Kinetics and Mechanisms of the Reactions of Nickel(II) and Pentane-2,4-dione

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The kinetics and mechanisms of the reactions of Ni^{II} and pentane-2,4-dione (Hpd) to form the mono complex have been investigated in water and aqueous methanol (mol fraction of methanol, 0.8). The keto tautomer does not react directly with Ni^{II}, and the kinetic data are consistent with a mechanism in which Ni^{II} reacts with the enol form of the ligand. The rate constants for reaction with the undissociated enol tautomer are 19.3 $dm^3 mol^{-1} s^{-1}$ in water and 17.0 $dm^3 mol^{-1} s^{-1}$ in aqueous methanol. The results suggest that, for the reaction of metal and oxometal ions with simple β-diketones, a mechanism whereby complex formation rates are closely related to solvent exchange rates is not operative. The results are discussed and rationalized in terms of previously published data for reactions of Cu^{II}, Fe^{III}, and U^{VI} with β-diketones.

A PERUSAL of the chemical literature dealing with the reactions of metal ions with β-diketones [1-11] shows that the kinetics and mechanisms of the reactions of Cu^{II} and Fe^{III} with pentane-2,4-dione (Hpd) and of Co^{II}, Cu^{II}, Ni^{II}, and Fe^{III} with 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione (Htftbd) have been investigated. The more recent papers show that factors other than the properties of the metal ion are important in complex formation by β-diketone ligands.[1-4] In most studies of the interactions of metal ions with non-β-diketone-type ligands, the loss of a water molecule from the metal ion was postulated to be the rate-determining step in complex formation.[12] Support for this view comes from the fact that for many metal ions the rates of complex formation parallel the rate of solvent exchange.[13] β-Diketones, however, have properties at variance with those of ' normal ' proton-containing ligands such as glycine, oxalic acid, and tartaric acid. The β-diketones can and do exist as keto or enol tautomers. The ratio of keto to enol varies with the ligand and the solvent.[14,15] The electronic properties and the reactivity towards metal ions of the keto and enol tautomers of any β-diketone are quite different. Also, the rates of proton loss or ionization of either the keto or enol tautomers of the more commonly encountered β-diketones such as Hdp, Htftbd, and trifluoroacetylacetone are very much less than ' normal ' proton-transfer reactions, which are generally quite rapid in aqueous and methanol solutions.[12] Thus the reactions of metal ions with β-diketones have a potential for mechanistic variations not present in other ligands.

The nickel(II)–pentane-2,4-dione system has previously been investigated by Pearson and Moore as part of their investigations into the hydrolysis of pentane-2,4-dionato-complexes.[10,11] However, the reaction was only investigated in the reverse direction, *i.e.* ' hydrolysis,' and the data are insufficient for the complete mechanistic interpretation of the reaction in the light of more recent developments in the kinetics and mechanisms of the interactions of metal ions with β-diketones. We have been investigating the kinetics and mechanisms of the reactions of metal and oxometal ions with β-diketones for some time, and have noted differences in the modes of reaction of Cu^{II} and $[UO_2]^{2+}$ on the one hand and of Ni^{II} with Hpd on the other.[1,16,17] Consequently, we have reinvestigated the reaction between Ni^{II} and Hpd in water and have also extended the work to aqueous methanol solutions.

EXPERIMENTAL

Stock solutions of Ni^{II} were prepared from AnalaR grade $NiCl_2 \cdot 6H_2O$. The solutions were standardized by gravimetric analysis using dimethylglyoxime. Reagent grade pentane-2,4-dione 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 l) and then diluting to the mark with dry methanol. The mol fraction of methanol in these solutions is 0.80. Standardized perchloric acid was used as a source of H^+ in aqueous solutions while toluene-*p*-sulphonic acid was the H^+ source in aqueous methanol solutions. Recrystallized sodium perchlorate was used to adjust the ionic strength to 1.0 mol dm^{-3} in aqueous solution and 0.5 mol dm^{-3} in aqueous methanol solutions.

