Kinetics and Mechanisms of the Reactions of Vanadyl Ion with β-Diketones

By **Michael J. Hynes** * and **Brigid D. O'Regan**, Chemistry Department, University College, Galway, Ireland

The kinetics and equilibrium constants of the reactions of vanadyl ion with 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione (Htftbd), 1,1,1-trifluoropentane-2,4-dione (Htfpd), and pentane-2,4-dione (Hpd) to form the mono complexes have been investigated in aqueous solution at 25 °C and I = 1.0 mol dm^{-3}. The values of the equilibrium constants, K_1, for the reaction $[VO]^{2+} + HL \rightleftharpoons [VO(L)]^{+} + H^{+}$ where HL represents the undissociated form of the β-diketone are 0.55 ± 0.09, 0.32 ± 0.05, and 0.11 ± 0.02 for Hpd, Htftbd, and Htfpd respectively. The kinetic data are consistent with a mechanism in which the vanadyl ion reacts with the enol forms of Htftbd and Htfpd by parallel acid-independent and inverse-acid paths. The rate constants for reaction of $[VO]^{2+}$ with HE, the undissociated enol tautomers of Htftbd and Htfpd, are 7.6 and 3.5 dm^3 mol^{-1} s^{-1} respectively. The $[VO]^{2+}$ ion reacts with the enolate ion of Htftbd and Hftpd with rate constants of 3.6×10^3 and 2×10^2 dm^3 mol^{-1} s^{-1} respectively, while it reacts with the keto-tautomer of Hpd with a rate constant of 4.4 dm^3 mol^{-1} s^{-1}.

ALTHOUGH a large number of oxo-metal species of the type $[MO_x]^{n+}$ are known for the transition metals many of them do not exist as discrete entities in solution or in the solid state.[1] The two most well known of these species are the oxovanadium(IV), or vanadyl, ion $[VO]^{2+}$, and the dioxouranium(VI), or uranyl, ion $[UO_2]^{2+}$. Complexes of these two oxo-metal ions have been extensively investigated.[1-5] As part of our continuing investigations into the kinetics and mechanisms of the complexation reactions of oxo-metal ions, particularly those involving β-diketones as ligands,[6,7] we have investigated the reactions of vanadyl ion with pentane-2,4-dione (Hpd), 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione (Htftbd), and 1,1,1-trifluoropentane-2,4-dione (Htfpd). Despite the fact that complexes of $[VO]^{2+}$ with β-diketones are numerous and that these, together with their adducts, have been widely studied,[8] there are little kinetic data available on the substitution reactions of vanadyl complexes with these ligands. A number of studies have reported solvent-exchange data and complex-formation rates of $[VO]^{2+}$ with various other ligands.[9-15] The kinetics of hydrolysis of $[VO(pd)]^{+}$ have been previously reported [16] but in view of the greatly increased understanding of the mechanisms of the interactions of metal ions with β-diketones since the original study was carried out it was decided to reinvestigate the reaction. Additionally, the formation reactions of the above complex were not investigated in the original work.

EXPERIMENTAL

Stock solutions of $[VO]^{2+}$ were prepared from vanadyl sulphate (B.D.H.). Aliquots of these solutions were analysed by adding an excess of ethylenediaminetetra-acetate solution and back-titrating the excess with an Mg^{2+} solution to an Eriochrome Black-T end-point. The Mg^{2+} solution was prepared by dissolving magnesium metal in dilute hydrochloric acid. The vanadyl sulphate from which the stock solutions of $[VO]^{2+}$ were prepared was found to contain approximately three molecules of water per molecule of $[VO][SO_4]$. In some of the kinetic runs $[VO][NO_3]_2$ was substituted for $[VO][SO_4]$. This was prepared by adding $Ba[NO_3]_2$ to aqueous solutions of $[VO][SO_4]$ and filtering off the precipitate. Within the experimental error, the rate constants did not display any effects due to the presence of sulphate.

Spectra were recorded on either Beckman DB-GT or Pye–Unicam SP 800 u.v.-visible spectrophotometers. pH Measurements were made with a Pye model 290 pH meter equipped with a Pye Ingold $E_0{}^7$ combined electrode.

All solutions were freshly prepared for the kinetic runs. Aqueous solutions containing $[VO]^{2+}$ were found to be stable for at least a period of 3 h. Pentane-2,4-dione was freshly distilled prior to use. The ionic strength of the solutions was adjusted using $Na[ClO_4]$ as the inert electrolyte. Initially it was found that there was an interaction between the $[VO]^{2+}$ and the sodium perchlorate used (Koch–Light). This was probably due to a trace of iron(III) present in the commercial salt. This was removed by passing an aqueous solution of $Na[ClO_4]$ over Zeo Karb 225 cation-exchange resin in the sodium form. The raffinate was then concentrated and the sodium perchlorate which crystallised was dried *in vacuo*. The water content was determined by thermogravimetric analysis. Sodium perchlorate purified in this manner gave no detectable reaction with $[VO]^{2+}$.

