Co(II) AND Cu(II) - PROMOTED BASE HYDROLYSIS OF 2-CYANO-1, 10-PHENANTHROLINE

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Abstract

Co(II) and Cu(II) promoted base hydrolysis of 2-cyano, 1,10-phenanthroline was studied. At 298.2°K, Cu(II) reaction is more efficient (by a factor of 20) than either Co(II) and its analogues Ni(II) in promoting base hydrolysis.

Introduction

In 1966, Correy reported the synthesis of 2-cyano-1,10-phenanthroline, and from this material a variety of 2-substituted 1,10-phenanthroline have been prepared [1]. These include the tridentate ligands 2-carboxy-1,10-phenanthroline, its amide, thioamide, amidoxide, carbaldehyde imines, carbaldehyde hydrazones and thiazole. The metal complexes of these substituted phenanthrolines have been investigated by Goodwin and coworkers, [2-5] and the Ni(II)-promoted hydrolysis of 2-cyano derivatives has been studied [6]. The advantage of 2-cyano-1, 10-phenanthroline is that it should be strongly and completely bound to various metal ions, and the cyano group is in a well-defined position in a metal complex, near the metal, but for reasons of geometry not coordinated with it.

In this paper the Co(II) and Cu(II)-promoted hydrolysis of 2-cyano-1,10-phenanthroline is described.

Experimental Section
Materials

2-Cyano-1,10-phenanthroline was prepared by the method cited in the literature [1], mp 238-9° C, yield 70%. Found C, 75.95; H, 3.40; N, 20.50 requires for $C_{13}H_7N_3$, C, 76.08; H, 3.44; N, 20.47%.

The solutions of Co(II) and Cu(II) were prepared from their salts and were standardized [7,8].

Physical Measurements

A radiometer pH-meter 26 was used to measure the pH of the solutions, which were contained in a beaker immersed in a water bath thermostated at the appropriate temperature. All kinetic measurements were carried out, using a Unicam SP 1800 spectrophotometer.

Kinetic Measurements and Results
(a) Co(II)-promoted base hydrolysis of 2-cyano-1,10-phenanthroline

Solutions of 2-cyano-1,10-phenanthroline in 0.1 M Co(II) at pH 4.8 undergo spectral changes characteristic of reaction(I). When this reaction was allowed to go to completion and edta added, a white precipitate of amide was obtained. Also the uv spectrum of the product of the above reaction was identical to that of a solution of the authentic amide sample in 0.1 M Co(II). These experiments confirm that the reaction investigated at pH 4.8 represents conversion of nitrile to amide.

Keywords: Hydrolysis of metal ion coordinated substrates
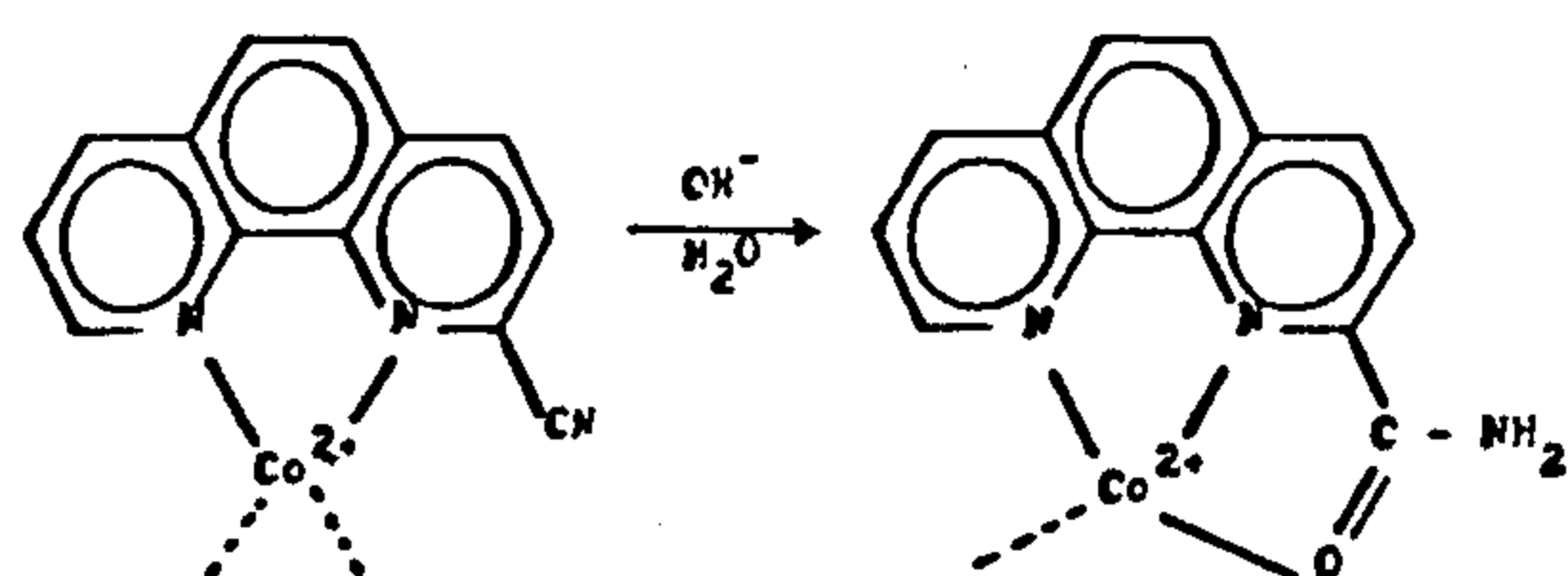
(I)

