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Kinetics and mechanisms of the reactions of dioxouranium(VI), $[UO_2]^{2+}$, with heptane-2,4,6-trione (H_2hto), 1-phenylhexane-1,3,5-trione (H_2phto) and 1,5-diphenylpentane-1,3,5-trione (H_2dppto) in methanol–water (70:30 vol./vol.) at 25 °C and $I = 0.5$ mol dm^{-3}

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Abstract

The equilibria and kinetics of the reactions of $[UO_2]^{2+}$ with heptane-2,4,6-trione (H_2hto), 1-phenylhexane-1,3,5-trione (H_2phto) and 1,5-diphenylpentane-1,3,5-trione (H_2dppto) have been investigated in methanol–water (70:30 vol./vol.) solution at 25 °C and ionic strength 0.5 mol dm^{-3}. A mechanism is proposed which accounts satisfactorily for the kinetic data. $[UO_2]^{2+}$ reacts with both the fully protonated and mono-anions of H_2hto, H_2phto and H_2dppto with rate constants of 3.67×10^3, 5.55×10^8, 1.78×10^3, 4.73×10^8, 0.419×10^3 and 2.16×10^8 dm^3 mol^{-1} s^{-1}, respectively. An alternative formulation is also discussed.

Introduction

Although the ligand exchange and complex formation reactions of dioxouranium(VI) have been the subject of a number of investigations [1–37] relatively little is still known regarding the intrinsic reactivity of this ion in aqueous solution. There are a number of reasons for this. Only a relatively small number of the previous investigations have been concerned with the complex formation of this ion with simple ligands in aqueous solution [1–3, 9, 11, 17, 20, 33, 34]. The remainder of the studies were concerned with ligand exchange reactions in non-aqueous solvents. These results have little relevance to the reactions of this ion in aqueous solution. Of the reactions carried out in aqueous solution, doubts have been cast [3, 9] on the results obtained by Hurwitz and Kustin [1]. The reactions of $[UO_2]^{2+}$ with β-diketones [9, 11, 20] cannot be considered typical of reactions in aqueous solution as it is well known that the reactions of metal ion with both the protonated keto and enol tautomers of these ligands proceed at rates which are considerably less than those predicted on the basis of the outer-sphere association constant and the solvent exchange rate [38]. Unfortunately, it did not prove possible to investigate the reactions of $[UO_2]^{2+}$ with the mono anions of 1,3-diketones. The reactions of metal species with these species have been shown to be 'normal' [38] and the results might be expected to give an indication of the inherent lability of the $[UO_2]^{2+}$ ion.

Recent kinetic work has been concerned with the reactions of $[UO_2]^{2+}$ with uranophiles [31, 32, 34, 37]. Most of these ligands are macrocycles and again due to the presence of steric and other constraints, the reactions are not typical of the reactivity of this ion in aqueous solution. In addition, some of the studies have been carried out in non-aqueous solvents such as propylene carbonate [31, 32].

Due to the fact that most of the uranium on earth is present in seawater as the uranyltricarbonato complex, $[UO_2(CO_3)_3]^{4-}$, the kinetics and mechanisms of the ligand exchange reactions of $[UO_2]^{2+}$ in aqueous solution are of considerable interest. Furthermore, a variety of mechanisms have been reported for the ligand exchange reactions of dioxouranium(VI) complexes [34]. We now report the results of our investigations of the reactions of $[UO_2]^{2+}$ with heptane-2,4,6-trione (H_2hto), 1-phenylhexane-1,3,5-trione (H_2phto) and 1,5-diphenylpentane-1,3,5-trione (H_2dppto) in methanol–water (70:30 vol./vol.) solution.

