Kinetics and Mechanism of the Reaction of Uranyl Ion with Thenoyltrifluoroacetone

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The kinetics and equilibrium of the reaction of thenoyltrifluoroacetone and uranyl ion $[UO_2]^{2+}$ to form the mono complex have been studied in aqueous solution at 25 °C and 1.0 mol dm^{-3} ionic strength. The value of the equilibrium constant, K_1 for reaction (i) where HA represents the undissociated form of thenoyltrifluoroacetone,

$$[UO_2]^{2+} + HA \rightleftharpoons [UO_2E]^+ + H^+ \qquad \text{(i)}$$

is 0.14 ± 0.02. The kinetic data are consistent with a scheme in which $[UO_2]^{2+}$ reacts with the enol form of the ligand. The rate constants for reaction of $[UO_2]^{2+}$ with HE, the undissociated form of the enol tautomer, and with E^- the enolate ion are $\geqslant 1 \times 10^4$ and $\geqslant 3 \times 10^5$ dm^3 mol^{-1} s^{-1} respectively.

ALTHOUGH the equilibria of formation of complexes of the uranyl ion $[UO_2]^{2+}$ have been extensively investigated,[1,2] with a wide variety of ligands, few kinetic studies of these systems have been made. Consequently, little is known about the mechanisms of formation of complexes of $[UO_2]^{2+}$. The kinetics of the reactions between 4-(2-pyridylazo)resorcinol have been reported recently,[3] although no detailed mechanism was proposed. A previous study reported on the relaxation spectra of complexes of $[UO_2]^{2+}$ with $[SO_4]^{2-}$, $[SCN]^-$, $MeCO_2^-$, and $ClCH_2CO_2^-$ in aqueous solution.[4] However, the reported rate data in this instance do not agree with the data obtained by us on the same systems using stopped-flow measurements.[5]

As part of our continued investigations of the chemistry of the uranyl ion, we have undertaken a detailed study of the kinetics and mechanisms of complex formation by this ion.[6-9] In this paper we report the results of equilibrium and kinetic studies of the interaction between $[UO_2]^{2+}$ and thenoyltrifluoroacetone (Htta) in aqueous solution. The ligand was selected because of its widespread use in solvent extraction of U^{VI} and other actinoid elements.[10]

EXPERIMENTAL

Stock solutions of $[UO_2]^{2+}$ were prepared from AnalaR grade $[UO_2][NO_3]_2 \cdot 6H_2O$ These solutions were standardized by igniting aliquot portions to U_3O_8 in platinum crucibles. Koch–Light reagent grade thenoyltrifluoroacetone (Htta) was used as purchased. Solutions were always freshly prepared for the kinetic runs.

Spectra were recorded on a Beckman DB-GT u.v.–visible spectrophotometer equipped with a chart recorder. pH Measurements were made with a Pye model 290 pH meter equipped with a Pye Ingold E_7° combined glass and reference electrode.

The rate constants were measured using an Applied Photophysics stopped-flow device. The drive syringes and mixing chamber were maintained at 25.0 ± 0.1 °C. Reaction conditions involved using a large excess of metal ion to ensure mono complex formation. Due to the low solubility of tta and of the mono complex formed between $[UO_2]^{2+}$ and Htta, ligand concentrations of *ca.* 1×10^{-4} mol dm^{-3} were used for all the runs. The pH of the $[UO_2]^{2+}$ and Htta solutions was adjusted using $HClO_4$ and Na[OH]. For the kinetic runs, aliquot portions of these solutions (containing the appropriate amount of $Na[ClO_4]$ to give the required ionic strength) were withdrawn into the reservoir syringes of the stopped-flow device from which they were transferred to the thermostatted drive syringes. The kinetic data were recorded using a Tektronix model 5100 storage oscilloscope. The stored traces were photographed and plots of $-\ln(A - A_\infty)$ against time were obtained. The best (least-squares) fit of straight-line plots and the standard errors were calculated as described in the literature.[11]

RESULTS AND DISCUSSION

The overall equilibrium constant for the reaction between $[UO_2]^{2+}$ and tta may be represented as in equation (1), where HA and E^- represent Htta and the

$$[UO_2]^{2+} + HA \overset{K_1}{\rightleftharpoons} [UO_2E]^+ + H^+ \qquad (1)$$

enolate ion respectively. Due to the fact that [HA] = [HK] + [HE], where HK and HE represent the keto- and enol tautomers respectively, equation (1) can be reduced to (2) and (3). It has been estimated that in

$$[UO_2]^{2+} + HK \overset{K_K}{\rightleftharpoons} [UO_2E]^+ + H^+ \qquad (2)$$

$$[UO_2]^{2+} + HE \overset{K_E}{\rightleftharpoons} [UO_2E]^+ + H^+ \qquad (3)$$

aqueous solution 98.5% of Htta exists as the keto-form while the remaining 1.5% exists as the enol form.[12] Thus, K_K may be approximated to K_1 without serious error.

