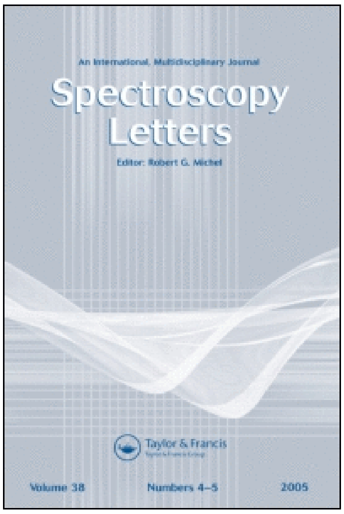

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Comparison of the Kinetics of the Exchange Mechanism of the Thallium Ion with 18C6 and with Pentaglyme in Acetonitrile Solutions

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COMPARISON OF THE KINETICS OF THE EXCHANGE MECHANISM OF THE THALLIUM ION WITH 18C6 AND WITH PENTAGLYME IN ACETONITRILE SOLUTIONS

Key Word: NMR; Kinetics; Macrocyclic complexes; Pentaglyme; Acetonitrile; Thallium(I).

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ABSTRACT

In acetonitrile solutions, the exchange reaction is bimolecular in the Tl^+ + 18C6 system, while in the Tl^+ + pentaglyme system the associative-dissociative and the bimolecular mechanisms coexist at room temperature and the bimolecular exchange reaction dominates at 263° K. For the bimolecular mechanism in the case of Tl^+ + 18C6 and the associative-dissociative mechanism in the case of Tl^+ + pentaglyme, the activation energies of the exchange reactions change with temperature. At 298° K, in the Tl^+ + 18C6 system the activation energy for the bimolecular exchange reaction is $\simeq$ 2 $kcal.mol^{-1}$ and exchange rate constant (k_1) is $(4.1 \pm 0.1) \times 10^7\ s^{-1}mol^{-1}$; in the Tl^+ + pentaglyme system, the activation energy for the associative-dissociative exchange reaction is $\simeq$ 5 $kcal\ mol^{-1}$ and the decomplexation rate constant (k_{-2}) is $(2.2 \pm 0.4) \times 10^5\ s^{-1}$. The activation energy for the bimolecular exchange in the Tl^+ + pentaglyme system was determined to be 3.00 ± 0.05 $kcal.mol_{-1}$ and the exchange rate constant $(3.0 \pm 0.1) \times 10^8\ s^{-1}\ mol^{-1}$.

INTRODUCTION

The "Macrocyclic Effect", i.e. the increase in the stability of a metal complex when a linear polyether ligand is replaced by its cyclic analogue,[1-6] is most often discussed in terms of the entropy or the enthalpy of complexation. However, at this time it is still not clear which of the above is the dominating factor for the enhanced stabilities of the macrocyclic polyether complexes over the linear polyether complexes. The effect of kinetics on the macrocyclic effect has been largely ignored. In particular, while many papers discuss kinetics of complexation reactions involving macrocyclic and nonmacrocyclic ligands,[7] except for the work of Tuemmler *et al.*[8], there is very little information on the complexation kinetics involving linear analogues of crown ethers. We therefore undertook a comparative NMR study of the exchange mechanisms and kinetics of thallium(I) complexes with 18-crown-6 and its linear analogue, pentaglyme, in acetonitrile solutions.

EXPERIMENTAL PART

NMR spectra of ^{205}Tl were obtained on a Bruker WH-180 FT spectrometer equipped with a temperature control unit for variable temperature operations. The spectrometer is operating at a field of 42.27 kG, and for the ^{205}Tl nucleus, the frequency of 103.88 MHz. Chemical shifts of ^{205}Tl were referenced to that of 0.1M $TlClO_4$ solutions in D_2O corrected for the differences in bulk magnetic susceptibilities of sample solutions and D_2O of the reference solution.[9]

Linewidths were measured by fitting a Lorentzian function to the resonance lines. A complete NMR lineshape analysis technique was used to determine the kinetic parameters for the exchange between the solvated and complexed cation sites. Equations were of similar format to those used by Cahen *et al.*[10] Some modifications were made to include exponential line broadening and delay time effect on the spectra.[11] A nonlinear least-squares program KINFIT[12] was used to fit the spectra to NMR exchange equations in order to extract the mean lifetime, τ, for each system at several temperatures.