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Experimental

H_2hto was prepared according to the method of Bethell and Maitland [39] and was purified prior to use by distillation under reduced pressure. H_2phto was prepared by condensation of pentane-2,4-dione with methyl benzoate as described by Hauser *et al.* [40]. H_2dppto was prepared by condensation of 1-phenyl-butane-1,3-dione with methyl benzoate as described by Hauser *et al.* [40]. Stock solutions of $[UO_2]^{2+}$ were prepared from AnalaR grade $UO_2(NO_3)_2 \cdot 6H_2O$ (BDH). These solutions were standardized by igniting aliquot portions to U_3O_8 in a platinum crucible on a Meker burner. Stock solutions of sodium hydroxide were prepared from reagent grade NaOH (Riedel–de Haën).

The ionic strength of all solutions was adjusted to 0.5 mol dm^{-3} using reagent grade sodium perchlorate (Riedel–de Haën). In order to remove any iron(III) impurities present, stock solutions, adjusted to pH 3 using perchloric acid, were passed over a column of Amberlite IR-120 (BDH) cation exchange resin in the sodium form.

Equilibrium and kinetic measurements were carried out in methanol–water (70:30 vol./vol.) solvent. Methanol was purified by distillation from magnesium and iodine. All solutions were prepared using distilled water which had been boiled for 15 min. Methanol–water solutions (70:30 vol./vol.) were prepared by adding water (300 cm^3) to a 1000 cm^3 volumetric flask and diluting to the mark with distilled methanol.

UV–Vis spectra were recorded on a Shimadzu UV260 spectrophotometer. pH measurements were made with a PTI6 pH meter equipped with a Russell combination electrode. The filling solution of the reference section was a 3 mol dm^{-1} aqueous solution of sodium chloride. The pH meter was calibrated to read hydrogen ion concentration directly by titrating solutions of perchloric acid (0.001–0.005 mol dm^{-3}) with standard sodium hydroxide solutions. The endpoints of these titrations were determined using the method of Johansson [41].

Metal ions stability constants were determined spectrophotometrically. Stability constants were determined using the computer program SQUAD [42]. The details are shown in Table 1.

Kinetic measurements were made on a Hi-Tech SF-20 stopped-flow apparatus interfaced to a BBC microcomputer. Pseudo-first-order rate constants were calculated by fitting the absorbance data (70–100 data points) to eqn. (1) using a three-parameter curve-fitting routine in which the absorbance at zero time, A_0, the absorbance at infinity time, A_∞, and the rate constants k were treated as variables. Data for from three to four half-lives were used in these calculations. The reported rate constants are the average of at least three determinations. The standard deviations in individual runs were usually less than 1%

$$A = A_\infty(1 - \exp(-kt)) + A_0 \exp(-kt) \qquad (1)$$

The reactions were investigated in the forward direction (complex formation) and in the reverse direction (hydrolysis). The complex formation reactions were monitored by reacting solutions of the ligands at the appropriate ionic strength and hydrogen ion concentration with solutions of the metal having the same ionic strength and hydrogen ion concentrations and observing the absorbance change at a wavelength which afforded a large absorbance change. Hydrolysis reactions were carried out by reacting solutions of the complexes, adjusted to a pH where there was appreciable complex formation, with solutions containing perchloric acid and observing the absorbance change at a suitable wavelength.

Results

Table 1 lists the equilibrium data for the 1:1 complexes of $[UO_2]^{2+}$ with H_2hto, H_2phto and

TABLE 1. Equilibrium data for reaction of $[UO_2]^{2+}$ with triketones

	H_2hto	H_2phto	H_2dppto
Solution composition			
$[T_L]$ range		1.00×10^{-4}–2.50×10^{-4} mol dm^{-3}	
$[T_M]$ range		2.00×10^{-5}–100×10^{-3} mol dm^{-3}	
ionic strength, electrolyte		0.5 mol dm^{-3} $NaClO_4$	
pH range		1.5–3.0	
Experimental method		spectrophotometric determination	
Temperature (°C)		25	
Total no. data points	210	210	210
Method of calculation		SQUAD [42]	
Stability constants log β_{MHL}	8.48 ± 0.02	8.79 ± 0.01	8.95 ± 0.02

