Pure Res. Iran.J.Chem & Chem.Eng. Oct 1987

KINETICS AND MECHANISM OF THE SUBSTITUTION OF LIGAND (UREA) OF $[Ti(ur)_6]^{3+}$ BY H_2O AND SCN^- IN ETHANOL SOLUTION.

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(Received 25th April,1987)

ABSTRACT

The kinetics of substitution of $[Ti(ur)_6]^{3+}$ by H_2O and SCN^- ion in ethanol solution have been measured spectrophotometrically by stopped- flow method.Water is a good nucleophile towards Ti(III) substrates.Even the solvent ethanol appears to be a poor ligand when compared to water.Substitution in general follows two parallel pathways : "direct" (second order) reaction,and solvolysis followed by rapid substitution (first order).Both mechanisms are important for H_2O substitution,but for SCN^- reaction is much more rapid and proceeds entirely by the "direct" route,probably because of the greater nucleophilic strength of SCN^- V.S. H_2O.

INTRODUCTION

Substitution Reactions

Substitution embraces the replacement of a ligand coordinated to a metal by a free ligand in solution or the replacement of the coordinated ion by a free metal ion.The replacement of one unidentate ligand by another is the simplest situation to envisage and this process has been used extensively to investigate the mechanism of substitution.Direct replacement appears to be rare with octahedral complexes.In this sort of complexes substitution can be multistaged ,so that at least one of the unidentate ligands will usually be a solvent molecule.In addition to this type of ligand interchange reaction,the replacement of one ligand by another without the direct intervention of solvent is also possible.

Such ligand interchange in metal complexes can occur in two ways,either by a combination of solvolysis and anation,or by simple interchange.Most of the examinations of solvolysis have been made in aqueous solution and with inert complexes since it is often easier to produce specific starting species in these cases.The relative simplicity of behaviour in aqueous solution is not usually duplicated in other solvents.

The Kinetics of Replacement Involving Unidentate ligands (1).

The rate law governing substitution in octahedral complexes often consists of two terms,one first-order in the metal complex (M) alone and the other first-order in both M and entering ligand Y:

$$v= \frac{-d(M)}{dt} = k_1(M) +k_2(M)(Y) \qquad 1$$

The experiments are invariably carried out using excess Y and therefore with pseudo-first-order conditions.The experimental first-order rate constant k_{obs} is given by

$$v= k_{obs}(M) \qquad 2$$

Therefore $k_{obs}=k_1+k_2(Y)$

A plot of k_{obs} vs (Y) will have an intercept k_1 and a slope k_2.

Significance of k_1:

The term containing k_1 represents substitution behaviour in octahedral complexes when ligand-ligand replacement takes place via the solvated complex:

$$ML_6 \overset{S}{\rightleftharpoons} L_5MS \xrightarrow{+Y} L_5MY+S \qquad 3$$

The rates of substitution reaction in non-aqueous solvents are often dependent upon the concentration of the entering nucleophile and this dependence can be quite complicated

$$\begin{tikzcd} L_5MS....S \arrow[r, shift left, "+Y"] \arrow[d, "k_0"'] & L_5ML....Y \arrow[l, shift left, "K_1"] \arrow[r, shift left, "+Y"] \arrow[d, "k_1"'] & L_5ML....2Y \arrow[l, shift left, "K"] \arrow[r, shift left] \arrow[d, "k_2"'] & etc. \arrow[l, shift left] \\ L_5MS & L_5MY....L & L_5M...L...Y & \\ (L_5MY) & (L_5MS...L...Y) & (L_5MS...L...2Y) & \end{tikzcd} \qquad 4$$

This would give rise to a general expression of the form:

$$k_{obs}= \frac{k_0+k_1K_1[Y]+k_2K_2[Y]^2...}{1+K_1[Y]+K_1K_2[Y]^2...} \qquad 5$$

Kinetic Measurements

The rates of the reactions of Ti(III)

in ethanol as solvent were determined spectrophotometrically by following the change in absorbance with time at the wavelength (λ) selected. The instrument used was an Aminco-Morrow stopped-flow spectrophotometer which was fitted to a data collection system (DASAR) and teletype. (See Figure 1). The measurements are stored digitally, displayed on a visual display, and output on paper tape on a teletype. Subsequent data treatment was carried out on a computer. In the present work, the chosen wavelength was usually that at which maximum changes in the transmittance occurred in going from starting materials to product, as obtained from preliminary experiments. The chosen time-base was usually the fastest time which allowed a complete reaction (or stages of reaction) to be monitored in a single run.

