

substantial amounts of π character, the contact shifts for the methyl group and β -CH will be of opposite sign and have a magnitude of several thousand hertz. Eaton's data¹¹ on the closely related transition metal acetylacetonates also show large isotropic contact shifts and delocalization in molecular orbitals of π symmetry. Thus, although π delocalization was least when the heteroatom was S in La Mar's system,¹⁷ we would still expect contact shifts of substantial magnitude if the unpaired electron was located in the d_{xy} orbital.

If one chooses our coordinate system, so that the x and y axes intersect the corners of the square-plane, the $d_{x^2-y^2}$ orbital is usually considered the "bonding orbital" in a square-planar geometry,¹⁸ and the σ_{ag} orbital, which is mainly $d_{x^2-y^2}$ in character, should be strongly antibonding. If the unpaired electron resided in this orbital, large contact shifts should occur. In $\text{Co}(\text{sacsac})_2$, the hyperfine coupling constants for the methyl group are of the same sign. This, together with the observation of relatively small contact shifts, leads us to conclude that the unpaired electron resides in the $3d_{z^2}$ metal orbital—rather than the $3d_{xy}$ orbital. This conclusion is in agreement with esr studies of the square-planar cobalt(II)-phthalocyanine complex^{2,10,11} which also showed that the unpaired electron was located in the $3d_{z^2}$ orbital. If the extended Hückel molecular orbital calculations of Cotton, *et al.*,¹⁹ on the square-planar (D_{2h}) bis(β -ketoenolate) complexes of nickel(II) and copper(II) can be extrapolated to $\text{Co}(\text{sacsac})_2$, then for a d^7 case the unpaired electron would also be in a σ_{ag} (d_{z^2}) orbital.

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Finally, we need to discuss the mechanism by which the unpaired electron spin density reaches the ligand protons. There are two probable mechanisms by which this may occur. The first is an admixture of the $4s$ and $3d_{z^2}$ orbitals which is possible since they both transform as A_g in the D_{2h} point group. Ingram, *et al.*,⁸ had calculated this admixture to be 4% in the β -cobalt(II)-phthalocyanine complex. However, this mechanism would place *positive* spin density in the σ_{ag} ($4s$) molecular orbital and would result in a *downfield* contact shift for the protons. The second is a "core polarization" mechanism that has been invoked by Watson and Freeman²⁰ to explain the hyperfine splitting observed in the atomic spectra of transition metal ions and atoms that contain no unpaired "s" electrons. Here, the unpaired electrons in the d orbitals contribute indirectly by polarizing the formally paired electron spins in the s orbitals, thus leading to negative spin density at the metal nucleus. Garito and Wayland²¹ have recently used such a mechanism to account for the observed negative hyperfine coupling constants in $\text{Cu}(t\text{-Bu}(\text{oac}))_2$ ($t\text{-Bu}(\text{oac}) = t\text{-butyl acetoacetate}$) and its 1:1 substituted pyridine type adducts.

Apparently, this indirect mechanism is dominant and negative spin density from the metal is mixed into the σ_{ag} ($4s$) molecular orbital. Such a mechanism would lead to the observed negative hyperfine coupling constants and upfield contact shifts.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for the partial support of this research under Grant No. 1155-G-3.

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CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY,
UNIVERSITY OF ADELAIDE, ADELAIDE, SOUTH AUSTRALIA 5001, AND THE
DEPARTMENT OF CHEMISTRY, WASHINGTON STATE UNIVERSITY, PULLMAN, WASHINGTON 99163

