Kinetic Studies of the Ligand Substitution Reaction of Some New Uranyl Schiff Base Complexes with Tri-*n*-butylphosphine

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ABSTRACT: Kinetics of the substitution reaction of solvent molecule in uranyl(VI) Schiff base complexes by tri-*n*-butylposphine as the entering nucleophile in acetonitrile at 10–40°C was studied spectrophotometrically. The second-order rate constants for the substitution reaction of the solvent molecule were found to be $(8.8 \pm 0.5) \times 10^{-3}$, $(5.3 \pm 0.2) \times 10^{-3}$, $(7.5 \pm 0.3) \times 10^{-3}$, $(6.1 \pm 0.3) \times 10^{-3}$, $(13.5 \pm 1.6) \times 10^{-3}$, $(13.2 \pm 0.9) \times 10^{-3}$, $(52.9 \pm 0.2) \times 10^{-3}$, and $(8.1 \pm 0.6) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at 40°C for [UO₂(Schiff base)(CH₃CN)], where Schiff base = L1–L8, respectively. In a temperature dependence study, the activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ for the reaction of PBu₃, the span of k_2 values and the large negative values of the activation entropy, an associative (A) mechanism is deduced for the solvent substitution. By comparing the second-order rate constants $k_{2,}$ it was concluded that the steric and the electronic properties of the complexes were important for the rate of the reactions. © 2013 Wiley Periodicals, Inc. Int J Chem Kinet 1–8, 2013

INTRODUCTION

Schiff base complexes have remained an important area of research because of their simple synthesis, versatility, and diverse range of applications in designing molecular ferromagnets [1], polymerization [2], catalysis [3–5], and as liquid crystals [6,7]. They also show broad biological activity [8–13].

Unsymmetrical Schiff base ligands have clearly offered many advantages over their symmetrical counterparts in the elucidation of the geometry of the metal ion binding sites in the metallo-proteins and the enzymes and the selectivity of the natural systems with synthetic materials [14].

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Interest in the coordination chemistry of uranium has recently increased owing to diversity of their structures and possible applications in nuclear industry, catalysis, anion and neutral molecule sensing, and small molecule activation [15–19]. These applications are causing less specialized and easier-to-appreciate motivation for carrying out actinide-related chemical research [20].

Ligand field effects in most d-transition elements favor an arrangement where the equatorial ligands are arranged in an almost square-planar geometry. But the much smaller ligand field effects in the f-block elements in combination with a much larger ionic size results in a different geometry for lanthanoid and actinoid elements [21-23]. This is further enhanced by the presence of the particularly strong, trans O=U=O apical bonds. The kinetic stabilization of the U=O bonds in uranyl complexes promotes an additional ligand coordination which typically occurs in the equatorial plane of the linear dioxo unit [24]. This unusual coordination geometry indicates that the pathway for ligand substitution reactions might be located in this plane, a very different situation from those encountered in most other coordination geometries.

The variation of the magnitudes of ΔH^{\neq} and ΔS^{\neq} , and the sign of the latter parameter within a series of similar ligand substitution reactions, can give a guide to mechanistic change. Thus, in reactions with an associative mechanism ΔH^{\neq} has smaller magnitudes compared with a dissociative one and ΔS^{\neq} tends to have negative and positive values for an associative and dissociative mechanism, respectively [25].

This paper investigates the kinetics and mechanism of solvent substitution in the equatorial plane by PBu_3 and considers the electronic and the steric effects on the rate of substitution reactions.

MATERIALS

All the materials were purchased commercially and used without further purification.

EXPERIMENTAL

All of the scanning UV–vis spectra were recorded on a Perkin–Elmer Lambda 2 spectrophotometer equipped with a Lauda-ecoline-RE 104 thermostat.

Schiff bases and uranyl complexes (Scheme 1) were synthesized by the following procedure.