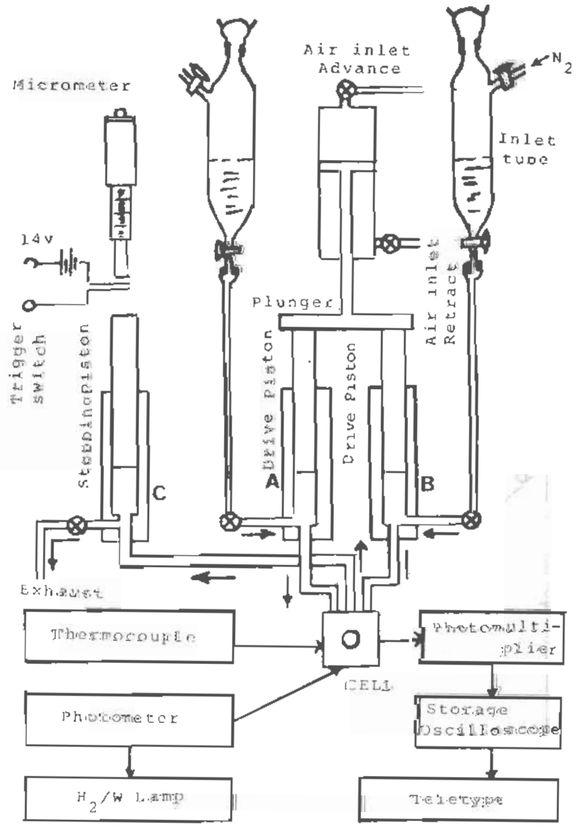


Fig. 1. stopped-flow photospectrometer apparatus

To measure and adjust the temperature a thermocouple was fitted to the cell, and the reservoir syringes and observation cell were thermostatted with water from a constant temperature bath. By balancing the heating and cooling effects, the temperature of the cell compartment was kept within ±0.2^0 during a particular run. Due to the air sensitive reactions a special type of inlet tube was used (Fig. 1). The tube was designed to be evacuated to 0.01 Torr and then filled with nitrogen. The solution introduced to the stopped-flow machine in this tube was, therefore, always under nitrogen. The arrangement used is shown in Fig. 1.

The complex was prepared using $TiCl_3$ (~15%) solution with adding recrystalized urea ligand from ethanol (absolutly pure) solution, under dry nitrogen free from oxygen. Complex crystalines were dissolved in absolute ethanol (100%) which was purified in the lab. Twice distilated water free from any gases in ethanol solvent was used.

RESULTS AND DISCUSSION

Kinetic investigations of redox reactions of Ti(III) as a reductant have aroused considerable interest in the last few years, (2-37). But reports about substitution reactions on Ti(III) as this work are very rare. Here we studied the kinetics of substitution of urea from $[Ti(Ur)_6]I_3$ by H_2O and SCN^- in ethanol solution. In general the rate equation was derived, rate constants measured at several temperatures, and activation parameters calculated.

(a) Reaction of $[Ti(ur)_6]I_3$ with H_2O in enthanol

The reaction was studied spectrophotometrically by monitoring the changes in absorbance with time at 625 nm. Pseudo first-order conditions (excess H_2O) were always used and plots of $\ln(A_\infty - A_t)$ versus time were usually linear for more than 80% of the reactions, (Fig. 2). The value of A_∞ was difficult to determine experimentally, and was treated as an "unknown". The method of least squares was used to calculate the best values of A_∞ and k_{obs} for each run. The plot of k_{obs} versus $[H_2O]$ (Fig. 3) was linear, and followed equation 6 :

$$k_{obs} = k_0 + k_2 [H_2O] \qquad 6$$

The value of k_0 was significant, and was determined from the intercept of the plot.

