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Kinetics and Mechanisms of the Reactions of Copper(II) and Oxovanadium(IV) with Heptane-3,5-dione in Aqueous Solution

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Abstract

The kinetics and mechanisms of the reactions of copper(II) and oxovanadium(IV), $[VO]^{2+}$ with heptane-3,5-dione to form the 1:1 complex have been investigated in aqueous solution at 25 °C and ionic strength 0.5 mol dm^{-2} $NaClO_4$ using the stopped-flow technique. In the case of copper(II), two separate reactions were observed, while only one reaction was observed when oxovanadium(IV) was the metal species.

A detailed mechanism is proposed to account for the kinetic data. Cu^{2+} reacts with the enol and keto tautomers of the ligand with rate constants of 1.14×10^4 and 8.9 dm^3 mol^{-1} s^{-1}, respectively. $[VO]^{2+}$ reacts with the enol and keto tautomers with rate constants of 5.33 and 0.986 dm^3 mol^{-1} s^{-1}, respectively, while $[VO(OH)]^+$ reacts with the keto tautomer with a rate constant of 7.64 dm^3 mol^{-1} s^{-1}. The results are discussed in the light of previous investigations.

Introduction

The kinetics and mechanisms of the reactions of metal ions with β-diketones have been the subject of a number of investigations during the past few years [1]. Although some of these investigations have been concerned with the reactions of copper(II) [2–8], it is only recently that the rate constants for reaction of Cu^{2+} with an enolate ion derived from a β-diketone have been determined [6, 7]. In previous investigations, rate constants for reaction of Cu^{2+} with both the keto and enol tautomers of various β-diketones have been reported. However only lower limits of the complex formation rate constants for reaction of this metal ion with the enolate form of the ligands could be estimated. Kinetic data for reaction of $[VO]^{2+}$ with β-diketones is quite limited [1, 8].

Recent work has concentrated on an investigation of the effect of chain length on the reactivity of β-diketones towards metal ions [9, 10]. To date, the kinetics and mechanisms of the reactions of nickel(II) [9] and cobalt(II) [10] with heptane-3,5-dione have been investigated. As a continuation of this work we now report the results of our investigation of the reactions of copper(II) and oxovanadium(IV) with this ligand. On the basis of their solvent exchange rates [11] copper(II) represents a labile metal ion while $[VO]^{2+}$ with a water exchange rate of approximately 500 s^{-1} [12–15] is a relatively inert metal ion.

Experimental

$Cu(NO_3)_2 \cdot 3H_2O$ (May and Baker) was used as the source of copper(II). Stock solutions were standardised by titration with sodium thiosulphate in the presence of starch indicator. The sodium thiosulphate had been previously standardised against potassium iodate. Stock solutions of $[VO]^{2+}$ were prepared from vanadyl sulphate (BDH). Aliquots of these solutions were analysed by adding an excess of standard ethylenediaminetetraacetate solution and backtitrating the excess with a standard Mg^{2+} solution to an Eriochrome Black T endpoint. The titration was carried out at pH > 10 in the presence of a NH_4OH/NH_4Cl buffer.

Reagent grade heptane-3,5-dione (Kodak) was freshly distilled under reduced pressure prior to use. Stock solutions were standardised by titration with standard sodium hydroxide. Endpoints were determined by the use of an iterative computer program based on the method of Gran and Johansson [16].

Perchloric acid was used as the source of hydrogen ions and all solutions were adjusted to an ionic strength of 0.5 mol dm^{-3} by the addition of $NaClO_4$.