Synthesis of the Ligands. All the tetradentate Schiff base ligands (L1–L8) were prepared by the condensation of diamines (1 mmol) and aldehydes (2 mmol) in



 $3 = H, 4 = H, 5 = H \longrightarrow [UO_2(L1)(CH_3CN)]$ $3 = OMe, 4 = H, 5 = H \longrightarrow [UO_2(L2)(CH_3CN)]$ $3 = H, 4 = OMe, 5 = H \longrightarrow [UO_2(L3)(CH_3CN)]$ $3 = H, 4 = H, 5 = OMe \longrightarrow [UO_2(L4)(CH_3CN)]$ $3 = H, 4 = H, 5 = Br \longrightarrow [UO_2(L5)(CH_3CN)]$ $3 = H, 4 = H, 5 = C1 \longrightarrow [UO_2(L6)(CH_3CN)]$



Scheme 1 Structural representations of the uranyl Schiff base complexes.

methanol (25 mL). The mixture was refluxed for about 5 h. The products were washed with methanol and diethyl ether. All the Schiff base ligands were dried at 50° C in vacuum.

Synthesis of the Uranyl Complexes. The uranyl complexes were synthesized by the condensation of Schiff base ligands (1 mmol) and uranyl acetate (1 mmol)





in methanol (25 mL). The mixture was refluxed for about 5 h in a 1:1 molar ratio. After being cooled, the product was precipitated and filtered; then washed with methanol (3 mL) and diethyl ether (3 mL). All the Schiff base complexes were dried at 50° C in a vacuum.

Synthesis of the Kinetic Product: $[UO_2(L7)(PBu_3)]$. PBu₃ (0.078 mL) was added to a refluxing solution of UO₂(L7)(solvent) in acetonitrile (25 mL) (1:1 molar ratio). The mixture was refluxed for 10 h under nitrogen atmosphere. Temperature was controlled at about 60°C. The product was characterized by different methods, and it was understood that PBu₃ was replaced the coordinated solvent.

[UO₂(L7)(PBu₃)]: Yield: 54%, Color: orange, mp >250°C, Anal. Found (Calcd): C₃₇H₄₇N₂O₄PU. 0.5H₂O (1): C, 51.62 (51.57); H, 5.42 (5.61); N, 3.41 (3.25). IR (KBr, cm⁻¹): 3429 (ν_{O-H}) (MeOH), 2869– 3055 (ν_{C-H}), 1612 ($\nu_{C=N}$), 1542 ($\nu_{C=C}$), 895 ($\nu_{U=O}$), 640 (ν_{U-N}), 463 (ν_{U-O}). ¹H NMR (250 MHz, DMSOd₆, room temperature): δ (ppm) = 0.77–0.97 (m, 9H, CH₃) (PBu₃), 1.26–1.48 (m, 18H, CH₂) (PBu₃), 1.54– 1.61 (d, 3H, CH₃^e), 4.63–4.77 (m, 2H, CH₂^c), 5.14 (m, 1H, CH^d), 7.25–8.36 (m, 12H, ArH), 10.25 (s, 1H, H^bC=N), 10.34 (s, 1H, H^aC=N). UV–vis. (acetonitrile): λ_{max} (nm), ε (M⁻¹ cm⁻¹) = 245 (22166), 323 (5145), 366 (sh), 404 (sh).

Kinetic Studies. A solution of the uranyl complexes with specific concentration $(2.5-5) \times 10^{-5}$ M in acetonitrile was prepared. 2.5 mL of each complex was poured in a cell, and a known excess concentration of PBu₃ solution in acetonitrile was added by using a microsyringe. After rapid stirring by a microsyringe,

the absorbance in the UV–vis region was monitored with time. The kinetics was followed at a wavelength of maximum absorbance, where the difference in the absorbance between the substrate and the product was the largest (λ_{max}). This wavelength was different for each complex.

It was found that the uranyl complexes have a pentagonal-bipyramidal geometry with an axial O=U=O moiety [26,27]. When PBu₃ was added to the solution of the complex as a nucleophile, it occupies the sixth position in the equatorial plane as a rate-determining step, then the solvent molecule is removed in a fast step. This was confirmed by synthesizing [UO₂(L7)(PBu₃)] as one of the kinetic product, separately.

The kinetics was followed as described in the following reaction:

> $[UO_2(Schiff base)(CH_3CN)] + PBu_3$ $\rightarrow [UO_2(Schiff base)(PBu_3)] + CH_3CN$

PBu₃ with the excess concentration at least (1:10 ratio) was added to the uranyl complex solution. Therefore, the kinetics was followed under pseudo–first-order conditions. The rate law was according to Eq. (1):

$$R = k_{\rm obs}[\rm Complex] \tag{1}$$

$$k_{\rm obs} = k_2 [\rm PBu_3] + k_1 \tag{2}$$

where k_1 is the first-order rate constant for a solvent path (Scheme 2, path 2), and k_2 is the second-order rate constant (Scheme 2, path 1).