TABLE 2. Kinetic data for reaction of $[UO_2]^{2+}$ with heptane-2,4,6-trione (H_2hto), 1-phenylhexane-1,3,5-trione (H_2phto) and 1,5-diphenylpentane-1,3,5-trione (H_2dppto) in methanol–water (70:30 vol./vol.) at 25 °C and $I=0.5$ mol dm^{-3}

Ligand	$10^3\times[UO_2]^{2+}$ (mol dm^{-3})	$10^3\times[H^+]$ (mol dm^{-3})	k_{obs} (s^{-1})	$k_{calc}{}^a$ (s^{-1})
H_2hto^b	2.00	50.0	128	122
	3.00	50.0	128	126
	4.00	50.0	129	129
	5.00	50.0	129	133
	6.00	50.0	128	137
	3.00	15.8	53.6	49.3
	5.00	15.8	57.0	57.0
	3.00	10.0	39.6	36.4
	5.00	10.0	51.5	44.3
	3.00	6.31	30.0	28.6
	5.00	6.31	39.3	36.8
	2.00	4.00	20.5	19.7
	3.00	4.00	27.0	24.2
	4.00	4.00	30.9	28.6
	5.00	4.00	34.5	33.0
	6.00	4.00	38.3	37.4
	2.00	3.98	22.4	19.7
	3.00	3.98	26.3	24.1
	5.00	3.98	36.9	33.0
	1.00	2.51	13.9	12.4
	2.00	2.51	18.9	17.3
	4.00	2.51	30.8	27.0
	1.0	1.58	12.1	11.0
	2.00	1.58	18.8	16.5
	4.00	1.58	29.4	27.6
	2.00	1.00	18.5	17.4
	3.56	1.00	27.4	27.8
	2.00	0.930	19.0	17.7
	3.00	0.930	24.0	24.6
	4.00	0.930	28.6	31.4
	5.00	0.930	34.0	38.3
	6.00	0.930	41.3	45.1
h_2phto^c	3.00	25.1	24.5	24.2
	4.00	25.1	25.7	26.0
	5.0	25.1	27.1	27.8
	2.90	15.8	18.4	17.5
	4.00	15.8	19.7	19.6
	5.00	15.8	20.9	21.5
	3.00	10.0	14.7	13.8
	4.00	10.0	16.0	15.8
	5.00	10.0	17.7	17.7
	2.04	6.31	9.86	9.51
	3.00	6.31	11.8	11.5
	4.00	6.31	13.8	13.6
	2.00	3.98	8.67	8.13
	3.00	3.98	10.6	10.4
	4.00	3.98	12.6	12.7
	2.00	2.51	7.54	7.65
	3.00	2.51	9.88	10.2
	4.00	2.51	12.2	12.7
h_2dppto^d	3.00	25.1	3.97	3.84
	4.00	25.1	4.34	4.30
	5.00	25.1	4.86	4.77
	2.90	15.8	3.10	3.06
	4.00	15.8	3.53	3.60
	5.00	15.8	4.03	4.09
	3.00	10.0	2.73	2.72
	4.00	10.0	3.03	3.26
	5.00	10.0	3.57	3.79
	2.04	6.31	2.10	2.03
	3.00	6.31	2.70	2.60
	4.00	6.31	3.20	3.21
	2.00	3.98	2.26	2.01
	3.00	3.98	2.80	2.72
	4.00	3.98	3.40	3.43
	2.00	2.51	2.24	2.23
	3.00	2.51	3.15	3.11
	4.00	2.51	3.92	3.99

[a] On the basis of Scheme 1. [b] $\lambda=375$ nm. [c] $\lambda=410$ nm. [d] $\lambda=490$ nm.