Acetonitrile (AN) (Specto purity, J.T. Baker) was of spectra grade and contained less than 0.0001% water; it was not further purified except for being stored over freshly activated molecular sieves before use. Thallium(I) perchlorate (K&K Chemical Company) was recrystallized from deionized water and then dried at 120°C for three days. Pentaglyme was synthesized and purified by a method described by Okoroafor.[13]

RESULTS AND DISCUSSIONS

Assuming the formation of a 1:1 complex, $M^+ + L \rightleftharpoons ML^+$, if the concentrations of the ligand L are smaller than the total concentrations of the salt, metal ions undergo exchange between the uncomplexed and complexed sites, which usually occurs by one of two mechanisms shown below:[14,15]

$$\text{(I)} \qquad {}^{*}M^+ + ML^+ \xrightleftharpoons{k_1} {}^{*}ML^+ + M^+$$

$$\text{(II)} \qquad M^+ + L \xrightleftharpoons[k_{-2}]{k_2} ML^+$$

where I and II are the bimolecular and the associative-dissociative exchange mechanisms respectively.

Table 1. The exchange rate constants(k_1) of the thallium ion in the system of $TlClO_4$ with pentaglyme in acetonitrile via the bimolecular exchange mechanism and the exchange or the decomplexation rate constant(k_d or k_{-2}) via the associative-dissociative mechanism, $TlClO_4$:0.01M

Temperature (k)	$k_1 \times 10^{-8}$ $M^{-1} \cdot s^{-1}$	$k_{-2} \times 10^{-5}$ s^{-1}
308	3.5 ± 0.1	3.1 ± 0.4
298	3.0 ± 0.1	2.2 ± 0.4
293	2.7 ± 0.1	1.9 ± 0.4
288	2.5 ± 0.2	1.6 ± 0.4
283	2.3 ± 0.3	1.3 ± 0.5
278	2.1 ± 0.2	1.0 ± 0.5
273	1.9 ± 0.2	0.8 ± 0.5
263	1.5 ± 0.2	0.4 ± 0.6

It was found that for the Tl^+ + 18C6 system the bimolecular exchange reaction predominates throughout the temperature range studied, while for the Tl^+ + pentaglyme system the two exchange reactions coexist at room temperature and the bimolecular one dominates at 263°K. The rate constants at different temperatures for the respective reactions for the $TlCFlO_4$ + 18C6 and $TlClO_4$ + pentaglyme systems are listed in Tables 1 and 2 respectively.

It was also observed that the Arrhenius plot (ln k_1 vs. 1/T) for the $TlClO_4$ + 18C6 system is not linear (See Figure 1). Figures 2 and 3 show the Arrhenius plots of the two exchange mechanisms for the system $TlClO_4$ + pentaglyme in acetonitrile solution. It can be

Table 2. The exchange rate constants of the thallium ion in the system of $TlClO_4$ with 18C6 in acetonitrile, $TlClO_4$:0.01M