The base hydrolysis of 2-cyano-1,10-phenanthroline in the presence of Co(II) was followed by monitoring the absorbance change at 380 nm at temperatures in the range 288.2-308.2°K, using solutions between pH 6.03 and 7.32. Hepes (N-2-hydroxyethylpiperazine-N'-2-ethane sulphonic acid) buffer was used to control pH.

The general technique employed in the kinetic measurements has already been outlined [6]. All the kinetic studies were carried out at I=0.3 (using sodium perchlorate as the supporting electrolyte). Pseudo-first-order rate constants (k_{obs}) were obtained by the Guggenheim method [9], and the second order rate constants were calculated using the relationship $k_2 = k_{obs} / [OH^-]$. Values of $k_{obs} / [OH^-]$, (k_2

Table 1) were found to be reasonably constant at the given temperature. Determination of the activation parameters [10] from the data of Table 1 yields the values of $\triangle H^\#$ (59.3 kJmol^{-1}) and $\triangle S^\#$ (42JK^{-1} mol^{-1}).

(b) Cu(II)-promoted base hydrolysis of 2-cyano-1,10-phenanthroline

In preliminary investigations, about 20 µl of a stock solution of 2-cyano-1,10-phenanthroline was injected into a 1 cm cell containing a 0.02 M solution of Cu(II) buffered at pH 4.6 with acetate/acetic acid buffer. Repetitive scans after time intervals of 20 minutes were recorded in the range 333-368 nm (Figure 1). The wavelength of 355 nm was chosen for kinetic studies. Reaction solutions were 0.01 M in Cu(II), 0.27 M in NaClO$_4$ (was used to maintain the constant ionic strength of 0.3 during the reaction), and 2.5 x 10^{-3} M in NaCH$_3$CO$_2$. Plots of log (A_∞ -A_t) versus time (where A_t and A_∞ are the absorbances at the time t and the time infinity, respectively) were linear for three half lives. Pseudo-first-order rate constants (k_{obs}), were obtained by the same method used for Co(II), (Table 2).