Figure 1 Plot of $\ln[(A_0 - A_\infty)/(A_t - A_\infty)]$ versus t(s) for $[UO_2(L3)(CH_3CN)]$ at 40.0°C.



Figure 2 Absorption spectra of $[UO_2(L6)(CH_3CN)]$ with PBu₃ at 20.0°C in CH₃CN with the isosbestic points. Time interval: 1 min.

The pseudo-first-order rate constants were calculated by fitting the data to Eq. (3):

$$\ln[(A_0 - A_\infty)/(A_t - A_\infty)] = k_{\text{obs}}t \tag{3}$$

(where A_t is absorbance at time t, A_0 is absorbance at t = 0, and A_∞ is absorbance at $t = \infty$) by means of a linear least-squares computer program (Fig. 1). As an example, the variation of the electronic spectra for $[UO_2(L3)(CH_3CN)]$ reacted with the excess concentration of PBu₃ solution at 20.0°C in CH₃CN is shown in Fig. 2.

The second-order rate constants k_2 (M⁻¹ s⁻¹) were obtained from the slope of the linear plots of k_{obs} versus [PBu₃]. Figure 3 shows plots of k_{obs} versus [PBu₃] for [UO₂(L3)(CH₃CN)] at different temperatures in CH₃CN. k_{obs} and k_2 values for all the systems are presented in Tables I–VIII.



Figure 3 Plots of k_{obs} versus [PBu₃] for [UO₂(L3) (CH₃CN)] at different temperatures.

The activation parameters of the studied systems were calculated by using the Eyring equation:

$$\ln (k_2/T) = -\Delta H^{\#}/RT + \Delta S^{\#}/R + 23.8 \quad (4)$$

 $\Delta H^{\#}$ and $\Delta S^{\#}$ values were obtained from plots of ln(k_2/T) versus 1/T at four different temperatures in the range 10.0–40.0 (±0.1)°C. The Eyring plot for the reaction of [UO₂(L3)(CH₃CN)] with PBu₃ is shown in Fig. 4.

 $\Delta G^{\#}$ values were calculated using Eq. (5):

$$\Delta G^{\#} = \Delta H^{\#} - T \Delta S^{\#} \tag{5}$$

Table IX shows the activation parameters $\Delta G^{\#}$ (at 40.0°C), $\Delta H^{\#}$, and $\Delta S^{\#}$ for the reaction of the uranyl complexes with PBu₃ in CH₃CN.

RESULTS AND DISCUSSION

 k_2 values for different complexes [UO₂(L)(CH₃CN)], where L = L1–L8 with PBu₃ at 40.0°C, are as follows:

	L1	L2	L3	L4	L5	L6	L7	L8
k_2	8.8	5.3	7.5	6.1	13.5	13.2	52.9	88.1
$(\times 10^3 \text{ M}^{-1} \text{ s}^{-1})$) (0.5)	(0.2)	(0.3)	(0.3)	(1.6)	(0.0)	(0.2)	(0.6)

By comparing the rate constants (k_2) and the activation parameters, it can be concluded that two parameters are important in the rate of substitution reactions:

 The first parameter is the electronic factor. The electron-withdrawing groups such as Br and Cl make the uranium center more positive; therefore, the rate of the substitution reaction increases. The electron-releasing groups decrease it.

Table I Pseudo–First-Order Rate Constants $10^4 k_{obs}^a$, $k_1 (\times 10^4 s^{-1})$, and $k_2 (\times 10^3 M^{-1} s^{-1})$ for the Reaction of $[UO_2(L1)(CH_3CN)]$ with PBu₃ at Different Temperatures