Temperature (k)	$k_1 \times 10^{-7}$ $M^{-1}s^{-1}$
278	3.7 ± 0.5
288	4.2 ± 0.4
293	4.1 ± 0.5
298	4.1 ± 0.2
303	4.4 ± 0.3
308	4.7 ± 0.4
313	5.6 ± 0.3
318	7. ± 1.
323	8. ± 2.
328	6.8 ± 0.6

seen that the Arrhenius plot is linear for the bimolecular mechanism and slightly curved for the associative-dissociative mechanism. The activation energies E_a of reactions can be obtained from the Arrhenius plots, and then the other activation kinetic parameters ($\Delta H^{\dagger}$, $\Delta G^{\dagger}$, and $\Delta S^{\dagger}$) can be calculated using Eyring transition state theory. According to the equation:

$$\ln k = A - \frac{E_a}{RT}$$

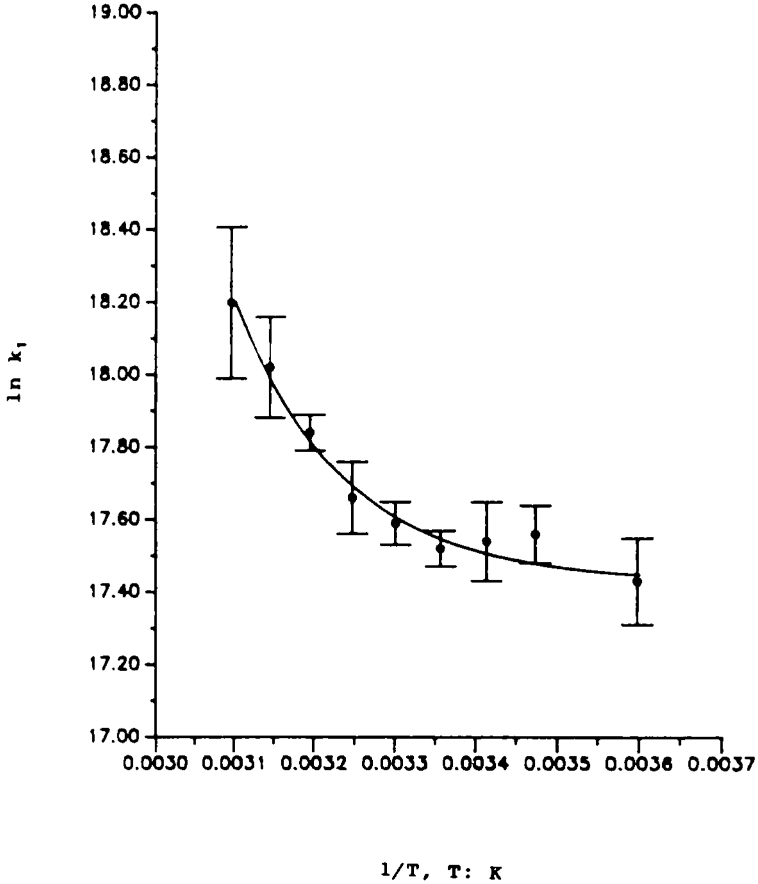

Figure 1 ln k_1 vs. 1/T for the system $TlClO_4$ + 18C6 in acetonitrile solution.
k_1: the exchange rate constant of the thallium ions by the bimolecular mechanism; T: temperature in K

