Kinetics and Mechanism of the Reactions of Uranyl Ion and β-Diketones in Methanol--Water (9 : 1 v/v)

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The rates of ketonization and enolization together with the enol to keto ratios of 1,1,1-trifluoropentane-2,4-dione (Htfpd) and 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione (Htftbd) have been determined in a range of methanol–water solutions. The equilibrium constants for formation of $[UO_2(tfpd)]^+$ and $[UO_2(tftbd)]^+$ have been determined in methanol–water solutions (9 : 1 v/v). The kinetics and mechanisms of the reactions of uranyl ion with pentane-2,4-dione (Hpd), Htfpd, and Htftbd in methanol–water solutions (9 : 1 v/v) have been investigated. The $[UO_2]^{2+}$ ion reacts with the enol tautomer of Hpd with a rate constant of 4 928 ± 727 dm³ mol⁻¹ s⁻¹, while it reacts with the keto tautomer with a rate constant of 18.1 ± 0.5 dm³ mol⁻¹ s⁻¹. However, $[UO_2]^{2+}$ reacts exclusively with the enol tautomers of Htfpd and Htftbd with rate constants estimated to be $\geqslant$1 000 dm³ mol⁻¹ s⁻¹.

In recent years a number of papers dealing with the kinetics and mechanisms of the reactions of metal and oxometal ions with β-diketones have appeared in the literature.[1-15] Most of these have dealt with reactions in aqueous solutions, although a number of them have also reported data in methanol and methanol–water media. The reactions of metal species with β-diketones have a greater potential for mechanistic variation than their reactions with most other ligands. β-Diketones exist as keto and enol tautomers and in many instances the keto to enol ratio is highly solvent dependent. For example, in water the keto to enol ratio is 4 : 1 for pentane-2,4-dione [16,17] while it is 0.25 : 1 in methanol.[18] We have extended our studies of the reactions of metal and oxometal ions with β-diketones in aqueous solutions to methanol–water solutions. This was done largely in the hope of elucidating some of the details of the intimate mechanisms of these reactions. We now report the kinetics of the reactions of dioxouranium(VI), $[UO_2]^{2+}$, with pentane-2,4-dione (Hpd), 1,1,1-trifluoropentane-2,4-dione (Htfpd), and 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione (Htftbd) in methanol–water solutions (9 : 1 v/v).

EXPERIMENTAL

Stock solutions of $[UO_2]^{2+}$ were prepared from AnalaR grade $[UO_2][NO_3]_2\cdot 6H_2O$. The solutions were standardized by igniting aliquot portions to U_3O_8 in platinum crucibles. Koch-Light Htfpd and Htftbd were used as purchased. Solutions were always freshly prepared for the kinetic runs. Hpd was freshly distilled prior to use. Methanol was purified by distilling from magnesium and iodine. Methanol–water solutions (9 : 1 v/v) were prepared by adding water (100 g) to a volumetric flask (1 dm³) and then diluting to the mark with dry methanol. The mole fraction (x) of methanol in these solutions is 0.80. Toluene-p-sulphonic acid was used as the H^+ source in these solutions. Sodium perchlorate purified as previously described [15] was used to adjust the ionic strength to 0.5 mol dm⁻³.

The apparatus and techniques were as previously described.[14] The metal species was maintained in at least ten-fold excess of the ligand to ensure formation of only the mono-complex. This also ensured that the reactions were carried out under pseudo-first-order conditions. The temperature was maintained at 25.0 ± 0.1 °C.

The following procedure was found to give the most satisfactory results for the determination of the rate constants for enolization of β-diketones (k_e) but at all times care was taken to ensure that none of the bromine evaporated. Bromine solutions were prepared by dissolving a known volume of bromine in a known volume of solvent. Aliquot portions of these solutions were standardized by titration with thiosulphate using acidified potassium iodide to liberate iodine. The extinction coefficients of bromine in solution were determined by reading the absorbance of solutions in 1-cm stoppered cells at the appropriate wavelength. The concentrations of these solutions were known and were checked by titration as described above after the absorbance was recorded.

Solutions containing bromine, acid, and sodium perchlorate to a total ionic strength of 0.5 mol dm⁻³ were allowed to equilibrate at 25 °C in stoppered cells. Following this, the initial absorbances of the solutions were determined at the appropriate wavelength. Aliquot portions of the diketone were then introduced using a micropipette, and the absorbance decreases recorded. The data were treated according to equation (4) and at least five different sets of concentrations were used to determine the final k_e value.

RESULTS AND DISCUSSION

Tautomerization Reactions.—The keto–enol tautomerization equilibrium of a β-diketone may be represented by equation (1) where HK and HE represent the keto and enol tautomers respectively. The enolization rates of β-diketones (k_e) are measured by a bromination procedure.[19]

$$\mathrm{HK} \underset{k_t}{\overset{k_e}{\rightleftharpoons}} \mathrm{HE} \qquad (1)$$

Usually, the enol tautomer and any enolate ion present react rapidly with bromine added. In order to maintain equilibrium some of the keto tautomer converts to the enol tautomer which then reacts with bromine; hence the rate of enolization parallels the rate of bromination. Therefore equations (2) and (3) hold

$$-\mathrm{d}[\mathrm{Br_2}]/\mathrm{d}t = -\mathrm{d}[\mathrm{HK}]/\mathrm{d}t = k_e[\mathrm{HK}] \qquad (2)$$

$$[\mathrm{Br_2}] = A/\varepsilon \text{ and } [\mathrm{HK}] = (A/\varepsilon + a - b) \qquad (3)$$

where A is the optical density at time t due to the absorbance of bromine, ε is the molar absorbtivity of bromine in a cell of 1 cm path length, a is the total concentration of β-diketone, and b is the total concentration of bromine. Making the appropriate substitution in equations (2) and (3), equation (4) can be derived. Thus,

$$-\ln(A/\varepsilon + a - b) = k_e t + \text{constant} \qquad (4)$$

a plot of the left-hand side of equation (4) against time gives a straight line of slope k_e, the rate of enolization of the β-diketone.

In order to determine the rate of ketonization of β-diketones (k_f), solutions of the diketone were adjusted to pH 6.5, at which stage they contained appreciable quantities of the enolate ion. On mixing with acid solution the enolate ion was rapidly converted to the enol tautomer and the subsequent slow conversion of the enol tautomer could be monitored at suitable wavelengths. Guggenheim plots of the absorbance changes yield values of $k_{obs.}$ which equal the rate of approach to equilibrium, $(k_e + k_f)$.[20] The rates of enolization of Htftbd and Htfpd in water–methanol solutions (9 : 1 v/v) are $(2.20 \pm 0.40) \times 10^{-3}$ s^{-1} and $(3.46 \pm 0.19) \times 10^{-3}$ s^{-1} respectively.