The rate constants were measured using an Applied Photophysics stopped-flow device. The drive syringes and mixing chamber were thermostatted at 25.0 ± 0.1 °C. Reaction conditions involved using a large excess of metal ion to ensure that only the mono complex was formed. The kinetic data were recorded using a Tektronix model 5100 storage oscilloscope. The stored traces were photographed on Polaroid film and plots of $-\ln(A - A_\infty)$ against time were obtained.

RESULTS AND DISCUSSION

Equilibrium Measurements.—The equilibrium constant for reaction (1) was determined by a spectrophotometric method. In the case of β-diketones existing in tautomeric keto- and enol forms, K_1 can be partitioned

$$[VO]^{2+} + HL \rightleftharpoons [VO(L)]^{+} + H^{+}\ (K_1) \qquad (1)$$

between the equilibrium constants K_K and K_E for the reactions of the keto- (HK) and enol (HE) forms respectively [equations (2)—(4)]. At equilibrium equations

$$[VO]^{2+} + HK \rightleftharpoons [VO(E)]^{+} + H^{+}\ (K_K) \qquad (2)$$

$$[VO]^{2+} + HE \rightleftharpoons [VO(E)]^{+} + H^{+}\ (K_E) \qquad (3)$$

$$\text{where } 1/K_1 = (1/K_E) + (1/K_K) \text{ and } [HE]/[HK] = K_K/K_E \qquad (4)$$

(5) and (6) hold where M^{2+} represents $[VO]^{2+}$ and $[HL]_0$ and $[M^{2+}]_0$ are the total ligand and metal concentrations respectively. In the absence of other absorbing species the concentration of $[ML]^+$ at equilibrium is

$$[HL] = [HL]_0 - [ML]^+ \qquad (5)$$

$$[M^{2+}] = [M^{2+}]_0 - [ML]^+ \qquad (6)$$

equal to A/ε where A is the absorbance per unit path length and ε is the molar absorptivity of the complex. Making the appropriate substitution in the preceding equation relationship (7) is obtained where $h = (1 +$

$$\frac{[M^{2+}]_0[HL]_0}{Ah[H^+]} = \frac{[M^{2+}]_0 + [HL]_0}{\varepsilon h[H^+]} + \frac{1}{\varepsilon K_1} \qquad (7)$$

$K_h/[H^+])$ and $K_h = 1.7 \times 10^{-5}$ mol dm^{-3} is the hydrolysis constant of $[VO]^{2+}$ in aqueous solution.[17] Hence a plot of the left-hand side of equation (7) against $([M^{2+}]_0 + [HL]_0)/h[H^+]$ should yield a straight line of slope $1/\varepsilon$ and intercept $1/\varepsilon K_1$. Figure 1 shows the plots suggested by equation (7) for reaction of $[VO]^{2+}$ with Htftbd, Htfpd, and Hpd while Table 1 gives the results obtained for K_1, K_E, and K_K.

TABLE 1

Equilibrium constants for formation of mono-β-diketone complexes of $[VO]^{2+}$ in aqueous solution at 25 °C and $I = 1.0$ mol dm^{-3}

Ligand	λ/nm	K_1	K_K	K_E
Hpd	330	0.55 ± 0.09	0.67 ± 0.10	3.14 ± 0.49
Htftbd	360	0.32 ± 0.05	0.32 ± 0.05	73.05 ± 10.73
Htfpd	330	0.11 ± 0.02	0.11 ± 0.02	10.39 ± 1.88

Kinetic Measurements.—(a) *Reaction of* $[VO]^{2+}$ *with* Htftbd *and* Htfpd *in aqueous solution*. When aqueous solutions of $[VO]^{2+}$ were treated with solutions of either Htftbd or Htfpd a one-step reaction was observed. Tables 2 and 3 contain the kinetic data. The kinetic data are consistent with a scheme in which the vanadyl ion does not react directly with the keto-tautomer. Complex formation takes place by a mechanism in which $[VO]^{2+}$ reacts with the enol form of the β-diketone according to equation (8) where $M^{2+} = [VO]^{2+}$, $k_{HE}' = k_{HE}[M^{2+}]$, $k_{-HE}' = k_{-HE}[H^+]$, and $k_{HE}/k_{-HE} = K_E$. The solution of equation (8) has been previously described.[18-20] Using the assumption that $k_f \gg k_c$ relationship (9) may be obtained for $k_{obs.}$ for the slower of the two possible relaxations. Equation (9) is more conveniently written

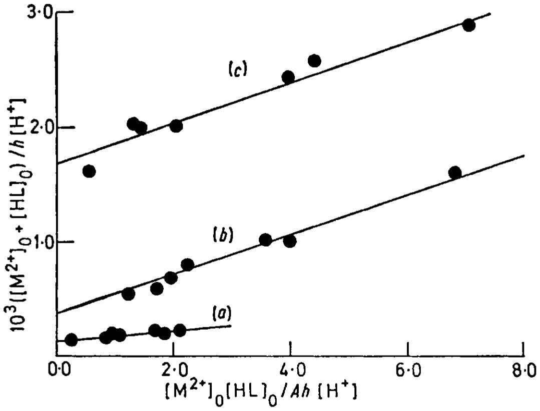


FIGURE 1 Plot of equation (7) for reaction of $[VO]^{2+}$ with β-diketones in aqueous solution at 25 °C and $I = 1.0$ mol dm^{-3}. β-Diketones: (*a*) Htftbd, (*b*) Hpd, and (*c*) Htfpd