The slope of the line was used to calculate the second order rate constant, k_2, and hence the activation parameters. The plot $k_{obs}/[H_2O]$ versus reciprocal temperatures is linear (Fig.4). The activation parameters were calculated using the transition theory.

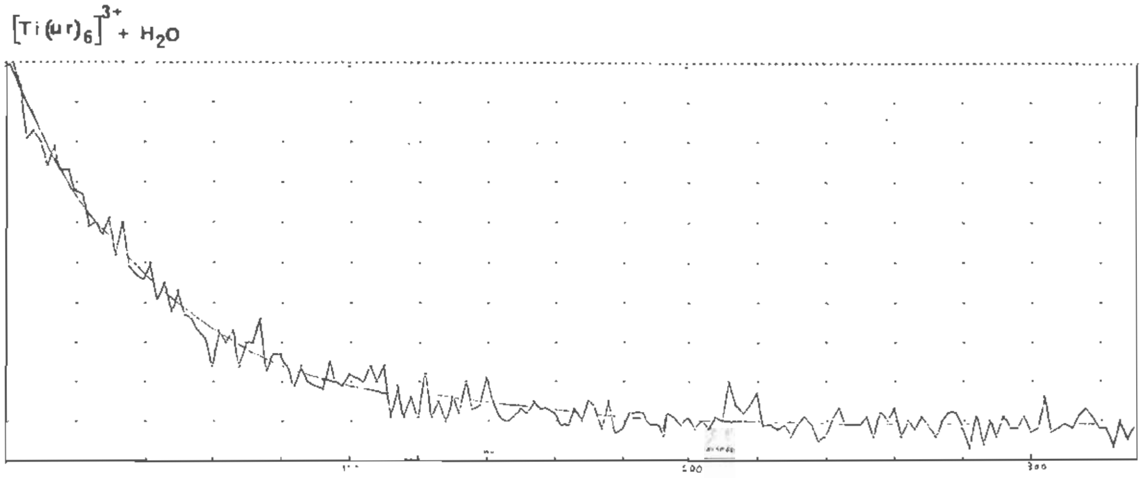
$$k_2 = k_{obs}/[H_2O] \qquad 7$$

Activation parameters:

$\Delta H^{\ddagger} = 3.67(\pm 0.8)$ kJ mol^{-1}

$\Delta S^{\ddagger} = -80.8(\pm 3)$ J mol^{-1} K^{-1}

No kinetic studies on Ti(III)-urea complexes have previously been reported. Water is a good nucleophile towards Ti(III) substrates, and undergoes a substitution reaction in $[Ti(ur)_6]I_3$ in an organic solvent. Even the solvent ethanol appears to be a poor ligand when compared to water. Although ethanol dominates the substitution the weakness of its bond to the metal causes it to dissociate repeatedly, thus giving the water a chance to enter the co-ordination sphere. As the equation 6 shows, the overall rate equation fits 8.



T = 21°c

Fig.2. Variations of absorbance vs time for the reaction of $[Ti(ur)_6]I_3$ with H_2O at 21 °C.

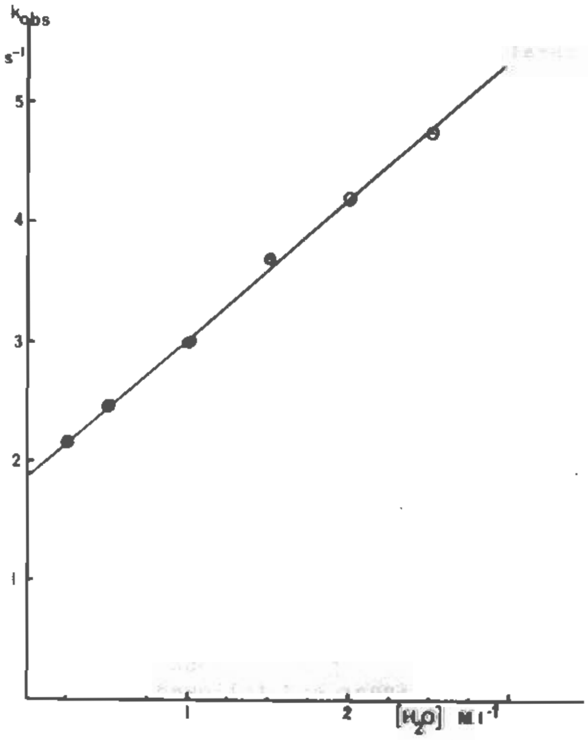


Fig.3. Variation of k_{obs}, for ligand substitution of $[Ti(ur)_6]I_3$ with H_2O, vs concentration of water.