TABLE 1

Rates of ketonization (k_f) of Htftbd and Htfpd in methanol–water solutions

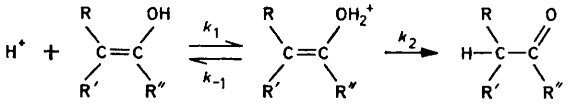
	Htftbd [a]		Htfpd [b]	
x_{MeOH}	$10^2[H^+]$/mol dm^{-3}	k_f/s^{-1}	$10^2[H^+]$/mol dm^{-3}	k_f/s^{-1}
0.8 [c]	0.39	0.051	0.38	0.055
	0.98	0.062	0.95	0.062
	1.56	0.078	1.90	0.070
	1.95	0.067	3.81	0.077
	2.93	0.080	5.71	0.088
	4.88	0.101	7.61	0.091
	7.81	0.101	9.52	0.098
	9.80	0.110	19.05	0.114
0.4 [c]	0.4	0.294	0.4	0.460
	1.0	0.322	1.0	0.510
	4.0	0.343	2.0	0.521
	6.0	0.377	4.0	0.522
	8.0	0.389	6.0	0.529
	10.0	0.435	8.0	0.570
	20.0	0.440	10.0	0.607
0.31	5.0	0.470	5.0	0.721
	10.0	0.578	10.0	0.727
	20.0	0.618	20.0	0.733
	50.0	0.605	50.0	0.774
0.13 [c]	4.0	0.996	4.0	1.509
	6.0	1.116	6.0	1.453
	10.0	1.026	10.0	1.411
	20.0	1.143	20.0	1.378
0.0 [d]	5.0	2.051	1.0	2.185
	10.0	2.022	10.0	1.990
	20.0	1.952	20.0	2.035

[a] λ = 342 nm. [b] λ = 296 nm. [c] I = 0.5 mol dm^{-3} Na[ClO$_4$]. [d] I = 1.0 mol dm^{-3} Na[ClO$_4$].

Preliminary investigations suggested that the ketonization rates (k_f) of Htftbd and Htfpd in methanol–water were dependent on the concentration of H$^+$ present in the solutions. Table 1 gives the experimental results. In order to test the accuracy of our experimental procedures and results we also redetermined k_f for Htftbd in aqueous solution at an ionic strength of 1.0 mol dm^{-3} in the [H$^+$] range 0.05—0.20 mol dm^{-3}. The average value obtained 2.01 ± 0.05 s^{-1} is in good agreement with the value of 1.96 ± 0.06 s^{-1} obtained by Sutin and co-workers [3] under similar conditions.

Both k_e and k_f decrease with increasing methanol content of the solvent. However, k_f decreases more rapidly than k_e, and since the ratio of enol to keto tautomer present is $k_e : k_f$ the enol fraction present increases with increasing methanol content of the solvent. A similar result is obtained for Hpd.[16-18] The relative increase in enol to keto ratio on going from pure water to methanol–water (9 : 1 v/v) is the same for both Htftbd and Htfpd within experimental error. Possible differences in the solvation of the two β-diketones do not appear to affect the influence of changing solvent composition on the keto to enol ratio.

It is apparent that in aqueous methanol the value of k_f increases with increasing acidity, levelling off at acidities <0.2 mol dm^{-3}. This effect is more marked in solutions having a high mol fraction of methanol. This effect has not previously been reported, probably because results to date have been largely confined to aqueous solutions. The general mechanism for keto–enol conversion is thought to be acid catalysed with rate-determining proton transfer to carbon.[19] It may be written as equation (5). Proton-transfer reactions to and from oxygen are



(5)

generally rapid and in this case the protonation equilibrium can be described by the equilibrium constant K, where $K = k_1/k_{-1}$. When the H$^+$ concentration is in pseudo-first-order excess $k_{obs.}$ will have the form of equation (6). It appears that under most conditions $K[H^+] \gg 1$ so that $k_{obs.} = k_2$. Consequently, the observed rate constant is not dependent on [H$^+$] and k_2 appears as the limiting rate. If however $K[H^+] \simeq 1$, equation (6) may be written as equation (7). A plot of $[H^+]/k_{obs.}$ against [H$^+$] should be linear with a slope of $1/k_2$ and intercept of $1/Kk_2$. Application of equation (7) to the results obtained for the ketonization studies of Htftbd and Htfpd gives one line for each solvent composition (Figures 1 and 2). The slopes of these lines gives the values of k_2, the limiting rate of ketonization at each solvent composition. The low values of the intercepts (<0.1 s mol dm^{-3} in all cases) lead to large errors in the determination of K. Table 2 summarizes the values obtained for k_e and k_f for both Htftbd and Htfpd and also gives the ratio of enol to keto tautomer at various solvent compositions.

$$k_{obs.} = Kk_2[H^+]/(1 + K[H^+]) \qquad (6)$$

$$[H^+]/k_{obs.} = [H^+]/k_2 + 1/Kk_2 \qquad (7)$$

Equilibrium Measurements.—The overall equilibrium constant K_1 for reaction (8) and the partitioned equilibrium constants K_E and K_K [equations (9) and (10)] were determined as previously described [13] using equation (11)

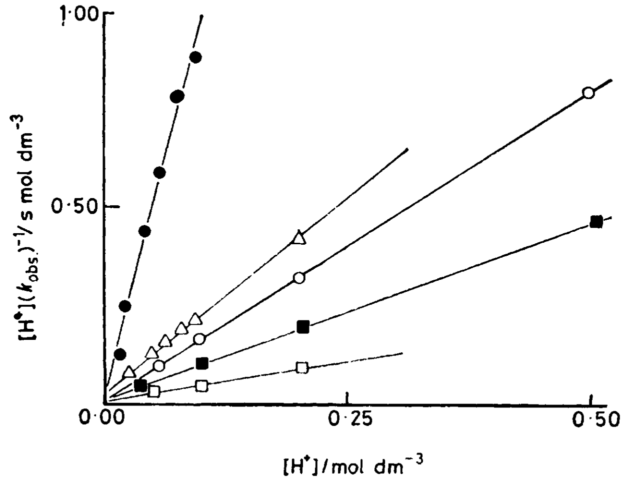


FIGURE 1 Plot of equation (7) for ketonization of Htftbd in methanol–water mixtures: $x_{MeOH} = 0.80$, $k_2 = 0.11$ (●); $x_{MeOH} = 0.4$, $k_2 = 0.44$ (△); $x_{MeOH} = 0.31$, $k_2 = 0.63$ (○); $x_{MeOH} = 0.13$, $k_2 = 1.27$ (■); $x_{MeOH} = 0.00$, $k_2 = 2.0$ (□)

where A is the absorbance per cm pathlength, ε_1 is the molar absorption coefficient of $[ME]^+$, and M^{2+} represents $[UO_2]^{2+}$; $[M^{2+}]_0$ and $[HL]_0$ represent the total concentrations of metal ion and ligand respectively. In these equations $[HL] = [HK] + [HE]$ is the total concentration of undissociated diketone and HK, HE, and E^- are the keto and enol tautomers and enolate ion respectively.

$$M^{2+} + HL \longrightarrow ME^+ + H^+ \ (K_1) \qquad (8)$$

$$M^{2+} + HK \longrightarrow ME^+ + H^+ \ (K_K) \qquad (9)$$

$$M^{2+} + HE \longrightarrow ME^+ + H^+ \ (K_E) \qquad (10)$$

$$\frac{[M^{2+}]_0[HL]_0}{A[H^+]} = \frac{[M^{2+}]_0 + [HL]_0}{\varepsilon_1[H^+]} + \frac{1}{\varepsilon_1 K_1} \qquad (11)$$

Figure 3 shows plots of the left-hand side of equation (11) against $([M^{2+}]_0 + [HL]_0)/[H^+]$ for reaction of $[UO_2]^{2+}$ with Htftbd and Htfpd in methanol-water (9 : 1 v/v). The values of K_1, K_K, and K_E are given in Table 3.