The Hydrolysis of Phosphatopentaamminecobalt(III) in Aqueous Solution

By STEPHEN F. LINCOLN,¹ JERROLD JAYNE, AND JOHN P. HUNT

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The kinetic parameters of the hydrolysis of phosphatopentaamminecobalt(III) in aqueous solution at unit ionic strength have been measured. The following hydrolysis constants were determined: for $\text{Co}(\text{NH}_3)_5\text{PO}_4^0$, $k(60^\circ) = 2.0 \times 10^{-6} \text{ sec}^{-1}$, $\Delta H^\ddagger = 39.6 \pm 1.4$, $\Delta S^\ddagger = 33.7 \pm 4.5$; for $\text{Co}(\text{NH}_3)_5\text{HPO}_4^+$, $k(60^\circ) = 1.05 \times 10^{-6} \text{ sec}^{-1}$, $\Delta H^\ddagger = 26.8 \pm 0.5$, $\Delta S^\ddagger = -6.6 \pm 1.5$; for $\text{Co}(\text{NH}_3)_5\text{PO}_4\text{H}_2^{2+}$, $k(60^\circ) = 1.57 \times 10^{-5} \text{ sec}^{-1}$, $\Delta H^\ddagger = 23.3 \pm 0.3$, $\Delta S^\ddagger = -11.2 \pm 1.0$; for the base-catalyzed hydrolysis of $\text{Co}(\text{NH}_3)_5\text{PO}_4^0$, $k(60^\circ) = 4.0 \times 10^{-4} M^{-1} \text{ sec}^{-1}$, $\Delta H^\ddagger = 36.8 \pm 0.7$, $\Delta S^\ddagger = 36.0 \pm 2.0$, where the units of ΔH^\ddagger and ΔS^\ddagger are kcal mol^{-1} and $\text{cal deg}^{-1} \text{ mol}^{-1}$, respectively.

Introduction

In aqueous solution phosphatopentaamminecobalt(III) exhibits four stages of protonation^{2,3} such that n varies from 0 to 4 in the formula $\text{Co}(\text{NH}_3)_5\text{PO}_4\text{H}_n^{n+}$.

This complex is eminently suited for a study of the effect of protonation upon the hydrolysis rate of the phosphato ligand from the cobalt moiety. Previous kinetic studies of this system have been mainly concerned with the species for which $n = 4$ and 3 and also with the base-catalyzed hydrolysis.^{3,4}

(1) Address inquiries to this author at the University of Adelaide.

(2) S. F. Lincoln and D. R. Stranks, *Australian J. Chem.*, **21**, 37 (1968).

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In this work the kinetic characteristics of the species in which $n = 2, 1,$ and 0 are examined using a ^{32}P -tracer technique. Thus comparison of the kinetic parameters for the entire range $n = 4-0$ is facilitated.

Experimental Section

Materials.—Phosphatopentaamminecobalt(III) was prepared as in the literature.⁵ Phosphorus-32-labeled phosphate was included in the preparation when the radioactive complex was required. Sodium perchlorate used in ionic strength adjustments was either prepared by the neutralization of analytical grade sodium carbonate with perchloric acid or was once recrystallized Fluka reagent. All other chemicals were high-purity commercial products and were used without further purification.

Acid Dissociation Constants.—The values of pK_{a1} and pK_{a2} were determined by standard potentiometric titrations of a $0.005 M$ solution of complex with $0.100 M$ perchloric acid. The ionic strength of both solutions was adjusted to unity with sodium perchlorate. The titration vessel was thermostated in a water bath during the titrations. Carbon dioxide free nitrogen was bubbled through the titration solution during all titrations.

The pH measurements were made on a Beckman pH meter, which was calibrated at the temperature at which the titrations were performed.

Kinetic Measurements.—The kinetic sampling and ion-exchange separation techniques for reaction runs 1-27 inclusive were as previously described.^{2,3} For reaction runs 28-50 the following procedure was adopted. For each reaction run the complete reaction solution was prepared at room temperature and ten 5-ml aliquots were measured into stoppered Teflon containers. These aliquots were simultaneously immersed in a water thermostat, and individual aliquots in their containers were then removed at measured time intervals and immersed in an ice bath to stop reaction. To each aliquot 5 ml of a $1 M \text{H}_3\text{PO}_4$ - $0.1 M \text{HClO}_4$ solution was added as a carrier for any adsorbed phosphorus-32-labeled phosphate, and this mixture was agitated at room temperature for 30 min, a time sufficient for complete desorption of phosphate, as shown by tests. Aliquots were withdrawn from each such mixture and "free" and complexed phosphate was separated as described in the literature.²

Phosphorus-32 was assayed either by counting in a skirted-wall Geiger-Müller tube in the standard β -counting setup or by counting in a liquid scintillator using a homogeneous scintillator agent.

Treatment of Data.—First-order rate constants, k_{obsd} , were derived from the slopes of plots of $\log [(C_\infty - C_0)/(C_\infty - C_t)]$ against time t , where C_∞ , C_0 , and C_t are the "free" phosphate count rates at infinite time, zero time, and a measured time t , respectively. Infinite time was taken as 8-9 half-lives at which time hydrolysis was complete. The error in k_{obsd} was $\pm 3\%$ or less.

