSO	85±9	1197±120
	MeCN		342±30
$[UO_2(hmpa)_4]^{2+}+SCN^-$	MeCN		42.7±4.0

a) The quoted errors represent the standard deviation. b) $K=[UO_2S_{n-1}L^+]/([UO_2S_n2^+][L^-]$. c) $K'=K\cdot[S]$. d) Measured in MeCN–DMF(50 vol%) mixed solvent.

Equilibrium of $[UO_2(hmpa)_4]^{2+}$ Ion with SCN^-. The ^1H NMR spectra of solutions containing $[UO_2(hmpa)_4]^{2+}$, HMPA, CD_3CN, and $(CD_3)_2CO$ were observed at −65 °C. From the area ratio of the methyl proton signals of the coordinated and free HMPA, the structure of $[UO_2(hmpa)_4]^{2+}$ was proved to the same as that reported by Williams *et al.*,[10] *i.e.*, square bipyramidal. In this reaction, the equilibrium constant was measured in MeCN under the conditions of $[UO_2(hmpa)_4^{2+}]>[SCN^-]$. The value of equilibrium constant (K) was calculated by using a similar equation to Eq. 3, and is listed in Table 1.

The equilibrium constants for the reactions of $[UO_2(dmf)_5]^{2+}$ and $[UO_2(dmso)_5]^{2+}$ ions with SCN^- were also measured in MeCN under the conditions of T=25 °C and ionic strength= 0.2 M ($NaClO_4$). The calculated values of K and K' are listed in Table 1, where K and K', denote the equilibrium constants defined as below.

$$K = \frac{[UO_2S_{n-1}NCS^+]}{[UO_2S_n^{2+}][SCN^-]}, \quad K' = K[S],$$

$$S = \text{DMF, DMSO, and HMPA}$$

As seen in Table 1, the equilibrium constants for the SCN^- anation reaction towards $[UO_2(dmf)_5]^{2+}$ ion in MeCN and DMF are consistent with each other within experimental errors. Moreover, the equilibrium constant measured in MeCN-DMF mixed solvent (50% in volume) was in good agreement with those measurcd in each solvent. The similar values of solubility parameters[11] and dielectric constants of MeCN and DMF might lead to the consistency of these results. The dielectric constant has an effect on the solvation of ions and the solubility parameter is concerned with the intermolecular forces. Thus, MeCN and DMF can be considered as almost equivalent solvents for the reactions containing relatively large ionic species. The order of K' values for the reactions of different uranyl complexes with thiocyanate ion in MeCN is consistent with the order of the donor property of the coordinated organic ligands, HMPA>TMP[12]>DMSO>DMF. Especially, the logarithmic values of the equilibrium constants showed a good linear relationship to the E_B parameter[13] of each organic ligand rather than the donor number (DN)[14] (Fig. 3).

Kinetic Study on the Reactions of $[UO_2(dmso)_5]^{2+}$ Ion with SCN^- and N_3^-. On the basis of the results of equilibrium constants measured spectrophotometrically, the pseudo-first order rate constant (k_{obsd}) for the anation reactions by SCN^- and N_3^- were measured under the conditions of $[UO_2(dmso)_5^{2+}] \ll [SCN^-]$ and $[UO_2(dmso)_5^{2+}] \gg [N_3^-]$, respectively.

Figures 4 and 5 show the plots of k_{obsd} vs. $[SCN^-]$ and $[UO_2(dmso)_5^{2+}]$, which do not display a simple linear relationship, and the values of k_{obsd} approach each limiting value at high concentration region of SCN^- and $[UO_2(dmso)_5]^{2+}$, respectively. Attempts were made to examine the effect of water on the anation reactions, in which the concentration of water was changed from 0.03 to 0.1 M. It was found that water made no effect on the present anation reactions in this concentration range.