Spectra were recorded on a Beckman DB-GT u.v.–visible spectrophotometer equipped with a chart recorder. pH Measurements were made with a Pye model 290 pH meter equipped with a Pye-Ingold $E^0{}_7$ combined glass-and-reference electrode. The electrode was calibrated using a series of solutions of various perchloric acid concentrations at an ionic strength of 1.0 mol dm^{-3}, adjusted using sodium perchlorate. For pH measurements in aqueous methanol solutions, the solution in the reference compartment of the electrode was replaced by a saturated solution of KCl in methanol and the electrode was calibrated as for use in aqueous solutions except that toluene-*p*-sulphonic acid solutions, adjusted to $I = 0.5$ mol dm^{-3} using $Na[ClO_4]$, were used as the source of hydrogen ions.

The rates of reactions were measured using an Applied Photophysics stopped-flow device and a Tektronix model 5100 storage oscilloscope. The stored traces were photographed using a polaroid camera and plots of $-\ln(A - A_\infty)$ against time were obtained.

The reactions were studied in the forward and reverse directions. Studying the reactions in the forward direction involved mixing solutions of Ni^{II} and Hpd, both of which were adjusted to the appropriate pH and ionic strength prior to mixing. The reverse reaction was studied by mixing a solution of the complex prepared *in situ* with an excess of acid. The metal was maintained in at least ten-fold excess of the ligand to ensure the 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.

RESULTS AND DISCUSSION

When aqueous solutions of Ni^{II} and Hpd were mixed in the stopped-flow device a single reaction step was observed in all cases. A similar result was obtained in aqueous methanol solutions. In both cases the measured absorbance change accounted for the total absorbance change between the reactants and products. Mechanism (1) is postulated to account for the kinetic data, where HK and HE represent the keto and enol tautomers

$$\mathrm{HK} \underset{k_f}{\overset{k_e}{\rightleftharpoons}} \mathrm{HE} \underset{k'_{-\mathrm{HE}}}{\overset{k'_{\mathrm{HE}}}{\rightleftharpoons}} \mathrm{ME} + \mathrm{H}^+ \qquad (1)$$

of Hpd respectively, $k'_{\mathrm{HE}} = k_{\mathrm{HE}}[\mathrm{Ni}^{2+}]$, $k'_{-\mathrm{HE}} = k_{-\mathrm{HE}}[\mathrm{H}^+]$, and $k_{\mathrm{HE}}/k_{-\mathrm{HE}} = K_{\mathrm{E}}$. The general solution for this system is [18,19] (2) which yields two rate constants.

$$\lambda_{1,2} = \tfrac{1}{2}(p \pm q) \qquad (2)$$

where
$$q = p - (2b/p) \qquad (3)$$

$$p = k_e + k_f + k'_{\mathrm{HE}} + k'_{-\mathrm{HE}} \qquad (4)$$

$$b = k_e k'_{\mathrm{HE}} + (k_e + k_f)k'_{-\mathrm{HE}} \qquad (5)$$

Thus two reactions should be observed, independent of whether the reaction is run in the forward (formation) or reverse (hydrolysis) direction. For the reaction of Ni^{II} with Hpd the kinetic data are consistent with the solution $\lambda = p - (b/p)$. Substituting from equations (4) and (5) one obtains (6).

$$\lambda_1 = k_e + k_f + k_{\mathrm{HE}}[\mathrm{Ni}^{2+}] + k_{-\mathrm{HE}}[\mathrm{H}^+] - \frac{k_e k_{\mathrm{HE}}[\mathrm{Ni}^{2+}] + (k_e + k_f)k_{-\mathrm{HE}}[\mathrm{H}^+]}{k_e + k_f + k_{\mathrm{HE}}[\mathrm{Ni}^{2+}] + k_{-\mathrm{HE}}[\mathrm{H}^+]} \qquad (6)$$

The stability constant of $[\mathrm{Ni(pd)}]^+$ and the dissociation constant of Hpd in water are given as $10^{5,92}$ dm^3 mol^{1} and $10^{-9.00}$ mol dm^{-3} respectively.[20] Using these values, K is estimated to be 8.32×10^{-4} where K is defined in (7). From relation (8), which holds for $[\mathrm{Ni(pd)}]^+$ in water, and 4.57 : 1 as the ratio of keto to enol tautomer in water, K_{K}

$$K = [\mathrm{Ni(pd)}^+]\,[\mathrm{H}^+]/[\mathrm{Ni}^{2+}][\mathrm{Hpd}] \qquad (7)$$