Table 1. Co(II)–promoted base hydrolysis of 2-cyano-1,10-phenanthroline

Temperature/°K	pH	$10^8[OH^-]/M$	$10^4 k_{obs}/s^{-1}$	$10^{-4} k_2/M^{-1}s^{-1}$
288.2	6.75	3.55	5.96	1.68
288.2	6.90	5.02	8.49	1.69
288.2	7.08	7.60	12.08	1.59
288.2	7.23	10.73	16.88	1.57
298.2	6.03	1.52	5.76	3.79
298.2	6.34	3.11	11.10	3.57
298.2	6.57	5.28	19.70	3.73
298.2	6.99	13.91	50.10	3.60
308.2	6.02	3.12	26.99	8.65
308.2	6.54	10.31	90.42	8.77

Table 2. Cu(II)-promoted base hydrolysis of 2-cyano-1,10-phenanthroline at 298.2°K

pH	$10^{10}(OH^-)/M$	$10^{10}[OH^-]/M$	$10^4 k_{obs}/s^{-1}$	$10^{-5} k_2/M^{-1}s^{-1}$
4.63	4.30	6.07	4.87	8.02
4.78	6.07	8.57	6.45	7.53
4.78	6.07	8.57	6.50	7.58
5.03	10.80	15.25	11.70	7.67

Results and Discussion

Breslow *et al.* [6] report a second order rate constant of $2.4 \times 10^4 M^{-1} s^{-1}$ for the Ni(II)-promoted base hydrolysis of 2-cyano-1,10-phenanthroline at 298.2°K. This represents a rate enhancement of 10^7 over the base hydrolysis of the

free ligand. The value of k_2 reported in this paper for the Co(II), ($k_2 = 3.67 \times 10^4 M^{-1}s^{-1}$), and Cu(II), ($k_2 = 7.70 \times 10^5 M^{-1} s^{-1}$)-promoted base hydrolysis of 2-cyano-1,10-phenanthroline also at 298.2° K represents rate enhancements of 1.4×10^7 and 3×10^8, respectively. In the case of Co(II) study, activation parameters $\Delta H^{\#}_{298.2} = 59.3k$ J mol^{-1} and $\Delta S^{\#}_{298.2} = 42 JK^{-1}mol^{-1}$ were obtained. The corresponding values for base hydrolysis of the ligand are $\Delta H^{\#}_{298.2} = 65.5 kJmol^{-1}$, and $\Delta S^{\#}_{298.2} = -83.6 JK^{-1}mol^{-1}$. The observed rate enhancement produced by Co(II) is therefore entirely accounted for by vastly increased entropy of activation with little change being observed in $\Delta H^{\#}$. The large entropic increase probably results from charge neutralization in the addition complex, and the resultant desolvation of hydroxide ion. It also seems probable that the transition state involves bonding of the developing imino anion, (II), to the metal ion with concomitant displacement of a water ligand at the adjacent site. The Ni(II)-promoted base hydrolysis of 2-cyano-1,10-phenanthroline is also due to a large positive $\Delta S^{\#}$ value. In the Co(II) and Ni(II)-promoted hydrolysis of 2-cyano-8-hydroxyquinoline the 10^5-fold rate enhancements were also found to be due to vastly increased $\Delta S^{\#}$ values, with little change being observed in $\Delta H^{\#}$ [11].

(II)

Direct coordination of nitrile to the metal ion e.g. $[Co(NH_3)_5N \equiv C-C_6H_5]^{3+}$ causes rate accelerations due to a combination of a lowering in $\Delta H^{\#}$ ($14 kJmol^{-1}$ in the above complex), and an increase in $\Delta S^{\#}$ ($50 JK^{-1}mol^{-1}$).