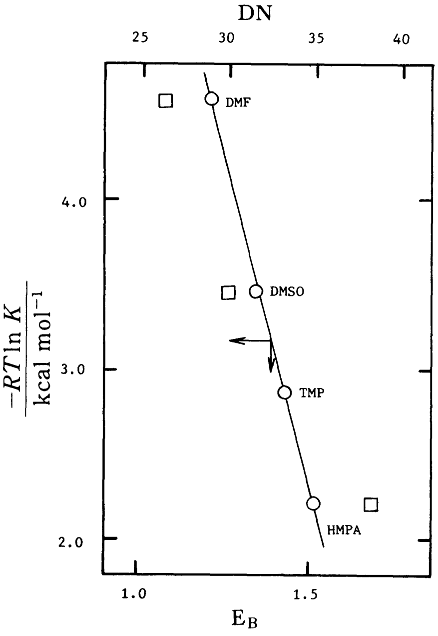

Fig. 3. The plot of $-RT\ln K$ vs. E_B and DN of the coordinated molecules: ○; E_B, □; DN.

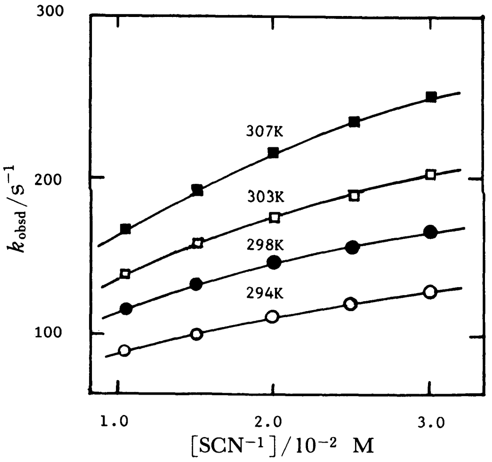

Fig. 4. Plots of k_{obs} vs. $[SCN^-]$ for the anation reaction of $[UO_2(dmso)_5]^{2+}$ by SCN^-. The solid lines denote the least-squares best-fit lines.

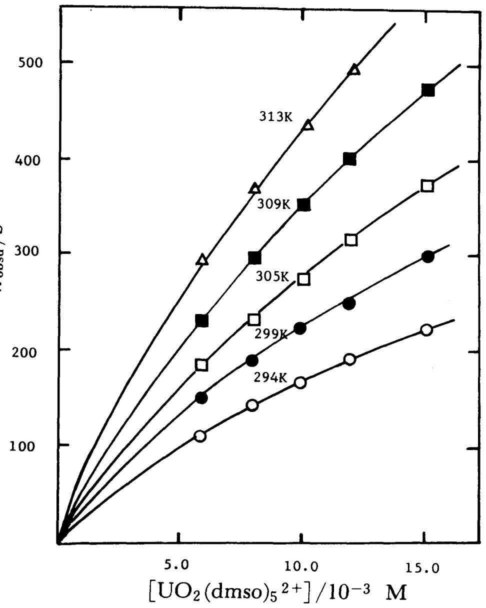

Fig. 5. Plots of k_{obsd} vs. $[UO_2(dmso)_5^{2+}]$ for the anation reaction by N_3^-. The solid lines denote the least-squares best-fit lines.

Taking into account the result that the anation reaction in $[UO_2(dmf)_5]^{2+}$ proceeded through the I_a mechanism,[9] the following I mechanism appears to be the most probable mehanism for the present anation reactions.

$$[UO_2(dmso)_5]^{2+} + L^- \overset{K_{os}}{\rightleftharpoons} [UO_2(dmso)_5]^{2+} \cdots L^-,$$

$$[UO_2(dmso)_5]^{2+} \cdots L^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [UO_2(dmso)_4L]^+ + \text{DMSO},$$

were L is SCN^- or N_3^- ion, and K_{os} is the outersphere complex formation constant. According to this mechanism, the observed rate constant, k_{obsd}, is given by Eq. 4.

$$k_{obsd} = \frac{k_{-1} + (k_1 + k_{-1})K_{os}[X]}{1 + K_{os}[X]}, \tag{4}$$

Table 2. Kinetic parameters of ligand substitution reactions[a)]