T .			[]						
(°C)	1.2	1.8	2.4	3	3.6	4.2	4.8	$k_1 (\times 10^4 \text{ s}^{-1})$	$k_2 (\times 10^3 \text{ M}^{-1} \text{ s}^{-1})$
10.0	6.7 (0.3)	7.0 (0.3)	7.1 (0.3)	7.3 (0.3)	7.4 (0.3)	7.6 (0.3)	7.8 (0.3)	6.4 (0.1)	2.9 (0.1)
20.0	8.8 (0.5)	9.0 (0.6)	9.3 (0.7)	9.5 (0.6)	9.8 (0.7)	10.0 (0.1)	10.4 (0.1)	8.2 (0.1)	4.3 (0.2)
30.0	9.8 (0.1)	10.2 (0.1)	10.5 (0.1)	10.7 (0.1)	11.1 (0.8)	11.4 (0.1)	11.8 (0.1)	9.2 (0.1)	5.4 (0.2)
40.0	10.4 (0.1)	10.9 (0.2)	11.1 (0.2)	11.8 (0.2)	12.4 (0.2)	13.1 (0.2)	13.4 (0.3)	9.2 (0.2)	8.8 (0.5)

 $[Complex] = 5.0 \times 10^{-5} \text{ M}, \lambda_{max} = 245.$

^aThe numbers in parentheses are the standard deviations.

Table II Pseudo–First-Order Rate Constants $10^4 k_{obs}^a$, k_1 (× 10^4 s⁻¹), and k_2 (× 10^3 M⁻¹ s⁻¹) for the Reaction of [UO₂(L2)(CH₃CN)] with PBu₃ at Different Temperatures

T ([]						
(°C)	1.2	1.8	2.4	3	3.6	4.2	4.8	$k_1 \ (\times 10^4 \ \mathrm{s}^{-1})$	$k_2 (\times 10^3 \text{ M}^{-1} \text{ s}^{-1})$
10.0	3.0 (0.0)	3.2 (0.0)	3.3 (0.0)	3.5 (0.1)	3.6 (0.0)	3.8 (0.1)	3.9 (0.1)	2.8 (0.1)	2.2 (0.1)
20.0	4.4 (0.1)	4.6 (0.1)	4.7 (0.1)	4.8 (0.1)	5.0 (0.1)	5.2 (0.1)	5.5 (0.1)	4.0 (0.1)	2.9 (0.2)
30.0	5.3 (0.2)	5.5 (0.3)	5.8 (0.4)	6.0 (0.4)	6.3 (0.0)	6.5 (0.5)	6.7 (0.5)	4.8 (0.3)	3.9 (0.1)
40.0	5.8 (0.6)	6.0 (0.8)	6.4 (1.0)	6.7 (1.0)	7.1 (1.0)	7.3 (1.0)	7.7 (1.0)	5.1 (0.1)	5.3 (0.2)

 $[Complex] = 3.0 \times 10^{-5} \text{ M}, \lambda_{max} = 244.$

^{*a*}The numbers in parentheses are the standard deviations.

Table III Pseudo–First-Order Rate Constants $10^4 k_{obs}{}^a$, k_1 (×10⁴ s⁻¹), and k_2 (×10³ M⁻¹ s⁻¹) for the Reaction of [UO₂(L3)(CH₃CN)] with PBu₃ at Different Temperatures

m ,			[]						
(°C)	1.2	2.1	3.0	3.9	4.8	5.7	6.6	$k_1 \ (\times 10^4 \ \mathrm{s}^{-1})$	$k_2 (\times 10^3 \text{ M}^{-1} \text{ s}^{-1})$
10.0	2.7 (0.0)	3.1 (0.0)	3.3 (0.2)	3.4 (0.1)	3.7 (0.1)	3.9 (0.2)	4.2 (0.3)	2.5 (0.1)	2.6 (0.2)
20.0	3.7 (0.2)	4.0 (0.4)	4.3 (0.1)	4.5 (0.0)	4.8 (0.2)	5.2 (0.2)	5.5 (0.3)	3.2 (0.1)	3.6 (0.1)
30.0	4.3 (0.0)	4.8 (0.1)	5.5 (0.0)	6.0 (0.3)	6.5 (0.3)	6.8 (0.4)	7.4 (0.5)	3.6 (0.1)	5.8 (0.2)
40.0	5.8 (0.1)	6.7 (0.3)	7.3 (0.4)	7.9 (0.3)	8.7 (0.6)	9.2 (0.8)	9.9 (1.1)	5.0 (0.1)	7.5 (0.3)

 $[Complex] = 3.0 \times 10^{-5} \text{ M}, \lambda_{max} = 258.$

^aThe numbers in parentheses are the standard deviations.