Results

The observed first-order rate constants k_{obsd} for the hydrolysis of phosphatopentaamminecobalt(III) are listed in Table I.

Phosphate buffer was employed to maintain a constant pH during the hydrolysis of the complex in a number of runs. Variation of the buffer concentration from 0.005 to $0.02 M$ at pH 5.94 at 80° (runs 24-26) caused no significant variation in k_{obsd} . At 60° reaction runs in $0.02 M$ phosphate buffer at pH 2.18 and 2.54 (runs 14, 15) yielded k_{obsd} values identical, within experimental error, with k_{obsd} values obtained from runs in 0.001 - $0.005 M \text{HClO}_4$ at the same temperature (runs 4-7). It is thus apparent that phosphate buffers

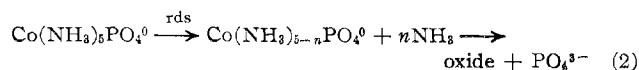
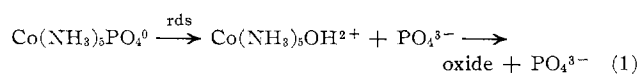
TABLE I
KINETIC DATA FOR HYDROLYSIS

Run	pH	Temp, °C	Solvent ^a	$10^3 k_{\text{obsd}}, 10^4 [\text{complex}],$ $\text{min}^{-1} M$	M
1	...	60.0	0.040 M HClO ₄	1.40	2.5
2	...	60.0	0.020 M HClO ₄	1.13	2.5
3	...	60.0	0.010 M HClO ₄	1.0	0.3
4	...	60.0	0.003 M HClO ₄	0.93	0.3
5	...	60.0	0.001 M HClO ₄	0.95	0.3
6	...	60.0	0.005 M HClO ₄	0.93	0.3
7	...	60.0	0.002 M HClO ₄	0.93	0.3
8	...	80.5	0.003 M HClO ₄	7.6	0.3
9	...	80.5	0.005 M HClO ₄	7.75	0.3
10	...	70.8	0.003 M HClO ₄	2.9	0.3
11	...	70.8	0.005 M HClO ₄	3.0	0.3
12	...	50.3	0.003 M HClO ₄	0.315	0.3
13	...	50.3	0.005 M HClO ₄	0.312	0.3
14	2.18	60.0	0.020 M H ₃ PO ₄ - H ₂ PO ₄	0.94	2.5
15	2.54	60.0	0.020 M H ₃ PO ₄ - H ₂ PO ₄	0.94	2.5
16	6.22	60.0	0.010 M Na ₂ HPO ₄ - NaH ₂ PO ₄	0.062	2.5
17	5.72	60.0	0.010 M Na ₂ HPO ₄ - NaH ₂ PO ₄	0.064	2.5
18	5.92	60.0	0.010 M Na ₂ HPO ₄ - NaH ₂ PO ₄	0.063	2.5
19	6.22	60.0	0.010 M Na ₂ HPO ₄ - NaH ₂ PO ₄	0.063	2.5
20	6.22	70.4	0.010 M Na ₂ HPO ₄ - NaH ₂ PO ₄	0.217	2.5
21	5.72	70.4	0.010 M Na ₂ HPO ₄ - NaH ₂ PO ₄	0.218	2.5
22	5.95	70.4	0.010 M Na ₂ HPO ₄ - NaH ₂ PO ₄	0.222	2.5
23	5.56	80.0	0.010 M Na ₂ HPO ₄ - NaH ₂ PO ₄	0.67	0.5
24	5.94	80.0	0.020 M Na ₂ HPO ₄ - NaH ₂ PO ₄	0.66	0.5
25	5.94	80.0	0.010 M Na ₂ HPO ₄ - NaH ₂ PO ₄	0.69	0.5
26	5.94	80.0	0.005 M Na ₂ HPO ₄ - NaH ₂ PO ₄	0.66	0.4
27	6.26	80.0	0.010 M Na ₂ HPO ₄ - NaH ₂ PO ₄	0.65	0.5
28	...	82.4	0.0010 M NaOH	6.1	0.5
29	...	82.4	0.0010 M NaOH	5.9	0.5
30 ^b	...	82.4	0.0010 M NaOH	5.8	0.5
31	...	82.4	0.0025 M NaOH	7.6	0.5
32	...	82.4	0.010 M NaOH	12.3	2.0
33	...	82.4	0.010 M NaOH	12.3	2.0
34	...	82.4	0.020 M NaOH	21.4	2.0
35 ^c	...	82.4	0.020 M NaOH	22.5	2.0
36	...	82.4	0.025 M NaOH	24.6	2.0
37	...	72.2	0.0010 M NaOH	1.24	1.0
38	...	72.2	0.0010 M NaOH	1.29	1.0
39	...	72.2	0.0025 M NaOH	1.70	1.0
40	...	72.2	0.0025 M NaOH	1.70	1.0
41	...	72.2	0.010 M NaOH	2.54	2.5
42	...	72.2	0.020 M NaOH	4.45	2.5
43	...	72.2	0.025 M NaOH	5.45	2.5
44	...	72.2	0.025 M NaOH	5.20	2.5
45	...	60.0	0.001 M NaOH	0.15	1.0
46	...	60.0	0.001 M NaOH	0.16	1.0
47	...	60.0	0.010 M NaOH	0.34	2.3
48	...	60.0	0.020 M NaOH	0.59	2.3
49	...	60.0	0.025 M NaOH	0.74	2.3
50	...	60.0	0.025 M NaOH	0.72	2.3