Activation parameters for the Cu(II)-promoted reaction have not been obtained due to problems with precipitation at higher temperatures. At 298.2°K however, it is more efficient (by a factor of 20) than either Co(II), or Ni(II) in promoting base hydrolysis. This is consistent with previously reported trends for such reactions. Angelici *et al.* [12] have synthesized a number of N,N-diacetic acid derivatives of amino acid esters NH_2-(CHR)$_n$ —COR', (n=1, R= –H,R'= –C$_2$H$_5$ Or –C$_4$H$_9$; n=1 R= –CH$_3$, R'= –C$_2$H$_5$; n=1, R= –CH(CH$_3$)$_2$, R'= –C$_2$H$_5$; n=2, R= –H, R'=
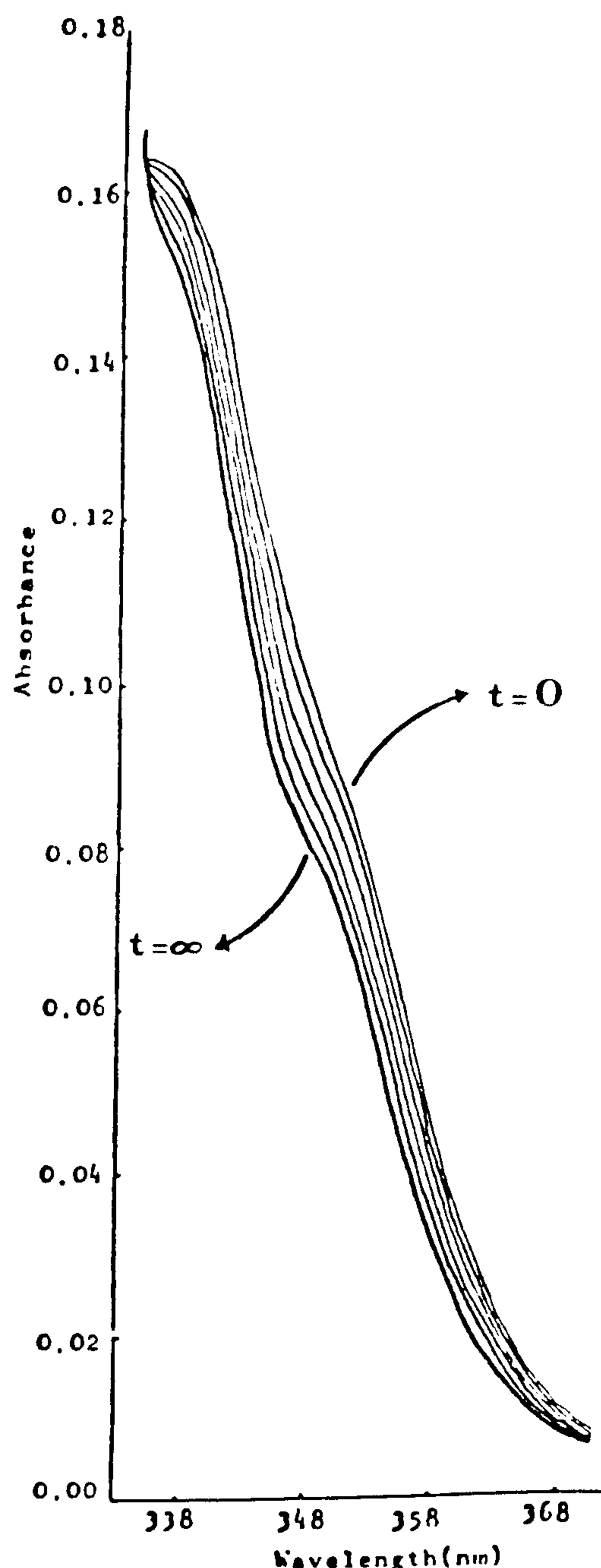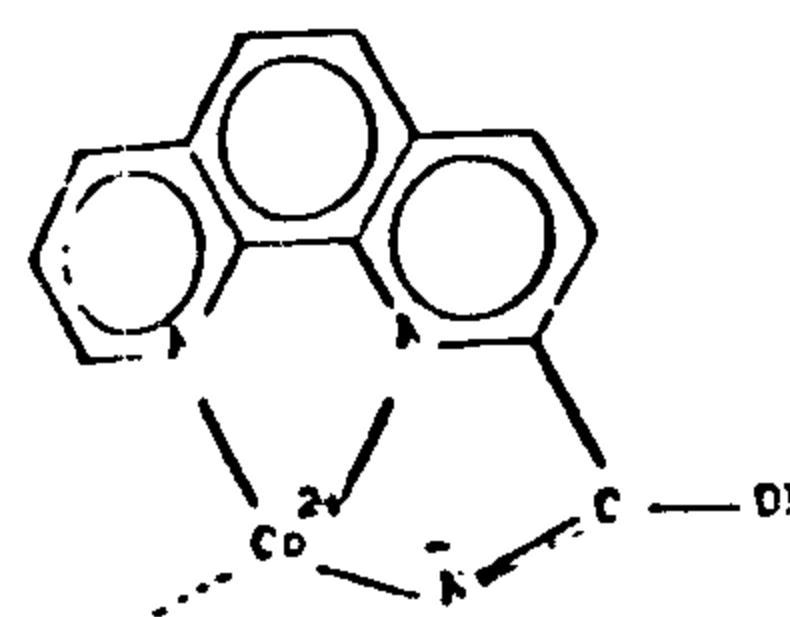
Figure 1. Cu(II)-promoted base hydrolysis of 2-cyano-1, 10-phenanthroline, at 298.2°K, pH 4.61, [NaClO$_4$]=0.24M, acetate buffer = 2x10^{-4}M, [Cu(II)] = 0.02M, Δt~10min.