Table IV Pseudo–First-Order Rate Constants $10^4 k_{obs}{}^a$, $k_1 (\times 10^4 \text{ s}^{-1})$, and $k_2 (\times 10^3 \text{ M}^{-1} \text{ s}^{-1})$ for the Reaction of $[UO_2(L4)(CH_3CN)]$ with PBu₃ at Different Temperatures

			[]						
(°C)	1.2	1.8	2.4	3	3.6	4.2	4.8	$k_1 \; (\times 10^4 \; \mathrm{s}^{-1})$	$k_2 (\times 10^3 \text{ M}^{-1} \text{s}^{-1})$
10.0	5.6 (0.1)	5.7 (0.3)	5.9 (0.2)	6.1 (0.1)	6.2 (0.0)	6.3 (0.2)	6.4 (0.4)	5.3 (0.1)	2.3 (0.1)
20.0	9.9 (0.4)	10.1 (0.1)	10.4 (0.0)	10.6 (0.1)	10.7 (0.3)	10.9 (0.5)	11.0 (0.8)	9.6 (0.1)	3.0 (0.2)
30.0	11.5 (0.1)	11.9 (0.1)	12.1 (0.3)	12.4 (0.4)	12.7 (0.4)	12.9 (0.7)	13.3 (0.8)	10.9 (0.1)	4.8 (0.2)
40.0	17.5 (0.4)	18.0 (0.3)	18.4 (0.6)	18.7 (0.4)	18.9 (0.9)	19.4 (1.1)	19.8 (0.9)	16.8 (0.1)	6.1 (0.3)

 $[Complex] = 2.5 \times 10^{-5} \text{ M}, \lambda_{max} = 254.$

^aThe numbers in parentheses are the standard deviations.

2. The second parameter is the steric hindrance. As the mechanism is an associative one, the steric hindrance plays an important role in producing the appropriate intermediate with a higher coordination number. This effect has been clearly observed by comparing k_2 values of the L2 complex with L3 and L4 complexes (Tables II–IV). Since the methoxy groups in L2 are close to the

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(°C)	1.2	1.8	2.4	3	3.6	4.2	4.8	$k_1 (\times 10^4 \text{ s}^{-1})$	$k_2 (\times 10^3 \text{ M}^{-1} \text{ s}^{-1})$
10.0	1.5 (0.0)	1.7 (0.0)	1.8 (0.1)	2.1 (0.0)	2.4 (0.2)	2.6 (0.1)	2.7 (0.1)	1.0 (0.1)	3.6 (0.2)
20.0	2.5 (0.0)	3.0 (0.1)	3.3 (0.0)	3.4 (0.3)	3.8 (0.1)	4.0 (0.2)	4.5 (0.3)	2.0 (0.1)	5.0 (0.4)
30.0	4.9 (0.0)	5.4 (0.0)	5.9 (0.1)	6.2 (0.1)	6.6 (0.1)	7.2 (0.2)	8.0 (0.2)	3.9 (0.2)	8.1 (0.5)
40.0	7.8 (0.0)	8.0 (0.1)	9.2 (0.1)	10.2 (0.3)	10.9 (0.2)	11.9 (0.3)	12.2 (0.4)	5.5 (0.2)	13.5 (1.6)

Table V Pseudo–First-Order Rate Constants $10^4 k_{obs}^a$, k_1 (× 10^4 s⁻¹), and k_2 (× 10^3 M⁻¹ s⁻¹) for the Reaction of $[UO_2(L5)(CH_3CN)]$ with PBu₃ at Different Temperatures

 $[Complex] = 5.0 \times 10^{-5} \text{ M}, \lambda_{max} = 420.$

^aThe numbers in parentheses are the standard deviations.

Table VI Pseudo–First-Order Rate Constants $10^4 k_{obs}{}^a$, k_1 (×10⁴ s⁻¹), and k_2 (×10³ M⁻¹ s⁻¹) for the Reaction of [UO₂(L6)(CH₃CN)] with PBu₃ at Different Temperatures