A spectrophotometric method was used to determine K_1.[13] If a wavelength is chosen where the aqueous

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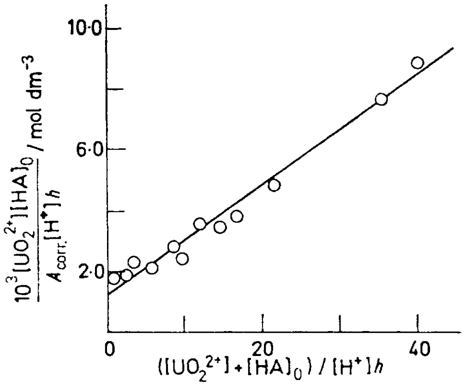
$[UO_2]^{2+}$ ion has no absorption, then $[UO_2E]^+ = A/\varepsilon_1$ where A is the absorbance per cm pathlength and ε_1 is the molar absorption coefficient of $[UO_2E]^+$. From equation (1), we obtain (4), where $[HA]_0$ is the total

$$\frac{[UO_2]^{2+}[HA]_0}{A[H^+]h} = \frac{[UO_2]^{2+} + [HA]_0}{\varepsilon_1[H^+]h} + \frac{1}{\varepsilon_2 K_1} \qquad (4)$$

concentration of Htta, $h = 1 + K_h[H^+]^{-1}$, and K_h is the hydrolysis constant of $[UO_2]^{2+}$ (2.0×10^{-5}).[14] Hence a plot of the left-hand side of equation (4) against $([UO_2]^{2+} + [HA]_0)/[H^+]h$ should yield a straight line of gradient $1/\varepsilon_1$ and intercept $1/\varepsilon_1 K_1$. In the present instance it was not possible to select a wavelength at which the absorbance of $[UO_2]^{2+}$ was zero. At the wavelength chosen, however (λ 400 nm), the absorbance of $[UO_2]^{2+}$ is at a minimum. Furthermore, in view of the fact that the concentration of $[UO_2]^{2+}$ was at all times in considerable excess of HA (in order to ensure that only the mono complex was formed), allowance could readily be made for the contribution of $[UO_2]^{2+}$ to the measured absorbance. The Figure shows a plot of $[UO_2]^{2+}[HA]_0/$-$A_{corr.}[H^+]h$ against $([UO_2]^{2+} + [HA]_0)/[H^+]h$ where $A_{corr.}$ is the measured absorbance corrected for the contribution from $[UO_2]^{2+}$. It is apparent that equation (4) is reasonably well obeyed over a wide range of pH and $[UO_2]^{2+}$. The value of K_1 obtained from a least-squares treatment of the data in the Figure was 0.14 ± 0.02.



$X = ([UO_2{}^{2+}] + [HA]_0)/[H^+]h$

$Y = 10^3[UO_2{}^{2+}][HA]_0/A_{corr.}[H^+]h$, mol dm^{-3}.

Plot suggested by equation (4) for the determination of K_1 in the formation of $[UO_2(tta)]^+$ at 25.0 °C and 1.0 mol dm^{-3} ionic strength; λ = 400 nm

Kinetics.—The reaction of an excess of $[UO_2]^{2+}$ with Htta was studied in aqueous solution at a number of different hydrogen-ion concentrations. In all cases a single reaction was observed which accounted for the calculated absorbance change between the reactants and products. The pH range in which these investigations were carried out was restricted at the lower end by the fact that at pH < 2.2 complex formation was negligible, while at pH > 3.5 hydrolysis of $[UO_2]^{2+}$ would be appreciable.[14] Such hydrolysis would greatly complicate the interpretation of the kinetic data. The reaction between $[UO_2]^{2+}$ and Htta was also studied in the reverse direction. This entailed preparing the complex *in situ* and treating it with excess of acid. In these experiments it was also necessary to have an excess of $[UO_2]^{2+}$ in order to ensure adequate formation of the mono complex. The kinetic data are given in the Table.