UV–Vis spectra were recorded on a Shimadzu UV260 spectrophotometer. pH measurements were made using a PTI6 pH meter equipped with a Russell combination electrode. The filling solution of the reference section was a 3 mol dm^{-3} aqueous solution

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TABLE 1. Ratio of enol to keto tautomers, equilibrium constants with Cu^{2+} and $[VO]^{2+}$ and rate constants for heptane-3,5-dione in aqueous solution

Solution composition	
$[L_L]$ range	0.0025–0.01 mol dm^{-3}
$[T_M]$ range	0.0046–0.0102 mol dm^{-3}
Ionic strength, electrolyte	0.5 mol dm^{-3}, $NaClO_4$
pH range	protonation: 8.3–10.7 complexation: 2.2–4.6
Experimental method	pH titration, calibrated in concentrations
Temperature	25 °C
Method of calculation	Superquad [18]
Total number of data points	protonation: 40, 2 titrations Cu complexation: 58, 3 titrations V complexation: 32, 2 titrations

$K_{HA} = 9.54 \times 10^{-11}$ mol dm^{-3}
$K_{HE} = 8.85 \times 10^{-10}$ mol dm^{-3}
$K_{HK} = 1.07 \times 10^{-10}$ mol dm^{-3}
$k_e = 5.78 \times 10^{-3}\ s^{-1}$
$k_f = 4.78 \times 10^{-2}\ s^{-1}$
$[HE]/[HK] = 0.121$

	Cu^{2+}	$[VO]^{2+}$
$\log \beta_1$	8.52(±0.04)	9.39(±0.01)
K_1	3.16×10^{-2}	0.234
K_E	2.93×10^{-1}	2.17
K_K	3.54×10^{-2}	0.262

$1/K_{HA} = 1/K_{HE} + 1/K_{HK}$
$1/K_1 = 1/K_E + 1/K_K$ where $K_1 = \beta_1 K_{HA}$

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 solution. The end-points of these titrations were determined using the method of Johansson [17].

Metal ion stability constants were determined by the potentiometric technique. Titrations were carried out in jacketed titration vessels through which water at 25 °C was circulating. All titrations were carried out in an atmosphere of oxygen-free nitrogen. Details of the titrations are shown in Table 1.

Most of the kinetic measurements were made on a Hitech SF-20 stopped-flow apparatus which was interfaced to a BBC microcomputer. However, some of the slower $[VO]^{2+}$ complex formation reactions were monitored with the Shimadzu UV260 spectrophotometer. 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 time zero, A_0, the absorbance at infinity time, A_∞, and the rate constant, k, were treated as variables. Data for from three to four half-lives were utilised in these calculations. The reported rate constants are the average of at least three determinations. The standard deviation in individual runs were usually less than one percent.

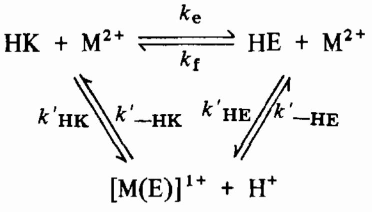
$$A = A_\infty(1 - \exp(-kt)) + A_0 \exp(-kt) \tag{1}$$

All solutions were freshly prepared for the kinetic runs. The water used to prepare the oxovanadium(IV) solutions was thoroughly saturated with nitrogen prior to the addition of the oxovanadium(IV) sulphate. The resultant solutions were found to be stable for at least 3 h. Repeat kinetic runs carried out within 1 h were found to be fully reproducible.

Results

Table 1 lists the equilibrium data for the Cu^{2+} and $[VO]^{2+}$ 1:1 complexes formed with heptane-3,5-dione. The proton equilibrium data together with the rate constants for enolization (k_e) and ketonization (k_f) previously determined are also included.

Tables 2 and 3 list the kinetic data for the Cu^{2+} and $[VO]^{2+}$ reactions, respectively. The mechanism proposed to account for the kinetic data is shown in Scheme 1. In this Scheme HK and HE represent the keto and enol tautomers respectively while M^{2+} represent the metal ion. $k'_{HE} = k_{HE}[M^{2+}]$, $k'_{-HE} = k_{-HE}[H^+]$, $K_E = k_{HE}/k_{-HE}$, $k'_{HK} = k_{HK}[M^{2+}]$, $k'_{-HK} = k_{-HK}[H^+]$ and $K_K = k_{HK}/k_{-HK}$. The general solution of the secular equations obtained from Scheme 1 yields eqns. (2), (3) and (4) [19, 20]. The λ_1 solution is trivial and need not be considered further.