-			[P] (× 10^{2} M					
Temperature (°C)	1.2	1.8	2.4	3	3.6	4.2	4.8	$k_1 (\times 10^4 \text{ s}^{-1})$	$k_2 (\times 10^3 \text{ M}^{-1} \text{ s}^{-1})$
10.0	2.6 (0.1)	2.9 (0.4)	3.1 (0.0)	3.2 (0.4)	3.4 (0.3)	3.6 (0.0)	3.9 (0.0)	2.2 (0.1)	3.3 (0.2)
20.0	4.1 (0.2)	4.5 (0.1)	4.9 (0.2)	5.2 (0.3)	5.4 (0.1)	5.6 (0.4)	6.1 (0.1)	3.5 (0.1)	5.2 (0.3)
30.0	5.4 (0.4)	5.7 (0.4)	6.4 (0.3)	6.9 (0.1)	7.5 (0.2)	7.8 (0.5)	8.1 (0.5)	4.4 (0.2)	8.0 (0.4)
40.0	5.3 (0.8)	6.7 (0.4)	7.3 (0.2)	7.8 (0.1)	8.6 (0.0)	9.0 (0.1)	10.5 (0.8)	4.5 (0.3)	13.2 (0.0)

 $[Complex] = 3.0 \times 10^{-5} \text{ M}, \lambda_{max} = 249.$

^{*a*}The numbers in parentheses are the standard deviations.

Table VII Pseudo–First-Order Rate Constants $10^4 k_{obs}{}^a$, $k_1 (\times 10^4 \text{ s}^{-1})$, and $k_2 (\times 10^3 \text{ M}^{-1} \text{ s}^{-1})$ for the Reaction of $[UO_2(L7)(CH_3CN)]$ with PBu₃ at Different Temperatures

			[]	P] (× 10^2 M	1)				
Temperature (°C)	1.2	1.8	2.4	3.0	3.6	4.2	4.8	$k_1 (\times 10^4 \text{ s}^{-1})$	$k_2 (\times 10^3 \text{ M}^{-1} \text{ s}^{-1})$
10.0	9.4 (0.5)	9.9 (0.4)	10.3 (0.5)	10.8 (0.2)	11.1 (0.1)	12.5 (0.1)	12.7 (0.1)	8.1 (0.1)	9.5 (0.2)
20.0	11.5 (0.1)	12.0 (0.1)	12.9 (0.0)	13.5 (0.1)	14.2 (0.0)	15.0 (0.1)	16.1 (0.2)	9.7 (0.2)	12.9 (0.0)
30.0	16.8 (0.1)	17.0 (0.1)	19.7 (0.1)	21.3 (0.1)	23.5 (0.1)	24.7 (0.1)	28.0 (0.1)	10.9 (0.1)	31.4 (0.2)
40.0	17.8 (0.1)	21.0 (0.1)	23.3 (0.1)	25.9 (0.1)	29.6 (0.1)	33.5 (0.0)	37.0 (0.0)	12.1 (0.3)	52.9 (0.2)

 $[Complex] = 5.0 \times 10^{-5} \text{ M}, \lambda_{max} = 422.$

^aThe numbers in parentheses are the standard deviations.

Table VIII Pseudo–First-Order Rate Constants $10^4 k_{obs}^a$, $k_1 (\times 10^4 s^{-1})$, and $k_2 (\times 10^3 M^{-1} s^{-1})$ for the Reaction of $[UO_2(L8)(CH_3CN)]$ with PBu₃ at Different Temperatures

_			[]	P] (× 10^2 M	1)				
Temperature (°C)	0.6	1.2	1.8	2.4	3.0	3.6	4.2	$k_1 \; (\times 10^4 \; \mathrm{s}^{-1})$	$k_2 (\times 10^3 \text{ M}^{-1} \text{ s}^{-1})$
10.0	11.6 (0.1)	12.5 (0.0)	13.1 (0.3)	14.7 (0.2)	15.2 (0.2)	17.1 (0.4)	17.8 (0.1)	10.3 (0.0)	17.8 (0.4)
20.0	21.0 (0.0)	25.5 (0.1)	26.6 (0.0)	29.0 (0.2)	32.0 (0.2)	34.2 (0.3)	35.1 (0.4)	19.7 (0.1)	38.7 (0.3)
30.0	34.6 (0.4)	37.1 (0.7)	39.9 (0.3)	43.0 (0.5)	51.6 (0.6)	57.7 (0.5)	59.7 (0.6)	27.9 (0.2)	76.3 (0.9)
40.0	38.1 (0.2)	40.4 (0.0)	45.7 (0.5)	49.3 (0.7)	55.7 (0.3)	62.8 (0.3)	69.2 (0.7)	30.4 (0.1)	88.1 (0.6)

 $[Complex] = 5.0 \times 10^{-5} \text{ M}, \lambda_{max} = 419.$

^aThe numbers in parentheses are the standard deviations.