TABLE 2

Observed rate constants for the reaction of $[VO]^{2+}$ with Htftbd in aqueous solution [a]

Expt. no.[b]	$10^3[VO^{2+}]$/ mol dm^{-3}	$10^3[H^+]$/ mol dm^{-3}	$10^2k_{obs.}$/ s^{-1}
1	2.0	2.24	0.55
2	5.0	2.24	0.60
3	8.0	2.24	0.60
4	10.0	2.24	0.63
5	2.0	1.95	0.56
6	5.0	1.95	0.60
7	10.0	1.32	0.78
8	12.0	1.32	0.74
9	2.5	50.0	1.15
10	2.5	75.0	1.27
11	2.5	100.0	1.34
12	2.5	125.0	1.61
13	5.0	125.0	1.43
14	5.0	150.0	1.74
15	5.0	200.0	1.98
16	5.0	100.0	1.54
17	8.0	100.0	1.66
18	10.0	100.0	1.68
19	16.0	100.0	1.78
20	5.0	200.0	2.83
21	8.0	200.0	2.76
22	10.0	200.0	2.86
23	16.0	200.0	2.84
24	5.0	300.0	3.67
25	10.0	300.0	3.67

[a] [Htftbd] = 1.0×10^{-4} mol dm^{-3}, λ = 366 nm, and $I = 1.0$ mol dm^{-3} Na[ClO$_4$]. [b] Experiments 1—8 were run in the forward direction, 9—25 in the reverse direction.

TABLE 3

Observed rate constants for the reaction of $[VO]^{2+}$ with Htfpd in aqueous solution [a]

Expt. no.[b]	$10^3[VO^{2+}]$/ mol dm^{-3}	$10^3[H^+]$/ mol dm^{-3}	$10^2k_{obs.}$/ s^{-1}
1	6.0	1.10	1.33
2	10.0	1.10	1.69
3	12.0	1.10	1.46
4	16.0	1.10	2.05
5	6.0	1.20	1.30
6	8.0	1.20	1.54
7	10.0	1.20	1.46
8	12.0	1.20	1.55
9	5.0	1.58	1.25
10	8.0	1.58	1.64
11	6.0	1.95	1.19
12	10.0	1.95	1.73
13	12.0	1.95	1.89
14	16.0	1.95	2.11
15	10.0	5.00	1.00
16	10.0	10.00	1.03
17	10.0	20.00	1.20
18	10.0	40.00	2.14
19	10.0	100.00	4.51
20	10.0	200.00	7.18
21	5.0	200.00	6.45
22	8.0	200.00	7.40
23	5.0	300.00	9.88
24	10.0	300.00	9.05
25	20.0	300.00	9.05
26	10.0	100.00	3.90
27	8.0	10.00	4.15
28	10.0	400.00	12.60

[a] [Htfpd] = 1.0×10^{-4} mol dm^{-3}, λ = 366 nm, and $I = 1.0$ mol dm^{-3}. [b] Experiments 1—14 were run in the forward direction, 15—28 in the reverse direction.

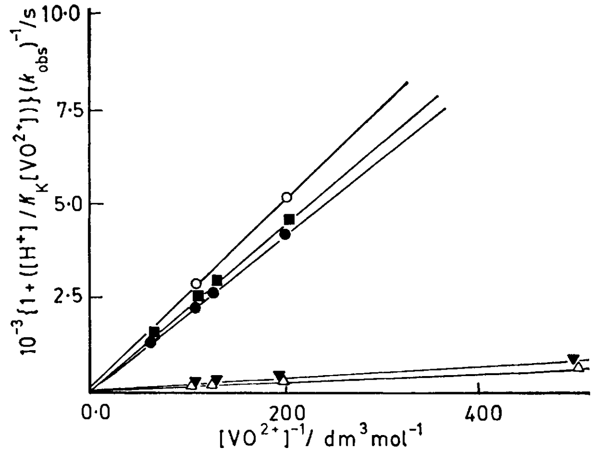


FIGURE 2 Plot of equation (10) for reaction of $[VO]^{2+}$ with Htftbd in aqueous solution at 25 °C and $I = 1.0$ mol dm^{-3}. $[H^+] = 1.95 \times 10^{-3}$ (△), 2.24×10^{-3} (▼), 0.10 (●), 0.20 (■), and 0.30 (○) mol dm^{-3}

as in (10). The data in Tables 2 and 3 are consistent with equation (10) and plots of the left-hand side against $1/[M^{2+}]$ are in fact linear (Figures 2 and 3) with common

$$HK \underset{k_f}{\overset{k_e}{\rightleftharpoons}} HE \underset{k_{-HE'}}{\overset{k_{HE'}}{\rightleftharpoons}} [ME]^+ \qquad (8)$$

$$k_{obs.} = \left\{\frac{k_e k_{HE}[M^{2+}]}{k_{HE}[M^{2+}] + k_f + (k_{HE}[H^+]/K_E)}\right\} \{1 + ([H^+]/K_K[M^{2+}]\} \qquad (9)$$

