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Kinetics and Mechanisms of the Reactions of Cobalt(II) and Pentane-2,4-dione in Aqueous Solution

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The kinetics and mechanisms of the reactions of Co(II) with pentane-2,4-dione (Hpd) to form the mono complex have been investigated in aqueous solution at 25 °C and ionic strength 0.5 mol dm^{-3}. Mechanisms have been proposed which account satisfactorily for the kinetic data. Co^{2+} reacts with the enol and keto tautomers of Hpd with rate constants of 136 and 0.84 dm^3 mol^{-1} s^{-1} respectively. These rate constants are considerably lower than would be predicted on the basis of the solvent exchange rate of Co^{2+}.

Introduction

To date, the complex formation reactions of pentane-2,4-dione (Hpd) with iron(III) [1, 2], copper(II) [3, 4], nickel(II) [5, 6], uranium(VI) [7], and vanadium(IV) [8] have been investigated in aqueous solution. Thus, kinetic data are only available for the reactions of two divalent first row transition metal ions with this ligand. In order to compare and contrast the reactivity of metal ions with pentane-2,4-dione we are investigating the complex formation reactions of a number of metal ions with this ligand. In contrast to other β-diketones such as 1,1,1-trifluoropentane-2,4-dione (Htfpd) and 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione (Htftbd) many metal ions appear to undergo reaction with both the keto and enol tautomers of Hpd. Although Ni^{II} appears to react with only the enol tautomer, Fe^{III}, Cu^{II} and U^{VI} undergo direct reaction with both the keto and enol tautomers.

We now report the results of our investigations of the reactions of Co^{II} with Hpd.

Experimental

Solutions of Co^{II} were prepared from cobalt(2+) perchlorate prepared as previously described [9]. The Co^{II} solutions were standardized against ethylenediaminetetraacetate using Xylenol Orange indicator [10]. Pentane-2,4-dione (Merck) was freshly distilled prior to use. Sodium perchlorate which had been passed over a bed of Zerolit 225 cation exchange resin in the sodium form was used to adjust the ionic strength to 0.5 mol dm^{-3}. Other procedures were as previously described [6–9].

The reactions could be studied in the forward (formation) or reverse (hydrolysis) directions. However, due to the very low formation constant of the mono complex formed between Co^{II} and Hpd, complex formation was insignificant below pH 4, and consequently the reactions could not be studied in the forward direction. Attempts were made to study the reaction in the forward direction at pH's 5.0, 5.5 and 6.0 using cacodylic acid as a buffering agent to maintain constant pH. Unfortunately however, the kinetic data were not reproducible and they could not be used. The reasons for this are not apparent, but may have their origin in the formation of hydrolytic species of Co^{II} or in interactions between Co^{II} and cacodylic acid. By using low concentrations of Hpd ($1-2 \times 10^{-4}$ mol dm^{-3}) the reactions could be studied in the forward direction at pH 4 while maintaining the hydrogen ion concentration relatively constant (due to the relatively small degree of complex formation). The absorbance changes although small, afforded reliable and reproducible kinetic data.

The metal was maintained in at least ten-fold excess of the ligand to ensure the formation of only the mono complex and the maintenance of pseudo-first-order conditions.

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TABLE I. Observed (λ_3) and Calculated (k_{calc}) Rate Constants for Reaction of Co^{II} with the Keto Tautomer of Hpd in Aqueous Solution at 25 °C and I = 0.5 mol dm^{-3}.