H_2dppto. When solutions of the ligands were reacted with solutions containing a pseudo-first-order excess of $[UO_2]^{2+}$ in the stopped-flow apparatus a single first-order reaction was observed. Table 2 lists the kinetic data for formation of the 1:1 complexes with all three ligands. The mechanism proposed to account for the kinetic data is shown in Scheme 1. In this Scheme, H_2L represents the triketone.

$$\begin{tikzcd}
{[UO_2]^{2+} + H_2L} \arrow[r, shift left, "k_1"] \arrow[d, shift right, "K_a"'] & {[UO_2(HL)]^+ + H^+} \arrow[l, shift left, "k_{-1}"] \\
{[UO_2]^{2+} + HL^-} \arrow[u, shift right] \arrow[r, shift left, "k_2"] & {[UO_2(HL)]^+} \arrow[l, shift left, "k_{-2}"]
\end{tikzcd}$$

Scheme 1.

For the mechanism in Scheme 1, k_{obs} has the form of eqn. (2) where $K_f=[UO_2(HL)]^+/[UO_2]^{2+}[HL^-]$, K_a is the first dissociation constant of the ligand ($10^{-8.27}$ for H_2hto and H_2dppto and $10^{-8.39}$ for H_2phto) and $[U]_o$ is the total uranium concentration.

$$k_{obs}=\{k_1[H^+]+k_2K_a\}\{[U]_o/(K_a+[H^+])+(K_aK_f)^{-1}\} \tag{2}$$

Equation (2) predicts that a plot of $k_{obs}\{[U]_o/(K_a+[H^+])+(K_aK_f)^{-1}\}^{-1}$ against $[H^+]$ should give a straight line of slope k_1 and intercept k_2K_a. Figure 1 show this to be the case for reaction of $[UO_2]^{2+}$ with heptane-2,4,6-trione. Even though $[H^+]$ varies by over a factor of 10, there is no deviation from linearity. Similar plots are obtained for the other

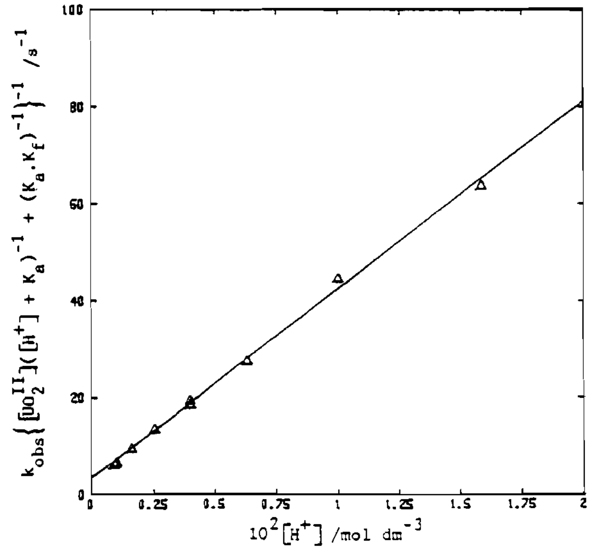

Fig. 1. Plot suggested by eqn. (2) for reaction of $[UO_2]^{2+}$ with heptane-2,4,6-trione in methanol–water solution (70:30 vol./vol.) at 25 °C and $I=0.5$ mol dm^{-3} $NaClO_4$. *x* axis: $10^2\times[H^+]$ (mol dm^{-3}); *y* axis: $k_{obs}\{[U]_o/(K_a+[H^+])+(K_aK_f)^{-1}\}^{-1}$ (s^{-1}).

ligands. Fitting the kinetic data to eqn. (2) using a non-linear curve fitting routine, give the values for k_1 and k_2 shown in Table 3 for all three ligands. The k_{calc} values obtained using the fitted values of the parameters are also given in Table 2 and it is apparent that the agreement between the k_{obs} and k_{calc} values is excellent over the hydrogen ion and metal concentrations used.