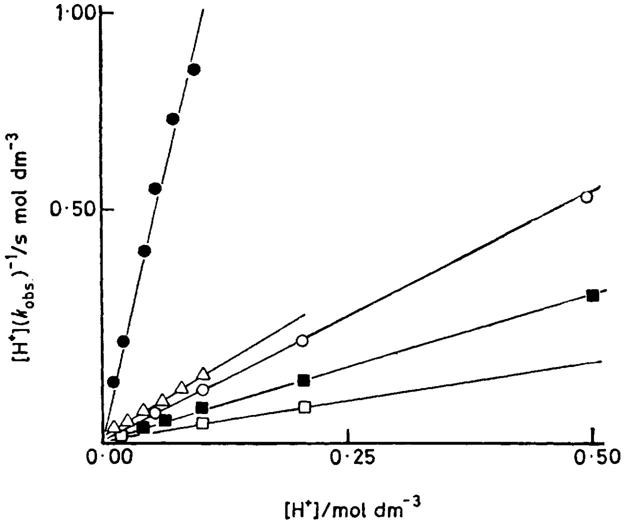


FIGURE 2 Plots of equation (7) for ketonization of Htfpd in methanol–water mixtures: $x_{MeOH} = 0.80$, $k_2 = 0.10$ (●); $x_{MeOH} = 0.40$, $k_2 = 0.65$ (△); $x_{MeOH} = 0.31$, $k_2 = 1.25$ (○); $x_{MeOH} = 0.13$, $k_2 = 1.25$ (■); $x_{MeOH} = 0.00$, $k_2 = 2.30\ s^{-1}$ (□)

Kinetics of the Reaction between $[UO_2]^{2+}$ *and* Hpd *in Methanol–Water* (9 : 1 $^v/v$).—When solutions of $[UO_2]^{2+}$ were treated with Hpd a two-step reaction was observed. A similar result was obtained when solutions containing Hpd and an excess of $[UO_2]^{2+}$ were treated with an excess of H^+. In some of the kinetic runs the half-lives of the two reaction stages were comparatively close and it proved difficult to separate the two reaction steps on the screen of the oscilloscope. This was particularly true for some of the kinetic runs in the reverse direction (*i.e.* hydrolysis) where the absorbance change due to the slow step was very small. The small absorbance change is due to the fact that there is approximately half as much keto tautomer (HK) as enol tautomer (HE) present in methanol–water (9 : 1 v/v) in the case of Hpd. Consequently the results for this slow reaction in the reverse direction are considered as qualitative only. Table 4 summarizes the kinetic data.

TABLE 2

Ratios of enol to keto tautomer present in methanol–water solutions of Htftbd and Htfpd

x_{MeOH}	$10^3k_e/s^{-1}$	k_f/s^{-1}	$10^3([HE]/[HK])$
(*a*) Htftbd			
0.80	2.20	0.11	20.0
0.40	4.32	0.44	9.9
0.31	5.01	0.58	8.6
0.13	6.84	1.03	6.6
0.00	8.40 [a]	2.03	4.1
(*b*) Htfpd			
0.80	3.46	0.098	35.3
0.40	7.24	0.61	11.9
0.31	8.51	0.73	11.6
0.13	11.75	1.42	8.3
0.00	14.90 [b]	1.99	7.5

[a] Ref. 3. [b] J. C. Reid and M. Calvin, *J. Amer. Chem. Soc.*, 1950, **72**, 2948.

TABLE 3

Equilibrium constants for the formation of $[UO_2(tftbd)]^+$ and $[UO_2(tfpd)]^+$ in methanol–water (9 : 1 v/v) at 25 °C and ionic strength 1.0 mol dm^{-3}

Ligand	λ/nm	K_1	K_K	K_E
Htftbd	410	6.85 ± 0.68	6.99 ± 0.69	349.4 ± 34.7
Htfpd	360	2.39 ± 0.24	2.47 ± 0.25	70.67 ± 7.1

The reaction between $[UO_2]^{2+}$ and Hpd in methanol–water (9 : 1 v/v) is best interpreted in terms of Scheme 1, where M^{2+} represents $[UO_2]^{2+}$. The non-trivial solutions

$$\begin{aligned}\lambda_2 = \{&k_e + k_f + k_{HK}[M^{2+}] + k_{HE}[M^{2+}] + k_{-HK}[H^+] + \\ &k_{-HE}[H^+]\} - \{k_e(k_{HE}[M^{2+}] + k_{-HK}[H^+] + \\ &k_{-HE}[H^+]) + k_{HK}[M^{2+}](k_f + k_{HE}[M^{2+}] + \\ &k_{-HE}[H^+]) + k_f(k_{-HK}[H^+] + k_{-HE}[H^+]) + \\ &k_{HE}k_{-HK}[M^{2+}][H^+]\}/(k_e + k_f + k_{HK}[M^{2+}] + \\ &\qquad k_{HE}[M^{2+}] + k_{-HK}[H^+] + k_{-HE}[H^+])\end{aligned} \qquad (12)$$

for the secular equations arising from this scheme are given by equations (12) and (13) where λ_1 and λ_2 correspond to the fast and slow relaxations respectively. If these fast and slow relaxations are attributed to the reaction of HE and HK respectively with $[UO_2]^{2+}$ then equations (12) and (13) should describe the observed rate