$$1/K = 1/K_{\mathrm{E}} + 1/K_{\mathrm{K}} \qquad (8)$$

where
$$K_{\mathrm{K}} = [\mathrm{Ni(pd)}^+]\,[\mathrm{H}^+]/[\mathrm{Ni}^{2+}][\mathrm{HK}] \qquad (9)$$

$$K_{\mathrm{E}} = [\mathrm{Ni(pd)}^+]\,[\mathrm{H}^+]/[\mathrm{Ni}^{2+}][\mathrm{HE}] \qquad (10)$$

and K_{E} are calculated as 1.01×10^{-3} and 4.63×10^{-3} respectively. Now, since $K_{\mathrm{E}} = k_{\mathrm{HE}}/k_{-\mathrm{HE}}$, under the experimental conditions employed, terms in k_{HE} may be neglected. Carrying out this simplification of equation (6) gives (11) or (12). A plot of the left-hand side of equation (12) against $[\mathrm{H}^+]/[\mathrm{Ni}^{2+}]$ should yield a straight

$$\lambda = \{(k_{-\mathrm{HE}})^2[\mathrm{H}^+]^2 + 2k_{\mathrm{HE}}k_{-\mathrm{HE}}[\mathrm{Ni}^{2+}][\mathrm{H}^+] + (k_e + k_f)k_{-\mathrm{HE}}[\mathrm{H}^+]\}/k_{-\mathrm{HE}}[\mathrm{H}^+] \qquad (11)$$

$$\frac{\lambda}{[\mathrm{Ni}^{2+}]} - \frac{k_e + k_f}{[\mathrm{Ni}^{2+}]} = k_{-\mathrm{HE}}\frac{[\mathrm{H}^+]}{[\mathrm{Ni}^{2+}]} + 2k_{\mathrm{HE}} \qquad (12)$$

line of slope $k_{-\mathrm{HE}}$ and intercept $2k_{\mathrm{HE}}$. Table 1 gives the experimental data for the reaction between Ni^{II} and Hpd in water and Figure 1 shows the plot suggested by equation (12). It is apparent that the data fit this equation satisfactorily over a wide range of [Ni^{II}] and [H$^+$]. The gradient of the line is 4 160 ± 70 dm^3 mol^{-1} s^{-1}. Using the value of K_{E} calculated above, k_{HE} is estimated to be 19.3 dm^3 mol^{-1} s^{-1}. Due to the very small value of k_{HE} the intercept of the experimental plot shown in Figure 1 cannot be considered significant, and thus is not used to calculate k_{HE}.

TABLE 1

Observed rate constants for reaction of Ni^{2+} and Hpd in aqueous solution

Experiment no.	$10^3[\mathrm{Ni}^{2+}]$	$10^3[\mathrm{H}^+]$	$k_{\mathrm{obs.}}$/s^{-1}
	mol dm^{-3}		
1	19.35	0.85	3.57
2	38.71	0.85	3.73
3	58.06	0.85	3.88
4	77.41	0.85	4.10
5	96.77	0.85	4.09
6	19.35	1.45	6.65
7	38.71	1.45	7.39
8	58.06	1.45	7.75
9	77.41	1.45	8.20
10	96.77	1.45	8.53
11	19.35	1.95	6.40
12	38.71	1.95	8.99
13	77.41	1.95	9.59
14	96.77	1.95	10.86
15	19.35	1.00	3.60
16	19.35	2.50	11.00
17	19.35	5.00	27.40
18	19.35	5.75	18.64
19	38.71	5.75	20.30
20	58.06	5.75	21.81
21	77.41	5.75	23.56
22	96.77	5.75	24.50
23	19.35	8.00	35.00
24	19.35	12.00	50.4
25	38.71	12.00	54.6
26	58.06	12.00	51.6
27	77.41	12.00	49.6
28	96.77	12.00	46.6
29	19.35	20.00	86.5
30	19.35	25.00	108.3
31	38.71	25.00	104.1
32	58.06	25.00	100.8
33	77.41	25.00	108.0
34	96.77	25.00	101.0
35	38.71	50.00	230.0
36	58.06	50.00	203.0
37	77.41	50.00	195.0
38	96.77	50.00	216.0
39	19.35	10.00	47.25
40	19.35	15.00	63.5

Experiments 1—14 were carried out in the forward direction, 15—40 in the reverse direction. [Hpd] = 5.0×10^{-4} mol dm^{-3}, λ = 310 nm, and I = 1.0 mol dm^{-3} Na[ClO$_4$].