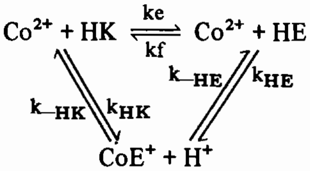
Experiment No.	Co^{II} mol dm^{-3}	$[H^+]$ mol dm^{-3}	λ_3 s^{-1}	k_{calc}[a] s^{-1}
1	5.13×10^{-3}	9.25×10^{-4}	0.124	0.160
2	9.04×10^{-3}	9.25×10^{-4}	0.149	0.186
3	13.88×10^{-3}	9.25×10^{-4}	0.166	0.218
4	19.16×10^{-3}	9.25×10^{-4}	0.195	0.253
5	23.13×10^{-3}	9.25×10^{-4}	0.256	0.278
6	27.58×10^{-3}	9.25×10^{-4}	0.266	0.307
7	5.13×10^{-3}	4.68×10^{-3}	0.127	0.160
8	9.04×10^{-3}	4.68×10^{-3}	0.150	0.187
9	13.88×10^{-3}	4.68×10^{-3}	0.166	0.221
10	19.16×10^{-3}	4.68×10^{-3}	0.188	0.257
11	23.13×10^{-3}	4.68×10^{-3}	0.250	0.284
12	27.58×10^{3}	4.68×10^{-3}	0.268	0.315
13	4.60×10^{-3}	0.147	0.125	0.157
14	9.25×10^{-3}	0.147	0.143	0.189
15	13.80×10^{-3}	0.147	0.166	0.221
16	18.40×10^{-3}	0.147	0.236	0.253
17	22.80×10^{-3}	0.147	0.250	0.283
18	27.35×10^{-3}	0.147	0.243	0.315
19	4.60×10^{-3}	0.234	0.116	0.157
20	9.25×10^{-3}	0.234	0.128	0.189
21	13.80×10^{-3}	0.234	0.179	0.221
22	18.40×10^{-3}	0.234	0.195	0.253
23	22.80×10^{-3}	0.234	0.220	0.283
24	27.35×10^{-3}	0.234	0.246	0.314
25	4.90×10^{-3}	0.238	0.129	0.159
26	9.00×10^{-3}	0.238	0.170	0.187
27	13.50×10^{-3}	0.238	0.209	0.219
28	17.80×10^{-3}	0.238	0.235	0.249
29	22.40×10^{-3}	0.238	0.257	0.281
30	4.90×10^{-3}	0.453	0.138	0.159
31	9.00×10^{-3}	0.452	0.169	0.188
32	13.50×10^{-3}	0.452	0.203	0.219
33	17.80×10^{-3}	0.453	0.232	0.249
34	22.40×10^{-3}	0.452	0.271	0.281
35	4.75×10^{-2}	1.36×10^{-4}	0.308	0.338
36	9.08×10^{-2}	1.36×10^{-4}	0.466	0.464
37[d]	15.20×10^{-2}	1.36×10^{-4}	0.685	0.593
38	6.39×10^{-2}	1.36×10^{-4}	0.372	0.391
39	7.41×10^{-2}	1.36×10^{-4}	0.484	0.420
40[b]	10.95×10^{-2}	1.36×10^{-4}	0.585	0.507
41[c]	12.69×10^{-2}	1.36×10^{-4}	0.650	0.545

λ = 320 nm. [Hpd] = 1–2 × 10^{-4} mol dm^{-3}. [a]Calculated using eqn. (5). [b]I = 0.58 mol dm^{-3}. [c]I = 0.63 mol dm^{-3}. [d]I = 0.70 mol dm^{-3}.

Results and Discussion

When the reaction between Co^{II} and Hpd was monitored on the stopped-flow apparatus in the vicinity of 320 nm it was apparent that under certain conditions two separate reaction stages could be observed. When the reaction was studied in the reverse direction using high (>0.1 mol dm^{-3}) concentration of H^+ only a single reaction was observed. Where the amplitude of the faster of the two relaxations observed was sufficiently large, the two reaction stages were sufficiently well separated to permit the evaluation of both pseudo-first-order rate constants.

The kinetic data for the reaction between Co^{II} and Hpd are consistent with the mechanisms outlined in Scheme I. The non-trivial solutions for the secular equations arising from this scheme are given by equations (1) and (2) [11, 12]



Scheme 1

$$\lambda_2 = p - b/p \tag{1}$$

$$\lambda_3 = b/p \tag{2}$$

where

$$p = k_e + k_f + (k_{HK} + k_{HE})[Co^{2+}] + (k_{-HK} + k_{-HE})[H^+] \tag{3}$$

and

$$b = k_e\{k_{HE}[Co^{2+}] + (k_{-HE} + k_{-HK})[H^+]\} + k_{HK}[Co^{2+}]\{k_f + k_{HE}[Co^{2+}] + k_{-HE}[H^+]\} + k_f(k_{-HE} + k_{-HK})[H^+] + k_{HE}k_{-HK}[Co^{2+}][H^+] \tag{4}$$