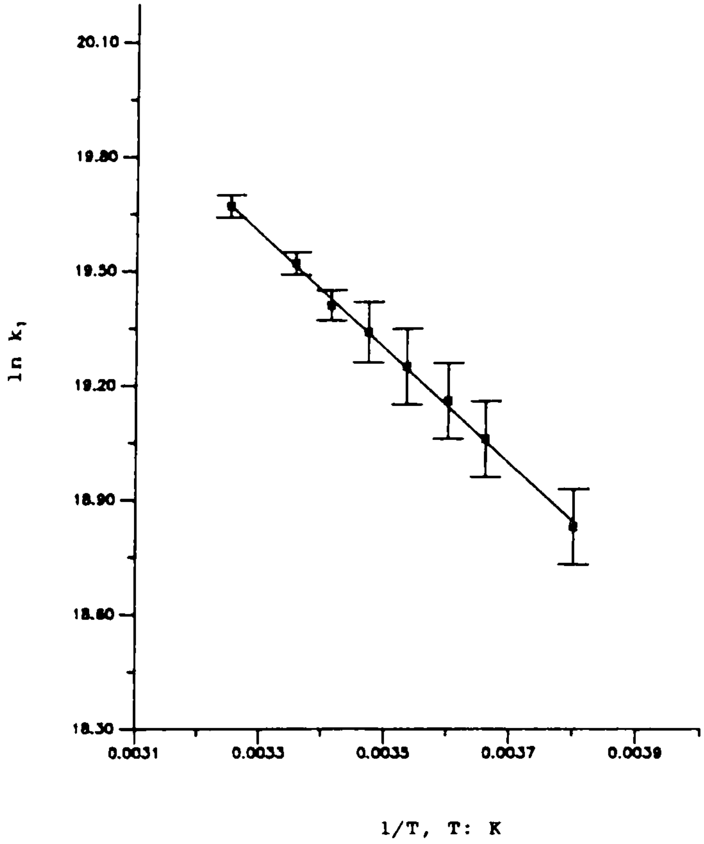

Figure 2 ln k_1 vs. 1/T for the bimolecular exchange mechanism in the system $TlClO_4$ + pentaglyme in acetonitrile solution
k_1: the exchange reaction rate constant of the thallium ions by the bimolecular exchange mechanism; T: temperature in K

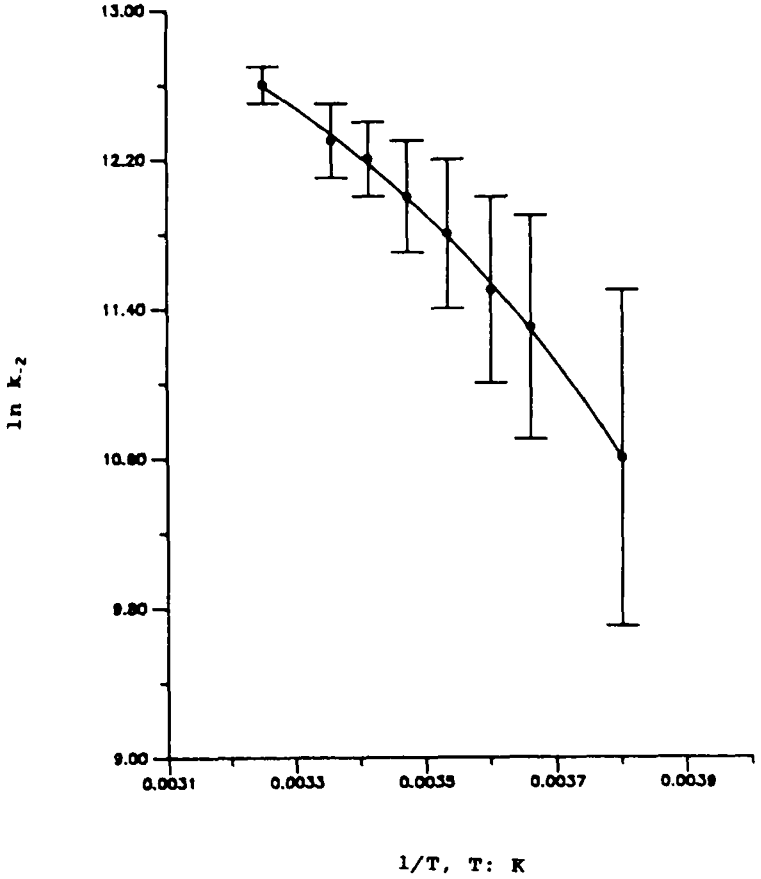

Figure 3 ln k_{-2} vs. 1/T for the associative-dissociative mechanism in the system $TlClO_4$ + pentaglyme in acetonitrile solution
k_{-2}: the exchange or the decomplexation rate constant of $TlClO_4$·Pentaglyme complex by the associative-dissociative exchange mechanism; T: temperature in K

(k is the rate constant, E_a is the activation energy of the reaction, R and T are the gas constant and the temperature respectively); ln k should be linearly dependent on 1/T. The nonlinearity of Arrhenius plots can be caused by the variation of either A or E_a, or both, with temperature. However, at this time the data are insignificant to unambiguously identify the cause.