$$\frac{1 + [H^+]/K_K[M^{2+}]}{k_{obs.}} = (1/k_e) + \left(\frac{1}{[M]}\right)\left(\frac{k_f}{k_e k_{HE}} + \frac{[H^+]}{k_e K_E}\right) \qquad (10)$$

intercepts of $1/k_e$ and slopes S [equation (11)]. Equation (11) may be rewritten as (12). In order to determine the dependence of k_{HE} on $[H^+]$, trial substitutions were made for k_{HE} for example, equations (13) and (14). Plots of $1/\{S - ([H^+]/k_eK_E)\}$ against $1/[H^+]$ are linear (Figures 4 and 5) showing that k_{HE} has the form indicated

$$S = \left(\frac{k_f}{k_e k_{HE}} + \frac{[H^+]}{k_e K_E}\right) \qquad (11)$$

$$1/\{S - ([H^+]/k_eK_E)\} = k_e k_{HE}/k_f \qquad (12)$$

$$k_{HE} = a + (b/[H^+]) \qquad (13)$$

$$k_{HE} = a + b[H^+] \qquad (14)$$

in equation (13). Therefore equation (12) may be written as equation (15). From the slopes and intercepts of the plots shown in Figures 4 and 5 values of a and b are found to be 7.6 dm^3 mol^{-1} s^{-1} and 0.35 s^{-1}

$$1/\{S - ([H^+]/k_eK_E)\} = (k_e/k_f)a + \{(k_e/k_f)b/[H^+]\} \qquad (15)$$

respectively, in the case of Htfbd, and 3.5 dm^3 mol^{-1} s^{-1} and 0.1 s^{-1} respectively in the case of Htfpd.

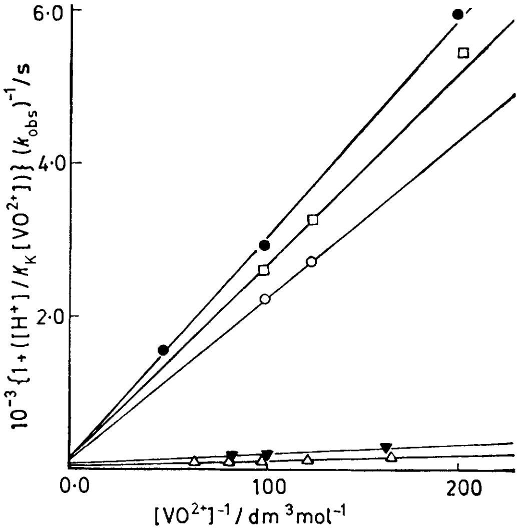


FIGURE 3 Plot of equation (10) for reaction of $[VO]^{2+}$ with Htfpd in aqueous solution at 25 °C and $I = 1.0$ mol dm^{-3}. $[H^+] = 1.20 \times 10^{-3}$ (△), 1.95×10^{-3} (▼), 0.10 (○), 0.20 (□), and 0.30 mol dm^{-3} (●)

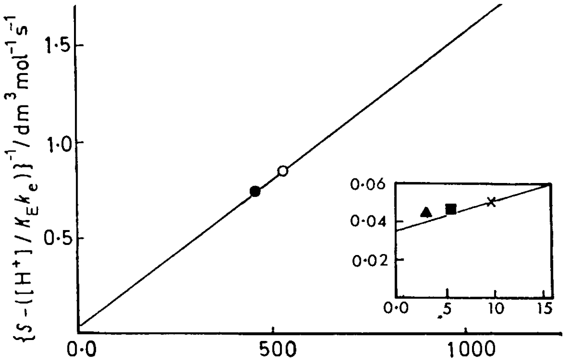


FIGURE 4 Plot of equation (11) for reaction of $[VO]^{2+}$ with Htftbd in aqueous solution at 25 °C and $I = 1.0$ mol dm^{-3}. $[H^+] = 1.95 \times 10^{-3}$ (○), 2.24×10^{-3} (●), 0.10 (×), 0.20 (■), and 0.30 mol dm^{-3} (▲)

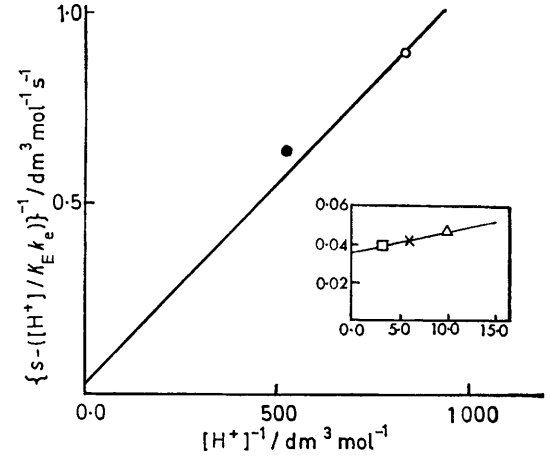


FIGURE 5 Plot of equation (11) for reaction of $[VO]^{2+}$ with Htfpd at 25 °C and $I = 1.0$ mol dm^{-3}. $[H^+] = 1.20 \times 10^{-3}$ (○), 1.95×10^{-3} (●), 0.10 (△), 0.20 (×), and 0.30 mol dm^{-3} (□)