The Slow Relaxation λ_3

The expression for the slow relaxation may be considerably simplified by making the assumption that $k_{HE} \gg k_{HK}$. This also implies that $k_{-HE} \gg k_{-HK}$ since K_K (=k_{HK}/k_{-HK}) and K_E (=k_{HE}/k_{-HE}) only differ by the ratio k_e/k_f which is approximately 7.3 under the conditions used in this investigation. The equilibrium constant for reaction of Co^{II} with Hpd at an ionic strength of 0.5 mol dm^{-3} is 1.36×10^{-4} [13] so that K_K and K_E are 1.55×10^{-4} and 11.3×10^{-4} respectively. Applying the above approximations to the expression for λ_3 eqn. (5) is obtained. Under conditions where

$$\lambda_3 = \frac{k_{HK}k_E[Co^{2+}]^2 + k_{HK}(1 + K_E/K_K)[Co^{2+}][H^+]}{[H^+] + K_E[Co^{2+}]} + \frac{(k_e + k_f)[H^+]}{[H^+] + K_E[Co^{2+}]} \tag{5}$$

$[H^+] \gg K_E [Co^{2+}]$ and where the term in $[Co^{2+}]^2$ is small compared to the other terms in the numerator, eqn. (5) reduced to eqn. (6). Thus a plot of λ_3 against

$$\lambda_3 = k_{HK}(1 + K_E/K_K)[Co^{2+}] + (k_e + k_f) \tag{6}$$

$[Co^{2+}]$ should yield a straight line of slope $(1 + K_E/k_K)k_{HK}$ and intercept $(k_e + k_f)$.

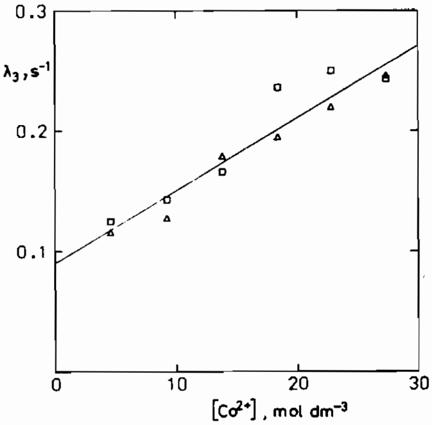


Fig. 1. Plot suggested by eqn. (6) for reaction of Co^{2+} with the keto tautomer of Hpd in aqueous solution at 25 °C and I = 0.5 mol dm^{-3}. $[H^+]$ = 0.147 (□), 0.234 mol dm^{-3} (△).

Table I gives the kinetic data for the slow relaxation observed when Co^{II} is reacted with Hpd. Figure 1 shows a plot of λ_3 against $[Co^{2+}]$ for reactions carried out in the reverse direction using H^+ concentrations of 0.147 and 0.234 mol dm^{-3}. It is evident that the data fit the plot suggested by eqn. (6) and the intercept of 0.09 s^{-1} is in good agreement with the directly determined values of 0.125 s^{-1} for $(k_e + k_f)$ [2]. At lower H^+ concentration it is necessary to use the full eqn. (5) to evaluate k_{HK}. The kinetic data in Table I were fitted to eqn. (5) using a least squares fitting routing [14]. This gives a value of 0.84 ± 0.03 dm^3 mol^{-1} s^{-1} for k_{HK} in good agreement with the value of 0.7 dm^3 mol^{-1} s^{-1} obtained at high $[H^+]$ using eqn. (6).

The Fast Relaxation λ_2

Using the value of 0.84 dm^3 mol^{-1} s^{-1} for k_{HK} and setting $k_{-HK} = 5.4 \times 10^3$ s^{-1} the kinetic data for the faster of the two observed relaxations (Table II) were fitted to eqn. (1). k_{HE} was allowed to vary

TABLE II. Observed (λ_2) and Calculated (k_{calc}) Rate Constants for Reaction of Co^{II} with the Enol Tautomer of Hpd in Aqueous Solution at 25 °C and I = 0.5 mol dm^{-3}.