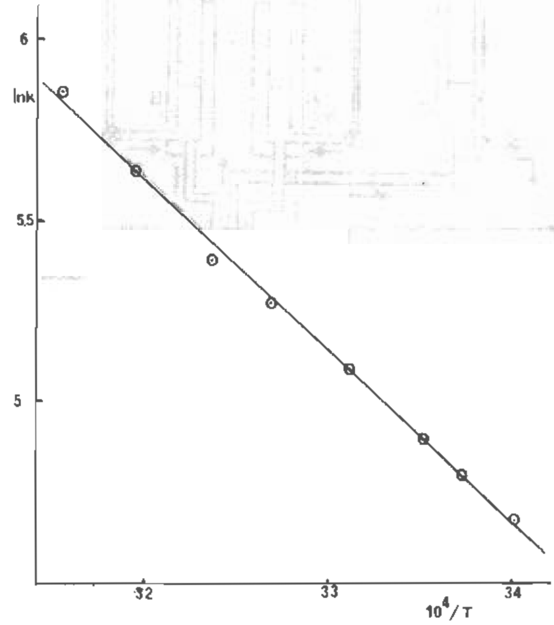


Fig.4. Arrhenius plot for ligand substitution of $[Ti(ur)_6]I_3$ with H_2O.

$$\text{rate}=k_o[\text{Ti(III)}]+k_2[H_2O][\text{Ti(III)}] \qquad 8$$

The first term of the equation shows that the rate is partly independent of $[H_2O]$ and this is probably due to the solvolysis of the complex. (However, this is not seen for the substitution by KSCN).

The process for the solvent ethanol is generally reversible:

$$[\text{Ti(ur)}_6]^{3+}+\text{EtOH} \rightleftharpoons [\text{Ti(ur)}_5\text{EtOH}]^{3+}+\text{ur} \qquad 9$$

In the presence of water, the equilibrium is over to the right (Fig.2) because water is generally a better solvent for solvolysis than ethanol. The position of equilibrium is strongly dependent upon the nature of the leaving group (urea) which is itself in competition with the solvent (ethanol) and the entering group (water).

The following equations are suggested for this reaction:

$$[\text{Ti(ur)}_6]^{3+}+\text{EtOH} \rightleftharpoons [\text{Ti(ur)}_6]^{3+}\text{....EtOH} \qquad 10$$

$$[\text{Ti(ur)}_6]^{3+}\text{...EtOH} \longrightarrow [\text{Ti(ur)}_5\text{EtOH}]^{3+}\text{...ur} \qquad 11$$

$$[\text{Ti(ur)}_5\text{EtOH}]^{3+}\text{..ur}+\text{EtOH} \longrightarrow [\text{Ti(ur)}_5\text{EtOH}]^{3+}\text{..EtOH}+\text{ur} \qquad 12$$

$$[\text{Ti(ur)}_5\text{EtOH}]^{3+}\text{...EtOH} \xrightarrow{k_O} [\text{Ti(ur)}_5\text{EtOH}]^{3+}+\text{EtOH} \qquad 13$$

$$[\text{Ti(ur)}_5\text{EtOH}]^{3+}+H_2O \overset{K}{\rightleftharpoons} [\text{Ti(ur)}_5\text{EtOH}]^{3+}\text{....}H_2O \text{ or } [\text{Ti(ur)}_5H_2O]^{3+}\text{....EtOH} \qquad 14$$

$$[\text{Ti(ur)}_5\text{EtOH}]^{3+}\text{....}H_2O \xrightarrow{k_1} [\text{Ti(ur)}_5H_2O]^{3+}+\text{EtOH} \text{ or } [\text{Ti(ur)}_5H_2O]^{3+}\text{....EtOH} \qquad 15$$