Reaction	Temp	k_1	k_{-1}	K_{os}	k_f	k_b
	°C	s^{-1}	s^{-1}	M^{-1}	10^4 M^{-1} s^{-1}	10^2 M^{-1} s^{-1}
$[UO_2(dmso)_5]^{2+}+SCN^-$	21.0	160±15	41±9	41		
	25.0	206±18	62±12	35		
	30.2	281±21	73±8	29		
	34.2	404±28	85±11	35		
$[UO_2(dmso)_5]^{2+}+N_3^-$	21.0	544±35	0.0±5.0	44		
	26.3	762±20	−1.0±3.0	41		
	32.6	1035±51	3.0±5.3	35		
	36.5	1345±51	−5.1±7.2	36		
	40.0	1751±75	11.0±10.5	32		
$[UO_2(hmpa)_4]^{2+}+SCN^-$	25.0				0.97±0.03	9.05±0.50
	30.0				1.57±0.05	9.82±0.50
	34.0				2.18±0.07	11.6±0.8
	38.0				2.89±0.07	13.4±0.7

a) The quoted errors represent the standard deviation.

Table 3. Kinetic data for the ligand substitution reactions in uranyl complexes at 25 °C[a)]

Reactions	Solvents	Rate constant	$\Delta H^{\neq}$	$\Delta H^{\neq}$	Mechanism
		s^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}	
$[UO_2(dmso)_5]^{2+}+SCN^-$	DMSO	$k_1=2.1\times10^2$	49.6±0.8	−35.7±4.5	I_a
$[UO_2(dmso)_5]^{2+}+N_3^-$	DMSO	$k_1=7.5\times10^2$	43.3±0.9	−45.8±5.0	I_a
$[UO_2(hmpa)_4]^{2+}+SCN^-$	MeCN	$k_f=9.7\times10^3/M^{-1}$	62.6±1.5	41.1±5.3	A

a) The quoted errors respresent the standard deviation. Ionic strength=0.2 M($NaClO_4$).

where X is SCN^- and $[UO_2(dmso)_5]^{2+}$ for the anation reactions by SCN^- and N_3^-, respectively, since the measurements were carried out under the conditions of $[UO_2(dmso)_5^{2+}]<[SCN^-]$ and $[UO_2(dmso)_5^{2+}]>[N_3^-]$. When $K_{os}[X]\ll1$, Eq. 4 can be simplified to $k_{obsd}=k_{-1}+(k_1+k_{-1})K_{os}[X]$. This agrees with the dependence of k_{obs} on [X] in the low concentration region. If the values of $K_{os}[X]$ are much larger than unity, Eq. 4 becomes $k_{obsd}=k_1+k_{-1}$, which is consistent with the fact that limiting values of k_{obsd} are obtained at high [X].

The values of k_1, k_{-1}, and K_{os} were calculated by the nonlinear least-squares method and are listed in Table 2. The solid lines in Figs. 4 and 5 obtained from the calculated values agree with the experimental results. The activation parameters for k_1 obtained from the Eyring plot are shown in Table 3.

The outersphere complex formation constants for both reactions are similar as shown in Table 2. This seems to be reasonable since SCN^- and N_3^- ions have the same charge, similar size and structure. Thus the interatomic distance between $[UO_2(dmso)_5]^{2+}$ and SCN^- or N_3^- in the outersphere complexes is assumed to be the same. In this case, the Fuoss equation[15)] gives the same value for the outersphere association constant.

The interchange rate constants of the present reactions depended on the nature of the entering ligands, SCN^- and N_3^-. The difference of the reactivities, *i.e.*, $k_1^{N_3^-}/k_1^{SCN^-}\simeq3.8$ cannot be attributed to the outersphere complex formation, because the value of this ratio is larger than the corresponding value for K_{os}, $K_{os}^{N_3^-}/k_{os}^{SCN^-}\simeq1.2$ at 25 °C. Thus the different reactivity may be due to a difference in nucleophilicity of SCN^- and N_3^-.