^a μ adjusted to 1 with NaClO₄. ^b Concentration $5 \times 10^{-8} M$ with reference to $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ initially. ^c Concentration $2 \times 10^{-4} M$ with reference to $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{ClO}_4)_3$ initially.

do not affect the hydrolysis rate under the experimental conditions.

In basic solution cobalt oxide is produced at a rate consistent with two reaction schemes



where rds indicates the rate-determining step for the production of cobalt oxide. In support of the scheme outlined in eq 1 is a similar study⁴ of *cis*-Co(NH₃)₄(OH)PO₄⁻ and *cis*-Co(en)₂(OH)PO₄⁻. Under basic conditions, hydrolysis of the tetraammine is accompanied by the formation of cobalt oxide, while in the case of the bis(ethylenediamine) analog no such decomposition occurs. The ΔH^\ddagger values for the tetraammine and the bis(ethylenediamine) analog for the uncatalyzed hydrolysis are within 1.5 kcal mol⁻¹, and for the base hydrolysis within 0.3 kcal mol⁻¹. Such similarities in ΔH^\ddagger tend to argue against radically different hydrolysis mechanisms, *i.e.*, loss of ammonia in the rds in one case and loss of phosphate in the other. In two^{6,7} other studies of acidopentaamminecobalt(III) complexes loss of coordinated ammonia was observed in hydrolysis reactions, and in both cases it was concluded that this occurred subsequently to the hydrolysis rds. Hence in this paper the scheme in eq 1 will be considered to apply.

As metal oxides are known to adsorb phosphate⁸ the reactant-product phosphate separation method included the use of a phosphate carrier to eliminate the effects of any such adsorption on the rate data as outlined in the Experimental Section.

Under the conditions for the base hydrolysis of Co(NH₃)₅PO₄⁰, [Co(NH₃)₅H₂O](ClO₄)₃ decomposes within a few seconds. In runs 30 and 35 [Co(NH₃)₅H₂O](ClO₄)₃ was added at zero time in order that a relatively high concentration of cobalt oxide should be produced at the commencement of the hydrolysis run. It is apparent that the k_{obsd} values obtained from these two runs do not significantly differ from runs under identical conditions in the absence of added [Co(NH₃)₅H₂O](ClO₄)₃. It is concluded from this that the cobalt oxide does not catalyze hydrolysis of Co(NH₃)₅PO₄⁰.

The pK_a values for Co(NH₃)₅PO₄H⁺ (pK_{a1}) and Co(NH₃)₅PO₄H₂²⁺ (pK_{a2}) are given in Table II.

TABLE II
VALUES FOR pK_a^a

Temp, °C	pK_{a1}	pK_{a2}
21.0	7.95 ± 0.10	3.45 ± 0.05
45.0	7.91 ± 0.10	3.51 ± 0.05
60.0	8.00 ± 0.10	3.70 ± 0.05

^a All pK_a values determined at unit ionic strength (NaClO₄).