Observed rate constants for reaction between $[UO_2]^{2+}$ and Htta, in aqueous solution at 25 °C

Experiment no.	$10^3[UO_2{}^{2+}]$ / mol dm^{-3}	$10^3[H^+]$ / mol dm^{-3}	$k_{obs.}$ / s^{-1}
(1)	5.0	8.93	0.163
(2)	7.5	8.93	0.096
(3)	10.0	8.93	0.063
(4)	12.5	8.93	0.064
(5)	15.0	8.93	0.047
(6)	20.0	8.93	0.041
(7)	25.0	8.93	0.034
(8)	1.0	2.81	0.177
(9)	5.0	2.81	0.046
(10)	7.5	2.81	0.030
(11)	10.0	2.81	0.023
(12)	12.5	2.81	0.022
(13)	15.0	2.81	0.021
(14)	20.0	2.81	0.018
(15)	25.0	2.81	0.017
(16)	10.0	8.90	0.115
(17)	10.0	15.80	0.170
(18)	10.0	23.80	0.270
(19)	10.0	31.70	0.350
(20)	10.0	47.60	0.480
(21)	10.0	63.50	0.590
(22)	10.0	79.40	0.720
(23)	10.0	317.90	1.300
(24)	10.0	795.00	1.540

Reactions (1)—(15) were run in the forward direction; [Htta] = 2×10^{-4} mol dm^{-3}. Reactions (16)—(24) were run in the reverse direction; [Htta] = 1×10^{-4} mol dm^{-3}. Ionic strength 1.0 mol dm^{-3} in all experiments; λ = 390 nm.

The kinetic data are consistent with the reaction scheme previously proposed for the formation of monothenoyltrifluoroacetone complexes of Ni^{II}, Co^{II}, Cu^{II}, and Fe^{III}.[13] Although in aqueous solution 98.5% of Htta exists as the keto-tautomer, complex formation occurs exclusively through the interaction of the metal ion with the enol tautomer, as in equation (5) where $k'_{HE} = k_{HE}[UO_2]^{2+}$ and $k'_{-HE} = k_{-HE}[H^+]$; k_{HE} and k_{-HE} are defined as in equation (3), where $k_{HE}/k_{-HE} = K_E$.

$$HK \underset{k_f}{\overset{k_e}{\rightleftharpoons}} HE \underset{k'_{-HE}}{\overset{k'_{HE}}{\rightleftharpoons}} [UO_2E]^+ \qquad (5)$$

In terms of this reaction scheme $k_{obs.} = \frac{1}{2}(p \pm q)$ where $p = k_e + k_f + k'_{HE} + k'_{-HE}$, $q = (p^2 - 4b)^{\frac{1}{2}}$, and $b = k_e k'_{HE} + k_f k'_{-HE} + k_e k'_{-HE}$. Due to the fact that only one reaction step was observed in the present investigation and replacing $(k_e + k_f)$ by k_f one obtains equation (6)[15,16] for excess of $[UO_2]^{2+}$. If we assume that

$$k_{obs.} = \left\{\frac{k_e k_{HE}[UO_2{}^{2+}]}{k_{HE}[UO_2{}^{2+}] + k_f + (k_{HE}[H^+]/K_E)}\right\} \times \left\{1 + \frac{[H^+]}{K_K[UO_2{}^{2+}]}\right\} \qquad (6)$$

$k_{HE}[UO_2{}^{2+}] \gg k_f + (k_{HE}[H^+]/K_E)$, equation (6) becomes

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(7). Thus a plot of $k_{obs.}$ against $[H^+]/[UO_2^{2+}]$ should yield a straight line of intercept k_e and gradient k_e/K_K. This mechanism predicts that equation (7) should be obeyed