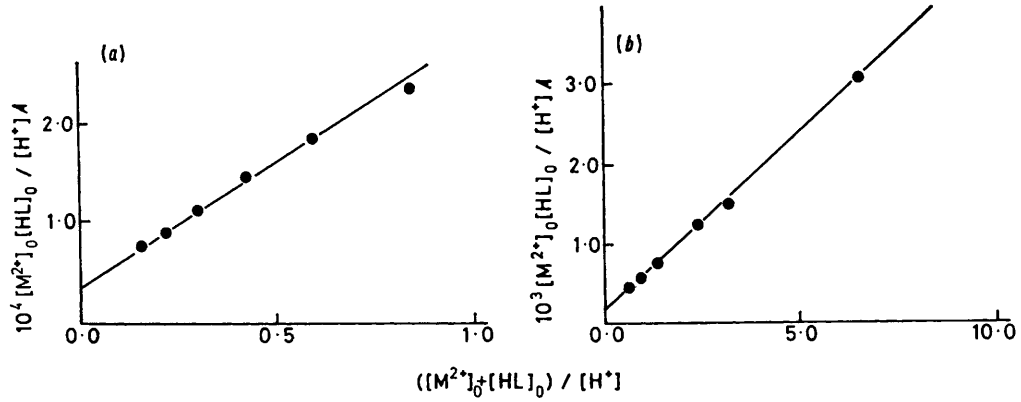


FIGURE 3 Plots of equation (11) for the determination of K_1 for the formation of mono-complexes in methanol–water (9 : 1 v/v): (*a*) $[UO_2(tftbd)]^+$; (*b*) $[UO_2(tfpd)]^+$

$$\lambda_3 = \{k_e(k_{HE}[M^{2+}] + k_{-HK}[H^+] + k_{-HE}[H^+]) + k_{HK}(k_f + k_{HE}[M^{2+}] + k_{-HE}[H^+]) + k_f(k_{-HK}[H^+] + k_{-HE}[H^+]) + k_{HE}k_{-HK}[M^{2+}][H^+]\}/\{k_e + k_f + k_{HK}[M^{2+}] + k_{HE}[M^{2+}] + k_{-HK}[H^+] + k_{-HE}[H^+]\} \quad (13)$$

constants for these reactions. Equations (12) and (13) may be simplified by making the reasonable assumption that $k_{HE} \gg k_{HK}$. Despite this simplification however, equation (12) remains extremely intractable and it did not prove possible to carry out a satisfactory analysis of the kinetic data for the fast step in terms of this equation. An additional complicating factor is the fact that the usual and useful simplification of $k_e \gg k_f$ is not applicable in this instance (k_e and k_f are equal to 0.005 6 and 0.010 4 s^{-1} respectively). Consequently the data were analysed as previously described [12] for the reactions in aqueous solution (Scheme 2). Applying the steady-state approximation to E^- and assuming that MHE^{2+} and ME^+ are in equilibrium, one obtains equation (14)

$$k_{obs.} = \frac{k_5k_a[M^{2+}] + k_{-5}k_a[H^+] + k_{-a}k_6[H^+][M^{2+}] + k_5k_6[M^{2+}] + k_{-a}k_6[H^+]^2/K + k_5k_6[M^{2+}][H^+]^2}{k_{-a}[H^+] + k_5[M^{2+}]} \quad (14)$$

for $k_{obs.}$. Since $k_{-a} = 3 \times 10^{-10}$ dm^3 mol^{-1} s^{-1} [20] it is reasonable to assume that $k_{-a}[H^+] \gg k_5[M^{2+}]$. Thus equations (15)—(18) are obtained. Experimentally it has been found that for reactions studied in the forward direction there is no dependence on $[M^{2+}]^2$ and that neither the slope or intercept of a plot of $k_{obs.}$ against $[M^{2+}]$ has any dependence on $[H^+]$. Taking $k_6 \gg (k_ak_5/k_{-a}[H^+] + k_5k_6/k_{-a})$ the only terms contributing to $k_{obs.}$ are those in equation (19). The kinetic data for experiments 1—11 (Table 4) were plotted as $k_{obs.}$ against $[M^{2+}]$ (Figure 4). The resultant plot has a slope of

$$k_{obs.} = a[M^{2+}]^2 + b[M^{2+}] + c \quad (15)$$

$$a = k_5k_6/k_{-a}[H^+] \quad (16)$$

$$b = k_6 + k_ak_5/k_{-a}[H^+] + k_5k_6/k_{-a} \quad (17)$$

$$c = k_{-5} + k_{-6}[H^+]/K \quad (18)$$

$$k_{obs.} = k_6[M^{2+}] + k_{-5} \quad (19)$$

4 928 ± 727 dm^3 mol^{-1} s^{-1} corresponding to k_6, the rate of reaction of $[UO_2]^{2+}$ with HE, the enol tautomer of Hpd. The intercept of the plot suggested by equation (15) is 24.8 ± 6.5 s^{-1}. Equation (15) suggests that this intercept is k_{-5}, which is independent of $[H^+]$. However, the metal-independent term $k_{-6}[H^+]/K$ in equation (15) may also contribute to the intercept of the $k_{obs.}$ against $[M^{2+}]$ plot. The effect of this term is within the experimental error of these fast reactions. Under the experimental conditions used to study the reactions in the forward direction the main dissociative pathway of the

TABLE 4

Observed rate constants for the reaction between $[UO_2]^{2+}$ and Hpd in methanol–water (9 : 1 v/v) [a]

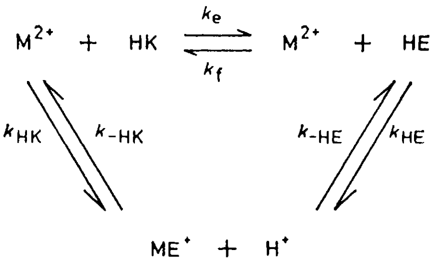
Experiment no. [b]	$10^3[UO_2^{2+}]$	$10^3[H^+]$	$k_{obs.}/s^{-1}$ (fast)	$k_{obs.}/s^{-1}$ (slow)
	mol dm^{-3}			
1	5.0	0.91	37.8	0.100
2	8.0	0.91	69.8	0.161
3	10.0	0.91	84.7	0.197
4	5.0	1.66	47.4	0.105
5	8.0	1.66	60.8	0.162
6	10.0	1.66	79.6	0.206
7	12.5	1.66	90.0	0.247
8	15.0	1.66	87.0	0.279
9	4.0	2.82	45.2	0.089
10	6.0	2.82	56.8	0.128
11	11.0	2.82	71.0	0.216
12	8.0	5.00	11.8	0.25
13	8.0	10.00	12.6	0.27
14	10.0	10.00	9.8	0.27
15	10.0	20.00	11.0	0.34
16	10.0	40.00	20.3	0.30
17	10.0	50.00	20.4	0.34
18	8.0	50.00	22.6	0.35
19	10.0	60.00	28.1	0.26
20	10.0	80.00	33.2	0.29
21	10.0	100.00	40.0	0.37
22	8.0	100.00	43.6	0.35
23	10.0	120.00	62.4	
24	10.0	150.00	66.0	
25	10.0	160.00	82.6	
26	10.0	200.00	99.5	

[a] Hpd = 2.5×10^{-4} mol dm^{-3}, $\lambda = 380$ nm, and $I = 0.5$ mol dm^{-3} Na[ClO$_4$]. [b] Experiments 1—11 were run in the forward direction, 12—26 in the reverse direction.

complex $[ME]^+$ to the free metal and the enolate ion is *via* the k_{-5} route.