$$k_{obs}=k_o+Kk_1[H_2O]\ (1+K[H_2O]) \qquad 16$$

$$k_{obs}=k_o+Kk_1[H_2O] \text{ if } K[H_2O] \lll 1 \qquad 17$$

$$k_{obs}=k_o+k_2[H_2O] \text{ where } k_2=Kk_1 \qquad 18$$

(b) Reaction of $[\text{Ti(ur)}_6]I_3$ with KSCN in Ethanol

The reaction was studied as in (a) Pseudo-first-order conditions (excess KSCN) were used and plots of $\ln(A_\infty-A_t)$ vs time for the first stage of the reaction were linear. The plot of absorbance vs time showed different stages for the reaction (Fig.5). The Plot of k_{obs} versus SCN^- (Fig.6) was linear in agreement with equation 19 :

$$k_{obs}=k[SCN^-] \qquad 19$$

The value of k was used to calculate the activation parameters. The plot of ln k versus the reciprocal of the temperature was linear up to 40°C (Fig.8) and after that, probably because the second stage of the reaction became more active, the real value of the k_{obs} was not found.

Activation parameters :

$\Delta H^{\ddagger}=75(\pm3)\ \text{kJ mol}^{-1}$

$\Delta S^{\ddagger}=73(\pm10)\ \text{J mol}^{-1}\text{K}^{-1}$

The activation parameters were calculated using only the points up to 40°C

In non-aqueous solvents solvolysis is reduced because ethanol is less coordinating and solvating than water.

It is often relatively easy to distinguish direct substitution from cryptosolvolysis (1). In the latter case solvolysis is followed by an anation under conditions where the solvento-complex is too reactive to be directly observable that is:

$$L_5ML+S \longrightarrow L_5MS+L \xrightarrow{L'} L_5ML'+S \qquad 20$$

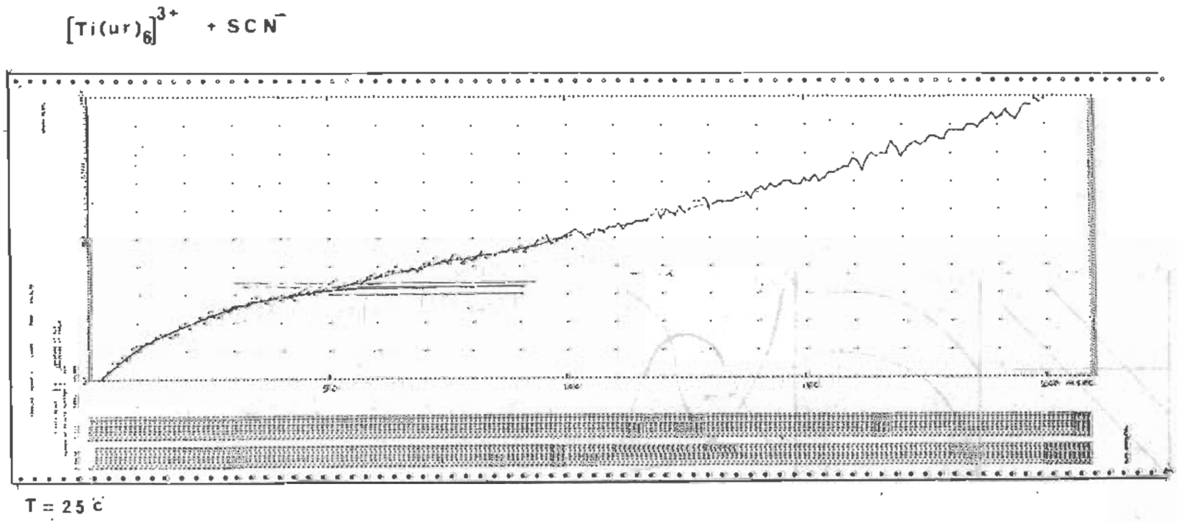


Fig.5. Variation of absorbance vs time for the reaction of $[\text{Ti(ur)}_6]I_3$ with KSCN at 25°C.