When solutions containing $[UO_2(HL)]^+$ were reacted with solutions containing an excess of perchloric acid, a single reaction was observed. Under these conditions, there is no excess $[UO_2]^{2+}$ so that the usual approach of setting $[U]_o$ in eqn. (2) to zero can be used. Noting that $K_f=k_2/k_{-2}$ and that $K_fK_a=k_1/k_{-1}$, the rate law for the hydrolysis reactions is thus given by eqn. (3).

$$k_{obs}=k_{-1}[H^+]+k_{-2} \tag{3}$$

The kinetic data are consistent with this rate law and eqns. (4), (5) and (6) give the experimental results.

$$H_2hto: k_{obs}=2.30(\pm 0.07)+2.68(\pm 0.01)\times 10^3[H^+] \tag{4}$$

$$H_2phto: k_{obs}=0.99(\pm 0.01)+6.63(\pm 0.06)\times 10^2[H^+] \tag{5}$$

$$H_2dphto: k_{obs}=0.31(\pm 0.01)+8.52(\pm 0.05)\times 10^1[H^+] \tag{6}$$

Although the water exchange rate, k_s, of $[UO_2]^{2+}$ has not been directly determined at 25 °C, using the reported values [17] of $\Delta H^‡$ (41.45 kJ mol^{-1}) and $\Delta S^‡$ (8.79 J K^{-1} mol^{-1}), it may be calculated to be 9.7×10^5 s^{-1}. In the present study, the solvent is methanol–water (70:30 vol./vol.), so it is expected that k_s would be somewhat greater. The values of the outer-sphere association constants (K_{os}) for +1/−1 and +2/0 interactions are approximately 2 and 0.5 dm^3 mol^{-1} in the above solvent when a distance of closest approach of 6 Å is assumed. From the foregoing, the Eigen–Wilkins mechanism [43] would predict that the second-order rate constant for complex formation, k_f $\{=(3/4)K_{obs}k_s\}$ [44] would be in the order of 10^6 dm^3 mol^{-1} s^{-1}.

From Table 3 it is evident that the reactions of $[UO_2]^{2+}$ with the fully protonated forms of all three ligands (k_1) proceed at rates that are greatly retarded when compared to those predicted on the basis of the Eigen–Wilkins mechanism [43]. The retardation factor is in the order of 10^4 and places them in the 'large effect' classification of Margerum *et al.* [43]. the rate constants for reaction of $[UO_2]^{2+}$ with the mono-anions of all three ligands to form the 1:1

TABLE 3. Summary of the rate constants for formation and dissociation of the mono-complexes of $[UO_2]^{2+}$ with heptane-2,4,6-trione (H_2hto), 1-phenylhexane-1,3,5-trione (H_2phto) and 1,5-diphenylpentane-1,3,5-trione (H_2dppto) in methanol–water (70:30 vol./vol.) at 25 °C and $I=0.5$ mol dm^{-3}

Rate constant (dm^3 mol^{-1} s^{-1})	H_2hto	H_2phto	H_2dppto
$k_1\times 10^{-3}$ (exp.)	3.67(±0.04)	1.78(±0.02)	0.419(±0.01)
$k_2\times 10^{-8}$ (exp.)	5.55(±0.49)	4.73(±0.42)	2.16(±0.09)
k_{-1} (exp.)	2680(±6)	663(±6)	85.2(±0.5)
k_{-1} (pred.)[a]	2263	709	87.6
k_{-2} (exp.)[b]	2.30(±0.07)	0.99(±(0.01)	0.31(±0.01)
k_{-2} (pred.)[b]	1.84	0.76	0.24
$k_3\times 10^{-6}$ (exp.)	2.97(±0.26)	1.92(±0.17)	1.16(±0.05)

[a] On the basis of log β and the rate of complex formation. [b] s^{-1}.

complex are all considerably greater than predicted by the Eigen–Wilkins mechanism. There are two possible reasons for this. An internal conjugate base may be formed between an oxygen on the ligand and the hydrogen of a coordinated water molecule. This can operate by either increasing the value of K_{os} or enhancing the rate of water exchange. It has been argued that enhanced solvent exchange rates are less important than increased K_{os} values [45]. Outer-sphere saturation, implying the presence of relatively large values of K_{os} have previously been reported for reactions of Cr^{3+} [46].