It has been shown [20] that the form of the rate law obtained here is consistent with the mechanism outlined in Scheme 1 where $[M(HE^*)]^{2+}$ and $[ME^*]^+$ are unstable intermediates in which one end of the diketone is attached to the metal centre. Assuming that equilibrium is maintained between both HE and E^-, and $[M(HE^*)]^{2+}$ and $[ME^*]^+$, and applying the steady-state approximation, equation (16) is obtained for k_{HE}. Two

$$k_{HE} = \frac{k_1 + (K_{HE}k_4/[H^+])}{1 + \dfrac{k_{-1} + K_{MHE}k_{-4}/[H^+]}{k_2 + K_{MHE}k_3/[H^+]}} \qquad (16)$$

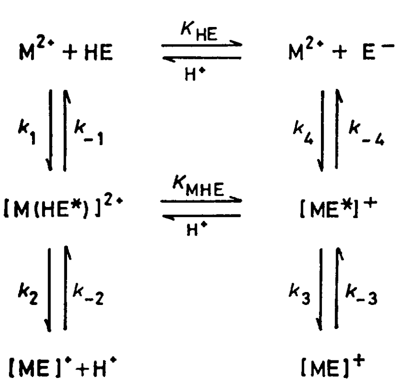
limiting cases of equation (16) are relevant.[20]

Case 1. If $\{k_2 + (K_{MHE}k_3/[H^+])\} \gg \{k_{-1} + (K_{MHE}k_{-4}/[H^+])\}$ equation (16) reduces to (17). In this

$$k_{HE} = k_1 + (K_{HE}k_4/[H^+]) \qquad (17)$$

instance $a = k_1$ and $b = k_{HE}k_4$. The implications are that formation of the singly bonded intermediate is slow and that the subsequent ring-closure reactions are rapid.

Case 2. Alternatively if $\{k_2 + (K_{MHE}k_3/[H^+])\} \ll \{k_{-1} + (K_{MHE}k_{-4}/[H^+])\}$ equation (16) reduces to (18). In this equation $K_1 = k_1/k_{-1}$ and $K_4 = k_4/k_{-4}$. Under



Scheme 1

$$k_{HE} = K_1k_2 + (K_{HE}K_4k_3/[H^+]) \qquad (18)$$

these conditions $a = K_1k_2$ and $b = K_{HE}K_4k_3$, and the rate-determining step is closure of the chelate ring.

With **Htfbd.** Comparison of equations (10) and (15) shows that in terms of the proposed reaction scheme the rate of the acid-independent reaction of the enol tautomer of Htfbd with $[VO]^{2+}$ is 7.6 dm^3 mol^{-1} s^{-1} while the rate of reaction of $[VO]^{2+}$ with the enolate ion of Htftbd is 3.6×10^3 dm^3 mol^{-1} s^{-1}.

The reactants in the acid-dependent reaction may be formulated as $[VO]^{2+}$ and E^- or alternatively as $[VO(OH)]^+$ and HE as shown in equations (19) and (20). If

$$[VO]^{2+} + E^- \xrightarrow{k_4} [VO(E)]^+ \qquad (19)$$

$$[VO(OH)]^+ + HE \xrightarrow{k_5} [VO(E)]^+ + H_2O \qquad (20)$$

the reaction pathway of equation (19) is adopted then $k_4 = 3.6 \times 10^3$ dm^3 mol^{-1} s^{-1}, whereas if the pathway of equation (20) is adopted $k_5 = b/K_h = 2.0 \times 10^4$ dm^3 mol^{-1} s^{-1} where K_h (1.7×10^{-5} mol dm^{-3}) is the hydrolysis constant of $[VO]^{2+}$.

With **Htfpd.** The kinetic data for this system were analysed in terms of the reaction of $[VO]^{2+}$ with the enol form of Htfpd exactly as was done for the reaction of Htftbd and $[VO]^{2+}$. Values of a and b in equation (15) were found to be 3.5 dm^3 mol^{-1} s^{-1} and 0.1 s^{-1} respectively. In terms of Scheme 1, k_1 the rate of reaction of $[VO]^{2+}$ with HE the enol tautomer is 3.5 dm^3 mol^{-1} s^{-1}, while k_4 the rate of reaction of $[VO]^{2+}$ with the enolate ion is 2×10^2 dm^3 mol^{-1} s^{-1}. The pathway represented by equation (20) involving reaction of $[VO(OH)]^+$ with HE gives a value of 5.9×10^3 dm^3 mol^{-1} s^{-1} for k_5.