It has previously been shown⁴ that the position of bond cleavage upon hydrolysis of phosphatopentaamminecobalt(III) in both acidic and basic solutions is exclusively between cobalt and oxygen.

Discussion

The complete rate equation over the solvent acidity range considered in this study (0.005 *M* HClO₄ to 0.025 *M* NaOH at an ionic strength made up to unity with NaClO₄) is

$$k_{\text{obsd}}[\text{complex}]_{\text{total}} = k_0[\text{P}_0] + k_1[\text{P}_1] + k_2[\text{P}_2] + k_{\text{OH}^-}[\text{P}_0][\text{OH}^-]$$

This may be rearranged to

$$k_{\text{obsd}} = \frac{k_0 K_1 K_2 + k_1 K_2 [\text{H}^+] + k_2 [\text{H}^+]^2 + k_{\text{OH}^-} K_1 K_2 K_w [\text{H}^+]^{-1}}{K_1 K_2 + K_2 [\text{H}^+] + [\text{H}^+]^2}$$

where brackets indicate concentration; P₀, P₁, and P₂ represent zero, mono-, and diprotonated phosphatopentaamminecobalt(III), respectively; k_0 , k_1 , and k_2 are the rate constants for the hydrolysis of zero, mono-, and diprotonated phosphatopentaamminecobalt(III), respectively; and k_{OH^-} is the rate constant for the base hydrolysis of the zero-charged complex, where $K_1 = [\text{P}_0][\text{H}^+]/[\text{P}_1]$; $K_2 = [\text{P}_1][\text{H}^+]/[\text{P}_2]$, and K_w is the self-ionization constant for water. The values of K_1 and K_2 are sufficiently different that the k_{obsd} values obtained in the pH ranges 5–6 and 2–2.7 correspond to k_1 and k_2 , respectively. Over the hydroxide concentration range 0.0025–0.025 *M* the rate equation reduces to $k_{\text{obsd}} = k_0 + k_{\text{OH}^-}[\text{OH}^-]$ such that a plot of k_{obsd} as abscissa with $[\text{OH}^-]$ as ordinate gives k_0 as the intercept on the abscissa and the slope yields k_{OH^-} . The derived kinetic parameters for P₀, P₁, and P₂, together with those from the literature for the triprotonated phosphato complexes, denoted P₃, are collected in Table III. It should be noted that runs 1–3 yield k_{obsd} values significantly greater than k_2 at 60°. This is attributable to the increasing participation of the more reactive Co(NH₃)₅H₃PO₃³⁺ species, P₃, as $[\text{H}^+]$ increases.³

TABLE III

Complex	DERIVED KINETIC PARAMETERS		
	10 ³ k , min ⁻¹ (60°)	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , cal deg ⁻¹ mol ⁻¹
P ₀	0.12	39.6 ± 1.4	33.7 ± 4.5
P ₁	0.063	26.8 ± 0.5	-6.6 ± 1.5
P ₂	0.94 ^c	23.3 ± 0.3	-11.2 ± 1.0
P ₃	9.0	25.6 ± 0.3	-0.2 ± 1.0 ^c
	10 ³ k_{OH^-} , M ⁻¹ min ⁻¹ (60°, base hydrolysis)		
P ₀	24.0	36.8 ± 0.7	36.0 ± 2.0
P ₀	23.0	35.0 ± 0.5	30.3 ± 1.5 ^b

^a From ref 3. ^b From ref 4. It should be noted that in ref 4 k_{OH^-} and ΔS^\ddagger are misquoted; the correct values are as in this table. Additionally for *cis*-Co(NH₃)₄(OH)PO₄⁻ the following correct values should be substituted in ref 4: $k_{\text{H}_2\text{O}}$ and k_{OH^-} should be multiplied by 10 and the corresponding ΔS^\ddagger values are 13 ± 1.5 and 19 ± 7 cal deg⁻¹ mol⁻¹, respectively. ^c Extrapolation to 25° yields $k = 1.31 \times 10^{-5}$ min⁻¹ which corresponds to a value of $k = 1.55 \times 10^{-5}$ min⁻¹ in ref 12.

It is seen from Table III that the hydrolyses of the protonated phosphato complexes are characterized by ΔH^\ddagger values some 10 kcal mol⁻¹ lower than the ΔH^\ddagger values observed for the hydrolysis and base hydrolysis of Co(NH₃)₅PO₄⁰.