For the $TlClO_4$ + 18C6 system, the activation energy decreases with decreasing temperature. It is $\approx$ 16 $kcal.mol^{-1}$ at 328K, $\approx$ 2 $kcal.mol^{-1}$ at 298K, and $\approx$ 0.3 $kcal.mol^{-1}$ at 278K respectively. For $TlClO_4$ + pentaglyme, system plots of ln k_1 (linear) and ln k_{-2} (nonlinear) vs. 1/T give activation energies of 3.00 ± 0.05 $kcal.mol^{-1}$ for the bimolecular exchange mechanism, and temperature dependent activation energy for the associative-dissociative mechanism ($\approx$ 5 $kcal.mol^{-1}$ at 298k and $\approx$ 11 $kcal.mol^{-1}$ at 263k). The other kinetic parameters of the exchange reactions are listed in Table 3.

The above results clearly show that the slope of the ligand has a strong influence on the complexation, decomplexation, and exchange mechanisms. In general, based on the electrostatic repulsions of the like charges and the entropy terms, the associative-dissociative mechanism is favored over the bimolecular mechanism. This preference can be changed if the charge-charge repulsion can be substantially reduced by the formation of contact-ion pairs, or the existance of strong solvent-cation interactions. The energy barrier for the decomplexation (E_a) is also determined by the easiness of the release of the ligand. If a ligand strongly interacts with a cation, the decomplexation step will be difficult, (especially in solvents of very poor solvating abilities), and the activation energy E_a will be high.

Table 3. Kinetic data for the exchange of the Tl^+ ion with 18C6 and pentaglyme in acetonitrile solutions at 298K.

Ligand	k^a	$E_a{}^b$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$
18C6	$(4.1\pm0.2) \times 10^7$	~ 2	~ 1.4	~ -19	7.06 ± 0.03
Pentaglyme[c]	$(3.0\pm0.1) \times 10^8$	3.00 ± 0.05	2.41 ± 0.05	-11.6 ± 0.2	5.88 ± 0.02
Pentaglyme[d]	$(2.2\pm0.4) \times 10^5$	~ 5	~ 4.4	~ -19	10.2 ± 0.1

[a] k: the decomplexation rate constant k_{-2} corresponding to the associative-dissociative mechanism in acetonitrile solutions with the units s^{-1} or the exchange reaction rate constant k_1 of the bimolecular exchange mechanism with the units $s^{-1}M^{-1}$;

[b] E_a, $\Delta H^\ddagger$ and $\Delta G^\ddagger$ units - kcal mol^{-1}; $\Delta S^\ddagger$ units - cal.mol^{-1} K^{-1};

[c] Bimolecular exchange mechanisn

[d] Associative-dissociative exchange mechanism

If ligands interact with cations sufficiently strongly so that the cation-cation repulsion can be reduced, it is possible that the bimolecular mechanism can still exist. In acetonitrile solutions, both the $TlClO_4$.18C6 complex and the $TlClO_4$.PG complex are relatively stable however the former is about 100 times more stable than the latter[13]. Therefore, the bimolecular mechanism becomes possible for both the Tl^+ + 18C6 and Tl^+ + pentaglyme systems. For the Tl^++ 18C6 system, the cation-ligand interactions are so strong that the bimolecular mechanism is the only exchange pathway throughout the studied temperature range. The situation for the $TlCl_4$ + PG system in acetonitrile solutions is a little different, i.e. the two exchange mechanisms coexist at room temperature while the bimolecular exchange mechanism dominates at low temperatures. In this system, the ligand-cation interaction is not as strong as that of 18C6 with Tl^+, and this interaction cannot effectively offset the cation-cation repulsion at the transition state of the bimolecular mechanism so that the associative-dissociative mechanism dominates. At low temperatures, the increase of the cation-ligand interaction can assist to decrease the cation-cation repulsion at the transition state and the bimolecular mechanism prevails.