(b) *Reaction of* $[VO]^{2+}$ *with* Hpd *in aqueous solution.* The reaction of $[VO]^{2+}$ with Hpd was carried out in aqueous solution over a wide range of metal-ion and H^+ concentrations. Under the experimental conditions used for most of the kinetic runs, a one-step reaction was observed and a single value of $k_{obs.}$ was calculated from a plot of $-\ln(A - A_\infty)$ against time (Table 4). However, under certain conditions, *e.g.* a combination of high H^+ and metal-ion concentrations, and particularly for reactions carried out in the 'reverse' direction, two reaction steps were observed. The half-lives of the two steps were usually quite close and the resulting values of $k_{obs.}$ are only considered to be qualitative (experiments 22—27 in Table 4). Attempts to treat the data

TABLE 4

Reaction of $[VO]^{2+}$ with Hpd in aqueous solution [a]

Expt. no.[b]	$10^3[VO^{2+}]$/ mol dm^{-3}	$10^3[H^+]$/ mol dm^{-3}	$k_{obs.}$ [c]/ s^{-1}	k_{HK} [d]/ dm^3 mol^{-1} s^{-1}
1	4.0	1.20	0.031	5.46
2	7.0	1.20	0.039	4.44
3	10.0	1.20	0.061	5.18
4	2.0	1.95	0.021	4.85
5	4.0	1.95	0.027	4.20
6	7.0	1.95	0.046	4.75
7	10.0	1.95	0.056	4.43
8	12.0	1.95	0.078	5.18
9	20.0	1.95	0.119	5.21
10	5.0	4.17	0.035	3.53
11	10.0	4.17	0.046	2.97
12	15.0	4.17	0.081	3.91
13	16.0	4.17	0.085	3.91
14	20.0	4.17	0.094	3.64
15	10.0	10.0	0.020	0.95
16	10.0	20.0	0.034	1.22
17	10.0	40.0	0.062	1.71
18	10.0	80.0	0.108	2.47
19	10.0	200.0	0.278	5.65
20	10.0	350.0	0.450	8.48
21	10.0	450.0	0.630	11.70
22	20.0	200.0	0.024 (0.48)	
23	20.0	100.0	0.023 (0.42)	
24	10.0	100.0	0.048 (0.24)	
25	10.0	10.0	0.060 (0.20)	
26	16.0	10.0	0.040 (0.40)	
27	10.0	10.0	0.040 (0.22)	

[a] $\lambda = 330$ nm, $[Hpd] = 2.0 \times 10^{-4}$ mol dm^{-3}, and $I = 1.0$ mol dm^{-3} $Na[ClO_4]$. [b] Experiments 1—14 were run in the forward direction, 15—21 in the reverse direction and one-step reaction was observed. Experiments 22—27 were run in the reverse direction and two steps were observed. [c] $k_{obs.}$ for faster reaction is given in parentheses. [d] Calculated from equation (21). $K_E = 3.14$, $K_K = 0.67$ (Table 1).

for these reactions in terms of the mechanism proposed for reaction of $[VO]^{2+}$ with both Htftbd and Htfpd were unsuccessful and the data do not obey equation (10).

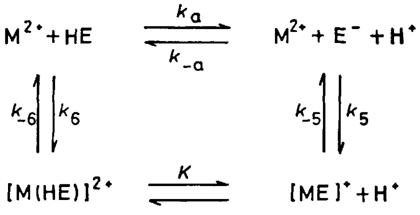
The kinetic data for experiments 1—14 in the forward direction may be analysed in terms of equation (21). In terms of this mechanism $k_{obs.}$ for the slow reaction is

$$[VO]^{2+} + HK \underset{k_{-HK}}{\overset{k_{HK}}{\rightleftharpoons}} [VO(E)]^{+} \underset{k_{HE}}{\overset{k_{-HE}}{\rightleftharpoons}} [VO]^{2+} + HE \qquad (21)$$

given by $\lambda = c/p$ where $c = (k_{HK}k_{-HE} + k_{-HK}k_{-HE})[H^+][M^{2+}] + k_{HK}k_{HE}[M^{2+}]$ and $p = (k_{-HK} + k_{-HE})[H^+] + (k_{HK} + k_{HE})[M^{2+}]$ and $[M^{2+}]$ represents $[VO]^{2+}$. Making the reasonable assumption that $[VO]^{2+}$ reacts more rapidly with HE than with HK to eliminate all but the largest terms in the expressions for c and p, expression (22) is obtained for k_{HK} where $k_{HE}/k_{-HE} = K_E$

$$k_{HK} = k_{obs.}\left\{\frac{[H^+] + K_E[M^{2+}]}{[1 + (K_E/K_K)][H^+][M^{2+}] + K_E[M^{2+}]^2}\right\} \qquad (22)$$

and $k_{HK}/k_{-HK} = K_K$. The data in experiments 1—14 (forward reaction) satisfy equation (22). The average value of k_{HK} is 4.4 ± 0.2 dm^3 mol^{-1} s^{-1}, and the constancy of the k_{HK} values (Table 4) supports the reaction pathway chosen in equation (21).