The reactions were also carried out in aqueous methanol solutions having 0.80 mol fraction of methanol. The experimental data are in Table 2, and Figure 2 shows the plot suggested by equation (12). The agreement is again satisfactory, and the gradient of the plot gives a value of 553 ± 7 dm^3 mol^{-1} s^{-1} for $k_{-\mathrm{HE}}$. Calculations similar to those carried out for the reactions in aqueous solutions using the data of Gentile and Dadger [21] gave k_{HE} = 17.0 dm^3 mol^{-1} s^{-1}. The intercept of the plot in Figure 2 is 52 ± 17 dm^3 mol^{-1} s^{-1} which gives a value of 26 ± 9 dm^3 mol^{-1} s^{-1} for k_{HE} in fair agreement with the value calculated from $k_{-\mathrm{HE}}$ and the published value of the stability constant.

A value of 2.7 dm^3 mol^{-1} s^{-1} has been quoted for the rate constant for reaction of Ni^{II} and HE in ref. 1, and the value is attributed to the original work of Pearson and Moore.[10] In this latter work the kinetic data for the hydrolysis of [Ni(pd)]$^+$ were interpreted in terms of H$^+$ trapping a half-opened chelate ring. This is the 'normal' mechanism observed for hydrolysis of metal chelates and $k_{obs.}$ can have the form [22] (13) where k' is an

$$k_{obs.} = k'[H^+] \qquad (13)$$

accumulation of rate constants. Pearson and Moore obtained a value of 3 500 dm^3 mol^{-1} s^{-1} for k' from a plot of $k_{obs.}$ against [H$^+$]. An examination of equation (12) shows that this gradient may be approximated to k_{-HE} without serious error. Carrying out the calculations previously described above results in a value of 23 dm^3 mol^{-1} s^{-1} for k_{HE}. The agreement with the result obtained in the present work is gratifying. Further support for the present mechanism comes from the fact that the data for both the formation and hydrolysis reactions fit equation (12) satisfactorily as demanded by the mechanism.

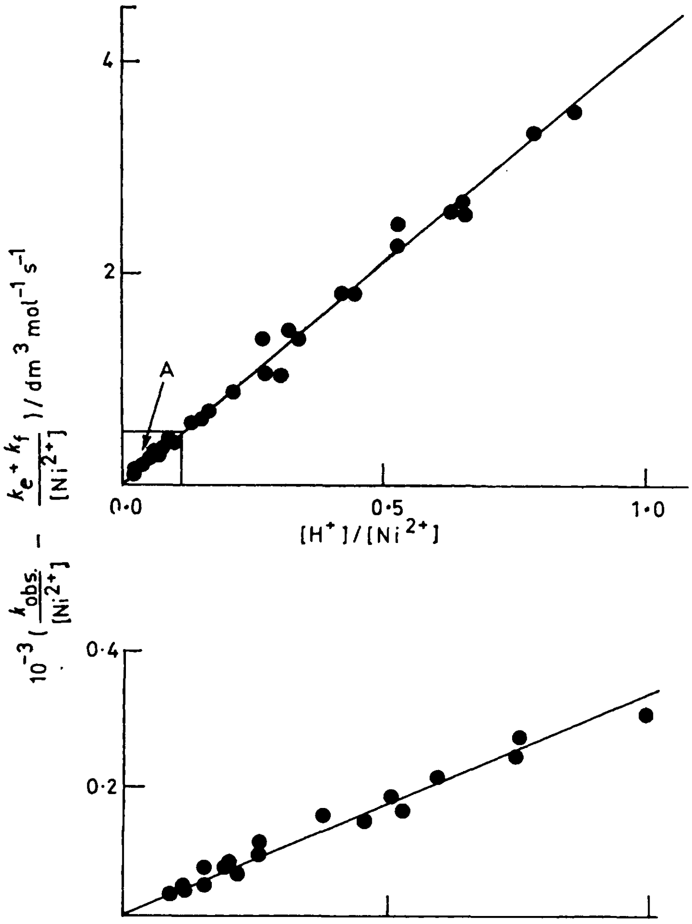

FIGURE 1 Plot suggested by equation (12) for reaction of Ni^{2+} with Hpd in aqueous solution. The lower diagram shows an expansion of region A in the upper