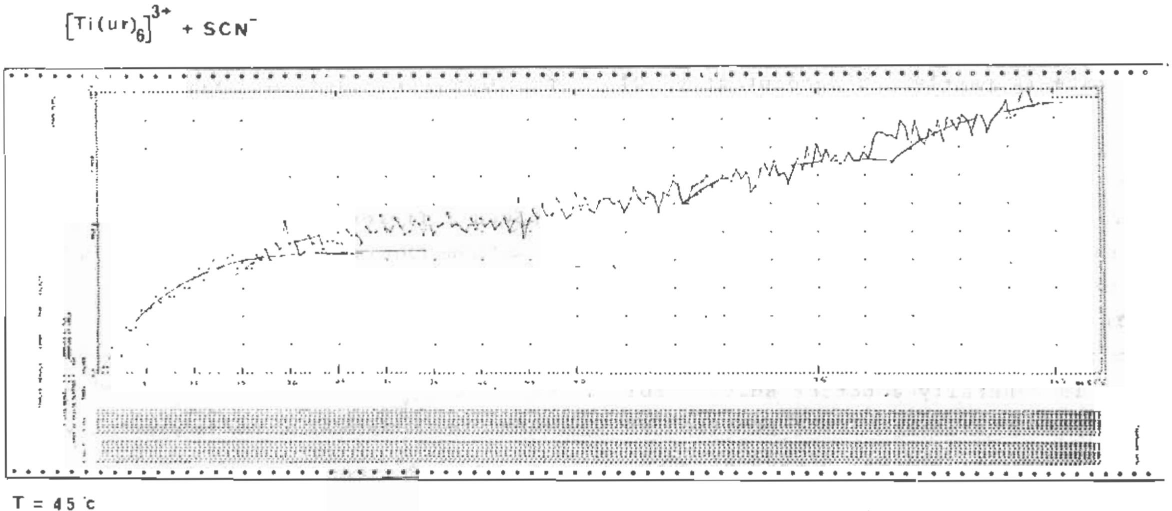


Fig.6.Variation of absorbance vs time for the reaction of $[Ti(ur)_6]I_3$ with KSCN at 45°C.

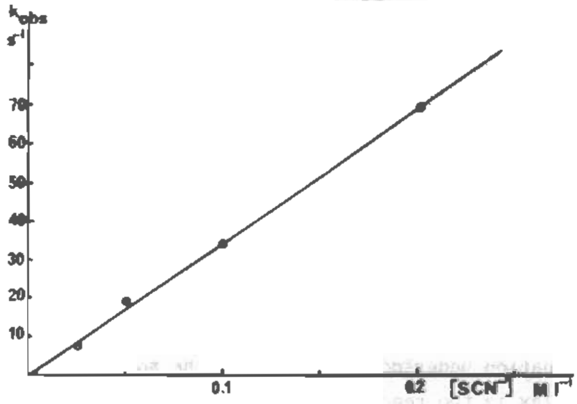


Fig.7:Variation of k_{obs} for ligand substitution of $[Ti(ur)_6]I_3$ with KSCN vs concentration of KSCN.

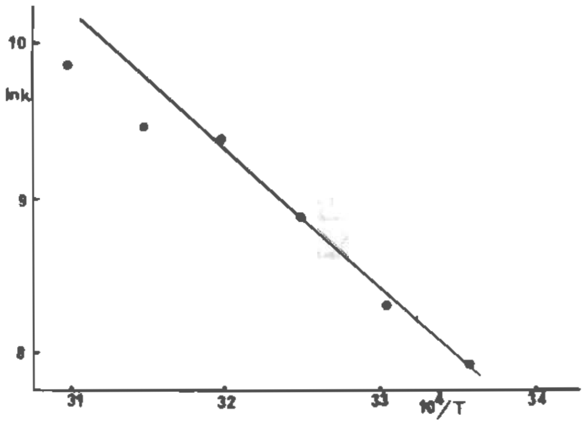


Fig.8.Arrhenius plot for ligand substitution of $[Ti(ur)_6]I_3$ with KSCN

The rate of substitution reactions is often dependent upon the concentration of the entering nucleophile and this dependence can be quite complicated.Fig.9 shows a number of curves for the plot of k_{obs} against [L'] which have been obtained (1).