Scheme 1.

$$\lambda_1 = 0 \tag{2}$$

$$\lambda_2 = 0.5(p + q) \tag{3}$$

$$\lambda_3 = 0.5(p - q) \tag{4}$$

$$p = k_e + k_f + (k_{HE} + k_{HK})[M^{2+}] + (k_{-HE} + k_{-HK})[H^+] \tag{5}$$

$$q = (p^2 - 4b)^{1/2} \tag{6}$$

$$b = k_e\{k_{HE}[M^{2+}] + (k_{-HK} + k_{-HE})[H^+]\} + k_{HK}[M^{2+}]\{k_f + k_{HE}[M^{2+}] + k_{-HE}[H^+]\} + k_f(k_{-HE} + k_{-HK})[H^+] + k_{HE}k_{-HK}[M^{2+}][H^+] \tag{7}$$

TABLE 2. Kinetic data for reaction of copper(II) with heptane-3,5-dione in aqueous solution at 25 °C and ionic strength 0.5 mol dm^{-3} NaClO$_4$

$10^3 \times [Cu^{2+}]$ (mol dm^{-3})	$10^3 \times [H^+]$ (mol dm^{-3})	λ_2		λ_3	
		k_{obs} (s^{-1})	k_{calc} (s^{-1})	k_{obs} (s^{-1})	k_{calc} (s^{-1})
1.02	1.04	55.4	52.2	0.102	0.110
1.02	2.08	91.5	92.8	0.128	0.122
1.02	2.60	107	113	0.126	0.124
1.02	3.12	129	133	0.135	0.126
1.02	3.64	147	154	0.135	0.128
1.02	4.16	163	174	0.138	0.129
1.02	5.20	206	215	0.140	0.130
2.03	1.04	71.7	63.8	0.141	0.149
2.03	2.08	103	104	0.171	0.176
2.03	2.60	126	125	0.190	0.184
2.03	3.12	145	145	0.201	0.189
2.03	3.64	162	165	0.203	0.193
2.03	4.16	181	186	0.209	0.196
2.03	5.20	216	226	0.210	0.200
3.05	2.08	123	116	0.204	0.222
3.05	2.60	141	136	0.233	0.234
3.05	3.12	159	157	0.244	0.243
3.05	3.64	179	177	0.259	0.250
3.05	4.16	190	197	0.266	0.256
3.05	5.20	223	238	0.280	0.264
4.06	2.08	140	128	0.241	0.261
4.06	2.60	159	148	0.273	0.279
4.06	3.12	172	168	0.282	0.292
4.06	3.64	191	189	0.306	0.302
4.06	4.16	210	209	0.320	0.310
4.06	5.20	232	249	0.344	0.322
5.08	2.08	158	139	0.269	0.296
5.08	2.60	172	160	0.303	0.318
5.08	3.12	191	180	0.321	0.335
5.08	3.64	208	200	0.349	0.349
5.08	4.16	233	220	0.351	0.360
5.08	5.20	265	261	0.387	0.377

TABLE 3. Kinetic data for reaction of oxovanadium(IV) with heptane-3,5-dione in aqueous solution at 25 °C and ionic strength 0.5 mol dm^{-3} NaClO$_4$