Figure 5 shows a plot of $k_{obs.}$ against $[H^+]$ for the reaction of $[UO_2]^{2+}$ and Hpd studied in the reverse direction; $k_{obs.}$ has the form of equation (20). Any variation in $k_{obs.}$ with change in metal concentration is within experimental error. It is apparent from Figure 5 that dissociation of the complex $[UO_2(pd)]^+$ occurs by both acid-dependent and acid-independent pathways.

$$k_{obs.} = (k_{-6}/K)[H^+] + k_{-5} \qquad (20)$$



SCHEME 1

The slope and intercept of the plot of equation (20) are 380 ± 17 dm^3 mol^{-1} s^{-1} and 5.3 ± 1.1 s^{-1} corresponding to k_{-6}/K and k_{-5} respectively. One would expect that if the mechanism in Scheme 2 was rigidly obeyed, the intercept obtained in Figure 4 would be the same as the intercept obtained in Figure 5. It is apparent that this is not so. Examination of the data for experiments 12—28 in Table 4 suggests that the intercept (5.3 s^{-1}) of the plot shown in Figure 5 is reliable. An obvious possibility is that there is a contribution from a reactive hydrolytic species of $[UO_2]^{2+}$ to the $k_{obs.}$ for the forward reactions, experiments 1—11 in Table 4. This would appear in the rate law as a metal-independent term. In theory this complication could be avoided by carrying out the formation reactions at higher $[H^+]$. However, under these conditions the degree of formation is relatively small and this, allied with the rapidity of the reaction (due to the necessity of using high $[UO_2]^{2+}$ concentration to achieve complex formation) results in the precision of the kinetic data being correspondingly reduced.

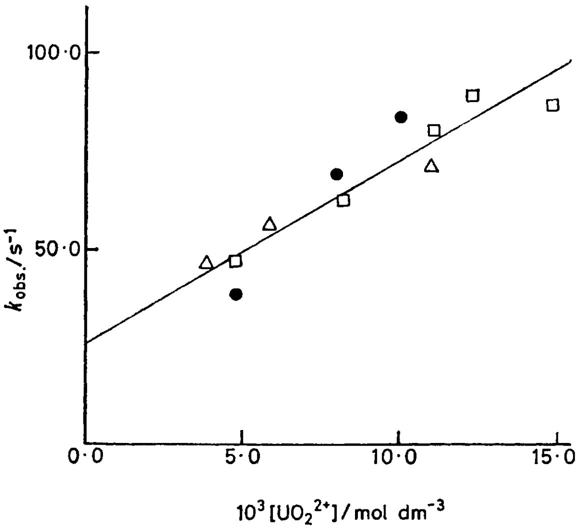
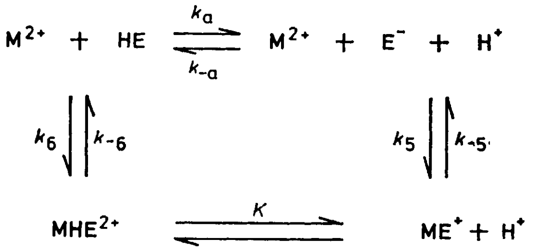


FIGURE 4 Plot of equation (19) for reaction of $[UO_2]^{2+}$ with the enol tautomer of Hpd in methanol–water (9 : 1 v/v): $[H^+] = 0.91 \times 10^{-3}$ (●); 1.66×10^{-3} (□); 2.82×10^{-3} mol dm^{-3} (△)



SCHEME 2

The observed rate constants for the slow reaction observed when $[UO_2]^{2+}$ is reacted with Hpd are included in Table 4. This slow reaction is attributed to the reaction of the metal with the keto tautomer, HK. The values of $k_{obs.}$ for the slow 'formation' reaction in methanol–water (9 : 1 v/v) are independent of H^+ concentration in contrast to their aqueous counterparts. Equation (13) may be reduced to equation (21) by putting $k_{-HE} = k_{HE}/K_E$ and $k_{-HK} = k_{HK}/K_K$ and allowing $k_{HE} \gg k_{HK}$ and $k_{HE}[M^{2+}] \gg (k_{HK}[M^{2+}] + k_e + k_f)$. Under the experimental conditions used the following approximations are valid: $[H^+]/[M^{2+}]K_K \ll 1$, $[H^+]/[M^{2+}]K_E \ll 1$, and $k_{HK}/k_{HE} < 1$. Using these approximations to eliminate all but the largest terms in equation (21) the expression for $k_{obs.}$ reduces to equation (22).

$$k_{obs.} = \frac{k_e k_{HE}[M^{2+}] + k_f k_{HK} + k_{HE}k_{HK}[M^{2+}]\{1 + [H^+]/K_K[M^{2+}] + [H^+]/K_E[M^{2+}]\}}{k_{HE}[M^{2+}]\{1 + [H^+]/[M^{2+}]K_E + [H^+]k_{HK}/[M^{2+}]K_K k_{HE}\}} \qquad (21)$$

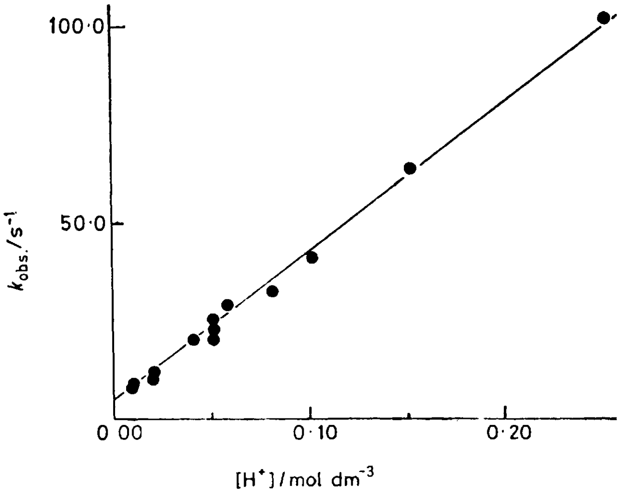


FIGURE 5 Plot of equation (20) for reaction of $[UO_2]^{2+}$ with the enol tautomer of Hpd in methanol–water (9 : 1 v/v)

The kinetic data for the slow reaction in experiments 1—11 (Table 4) fit the plot suggested by equation (22) (Figure 6). The slope, k_{HK} is 18.1 ± 0.5 dm³ mol⁻¹ s⁻¹

$$k_{\mathrm{obs.}} = k_e + k_f k_{\mathrm{HK}}/k_{\mathrm{HE}} + k_{\mathrm{HK}}[\mathrm{M}^{2+}] \qquad (22)$$

and represents the rate of reaction of $[\mathrm{UO_2}]^{2+}$ with the keto tautomer of Hpd. The value of k_{HK} obtained is about five times faster than that obtained in water. The intercept of the plot of $k_{\mathrm{obs.}}$ against $[\mathrm{M}^{2+}]$ in Figure 6 has a value of $(16.6 \pm 4.0) \times 10^{-3}$ s⁻¹ and is equal to $(k_e + k_f k_{\mathrm{HK}}/k_{\mathrm{HE}})$ where $k_e = 10.4 \times 10^{-3}$ s⁻¹. The values of $k_{\mathrm{obs.}}$ for the slow reaction studied in the reverse direction are relatively constant. This is as expected since equation (22) does not predict a $[\mathrm{H}^+]$ dependence for $k_{\mathrm{obs.}}$. Values of k_{HK} ranging from 24 to 35 dm³ mol⁻¹ s⁻¹ can be calculated from the kinetic data for experiments 12—22. Considering the qualitative nature of the $k_{\mathrm{obs.}}$ values in these experiments, these values of k_{HK} are in satisfactory agreement with k_{HK} derived from experiments carried out in the forward direction.