SCHEME 2

The data for experiments 15—21 (reactions run in the reverse direction) do not satisfy the above mechanism. The data may be analysed in terms of the mechanism shown in Scheme 2 as was done for reaction of $[UO_2]^{2+}$ with Hpd.[7] Applying the steady-state approximation to E^- and assuming that $[M(HE)]^{2+}$ and $[ME]^+$ are in equilibrium, equation (23) is obtained for k_{obs}. Since

$$k_{obs.} = \frac{k_5k_a[H^+][M^{2+}] + k_{-5}k_{-a}[H^+] + k_{-a}k_6[H^+][M^{2+}] + k_5k_6[M^{2+}]^2 + (k_{-a}k_{-6}[H^+]^2/K) + k_5k_6[M^{2+}][H^+]}{k_{-a}[H^+] + k_5[M^{2+}]} \qquad (23)$$

$k_{-a} = 3 \times 10^{10}$ dm^3 mol^{-1} s^{-1}, it is reasonable to assume that $k_{-a}[H^+] \gg k_5[M^{2+}]$ and that terms having k_{-a} in the numerator will be large compared to the other terms. Applying these approximations to equation (23), relationship (24) is obtained for $k_{obs.}$. For reactions in the

$$k_{obs.} = k_6[M^{2+}] + k_{-5} + (k_{-6}[H^+]/K) \qquad (24)$$

$$k_{obs.} = (k_{-6}[H^+]/K) + k_{-5} \qquad (25)$$

reverse direction the expression for $k_{obs.}$ reduces to equation (25). A plot of $k_{obs.}$ against $[H^+]$ is linear with a slope of 1.26 ± 0.02 dm^3 mol^{-1} s^{-1} (k_{-6}/K) and intercept of 0.010 ± 0.002 s^{-1} (k_{-5}) as shown in Figure 6. These values suggest that the main dissociative path of the complex $[VO(pd)]^+$ occurs *via* the protonated complex $[VO(Hpd)]^{2+}$ to Hpd and $[VO]^{2+}$ with a small contribution from the k_{-5} pathway, resulting in production of the enolate ion. The value of 1.26 dm^3 mol^{-1} s^{-1} obtained for the slope of the plot suggested by equation (25) is in fair agreement with the value of 2.37 dm^3 mol^{-1} s^{-1} obtained by Pearson and Moore[16] for the same plot at ionic strength 0.25 mol dm^{-3}.

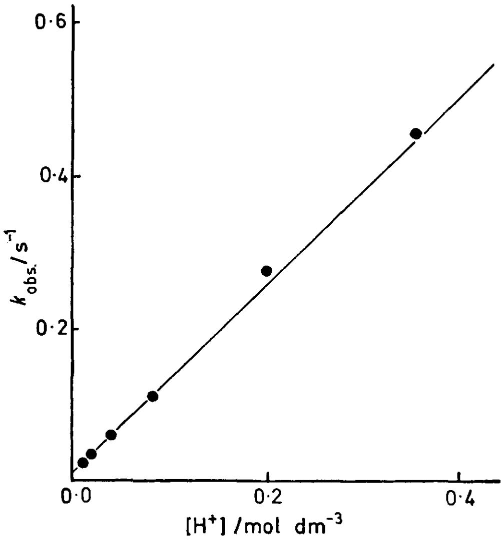


FIGURE 6 Plot of equation (24) for reaction of $[VO]^{2+}$ with Hpd in aqueous solution at 25 °C and $I = 1.0$ mol dm^{-3}

Table 5 summarises the kinetic data for reaction of $[VO]^{2+}$ with Htftbd, Htfpd, and Hpd. The solvent-exchange rate of $[VO]^{2+}$ has been previously reported in the range 500—590 s^{-1}.[11,12,14,15] In testing whether a formation rate constant is normal or not it is convenient to consider the dimensionless parameter R given by[21] $R = 4k_f/3K_0k_s$ where k_f is the rate of complex formation, K_0 is the outer-sphere association constant, and k_s is the rate of solvent exchange. For 'normal' substitution of co-ordinated water molecules R should have a value close to unity. The values of K_0 are usually calculated using the Eigen–Fuoss equation[22,23] in the case of charged ligands, and from Rorabacher's modification[24] for uncharged ligands. Table 5 gives the R values for the reactions studied in this work. The value of k_s for $[VO]^{2+}$ was taken as 500 s^{-1}. The rate of water exchange in $[VO(OH)]^+$ has not been reported but is probably close to the value of 2.3×10^4 s^{-1} obtained for water exchange in $[VO(Cl)]^+$.[14] This is the value used for the calculation in Table 5.

It is immediately obvious that the R values for reaction of $[VO]^{2+}$ with the enol tautomers of Htftbd and Htfpd, and with the keto-tautomer of Hpd, are within a factor of two of each other, but are considerably less than unity. The reduction in rate compared to ' normal ' reactions is however considerably less than the three orders of magnitude observed for reaction of Ni^{2+} with the enol tautomer of Htftbd.[25,*] The reaction of $[VO]^{2+}$ with the enolate form of Htfpd must be considered normal on this basis while the reaction with the enolate form of Htftbd is more rapid than would be expected. Although the solvent-exchange rate of $[VO(OH)]^+$ is uncertain, within the limits of the approximation made for it, the R values for reaction of $[VO(OH)]^+$ with the enol tautomers of Htftbd and Htfpd are relatively normal.