Experiment No.	10^2 $[Co^{2+}]$ mol dm^{-3}	10^4 $[H^+]$ mol dm^{-3}	λ_2 s^{-1}	k_{calc}[a] s^{-1}
1	4.75	1.36	21.0	23.6
2	9.08	1.36	28.3	29.4
3[d]	15.20	1.36	35.8	37.6
4	6.40	1.36	25.1	25.8
5	7.40	1.36	31.0	27.2
6[b]	10.45	1.36	34.2	31.9
7[c]	12.70	1.36	34.4	34.3

λ = 320 nm, [Hpd] = 1.2×10^{-4} dm^{-3}. [a]Calculated using eqn. (1). [b]I = 0.58 mol dm^{-3}. [c]I = 0.63 mol dm^{-3}. [d]I = 0.70 mol dm^{-3}.

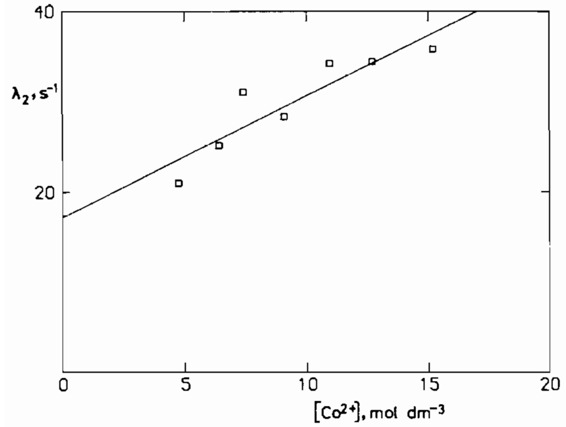


Fig. 2. Plot suggested by eqn. (7) for reaction of Co^{2+} with the enol tautomer of Hpd in aqueous solution at 25 °C, I = 0.5 mol dm^{-3}, and $[H^+]$ = 1.36×10^{-4} mol dm^{-3}.

while k_{-HE} was set equal to k_{HE}/K_E. This reduced the number of parameters to be fitted to one. The value of k_{HE} obtained was 136 ± 15 dm^3 mol^{-1} s^{-1}. An examination of the kinetic data shows that the b/p term in equation (1) makes only a small contribution to the expression for λ_2. Allowing $k_{HE} \gg k_{HK}$ and $k_{-HE} \gg k_{-HK}$ eqn. (1) may be approximated to eqn. (7). Thus at constant H^+ concentration, a plot of k_{obs} against $[Co^{2+}]$ should yield an approximate straight line of slope k_{HE} and intercept ($k_e + k_f + k_{-HE}[H^+]$). Figure 2 shows such a plot for the data in Table II. This gives a value of 134 ± 28 dm^3 mol^{-1} s^{-1} for k_{HE} and the value of K_E calculated (1.06×10^{-3}) is in good agreement

$$\lambda_2 = k_e + k_f + k_{HE}[Co^{2+}] + k_{-HE}[H^+] \qquad (7)$$

with the directly determined value of 1.13×10^3. The kinetic data give a value of 1.3×10^5 dm^3 mol^{-1} s^{-1} for k_{-HE}. Thus at a H^+ concentration of 0.1 mol dm^{-3} $k_{-HE}[H^+]$ = 1.3×10^4 s^{-1}, so that λ_2 for the fast relaxation would be very much greater than could be measured using our stopped-flow device. It is only at $[H^+] \cong 10^{-4}$ mol dm^{-3} that λ_2 becomes accessible using the stopped-flow technique. This explains the absence of a fast relaxation when the reactions were studied in the reverse direction using high concentrations of H^+.

Pearson and Anderson [4] in their investigation of the Cu^{II}–Hpd system omitted the equilibrium between the keto and enol tautomers in their proposed mechanism. We have fitted the kinetic data for this system to the equations used by these authors (using the complete equations) and we have then fitted the data to eqns. (1) and (2). The results are identical in both instances *e.g.* using all the data points, k_{HE} is found to be 2×10^4 dm^3 mol^{-1} s^{-1} and k_{HK} is found to be 15 dm^3 mol^{-1} s^{-1}. In the present investigation this is not the case and we have been unable to derive an equation which satisfies the kinetic data without taking the equilibrium between the keto and enol tautomers into consideration.

As far as we are aware this is the first instance in which the reaction of Co^{II} with a β-diketone has been directly determined. In all other instances only lower limits of the rate constants could be estimated.