It should be mentioned that configurations of ligands may also play an important role in determining the exchange mechanism. The crown ether 18C6 is nearly planar so that cations can approach the ring from either side. Pentaglyme is a linear ligand and it is more difficult to visualize symmetrical and simultaneous bonding of two cations to the ligand which occurs in the transition state of the bimolecular mechanism. At lower temperatures, the structure of the ligand is more rigid and more likely to take crown-ether like configurations, leading to the larger contribution of the bimolecular mechanism to the overall exchange process.

Another important factor that should be mentioned for the observed bimolecular mechanism is the charge density of the Tl^+ cation. It is known that K^+ and Tl^+ have very similar sizes (r_{K^+} = 1.33 Å, r_{Tl^+} = 1.40 Å), and therefore similar charge densities. It is known that the K^+ ion exchanges often proceeds by the bimolecular exchange mechanism.[16]

The ratio of the formation (k_2) and decomplexation (k_{-2}) reaction rate constants (mechanism II) yielded stability constant of a complex $K_f = k_2/k_{-2}$. If the exchange reactions proceed by the bimolecular mechanism, only the exchange reaction rate constants (k_1) can be determined by NMR measurement, and the complexation (k_2) and the decomplexation (k_{-2}) reaction rate constants are not obtainable. Therefore, in the Tl^+ + 18C6 and Tl^+ + pentaglyme systems, it is not possible to directly compare the complexation and decomplexation rate constants to see which of the two dominates the stability constants. the $Tl.PG^+$ complex (log K_f = 3.65 ± 0.05)[13] is less stable than the $Tl.18C6^+$ complex (log K_f = 5.8 ± 0.5)[13] and the decomplexation rate is faster for the former. The formation rate constant at 298 K for the $Tl.PG^+$ complex is 9.8×10^8 s^{-1}, as obtained by using the relationship $K_f = k_2/k_{-2}$ where K_f and k_{-2} are known. According to Tuemmler et al.,[8] the formation rate constant of the $Tl.PG^+$ complex is slower than the diffusion-controlled rate constants (10^9 to 10^{10} s^{-1}). The slower formation rate constants of linear ligands than the one expected for the diffusion-controlled processes probably results from the step-wise substitution of the solvent molecules in the solvation shells of cations. The pre-arrangement of the donor atoms of the macrocyclic ligands before complexing cations can more effectively replace the solvent molecules. It would be reasonable to expect that the complexation of the thallium ion by 18C6 is faster than the complexation by pentaglyme and may reach the diffusion-controlled limit. The faster complexation rate and the slower decomplexation rate in the Tl^+ + 18C6 system compared to the Tl^+ + pentaglyme system combine to give a 100-fold more stable complex in the case of the macrocyclic ligand.

CONCLUSIONS

By comparing the activation energies and their temperature-dependence for the exchange reactions of Tl^+ ions with 18C6 and pentaglyme, it seems that the strengths of the cation-ligand interactions and the structures of the ligand are important factors in determining the exchange mechanism. From the kinetic points of view, the bimolecular exchange reaction mechanism is not favored by the entropy factor, but the enthalpy factor is so strongly favored that it can overcome the entropy influence and the bimolecular exchange mechanism prevails for the system of $TlClO_4$ + 18C6 in acetonitrile solutions and for the $TlClO_4$ + pentaglyme system at low temperatures. Because of the bimolecular exchange mechanism in the system $TiClO_4$ + 18C6, the decomplexation rate constant of the complex cannot be obtained. Thus, we are not able to compare the two systems to conclude which factor, complexation or decomplexation, determines the macrocyclic effect in this case.

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