Figure 4 The Eyring plot for the reaction of $[UO_2(L3) (CH_3CN)]$ with PBu₃.

reaction center, therefore k_2 values are smaller compared with L3 and L4.

This effect has also been observed by comparing k_2 values for the L8 complex with the L7 complex (Tables VII and VIII). The methyl group in the L7 complex acts as an electron-releasing group; therefore, the k_2 values for L7 complex are smaller.

By comparing k_2 values for the L6 complex with the L5 one (Tables V and VI), it is clear that the two complexes approximately have the same k_2 values, because of the similarity of the steric hindrance and the electronic property.

By comparing the rate constants and the activation parameters, the following conclusions were reached:

- When the temperature is increased, the secondorder rate constant is increased too.
- 2. The low $\Delta H^{\#}$ values and the large negative $\Delta S^{\#}$ values are compatible with an associative mechanism, i.e., PBu₃ as a nucleophile entered in a rate-determining step with the k_2 rate constant then the solvent left the intermediate complex in a fast step. The uranyl complexes have a pentagonal bipyramidal structure with the trans-

UO₂ moiety in the axial positions. In the uranyl tetradentate Schiff base complexes, the fifth position of the equatorial plane is occupied by the solvent molecule [28], which is weakly coordinated to the UO₂ center. In a substitution reaction, PBu₃ can easily replace the solvent molecule (Scheme 2). The k_2 values obtained in this study were compared with our previous work [29]. It is clear that although the complexes were different in structure but the overall results were similar, i.e., the mechanism was an associative one.

CONCLUSIONS

The kinetics of some uranyl Schiff base complexes with PBu₃ was investigated spectrophotometrically in the UV–vis region. The span of k_2 values, the low $\Delta H^{\#}$ values, and the large negative $\Delta S^{\#}$ values revealed that the mechanism of the substitution reaction is an associative one.

By considering the electronic and the steric effects of the uranyl complexes, the following trends are observed:

- 1. Electronic effect:
 - $\circ [UO_2(L5)(CH_3CN)] > [UO_2(L1)(CH_3CN)]$ $> [UO_2(L4)(CH_3CN)].$
- 2. Steric hindrance:
 - $\circ [UO_2(L3)(CH_3CN)] > [UO_2(L4)(CH_3CN)]$ $> [UO_2(L2) (CH_3CN)].$
 - $[UO_2(L8)(CH_3CN)] > [UO_2(L7)(CH_3CN)].$
- 3. Electronic and steric effect:
 - $[UO_2(L5)(CH_3CN)] \approx [UO_2(L6)(CH_3CN)]$

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$\Delta G^{\#b}$ (kJ mol ⁻¹)	$\Delta S^{\#} (\mathbf{J} \mathbf{K}^{-1} \mathbf{mol}^{-1})$	$\Delta H^{\#} (\times 10^4 \text{ kJ mol}^{-1})$	Complexes
65.6 (3.0)	-209.7 (9.6)	2.4 (0.3)	[UO ₂ (L1)(CH ₃ CN)]
71.0 (1.0)	-226.8 (3.3)	2.0 (0.1)	$[UO_2(L2)(CH_3CN)]$
64.8 (2.5)	-206.9 (7.9)	2.5 (0.2)	$[UO_2(L3)(CH_3CN)]$
67.6 (2.1)	-215.9 (6.6)	2.2 (0.2)	$[UO_2(L4)(CH_3CN)]$
57.9 (2.8)	-185.1 (9.0)	3.0 (0.3)	$[UO_2(L5)(CH_3CN)]$
57.0 (1.4)	-182.2(4.5)	3.1 (0.1)	$[UO_2(L6)(CH_3CN)]$
42.7 (6.4)	-136.5 (2.1)	4.2 (0.6)	$[UO_2(L7)(CH_3CN)]$
44.6 (0.9)	-142.5 (2.6)	3.8 (0.5)	[UO ₂ (L8)(CH ₃ CN)]

Table IX Activation Parameters^{*a*} $\Delta G^{\#}$, $10^{4} \Delta H^{\#}$, and $\Delta S^{\#}$ for the Reaction of Uranyl Complexes with PBu₃ in CH₃CN

 $^{\it a} The numbers in parentheses are the standard deviations.$

^bCalculated at 40.0°C.

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