Table III is a summary of the rate constants for formation of the monocomplexes of a number of metal ions with Hpd. The values for U^{VI} are slightly different to those published in the original paper [7] (k_{HE} and k_{HK} = 5.3×10^3 and 3.58 dm^3 mol^{-1} s^{-1} respectively). In the case of k_{HE} due to our inability at that time to fit the kinetic data to the full equation a simplified version of the mechanism was used. The new value of 6×10^3 dm^3 mol^{-1} s^{-1} is independent of whether the equilibrium between the keto and enol tautomers is included in the mechanism or not. This is not the situation in the case of k_{HK}. Applying the curve fitting routine to the full equation used by Pearson and Anderson (neglecting the equilibrium between the keto and enol tauto-

TABLE III. Summary of Rate Constants for Formation of Mono Complexes of Hpd.

Metal Species	k_{HE} dm^3 mol^{-1} s^{-1}	R_{HE}	k_{HK} dm^3 mol^{-1} s^{-1}	R_{HK}	k_{HE}/k_{HK}	Ref.
Cu^{2+} [a]	2×10^4	1.1×10^{-5}	15	8.3×10^{-9}	1.3×10^3	4
Fe^{3+} [b]	5.2	0.014	0.29	8×10^{-3}	17.9	2
UO_2^{2+}	6×10^3	–	2.2	–	1.7×10^3	7
Ni^{2+} [c]	19.3	2.9×10^{-3}	–	–	–	5, 6
VO^{2+} [d]	–	–	4.4	0.04	–	8
Co^{2+} [e]	136	2.4×10^{-4}	0.84	1.5×10^{-6}	162	

[a] $k_s = 8 \times 10^9$ s^{-1} [22]. [b] $k_s = 165$ s^{-1} [23]. [c] $k_s = 3 \times 10^4$ s^{-1} [24]. [d] $k_s = 500$ s^{-1} [25]. [e] $k_s = 2.5 \times 10^6$ s^{-1} [26].

mers) gives a value of 3.47 dm^3 mol^{-1} s^{-1} for k_{HK} while using eqn. (2) a value of 2.2 dm^3 mol^{-1} s^{-1} is obtained. For convenience values of R are also included in Table III where $R = 4k_f/3K_o k_s$ [15], and k_f is the rate of complex formation, K_o is the ion pair equilibrium constant, and k_s is the rate of solvent exchange.

From Table III it is apparent that in all the reactions studied, the reactivity order is enol > keto. In all cases the reaction between the metal species and the keto tautomer is a direct reaction between the two species. Without exception, k_{HK} is considerably greater than the ionization rate constant of HK (0.015 s^{-1}) [2]. Inspection of the R values clearly shows that the reactions of both keto and enol tautomers with metal species are in all instances considerably slower than would be predicted on the basis of solvent exchange, in which case R would have a value close to unity. Somewhat surprisingly, the ratio k_{HE}/k_{HK} is not constant. This probably results from the fact that the electronic properties of the keto and enol tautomers of Hpd are quite different. Obviously, some of these differences are important in determining the relative reactivity of the two species towards metal ions. The ratio k_{HE}/k_{HK} is greatest for Fe^{III}. Since R_{HE} is greatest for Fe^{III}, this implies that reaction of Fe^{III} with the keto tautomer is even less retarded than for other metal ions. This may have its origin in the enhanced stability of the loosely bound precursor complex postulated when metal species react with keto tautomer of Hpd. In view of the fact that ketonic complexes of Hpd have been actually isolated [16–19], such an intermediate is not unreasonable. The complex formation reaction is completed by proton loss from the 3-carbon. This may be metal catalyzed.

In general protonated ligands are relatively unreactive towards metal species [20]. Based on the formation rate constants of the protonated ligand (k_{HL}) compared to those with the deprotonated species (k_L) two broad classifications have been made. In the first category k_L/k_{HL} is in the range 10–10^3 (moderate effect) while in the second category the ratio is >10^3 (large effect). The rate of reaction of Ni^{II} with the enolate ion of 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione (Htftbd) is relatively normal [21] (R ≅ 0.5). Assuming that in general the reactions of metal species with the enolate ions of β-diketones are normal, it is clear from Table III that with the exception of Fe^{III} the ratio k_L/k_{HL} for Hpd lies in the category 'large effect'. The ratio does appear to be inversely proportional to the lability of the metal species.

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