Run no.[a]	$10^3 \times [VO]^{2+}$ (mol dm^{-3})	$[H^+]$ (mol dm^{-3})	k_{obs} (s^{-1})	k_{calc} (s^{-1})
1	2.37	0.520×10^{-1}	1.55×10^{-1}	1.58×10^{-1}
2	2.37	1.04×10^{-1}	2.74×10^{-1}	2.79×10^{-1}
3	2.37	1.56×10^{-1}	3.92×10^{-1}	4.04×10^{-1}
4	2.37	2.08×10^{-1}	5.25×10^{-1}	5.30×10^{-1}
5	2.37	2.60×10^{-1}	6.43×10^{-1}	6.57×10^{-1}
6	4.72	0.520×10^{-1}	1.65×10^{-1}	1.73×10^{-1}
7	4.72	1.04×10^{-1}	2.93×10^{-1}	2.93×10^{-1}
8	4.72	1.56×10^{-1}	4.20×10^{-1}	4.17×10^{-1}
9	4.72	2.08×10^{-1}	5.49×10^{-1}	5.43×10^{-1}
10	4.72	2.60×10^{-1}	6.77×10^{-1}	6.70×10^{-1}
11	7.11	0.520×10^{-1}	1.74×10^{-1}	1.87×10^{-1}
12	7.11	1.04×10^{-1}	3.09×10^{-1}	3.07×10^{-1}
13	7.11	1.56×10^{-1}	4.28×10^{-1}	4.31×10^{-1}
14	9.44	0.520×10^{-1}	1.81×10^{-1}	2.01×10^{-1}
15	9.44	1.04×10^{-1}	3.26×10^{-1}	3.21×10^{-1}
16	9.44	1.56×10^{-1}	4.45×10^{-1}	4.45×10^{-1}
17	9.44	2.08×10^{-1}	5.92×10^{-1}	5.70×10^{-1}
18	9.44	2.60×10^{-1}	7.00×10^{-1}	6.97×10^{-1}
19	5.67	1.13×10^{-3}	1.32×10^{-2}	1.20×10^{-2}
20	5.67	6.81×10^{-4}	1.15×10^{-2}	1.05×10^{-2}
21	7.56	2.00×10^{-3}	1.80×10^{-2}	1.65×10^{-2}
22	7.56	1.16×10^{-3}	1.48×10^{-2}	1.38×10^{-2}
23	7.56	7.20×10^{-4}	1.25×10^{-2}	1.25×10^{-2}
24	9.45	2.02×10^{-3}	1.89×10^{-2}	1.82×10^{-2}
25	9.45	1.18×10^{-3}	1.49×10^{-2}	1.56×10^{-2}
26	9.45	7.62×10^{-4}	1.42×10^{-2}	1.45×10^{-2}
27	11.3	2.06×10^{-3}	1.99×10^{-2}	1.98×10^{-2}
28	11.3	1.20×10^{-3}	1.65×10^{-2}	1.73×10^{-2}
29	11.3	8.00×10^{-4}	1.58×10^{-2}	1.64×10^{-2}
30	3.13	2.95×10^{-3}	1.90×10^{-2}	1.59×10^{-2}
31	3.13	1.50×10^{-3}	1.13×10^{-2}	1.09×10^{-2}
32	3.13	9.60×10^{-4}	1.09×10^{-2}	0.90×10^{-2}
33	4.68	2.97×10^{-3}	1.77×10^{-2}	1.72×10^{-2}
34	4.68	1.51×10^{-3}	1.33×10^{-2}	1.24×10^{-2}
35	4.68	1.01×10^{-3}	1.20×10^{-2}	1.06×10^{-2}
36	6.24	2.96×10^{-3}	1.92×10^{-2}	1.84×10^{-2}
37	6.24	1.53×10^{-3}	1.47×10^{-2}	1.38×10^{-2}
38	6.24	1.04×10^{-3}	1.11×10^{-3}	1.22×10^{-3}
38	7.80	3.01×10^{-3}	2.01×10^{-2}	1.98×10^{-2}
38	7.80	1.51×10^{-3}	1.56×10^{-2}	1.52×10^{-2}
39	7.80	1.08×10^{-3}	1.30×10^{-2}	1.38×10^{-2}
40	9.36	3.03×10^{-3}	1.92×10^{-2}	2.11×10^{-2}
41	9.36	1.56×10^{-3}	1.46×10^{-2}	1.67×10^{-2}
42	9.36	1.13×10^{-3}	1.54×10^{-2}	1.54×10^{-2}
43	10.9	3.05×10^{-3}	1.93×10^{-2}	2.24×10^{-2}
44	10.9	1.62×10^{-3}	1.52×10^{-2}	1.82×10^{-2}
45	10.9	1.18×10^{-3}	1.58×10^{-2}	1.69×10^{-2}

[a] Runs 1–18 done in reverse direction using stopped flow apparatus, 19–29 done in forward direction using stopped flow apparatus, 30–45 done in forward direction using spectrophotometer.