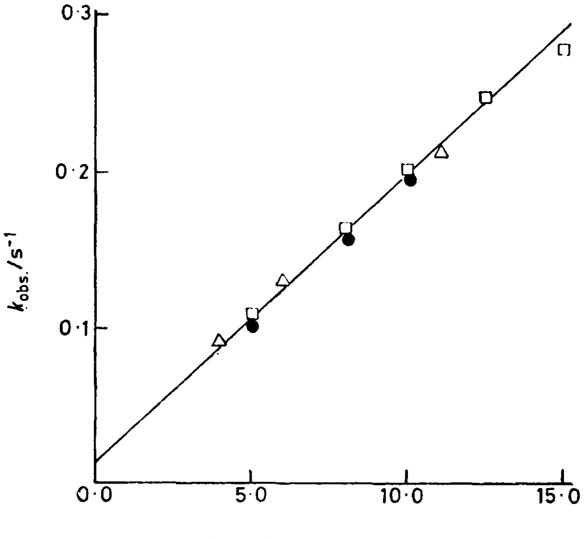


FIGURE 6 Plot of equation (22) for reaction of $[\mathrm{UO_2}]^{2+}$ with the keto tautomer of Hpd in methanol–water (9 : 1 v/v): $[\mathrm{H}^+] = 0.91 \times 10^{-3}$ (●); 1.66×10^{-3} (□); 2.82×10^{-3} mol dm⁻³ (△)

Kinetics of the Reaction of $[\mathrm{UO_2}]^{2+}$ *and* Htftbd *in Methanol–Water* (9 : 1 *v/v*).—A single reaction step was observed when $[\mathrm{UO_2}]^{2+}$ was treated with Htftbd in methanol–water (9 : 1 v/v), independent of whether the reaction was studied in the forward or reverse direction. The kinetic data are given in Table 5. They are consistent with a reaction scheme in which the metal ion reacts with the enol form of Htftbd as in equation (23)

$$\mathrm{HK} \underset{k_f}{\overset{k_e}{\rightleftharpoons}} \mathrm{HE} \underset{k_{-\mathrm{HE}}'}{\overset{k_{\mathrm{HE}}'}{\rightleftharpoons}} [\mathrm{M(tftbd)}]^+ \qquad (23)$$

where $\mathrm{M}^{2+} = [\mathrm{UO_2}]^{2+}$, $k_{\mathrm{HE}}' = k_{\mathrm{HE}}[\mathrm{M}^{2+}]$, and $k_{-\mathrm{HE}}' = k_{-\mathrm{HE}}[\mathrm{H}^+]$. This is comparable to the result obtained in aqueous solution.[13] Analyzing the secular equation arising from equation (23) as previously described [13] and allowing $k_f \gg k_e$, $k_{\mathrm{obs.}}$ is described by equation (24) and (25). The data in Table 5 for the reaction of $[\mathrm{UO_2}]^{2+}$

$$k_{\mathrm{obs.}} = \left[\frac{k_e k_{\mathrm{HE}}[\mathrm{M}^{2+}]}{k_{\mathrm{HE}}[\mathrm{M}^{2+}] + k_f + k_{\mathrm{HE}}[\mathrm{H}^+]/K_{\mathrm{E}}}\right] [1 + [\mathrm{H}^+]/K_{\mathrm{K}}[\mathrm{M}^{2+}]] \qquad (24)$$

$$\frac{1 + [\mathrm{H}^+]/K_{\mathrm{K}}[\mathrm{M}^{2+}]}{k_{\mathrm{obs.}}} = 1/k_e + \left[\frac{k_f}{k_e k_{\mathrm{HE}}} + \frac{[\mathrm{H}^+]}{k_e K_{\mathrm{E}}}\right]\left[\frac{1}{[\mathrm{M}^{2+}]}\right] \qquad (25)$$

and Htftbd could not be treated successfully in terms of equation (25). However, the approximations used to simplify this equation for the reaction in aqueous solution [13] are equally valid for the reaction in methanol–water (9 : 1 v/v), *i.e.* $k_{\mathrm{HE}}[\mathrm{M}^{2+}] \gg (k_f + k_{\mathrm{HE}}[\mathrm{H}^+]/K_{\mathrm{E}})$. Applying this condition to equation (25) results in equation (26) for $k_{\mathrm{obs.}}$. In spite of the small variations in the

$$k_{\mathrm{obs.}} = k_e + k_e[\mathrm{H}^+]/K_{\mathrm{K}}[\mathrm{M}^{2+}] \qquad (26)$$

$k_{\mathrm{obs.}}$ values for experiments 1—16, the data fit the plot suggested by equation (26). The values of k_e and K_{K} obtained from a plot of $k_{\mathrm{obs.}}$ against $[\mathrm{H}^+]/[\mathrm{M}^{2+}]$ are $(4.2 \pm 0.2) \times 10^{-3}$ s⁻¹ and 12.3 ± 2.3 respectively. These are in reasonable agreement with the directly determined values of k_e and K_{K}. Under the experimental conditions used for experiments 1—9, $K_{\mathrm{K}}[\mathrm{M}^{2+}] \gg k_e[\mathrm{H}^+]$ in equation (26) and $k_{\mathrm{obs.}} \approx k_e$. This is equivalent to saying that the reaction goes to completion in the forward direction and the rate of reaction is controlled by the rate of keto–enol conversion.

TABLE 5

Observed rate constants for the reaction of $[\mathrm{UO_2}]^{2+}$ with Htftbd in methanol–water (9 : 1 v/v) [a]

Experiment no.[b]	$10^3[\mathrm{UO_2}^{2+}]$ mol dm⁻³	$10^2[\mathrm{H}^+]$ mol dm⁻³	$10^2k_{\mathrm{obs.}}$/s⁻¹
1	5.0	1.62	
2	7.5	1.62	0.44
3	10.0	1.62	0.40
4	15.0	1.62	0.40
5	20.0	1.62	0.44
6	10.0	3.63	0.54
7	15.0	3.63	0.51
8	20.0	3.63	0.52
9	25.0	3.63	0.50
10	5.0	5.13	0.74
11	10.0	5.13	0.65
12	15.0	5.13	0.59
13	20.0	5.13	0.55
14	25.0	5.13	0.54
15	15.0	1.00	0.64
16	15.0	2.00	0.53
17	15.0	5.00	0.96
18	15.0	10.00	1.55
19	15.0	20.00	3.40
20	15.0	30.00	4.70
21	15.0	50.00	7.20

[a] Htftbd = 2.0×10^{-4} mol dm⁻³, λ = 410 nm, I = 0.5 mol dm⁻³ Na[ClO₄]. [b] Experiments 1—14 were run in the forward direction, 15—21 in the reverse direction.