The kinetics and mechanism of the reactions of Cu^{II} and [UO$_2$]$^{2+}$ with Hpd have previously been investigated and in both instances two separable reactions were observed.[1,17] These were attributed to the separate reactions of the metal ions with the keto and enol tautomers of pentane-2,4-dione. In the present investigation only one reaction step was observed and in this respect the reaction resembles that between Ni^{II} and Htftbd.[3] However, in the Ni^{II}–Hpd reaction it is the more rapid of the two possible relaxations which is seen, whereas in the reaction with Htftbd as ligand it is the slower of the two reactions which is observed, although Sutin has also observed two relaxations for the reaction of Cu^{II} with Htftbd.[3] There is little doubt that it is the faster relaxation that is observed here in this work since the data are not at all consistent with rate laws predicted by the slower reaction.

In order to evaluate the significance of the results obtained in this investigation it is necessary to compare them with data from other work. The characteristic rate constant for the reaction of Ni^{2+} with uncharged ligands is *ca.* 4 × 10^3 dm^3 mol^{-1} s^{-1}.[12] By comparison,

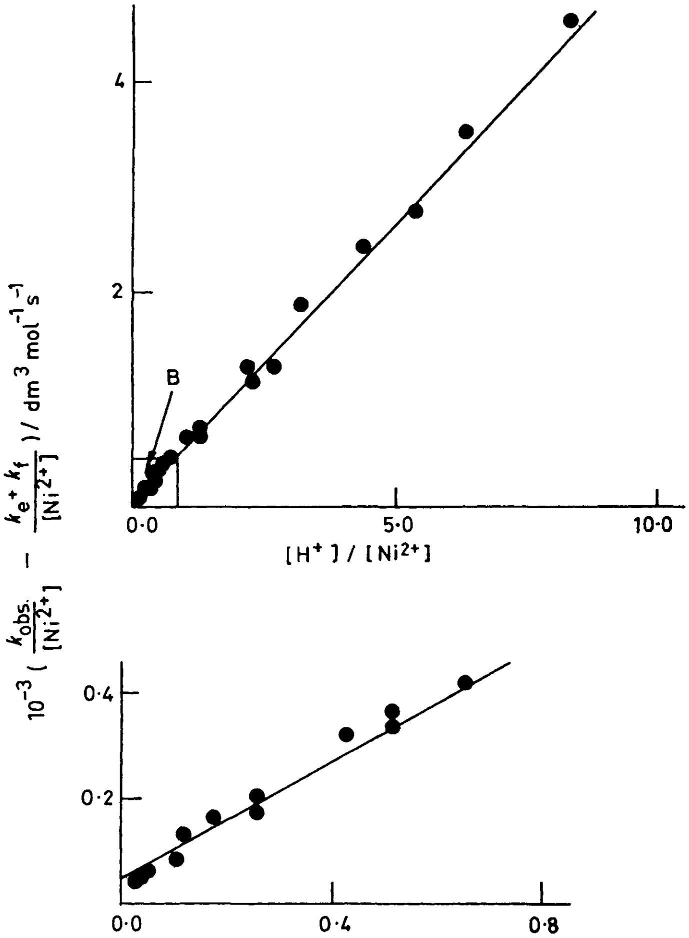

FIGURE 2 Plot suggested by equation (12) for reaction of Ni^{2+} with Hpd in aqueous methanol. The lower diagram shows an expansion of region B in the upper

the rate of reaction of Ni^{2+} with the enol tautomer of Hpd reported in this work, **19.3 $dm^3 mol^{-1} s^{-1}$**, is about two orders of magnitude lower. However, Sutin and his co-workers [3] obtained a similar result for the reaction of Ni^{2+} with the enol form of Htftbd. The reaction of Cu^{2+} with the enol form of Hpd was also considered to be abnormally slow (2×10^4 $dm^3 mol^{-1} s^{-1}$) and was explained in terms of a sterically controlled ring-closure mechanism.[1] This mechanism postulates that the closing of six- (and seven-) membered rings is in general sterically hindered,[23] and the difficulty encountered in effecting ring closure is sufficient to determine the overall rate of the reaction. This contrasts with the formation of five-membered rings where solvent release from the metal ion is rate determining.[12] However, a pure, sterically controlled, substitution mechanism predicts that the enolate ion should also react at an abnormally slow rate.[1] This is not found to be the case for the reactions of Ni^{2+} with the enolate ion of Htftbd and it is possible that factors other than ring closure are of importance.[3]