Factoring the q term (eqn. (6)), expanding the factor $(1-(4b/p^2))^{1/2}$ using the binomial expansion and retaining only the first two terms gives eqn. (8).

$$q \simeq p - 2b/p \tag{8}$$

It is apparent that the mechanism in Scheme 1 may give a maximum of two relaxations irrespective of whether the reaction is monitored in the forward direction (complex formation) or the reverse direction (hydrolysis). The faster of these two relaxations is described by eqn. (9) while the slower is described by eqn. (10).

$$\lambda_2 = p - b/p \tag{9}$$

$$\lambda_3 = b/p \tag{10}$$

Substituting for p and b in eqns. (9) and (10) from eqns. (5) and (7), respectively while noting that

$$\lambda_2 = k_e + k_f + (k_{HE} + k_{HK})[M^{2+}] + \{k_{HK}/K_K + k_{HE}/K_E\}[H^+] - \frac{[M^{2+}](k_e k_{HE} + k_f k_{HK} + k_{HE} k_{HK}[M^{2+}])\{1 + ([H^+]/[M^{2+}])(1/K_K + 1/K_E)\}}{k_e + k_f + (k_{HE} + k_{HK})[M^{2+}] + \{k_{HK}/K_K + k_{HE}/K_E\}[H^+]} \quad (11)$$

$$\lambda_3 = \frac{[M^{2+}](k_e k_{HE} + k_f k_{HK} + k_{HE} k_{HK}[M^{2+}])\{1 + ([H^+]/[M^{2+}])(1/K_K + 1/K_E)\}}{k_e + k_f + (k_{HE} + k_{HK})[M^{2+}] + \{k_{HK}/K_K + k_{HE}/K_E\}[H^+]} \quad (12)$$

$K_E = k_{HE}/k_{-HE}$ and $K_K = k_{HK}/k_{-HK}$ and rearranging the terms gives eqns. (11) and (12) for the fast and slow relaxations, respectively, as shown above.

An examination of the data published to date [1] shows that in general, the enol tautomer of β-diketones is considerably more reactive than the keto tautomer. Therefore one can reasonably assume that $k_{HE} > k_{HK}$. When this simplification is incorporated into eqn. (11), eqn. (13) is obtained. Equation (13) contains only one unknown parameter, k_{HE}.

$$\lambda_2 = k_e + k_f + k_{HE}[M^{2+}] + k_{HE}[H^+]/K_E - \frac{[M^{2+}]k_e k_{HE}(1 + ([H^+]/[M^{2+}])(1/K_K + 1/K_E)}{k_e + k_f + k_{HE}[M^{2+}] + k_{HE}[H^+]/K_E} \quad (13)$$

Reaction of Copper(II) with Heptane-3,5-dione

When the kinetic data for the faster of the two observed relaxations (Table 2) are fitted to eqn. (13), a value of 1.14(±0.01) × 10^4 dm^3 mol^{-1} s^{-1} is obtained for k_{HE}. The values of k_{calc} which are listed in Table 2 are obtained using eqn. (13) and the fitted value of k_{HE}. It is apparent that the agreement between the observed and calculated first-order rate constants is good over the range of metal and hydrogen ion concentrations studied.

The value of k_{HK}, 8.89(±0.01) dm^3 mol^{-1} s^{-1} is obtained by fitting the kinetic data for the slow relaxation to eqn. (12) while keeping the value of k_{HE} obtained above constant. In previous investigations of the reactions of metal ions with β-diketones, an inverse acid relationship was sometimes found for k_{HE} (eqn. (14)). This was ascribed to a reaction

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

pathway in which the metal species reacted with the enolate ion which is obtained on loss of a proton from either the keto or enol tautomers. It was further noted that in most instances, this pathway proceeded with rate constants close to those predicted on the basis of the Eigen–Wilkins mechanism. Based on this assumption, it can be readily shown that under the experimental conditions used in the present experiment, the inverse acid pathway would not compete with the pathway involving a direct reaction between the Cu^{2+} and the protonated enol tautomer.