For reactions in the reverse direction $[\mathrm{H}^+]/K_{\mathrm{K}}[\mathrm{M}^{2+}] \gg 1$ and $k_{\mathrm{HE}}[\mathrm{H}^+]/K_{\mathrm{E}} > k_f$, especially when $[\mathrm{H}^+] > 0.1$ mol dm⁻³. Under these conditions equation (24) reduces to equation (27). Data from experiments 17—21 were plotted as $1/k_{obs.}$ against $[M^{2+}]/[H^+]$ (Figure 7). Values

$$1/k_{obs.} = 1/k_f + K_E[M^{2+}]/k_f[H^+] \qquad (27)$$

of k_f and K_E calculated from the intercept and slope of the plot are 0.18 ± 0.12 s^{-1} and 60 ± 40 respectively. The directly determined values of k_f and K_E are 0.11 s^{-1} (at 0.1 mol dm^{-3} $[H^+]$) and 349.4 respectively. Obviously the value obtained for K_E from the plot suggested by equation (27) is in serious disagreement with the directly determined value. There is no obvious reason for this discrepancy in the K_E value obtained from equation (27) and the assumptions made in deriving this equation appear valid.

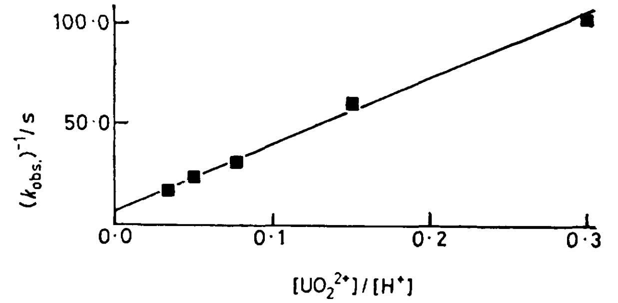
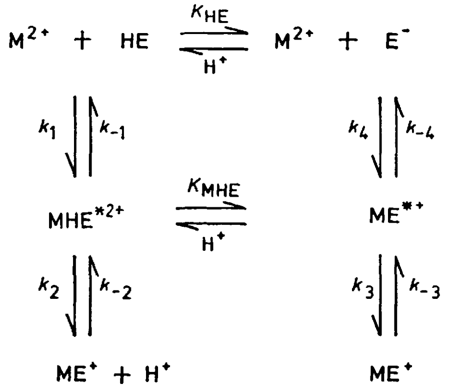


FIGURE 7 Plot of equation (27) for reaction of $[UO_2]^{2+}$ and Htftbd in methanol-water (9 : 1 v/v)

The $[H^+]$ dependence of k_{HE} should be the same in methanol-water (9 : 1 v/v) as in water, *i.e.* equation (28).

$$k_{HE} = a + b/[H^+] \qquad (28)$$

It has previously been shown [3] that this form of rate law is consistent with a mechanism of the type shown in Scheme 3, and that k_{HE} has the form of equation (29).



SCHEME 3

Using the assumption that the formation of the intermediates is rate determining and that the subsequent

$$k_{HE} = (k_1 + k_{HE}k_4/[H^+])/\{1 + (k_{-1} + K_{MHE}k_{-4}/[H^+])(k_2 + K_{MHE}k_3/[H^+])^{-1}\} \qquad (29)$$

ring closure is rapid, *i.e.* $(k_2 + K_{MHE}k_3/[H^+]) \gg (k_{-1} + K_{MHE}k_{-4}/[H^+]$, equation (29) reduces to equation (30). Under the experimental conditions used for most of the

$$k_{HE} = k_1 + K_{HE}k_4/[H^+] \qquad (30)$$

reactions between $[UO_2]^{2+}$ and Htftbd, $k_{HE}[M^{2+}] \gg k_f$ or $k_{HE}[M^{2+}] > 1.0$ s^{-1}. The lowest metal concentration used in the investigation was 5×10^{-3} mol dm^{-3}, so that k_{HE} is estimated to be $\geqslant$1 000 dm^3 mol^{-1} s^{-1}. If however $b/[H^+] \gg a$ then $k_{HE} = K_{HE}k_4$. The value of K_{HE} in methanol-water (9 : 1 v/v) is not available, but considering that K_{HE} in methanol is 1.3×10^{-7}, k_4, the rate constant for reaction of $[UO_2]^{2+}$ with the enolate ion of Htftbd, must be very rapid indeed.

Kinetics of the Reaction of $[UO_2]^{2+}$ *and* Htfpd *in Methanol–Water* (9 : 1 *v/v*).—The reaction between $[UO_2]^{2+}$ and Htfpd was very similar to the reaction between $[UO_2]^{2+}$ and Htftbd. The kinetic data are given in Table 6. They were plotted according to equation (26) (Figure 8). Values of k_e $[(3.9 \pm 0.2) \times 10^{-3}$ s$^{-1}]$ and K_K (1.86 ± 0.19) were determined from the intercept and slope respectively of the plot of $k_{obs.}$ against $[H^+]/[M^{2+}]$. These values agree well with the directly determined values of k_e and K_K (3.46×10^{-3} s^{-1} and 2.47 respectively). The assumptions used to derive equation (27) from equation (24) are again valid in this case and data from experiments 19—26 satisfy the plot, suggested by equation (27) (Figure 9). The values of k_f (0.33 s^{-1}) and K_E (61 ± 20) calculated from the intercept and slope respectively are in reasonable agreement with directly determined values of k_f and K_E (0.1 s^{-1} and 71 respectively). Applying the condition $k_{HE}[M^{2+}] \gg k_f$, k_{HE} is estimated to be $\geqslant$1 000 dm^3 mol^{-1} s^{-1}. If however, $b/[H^+] \gg a$, then $k_{HE} = K_{HE}k_4$ and the value of k_4, the rate of reaction of

TABLE 6

Observed rate constants for the reaction of $[UO_2]^{2+}$ with Htfpd in methanol–water (9 : 1 v/v) [a]

Experiment no.[b]	$10^3[UO_2^{2+}]$	$10^2[H^+]$	$10^2k_{obs.}/s^{-1}$
	mol dm^{-3}		
1	5.0	0.32	0.51
2	7.5	0.32	0.43
3	10.0	0.32	0.44
4	15.0	0.32	0.43
5	20.0	0.32	0.42
6	25.0	0.32	0.44
7	5.0	1.19	0.81
8	7.5	1.19	0.63
9	10.0	1.19	0.60
10	15.0	1.19	0.54
11	20.0	1.19	0.48
12	25.0	1.19	0.50
13	5.0	1.62	1.15
14	7.5	1.62	0.93
15	10.0	1.62	0.82
16	15.0	1.62	0.68
17	20.0	1.62	0.57
18	25.0	1.62	0.56
19	20.0	4.00	1.00
20	20.0	6.00	1.40
21	20.0	10.00	2.40
22	20.0	15.00	3.40
23	20.0	20.00	4.60
24	20.0	36.00	8.10
25	20.0	42.00	9.40
26	20.0	48.00	10.80
27	20.0	55.00	12.90
28	20.0	64.00	14.10

[a] Htfpd = 4.1×10^{-4} mol dm^{-3}, $\lambda = 260$ nm, $I = 0.5$ mol dm^{-3} Na[ClO$_4$]. [b] Experiments 1—18 were run in the forward direction, 19—28 in the reverse direction.