A mechanism leading to significant weakening of the cobalt-oxygen bond (the Co-O bond is broken) and probably a lower ΔH^\ddagger value would be one in which a proton is situated on the bridging phosphato oxygen in the transition state. Certainly a proton sited on this oxygen ought to be more effective in catalyzing

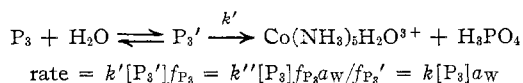
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the release of the phosphato ligand than would be the case for a proton sited on a nonbridging oxygen. It seems reasonable to postulate that the greater the protonation of the complex the greater is the probability that the bridging oxygen will be protonated. One cannot, of course, rule out the possibility that protonation of the oxygens on phosphorus is sufficient. The activation parameters for the three protonated species are rather similar which fact may be due to a combination of bond weakening and solvation effects.

An insight into the role of water in the hydrolysis of P_3 was perhaps gained by the observation that the hydrolysis rate law for this species is:³ $\text{rate} = k_3 \cdot [P_3]a_w$. This was rationalized in terms of an equilibrium being established between P_3 and an intermediate P_3' consisting of P_3 and a water molecule combined in a seven-coordinated species, *i.e.*



where f_{P_3}/f_{P_3}' is assumed to remain constant, f and a_w represent an activity coefficient and the activity of water, respectively, and k is the experimental rate constant. Similar mechanisms have been proposed for the hydrolysis of several other complex cobalt(III) species.^{9,10} A dissociative or solvent-assisted dissociative mechanism would also be possible as has been most often postulated. Perhaps one should keep an open mind on this question for these systems.

The ΔS^\ddagger values for both P_2 and P_1 are more negative

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than that for P_3 , which suggests that these species might also hydrolyze *via* an associative mechanism.

The markedly higher ΔH^\ddagger values observed for the hydrolysis and base-catalyzed hydrolysis of $Co(NH_3)_5PO_4^0$ might well be attributable to the fact that no protonation of the bridging oxygen is possible, and consequently a greater cobalt-oxygen bond energy exists than was the case for the protonated analogs. It could be argued that as a result an even greater amount of nucleophilic assistance from the incoming water molecule would be required in the transition state, leading to an associative activation process. The small differences between the base hydrolysis and hydrolysis are worth noting.

The base-catalyzed hydrolysis of $Co(NH_3)_5PO_4^0$ is kinetically consistent with most of the proposed base hydrolysis mechanisms.¹¹ The zero charge of this complex would presumably reduce the effect of ion pairing with hydroxide to a minimum. Green and Taube¹² have suggested that the slower base-catalyzed hydrolyses of acidopentaamminecobalt(III) complexes may proceed *via* an associative mechanism. In the case of $Co(NH_3)_5PO_4^0$ an associative mechanism would be in keeping with the trend suggested for its protonated analogs, although the ΔS^\ddagger value is not easily explained by any mechanism.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BEDFORD COLLEGE, REGENT'S PARK, LONDON N.W.1, ENGLAND

Mechanism of the Reactions of Dihydroxobis(ethylenediamine)cobalt(III) Cations in Highly Basic Aqueous Solution

BY M. E. FARAGO, B. A. PAGE, AND C. F. V. MASON

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The rates of isomerization and of the racemization of the $Co(en)_2(OH)_2^+$ ions have been measured over the temperature range 25–70°. The observed rates are independent of hydroxide concentration. The activation energies for the *cis* → *trans* change and for the *trans* → *cis* change are 29.5 and 28.5 kcal mol⁻¹, respectively. The activation energy for the racemization is not constant over the temperature range. The mechanisms of oxygen exchange with solvent and of stereochemical change are discussed. The mechanism of the latter is intramolecular, and it is proposed that a twisting process is the most likely one.

Introduction

Three studies of the system containing the *cis*- and *trans*- $Co(en)_2(OH)_2^+$ ions are reported in the literature.^{1–3} Bjerrum and Rasmussen¹ investigated the

equilibrium and estimated the rate constant for *cis* ⇌ *trans* isomerization at 25°. Tong and Yankwich² showed that the rate of isomerization at 35° was independent of hydroxide concentration between 1.0 and 0.0005 *M*.

In a more detailed study Kruze and Taube³ found that during the *cis* ⇌ *trans* isomerization of the Co-

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