If the alternative mechanism [case 2, equation (18)] is considered for reaction of $[VO]^{2+}$ with Htftbd and assuming that k_1 has a normal value of 113 dm^3 mol^{-1} s^{-1}, k_{-1} is equal to 1.55 s^{-1} and k_2 is equal to 0.104 dm^3 mol^{-1} s^{-1}. Therefore k_2/k_{-1} is 6.7×10^{-2} dm^3 mol^{-1}. For the reaction of $[VO]^{2+}$ with Htfpd the values of k_2 and k_2/k_{-1} are 0.34 dm^3 mol^{-1} s^{-1} and 3.1×10^{-2} dm^3 mol^{-1} respectively. Due to the fact that the rate constant for reaction of $[VO]^{2+}$ with the enolate form of either Htftbd or Htfpd is not depressed below the normal value, we must assume that $k_3/k_{-4} \sim 1$. Thus, the conditions for the case 2 mechanism is $k_2/k_{-1} \ll 1$. As noted by Sutin and co-workers,[20] this implies that the two monosubstituted intermediates $[M(NH^*)]^{2+}$ and $[ME^*]^+$ (Scheme 1) have rather different kinetic properties. Although it is likely that the enol (and keto-) tautomers of β-diketones are poor entering groups with the result that $k_1 < k_4$, due to the fact that the co-ordinated enolic oxygen is less basic in $[M(HE^*)]^{2+}$ than in $[ME^*]^+$, k_{-1} is probably much larger than k_{-4}. It follows that $k_1/k_{-1} \ll k_4/k_{-4}$.

TABLE 5

Kinetic data for reaction of $[VO]^{2+}$ with β-diketone species [a]

Metal species [b]	Ligand	Ligand species	k_f/dm^3 mol^{-1} s^{-1}	K_0/ dm^3 mol^{-1}	R
$[VO]^{2+}$	Htftbd	HE	7.6	0.3	0.07
		E^-	3.6×10^3	0.9	11
$[VO]^{2+}$	Htfpd	HE	3.5	0.3	0.03
		E^-	2×10^2	0.9	0.6
$[VO]^{2+}$	Hpd	HK	4.4	0.3	0.04
$[VO(OH)]^+$	Htftbd	HE	2×10^4	0.3	3.9
$[VO(OH)]^+$	Htfpd	HE	5.9×10^3	0.3	1.1

[a] I = 1.0 mol dm^{-3}, 298 K; distance of closest approach = 500 pm. [b] k_s for $[VO]^{2+}$ is taken as 500, k_s for $[VO(OH)]^+$ as 2.3×10^4 s^{-1}.

The results show that the keto-forms of both Htftbd and Htfpd are inert to attack by metal ions and that reaction of metal (and oxo-metal) ions with these ligands occurs by a mechanism in which the metal ions react with the enol form of the β-diketone. It is also consistent with the conclusions of earlier work that the rates of reaction of the enol and keto-tautomers of β-diketones with metal ions are generally slower than would be predicted on the basis of the Eigen–Wilkins mechanism. However, the rates of complex formation when the enolate ion is the ligand are relatively normal.

Sutin and co-workers [25] have stated that there are three factors which must be considered when investigating the kinetics of metal complex formation with protonated multidentate ligands: (*i*) strong intramolecular bonds which convert the protonated ligand into a poor entering group; (*ii*) the energetics of proton release from a unidentate intermediate which may slow down the rate of ring closure (proton-controlled ring closure); and (*iii*) ring strain associated with the formation of a six-membered ring chelate. Although it is often difficult to distinguish between these effects, the present work clearly shows that factor (*iii*) is not of paramount importance in determining the overall slow rate of complex formation with β-diketones. Sutin and co-workers [20] interpret their results in terms of factor (*ii*) on the basis that intramolecular hydrogen bonding would not slow the reactions by the three orders of magnitude observed for reaction of Ni^{2+} with the enol tautomer of Htftbd. However, it is now also clear that, for some metal ions at least, the reduction in rate is very much less than this, for example the reactions of Fe^{3+} and $[Fe(OH)]^{2+}$ with the enol tautomer of Hpd are described as ' normal '.[25] The situation is further complicated by the fact that slower reactions such as the formation of complexes of Fe^{3+} and $[VO]^{2+}$ are not likely to be as affected by steric factors as more rapid reactions, *e.g.* those involving the formation of complexes of Cu^{2+}. Additionally, the stability of the precursor complex will affect the overall rate of complex formation. It appears that the relative importance of these various factors is dependent on the lability of the metal species. As has previously been pointed out,[20] kinetic data on the direct reaction of the various metal species with the enolate forms of β-diketones would be very valuable in elucidating the intimate details of the mechanisms of these very interesting reactions.

One of us (B. D. O'R.) thanks the Department of Education for a studentship.

[8/1799 *Received, 13th October,* 1978]

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[*] Using $R = 4k_f/3K_0k_s$, k_f for reaction of $[VO]^{2+}$ with neutral and singly charged ligands should be 113 and 338 dm^3 mol^{-1} s^{-1} respectively. However, the experimental results reported to date vary somewhat: $[VO]^{2+} + [SCN]^-$, k_f = 160;[9] $[VO]^{2+}$ + glycine, k_f = 1 300;[15] $[VO]^{2+}$ + tartaric acid monoanion, k_f = 170 dm^3 mol^{-1} s^{-1}.[13]

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