$[UO_2]^{2+}$ with the enolate ion of Htfpd, is expected to be very large.

Table 7 summarizes the rate constants for the formation of mono-complexes of the uranyl ion with β-diketones. The results of studies carried out in aqueous solution [12,13,21] are also included for comparison purposes. It is apparent that there is no great difference between the mechanisms followed by these reactions in either water or methanol–water (9 : 1 v/v). The rate of reaction of $[UO_2]^{2+}$ with the enol tautomer of Hpd is approximately the same in both media. There is a definite increase in the rate of reaction of $[UO_2]^{2+}$ with the keto tautomer of Hpd on going from water to methanol–water (9 : 1 v/v), but the increase is considerably less than the two orders of magnitude observed for the same reaction when copper(II) is the metal. However, it is conceivable that the change to pure methanol would produce a drastic increase in the rate of reaction. It is unfortunate that precise rate constants cannot be obtained for the reaction of $[UO_2]^{2+}$ with the enol tautomers and enolate ions of Htftbd and Htfpd in either water or methanol–water (9 : 1 v/v) and that only lower limits can be quoted. A similar problem existed for the reactions of Co^{2+} and Cu^{2+} with Htftbd.[3]

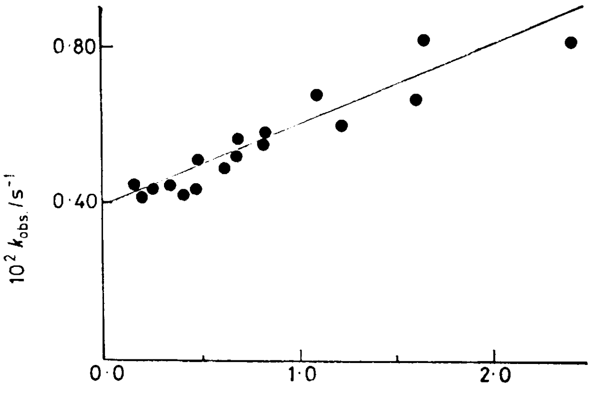


FIGURE 8 Plot of equation (26) for reaction of $[UO_2]^{2+}$ and Htfpd in methanol–water (9 : 1 v/v)

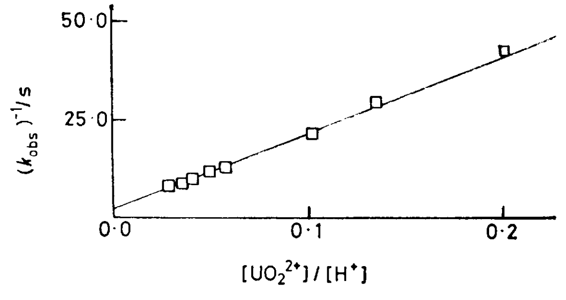


FIGURE 9 Plot of equation (27) for reaction of $[UO_2]^{2+}$ and Htfpd in methanol–water (9 : 1 v/v)

Two effects can be distinguished: (*a*) the effect of metal reactivity and (*b*) the effect of ligand reactivity. In a normal complex-formation reaction involving +2 metal ions of the 3*d* transition series the latter effect is relatively unimportant and the kinetics are dominated by the reactivity of the metal ion as measured by the solvent-exchange rate. For a given β-diketone ligand there is not a linear relationship between the rate of complex formation (k) and the solvent-exchange rate (k_s). In the case of Hpd the value of log (k/k_s) varies in the following order: Cu^{2+}, $10^{-5.6}$; Ni^{2+}, $10^{-3.2}$; Fe^{3+}, $10^{-2.8}$; $[UO_2]^{2+}$, $10^{-1.9}$. For +2 cations of the 3*d* transition series the relationship between k and k_s is $k = \frac{3}{4}K_0k_s$,[22] where K_0 is the outer-sphere association constant, and frequently lies in the range 1—10.

The general order of reactivity of the various forms of β-diketones appears to be enolate ion > enol tautomer > keto tautomer. In the case of Htftbd and Htfpd the keto tautomers are exceedingly unreactive or do not react at all and complex formation occurs exclusively by reaction between the metal ion and the enol tautomer. Both the keto and enol tautomers of Hpd react with some metal ions, and there appears to be a correlation between the complex forming ability of the metal ion and its reactivity with the keto tautomer. The species Fe^{3+}, $[UO_2]^{2+}$, and Cu^{2+} all react directly with the keto tautomer of Hpd but Ni^{2+} does not. This factor is probably due to the ability of the metal to stabilize the proposed precursor complex.[1]

TABLE 7

Rate constants for the formation of mono complexes of $[UO_2]^{2+}$ with β-diketones

Reaction	Solvent	k/dm^3 mol^{-1} s^{-1}	Reference
(*a*) Pentane-2,4-dione system			
$[UO_2]^{2+}$ + HE	Water	5 330	12
$[UO_2]^{2+}$ + HK	Water	3.6	12
$[UO_2]^{2+}$ + HE	Methanol–water (9 : 1 v/v)	4 930	This work
$[UO_2]^{2+}$ + HK	Methanol–water (9 : 1 v/v)	18.1	This work
(*b*) 4,4,4-Trifluoro-1-(2-thienyl)butane-1,3-dione			
$[UO_2]^{2+}$ + HE	Water	$\geqslant 1 \times 10^4$	13
$[UO_2]^{2+}$ + E^-	Water	$\geqslant 3 \times 10^5$	13
$[UO_2]^{2+}$ + HE	Methanol–water (9 : 1 v/v)	$\geqslant 1 \times 10^3$	This work
$[UO_2]^{2+}$ + E^-	Methanol–water (9 : 1 v/v)	Very rapid	This work
(*c*) 1,1,1-Trifluoropentane-2,4-dione			
$[UO_2]^{2+}$ + HE	Water	$\geqslant 1.3 \times 10^3$	21
$[UO_2]^{2+}$ + E^-	Water	$\geqslant 1.6 \times 10^4$	21
$[UO_2]^{2+}$ + HE	Methanol–water (9 : 1 v/v)	$\geqslant 1 \times 10^3$	This work
$[UO_2]^{2+}$ + E^-	Methanol–water (9 : 1 v/v)	Very rapid	This work

Many of the factors controlling the rates of reaction of metal–β-diketonate complexes are still not well understood. However, the number of systems studied to date is still rather limited and further work will lead to the solution of the intimate details of the mechanisms of these very interesting reactions.

[9/1136 *Received*, 18*th July*, 1979]

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