Reactions of $[VO]^{2+}$ with Heptane-3,5-dione

When the kinetic data for runs 1–18 are fitted to eqn. (13) for the faster of the two possible relaxations, a value of 5.33(±0.03) dm^3 mol^{-1} s^{-1} is obtained for k_{HE}. There is no contribution from an inverse-acid term. The k_{calc} values listed in Table 3 were obtained using this procedure. Using the value for k_{HE} obtained from eqn. (13) and fitting the data for runs 19–45 to eqn. (12) (slow relaxation) shows that k_{HK} has the form of eqn. (14) where a = 0.986(0.059) and b = 1.29(0.80) × 10^{-4}. Using the previously reported mechanisms for reaction of metal ions with β-diketones [1], a is the complex formation rate constant for direct reaction of the metal species with the protonated keto tautomer. Two alternative formulations are possible for the inverse-acid pathway represented by b. It may represent reaction of the metal species with the enolate ion formed by loss of a proton from either the keto or enol tautomers (k_4) in which case $b = K_{HA}k_4$. Using the value of b obtained above together with the value of K_{HA} from Table 1 results in value of 1.21 × 10^6 dm^3 mol^{-1} s^{-1} for k_4. This is clearly an unreasonably high complex formation rate constant for a metal ion having a water exchange rate in the order of 500 s^{-1}. The alternative formulation involves reaction of $[VO(OH)]^+$ with the keto tautomer (k_5). In this instance $b = K_h K_5$ where K_h is the hydrolysis constant of $[VO]^2$ (1.7 × 10^{-5} mol dm^{-3}). This results in a value of 7.64(4.72) for k_5. Calculations show that even at the lowest hydrogen ion concentration used in this investigation, less than 20% of the complex formation takes place by the inverse acid pathway. This results in a relatively large uncertainty in the value of k_5.

Discussion

Table 4 lists the previously published values of the rate constants for complex formation reactions of Cu^{2+} and $[VO]^{2+}$ with various β-diketones, together with the results obtained in this investigation. The analysis of the kinetic data for the copper(II)

TABLE 4. Rate constants for formation of 1:1 complexes of Cu^{2+} and $[VO]^{2+}$ with β-diketones at 25 °C

Metal	Ligand[a]	Solvent	Ionic strength (mol dm^{-3})	k ($dm^3\ mol^{-1}\ s^{-1}$)	Reference
Cu^{2+}	Hpd(keto)	H_2O	variable	12	2
Cu^{2+}	Hpd(keto)	MeOH	variable	1300	2
Cu^{2+}	Hpd(enol)	H_2O	variable	2×10^4	2
Cu^{2+}	Hpb(enol)	MeOH	variable	2×10^4	2
Cu^{2+}	$tftbd^{1-}$	H_2O	1.0 ($LiClO_4$)	$\geqslant 3 \times 10^6$	3
Cu^{2+}	Htfpd(enol)	H_2O	0.5 ($NaClO_4$)	[b]	4
Cu^{2+}	$tfpd^{1-}$	H_2O	0.5 ($NaClO_4$)	[b]	4
Cu^{2+}	Htftbd [c]	H_2O	0.2 (Na_2SO_4)	0.5	5
Cu^{2+}	$tftbd^{1-}$	H_2O	0.2 (Na_2SO_4)	2.0×10^3	5
Cu^{2+}	Hpbd(keto)	H_2O	0.1 ($NaClO_4$)	12	6
Cu^{2+}	Hpbd(enol)	H_2O	0.1 ($NaClO_4$)	2000	6
Cu^{2+}	pbd^{1-}	H_2O	0.1 ($NaClO_4$)	1.1×10^9	6
Cu^{2+}	Hpbd(enol)	$MeOH:H_2O$	0.5 ($NaClO_4$)	5.03×10^3	7
Cu^{2+}	pbd^{1-}	$MeOH:H_2O$	0.5 ($NaClO_4$)	3.2×10^9	7
Cu^2	Hhptd(enol)	H_2O	0.5 ($NaClO_4$)	1.14×10^4	this work
Cu^{2+}	Hhptd(keto)	H_2O	0.5 ($NaClO_4$)	8.9	this work
$[VO]^{2+}$	Hpb(keto)	H_2O	0.5 ($NaClO_4$)	4.4	8
$[VO]^{2+}$	Htftbd(enol)	H_2O	0.5 ($NaClO_4$)	7.6	8
$[VO]^{2+}$	$tftbd^{1-}$	H_2O	0.5 ($NaClO_4$)	3.6×10^3	8
$[VO(OH)]^{1+}$	Htftbd(enol)	H_2O	0.5 ($NaClO_4$)	2.0×10^4	8
$[VO]^{2+}$	Htfpd(enol)	H_2O	0.5 ($NaClO_4$)	3.5	8
$[VO]^{2+}$	$tfpd^{1-}$	H_2O	0.5 ($NaClO_4$)	2.0×10^2	8
$[VO(OH)]^{1+}$	Htfpd(enol)	H_2O	0.5 ($NaClO_4$)	5.9×10^3	8
$[VO]^{2+}$	Hhptd(enol)	H_2O	0.5 ($NaClO_4$)	5.33	this work
$[VO]^{2+}$	Hhptd(keto)	H_2O	0.5 ($NaClO_4$)	0.986	this work
$[VO(OH)]^{+}$	Hhptd(keto)	H_2O	0.5 ($NaClO_4$)	7.64	this work