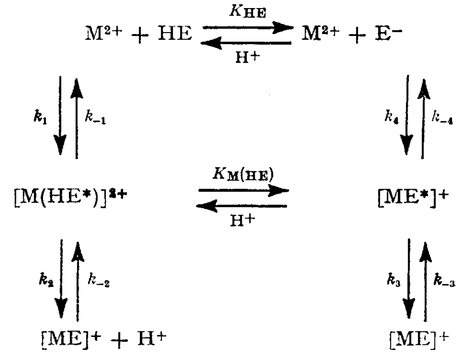
$$k_{obs.} = k_e + (k_e[H^+]/K_K[UO_2^{2+}]) \qquad (7)$$

for a given hydrogen-ion and uranyl-ion concentration independent of whether the formation or dissociation (hydrolysis) of the complex is being observed. The data in the Table conform to this prediction over a wide range of $[H^+]/[UO_2^{2+}]$. Under the reaction conditions used, it can readily be predicted that deviation from equation (7) should occur at $[H^+] > 0.1$ mol dm^{-3}. Such behaviour was observed for runs (23) and (24) of the Table. A plot of equation (7) gave a value of $(6.3 \pm 1.9) \times 10^{-3}$ s^{-1} for k_e which is in fair agreement with the published values,[13] while the value obtained for K_K is 0.09 ± 0.02. Taking the uncertainty in the value of the intercept into account, this is in satisfactory agreement with the value obtained directly, by equation (4).

It is readily apparent that under the reaction conditions used, $k_{HE}[UO_2^{2+}] \gg k_{HE}[H^+]/K_E$. Thus the condition for obtaining equation (7) from (6) reduces to $k_{HE}[UO_2^{2+}] \gg k_f$. Hence $k_{HE}[UO_2^{2+}] \gg 10$ s^{-1}, since $k_f = 1.9$ s^{-1}. It has previously been shown [13] that k_{HE}

$$k_{HE} = a + b[H^+]^{-1} \qquad (8)$$

has the form (8), which is consistent with the mechanism shown in the Scheme. Here $[M(HE^*)]^{2+}$ and $[ME^*]^+$ represent intermediates in which one end of the entering nucleophile is bonded to the uranyl ion. Applying the steady-state assumption to $[M(HE^*)]^{2+}$ and $[ME^*]^+$, and assuming that the reactions represented by K_{HE} and $K_{M(HE)}$ are in rapid equilibrium, one obtains [13] $k_{HE} = (k_1 + K_{HE}k_4[H^+]^{-1})/\left(1 + \dfrac{k_{-1} + K_{M(HE)}k_{-4}[H^+]^{-1}}{k_2 + K_{M(HE)}k_3[H^+]^{-1}}\right)$. If $(k_2 + K_{M(HE)}k_3[H^+]^{-1}) \gg (k_{-1} + K_{M(HE)}k_{-4}[H^+]^{-1})$, then $k_{HE} = k_1 + K_{HE}k_4[H^+]^{-1}$. Thus $a = k_1$ and $b = K_{HE}k_4$.



SCHEME

The lowest metal concentration used in the present investigation was 1×10^{-3} mol dm^{-3}. Thus $k_{HE} \geqslant 1 \times 10^4$ dm^3 mol^{-1} s^{-1}. If it is assumed that $a \gg b[H^+]^{-1}$, then $k_{HE} = k_4$. Therefore one estimates $k_4 \geqslant 1 \times 10^4$ dm^3 mol^{-1} s^{-1}. If on the other hand one assumes that $a \ll b[H^+]^{-1}$, then, using a published value of K_{HE} (9.6×10^{-5}),[8] k_4 is calculated to be $\geqslant 3 \times 10^5$ dm^3 mol^{-1} s^{-1}.

There are little data in the literature dealing with the solvent-exchange rates of $[UO_2]^{2+}$. However, extrapolating the tentative value reported by Fratiello *et al.*[17] to room temperature, the rate of water exchange can be approximated to 3×10^5 s^{-1} at 25 °C. Thus, the rate of reaction of $[UO_2]^{2+}$ with uncharged ligands might reasonably be expected to be of the order of 3×10^4 dm^3 mol^{-1} s^{-1}. This value is in fact quite similar to those reported for the reaction between $[UO_2]^{2+}$ and 4-(pyridylazo)resorcinol.[3] It thus appears that the reaction between $[UO_2]^{2+}$ and the enol tautomer of Htta is quite rapid. The question of whether or not the rate is 'normal' cannot be definitely decided until there are accurate data on the rate of water exchange of the $[UO_2]^{2+}$ ion. It would appear however that the rate is not reduced by the three orders of magnitude observed in the case of the reaction between Ni^{2+} and the enol tautomer of Htta.

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