Kinetic Study on the Reaction of $[UO_2(hmpa)_4]^{2+}$ Ion with SCN^-. On the basis of the spectrophotometric measurement of the equilibrium constant, the pseudo-first order rate constants, k_{obsd}, for the anation reaction in $[UO_2(hmpa)_4]^{2+}$ with SCN^- were measured under the conditions of $[UO_2(hmpa)_4^{2+}]>[SCN^-]$ in MeCN. The plots of k_{obsd} against the concentration of $[UO_2(hmpa)_4]^{2+}$ in Fig. 6 show a simple linear relationship. The effect of water on the present anation reaction was also examined, where the concentration of water was changed from 0.05 to 0.1 M. It was found that water made no evident effect on this reaction in this concentration range.

The simple relationship shown in Fig. 6 can be explained by an A or an I mechanism. In the A mechanism,

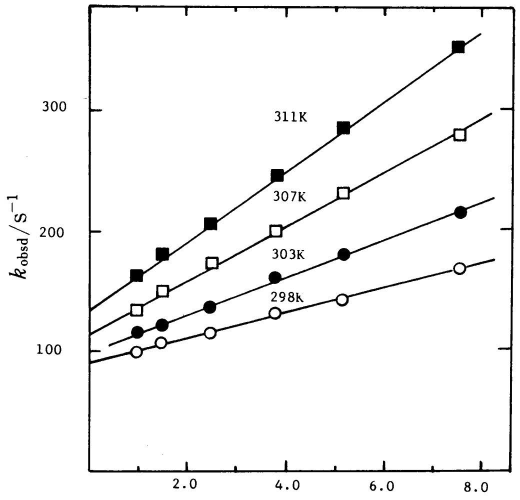

Fig. 6. Plots of k_{obsd} *vs.* $[UO_2(hmpa)_4^{2+}]$ for the anation reaction by SCN^-. The solid lines denote the least-squares best-fit lines.

$$[UO_2(hmpa)_4]^{2+} + SCN^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [UO_2(hmpa)_4NCS]^+,$$

$$[UO_2(hmpa)_4NCS]^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [UO_2(hmpa)_3NCS]^+ + HMPA,$$

where $k_{obsd}=k_f[UO_2(hmpa)_4^{2+}]+k_b[HMPA]_{free}$ in which k_f and k_b are $k_1k_2/(k_{-1}+k_2)$ and $k_{-1}k_{-2}/(k_{-1}+k_2)$, respectively. In the I mechanism,

$$[UO_2(hmpa)_4]^{2+} + SCN^- \overset{K_{os}}{\rightleftharpoons} [UO_2(hmpa)_4]^{2+}\cdots NCS^-,$$

$$[UO_2(hmpa)_4]^{2+} \cdots NCS^- \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}}$$

$$[UO_2(hmpa)_3NCS]^+ + HMPA,$$

where $k_{obsd}=k'_1K_{os}[UO_2(hmpa)_4^{2+}]/(1+K_{os}[UO_2(hmpa)_4^{2+}])+k'_{-1}[HMPA]_{free}$. When $K_{os}[UO_2(hmpa)_4^{2+}]$ is much smaller than unity, k_{obsd} can be simplified as follows:

$$k_{obsd} = k'_1K_{os}[UO_2(hmpa)_4^{2+}]+k'_{-1}[HMPA]_{free}.$$

Thus, both the two mechanisms can explain the experimental results shown in Fig. 6. On the other hand, as mentioned in the study on the equilibrium constant, it is shown that DMF and MeCN can be regarded as solvents having similar effect on the solvation of the species in the present study. Therefore, if the reaction proceeded through the I mechanism, the outersphere complex formation constant for this reaction is expected to be of the same order as that for the anation reaction in $[UO_2(dmf)_5]^{2+}$ with SCN^- in DMF. Since the K_{os} value for the latter reaction was $148M^{-1}$ at 25°C[9] and the concentration range of $[UO_2(hmpa)_4]^{2+}$ is larger than $7.58\times10^{-3}M$, the product of K_{os} and $[UO_2(hmpa)_4^{2+}]$ has much the same value as unity. Thus it is not likely that this reaction proceeds through the I mechanism. The HMPA concentration dependence of the pseudo-first order rate constants based on the A mechanism is shown in Fig. 7 and the calculated values of k_f and k_b are listed in Table 2.