[a] Hpd = pentane-2,4-dione, Hpbd = 1-phenylbutane-1,3-dione, Htfpd = 1,1,1,-trifluoropentane-2,4-dione, Htftbd = 4,4,4,-trifluoro-1-(2-thienyl)butane-1,3-dione, Hhptd = heptane-3,5-dione. [b] No rate constants or limits could be determined. [c] Mechanism does not indicate what the reacting species is.

reactions is entirely satisfactory, and it is apparent that the rate constants obtained for reaction of Cu^{2+} with both the keto and enol tautomers of heptane-3,5-dione in aqueous solution are of similar magnitude to the rate constants obtained for its reactions with other β-diketones. Over the range of ligands investigated, the chain length does not appear to exert any significant influence on the reactivity of β-diketones towards metal species.

In a previous investigation of the reactions of $[VO]^{2+}$ with β-diketones certain difficulties arose when an attempt was made to analyse the kinetic data in terms of a mechanism similar to that shown in Scheme 1 [8]. Analysis of the kinetic data was satisfactory when either Htfbd or Htfpd was the ligand. However, when pentane-2,4-dione was the ligand, the kinetic data could not be analysed in this fashion. Some of the difficulty was due to the fact that two overlapping relaxations were observed and it was not possible to separate these satisfactorily. When the fitted values for k_{HE} and k_{HK} together with the experimental metal and hydrogen ion concentrations are used in eqn. (11), the values obtained for λ_3 are not in total agreement with the experimentally determined values. Extensive analysis of the kinetic data using a variety of reaction schemes including those proposed by Chopra and Jordan [21] for similar situations has failed to elucidate the reason for this. It may be that the exponentials observed for either the forward or reverse reactions are not 'pure' and that this has introduced a degree of error in the pseudo-first-order rate constants determined using eqn. (1). The rate constants are however reproducible within experimental error.

While accepting the limitations of the kinetic analysis, Table 4 shows that the rate constants for reaction of $[VO]^{2+}$ with the enol tautomer of all four β-diketones investigated to date differ by less than a factor of two. The rate constants are some thirty times less than those predicted by the Eigen–Wilkins mechanism (113 $dm^3\ mol^{-1}\ s^{-1}$) from the outer sphere association constants and the solvent exchange rate. This is, however, considerably less than the 10^3 fold reduction observed for reaction of Ni^{2+} with a variety of β-diketones [1, 22] and is consistent with previous work [1].

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