TABLE 2

Observed rate constant for the reaction of Ni^{2+} with Hpd in aqueous methanol

Experiment no.	$10^3[Ni^{2+}]$	$10^3[H^+]$	$k_{obs.}/s^{-1}$
	mol dm^{-3}		
1	29.00	1.00	0.88
2	29.00	1.00	0.93
3	38.71	1.00	1.00
4	19.35	2.00	1.55
5	38.71	2.00	1.66
6	9.67	5.00	3.59
7	19.35	5.00	3.88
8	29.00	5.00	4.80
9	38.71	5.00	5.00
10	19.35	5.00	3.49
11	19.35	10.00	6.45
12	19.35	25.00	14.03
13	19.35	40.00	25.95
14	19.35	60.00	38.10
15	19.35	100.00	52.10
16	4.84	25.00	12.01
17	19.35	25.00	13.68
18	38.71	25.00	16.12
19	58.06	25.00	18.71
20	4.84	40.00	22.30
21	9.67	40.00	22.30
22	19.35	40.00	22.95
23	38.71	40.00	25.96
24	58.06	40.00	27.92
25	4.84	30.00	17.28
26	58.06	30.00	24.81
27	9.67	50.00	27.41
28	38.71	50.00	30.45

Experiments 1—9 were run in the forward direction, 10—28 in the reverse direction. [Hpd] = 4×10^{-4} mol dm^{-3}, $\lambda = 310$ nm, $I = 0.5$ mol dm^{-3} $Na[ClO_4]$, and mol fraction of methanol = 0.80.

The rates of reaction of Fe^{3+} with the enol forms of Hpd and Htftbd were considered normal by comparison with other iron(III) systems.[2,3] The rates of reaction of the uranyl ion, $[UO_2]^{2+}$, with the enol tautomers of both Hpd and Htftbd (5.3×10^3 and $>1 \times 10^4$ $dm^3 mol^{-1} s^{-1}$ respectively) do not fall far below the rate of water exchange at the $[UO_2]^{2+}$ ion,[24] and are thought to be relatively normal,[16,17] although the paucity of published data makes it difficult to evaluate whether a particular reaction involving $[UO_2]^{2+}$ is normal or not. It has been reported that the keto form of Hpd reacts with Cu^{2+} at an abnormally slow rate and complex formation is thought to occur *via* a precursor complex in which the metal ion is loosely bound to the protonated keto tautomer.[1]

When solutions containing Ni^{II} are mixed with solutions containing Hpd no reaction attributable to direct interaction of Ni^{2+} with the keto tautomer is observed. The difference in the behaviour of Ni^{II} compared with that of Cu^{II}, $[UO_2]^{2+}$, and Fe^{III} (where separate reactions are assigned to reactions of the metal species with the keto and enol tautomers) may be attributed to the relative inertness of Ni^{2+}. Alternatively, it may be due to the relatively weak complexing ability of Ni^{2+} which is reflected in its inability to stabilize the precursor to the transition state, *i.e.* the loosely held complex with the keto tautomer.

The question still remains as to why certain metal ions react with β-diketones at what are considered ' normal ' rates while reactions involving other metal ions are severely retarded or do not occur to any appreciable extent. One could attempt to rationalize the situation in terms of the stability of a precursor complex with either the keto or enol tautomers. The stability of such a complex might be related to the hard-acid hard-base compatability of the reacting species as outlined by Pearson,[25] and indeed the degree of reduction of the rate constant for metal-complex formation from that expected on the basis of solvent-exchange rates is least for the hardest metal species, $[UO_2]^{2+}$ and Fe^{3+}. However, it must also be borne in mind that, since the observed complexation rates are much slower than solvent exchange, attack by the diketone (enol or keto) on highly reactive five-co-ordinate species such as $[Ni(OH_2)_5]^{2+}$ is unlikely to be influenced by their hard or soft character. The fact that Ni^{II} reacts with the enol tautomer of pentane-2,4-dione at approximately the same rate in water and aqueous methanol suggests that neither proton-transfer steps or solvent basicity greatly influence the reaction. Additional data are needed before the problem can be resolved.

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