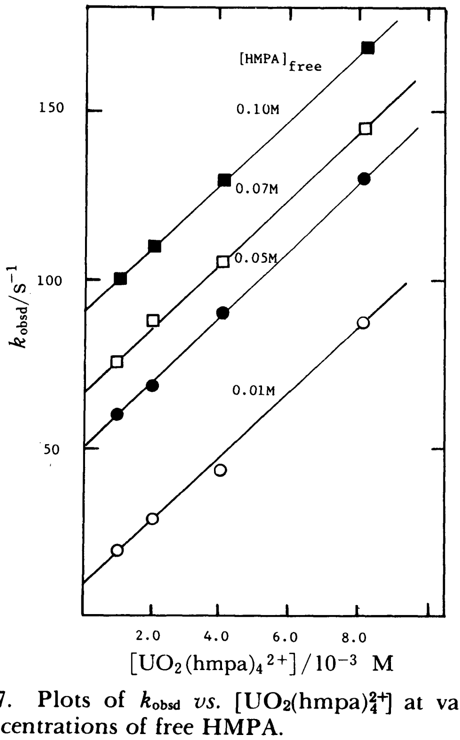

Fig. 7. Plots of k_{obsd} *vs.* $[UO_2(hmpa)_4^{2+}]$ at various concentrations of free HMPA.

It is concluded that the anation reactions in $[UO_2(dmso)_5]^{2+}$ proceeded through the Ia mechanism since the interchange rate constants depended on the nature of entering ligands, SCN^- and N_3^-. The anation reaction in $[UO_2(hmpa)_4]^{2+}$ with SCN^- ion was observed to proceed through the A mechanism, which is consistent with the results obtained by NMR[10] for the ligand exchange reaction in this complex.

It is proposed that the ligand substitution reactions in uranyl complexes with five ligands in the equatorial plane proceed through the associative interchange mechanism, while $[UO_2(hmpa)_4]^{2+}$ with less coordination number than five, reacts *via* the associative mechanism by forming a pentacoordinated intermediate.

The authors wish to express their thanks to Dr. Roderick D. Cannon of the University of East Anglia, U. K., Messrs. Takashi Kojima and Naoshi Fujiwara for their helpful discussions. This work was partly supported by the Grant-in-Aid for Developmental Scientific Research No. 584024 from the Ministry of Education, Science and Culture.

References

1) Y. Ikeda, S. Soya, H. Tomiyasu, and H. Fukutomi, *J. Inorg. Nucl. Chem.*, **41**, 1333 (1979).

2) Y. Ikeda, H. Tomiyasu, and H. Fukutomi, *Bull. Res. Lab. Nucl. Reactor*, **4**, 47 (1979).

3) R. P. Bowen, S. F. Lincoln, and E. H. Williams, *Inorg. Chem.*, **15**, 2126 (1976).

4) R. P. Bowen, G. J. Honan, S. F. Lincoln, T. M. Spotwood, and E. H. Williams, *Inorg. Chim. Acta*, **33**, 235 (1979).

5) G. J. Honan, S. F. Lincoln, and E. H. Williams, *J. Chem. Soc., Dalton Trans.*, **1979**, 1220.

6) J. Crea, R. Digiusto, S. F. Lincoln, and E. H. Williams, *Inorg. Chem.*, **16**, 2825 (1977).

7) A. M. Hounslow, S. F. Lincoln, P. A. Marshall, and E. H. Williams, *Aust. J. Chem.*, **34**, 2543 (1981).

8) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," Benjamin, London (1974).

9) H. Doine, Y. Ikeda, H. Tomiyasu, and H. Fukutomi, *Bull. Chem. Soc. Jpn.*, **56**, 1989 (1983).

10) G. H. Honan, S. F. Lincoln, and E. H. Williams, *Inorg. Chem.*, **17**, 1855 (1978).

11) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Reinhold, Dover (1950).

12) Unpublished data. TMP=Trimethyl phosphate.

13) a) R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965); b) R. S. Drago, *Coord. Chem. Rev.*, **33**, 252 (1980).

14) V. Gutmann and R. Schmidt, *Coord. Chem. Rev.*, **12**, 263 (1974).

15) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).