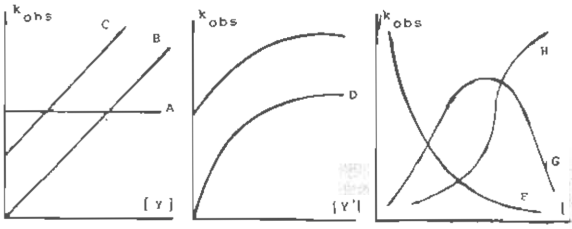


Fig.9.Dependence of pseudo-first-order rate constant k_{obs} for entry of L' upon the concentration (1)

However,the water case was in agreement with curve C and the present case (SCN^-) with curve B.As the plot of absorbance versus time shows this is a step-wise reaction,and these stages are clearest at higher temperatures (Fig.6) as k_{obs} was calculated for the first stage.The overall rate law for the reaction is shown in equation 21

$$\frac{-d[Ti(III)]}{dt} = k[Ti(III)][SCN^-] \qquad 21$$

The reaction scheme shown below is postulated to explain the stages:

$$[Ti(ur)_6]^{3+} + SCN^- \rightleftharpoons [Ti(ur)_5SCN]^{2+} + ur \qquad 22$$

$$[Ti(ur)_5SCN]^{2+} + SCN^- \longrightarrow [Ti(ur)_4(SCN)_2]^+ + ur \qquad 23$$

This is a rather fast reaction when compared to the reaction of water (k_2=2770 l $mol^{-1}s^{-1}$ at 25°C for SCN^- v.s.k_2=135 l$mol^{-1}s^{-1}$at 25°C for water).The solvolytic interference can be considerable,as in the case of ethanol water,or negligible as indicated here. When the complex reacts with water,the reaction is a cryptosolvolysis and the rate law is rather complicated but for SCN^- the results show a direct substitution. A direct associative or SN_2,process is possible:

$$[Ti(ur)_6]^{3+} + SCN^- \longrightarrow [Ti(ur)_6]^{3+}...SCN^- \quad 24$$

$$[Ti(ur)_6]^{3+}...SCN \longrightarrow [Ti(ur)_6SCN]^{2+} \quad 25$$

$$[Ti(ur)_6SCN]^{2+} \longrightarrow [Ti(ur)_5SCN]^{2+}...ur \quad 26$$

$$[Ti(ur)_5SCN]^{2+}...ur \longrightarrow [Ti(ur)_5SCN]^{2+} + ur \quad 27$$

Taking first the substitution reactions,it is clear that although substitution by SCN^- proceeds over tewnty times faster (at 25 °C)than substitution by H_2O but probably this is not due to a lower activation energy.In fact, $\Delta H^{\ddagger}$ for the SCN^- substitution is approximately double that for the aquation.The greater rate of the SCN^- reaction is a reflection of the large,positive,entropy of activation for this reaction, compared to the negative entropy of activation in the case of H_2O.That is, the two reactions proceed by different mechanisms (the difference being characterised by the very different $\Delta S^{\ddagger}$ values). Furthermore,because the SCN^- substitution is the faster,it is probable that some mechanism is open to this nucleophile which is not,for some reason,open to the H_2O nucleophile.

It has already been argued that in the aquation,two pathways must be operating independently,namely a "direct" substitution of a urea ligand by H_2O,and an "indirect" pathway involving prior solvolysis by ethanol.The negative $\Delta S^{\ddagger}$ and rather small $\Delta H^{\ddagger}$ suggest an associative(25) (A,or SN_2)mechanism for the "direct" substitution. However,in the SCN^- substitution, the "direct"pathway was observed only which,if taken with the rather larger $\Delta H^{\ddagger}$ and positive $\Delta S^{\ddagger}$,probably indicates a more dissociative activation step (D/I_d, or SN_1).It must be concluded that the greater nucleophilic strength of SCN^- in relation to H_2O allows the former to take advantage of and react with,an activated state which the H_2O apparently cannot react with.This is consistent with the observation of a simple reaction pathway for the SCN^- reaction,whilst in the H_2O case, with the slower direct reaction resulting from the lower nucleophilic strength of H_2O,the solvolysis reaction also becomes important.

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