Alternatively, an A or I_a mechanism may be operative, in which case the rate of solvent exchange is not rate-determining. Previous investigations of the ligand exchange mechanisms of complexes of $[UO_2]^{2+}$ have reported the presence of both associative and dissociative mechanisms [34]. In the case of an associative mechanism for complex formation, rate constants greater than those predicted on the basis of the rate of solvent exchange may be obtained. This has been observed in the case of complex formation reactions of Cr^{3+} which proceed by an I_a mechanism [47]. Some support for the latter proposal comes from a comparison of the rate constants for the three ligands. For the reactions with the protonated forms of the ligands, there is a significant decrease in rate on going from the least sterically hindered ligand, H_2hto to the most sterically hindered H_2dppto. A similar trend is observed for the mono anions and although the decrease in this cases is only a factor of 2.5 compared to a factor of 9 for the protonated ligands, the accord between the trends is gratifying.

An alternative formulation of the mechanism would involve a mechanism in which both $[UO_2]^{2+}$ and its hydrolytic product $[UO_2(OH)]^{1+}$ react with the protonated form of the ligand with rate constants of k_1 and k_3, respectively. In this situation k_{obs} would have the form of eqn. (7) where K_h is the hydrolysis constant for formation of $[UO_2(OH)]^{1+}$. The value of log K_h is -6.0 [48].

$$k_{obs} = \{k_1[H^+] + k_3K_h\}\{[U]_o/(K_a + [H^+]) + (K_aK_f)^{-1}\} \tag{7}$$

Fitting the kinetic data to this mechanism gives the results shown in Table 3 for k_3. The values obtained for k_3 seem surprisingly small when compared with the values obtained for reactions of the hydrolytic products of iron(III) with ligands. The solvent exchange rate of Fe^{3+} is 160 s^{-1} ($\Delta V^{\ddagger} = -5.4$ cm^3 mol^{-1}) while that for $Fe(OH)^{2+}$ is 1.2×10^5 s^{-1} ($\Delta V^{\ddagger} = +5.3$ cm^3 mol^{-1}) [49]. This represents a labilization factor of 750 on going from Fe^{3+} to the hydrolytic product and a change in mechanism from I_a to I_d. For Cr^{3+} and $Cr(OH)^{2+}$ the values of k_s are 2.4×10^{-6} ($\Delta V^{\ddagger} = -9.6$ cm^3 mol^{-1}) and 1.8×10^{-4} s^{-1} ($\Delta V^{\ddagger} = +2.7$ cm^3 mol^{-1}), respectively [50], an acceleration factor of 75. It is not unreasonable to expect a similar increase in the case of $[UO_2]^{2+}$ on formation of the hydrolytic species and this would normally be reflected in an increase in the rates of complex formation. However, if the mechanism for solvent exchange changed from an I_a to an I_d mechanism on going to the hydrolytic species, the expected increase in lability could be masked in the case of a good nucleophile. The dioxouranium ion is a hard acid while the triketones are hard bases. This matching in acid–base properties would result in a high reactivity in the case of an I_a mechanism.

The agreement between the experimentally determined values of k_{-1} and k_{-2} and those calculated on the basis of the rate constants for complex formation and the spectrophotometrically determined equilibrium constants gives further support to the proposed mechanism. It is unnecessary to invoke the more complex mechanism proposed by Chopra and Jordan [51] as was necessary for the reactions of copper(II) with triketones [52]. It is not possible to decide between the two possible mechanisms on the basis of the kinetic data alone. However, the balance of probability appears to favour the mechanism shown in Scheme 1.

Ekstrom and Johnson [3], depending on the mechanism used, obtained values of either 3.6×10^5 dm^3 mol^{-1} s^{-1} or 4.4×10^5 dm^3 mol^{-1} s^{-1} for reaction of $[UO_2]^{2+}$ with the molecular form of 4-(2-pyridylazo)resorcinol in aqueous solution. As might be expected, these rates are intermediate between those obtained for reaction of $[UO_2]^{2+}$ with the protonated and mono-anionic forms of the triketones investigated here.

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