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$-C_2H_5$; n=3, R= $-H$, R'= C_2H_5) and have found that base hydrolysis of metal complexes (reaction (II)) follow the order Cu(II)>> Co(II)> Ni(II) with Cu(II) complexes being generally 20-fold more susceptible to base hydrolysis than their Co(II) analogues(III).

(III)
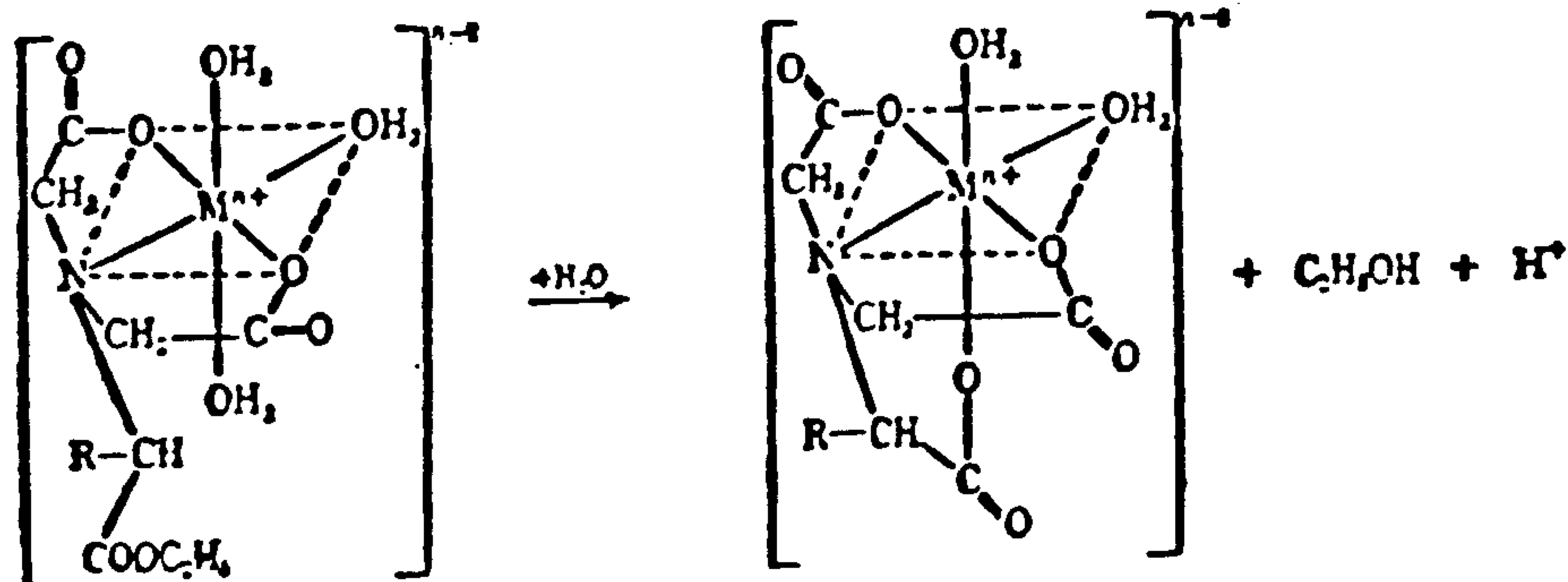
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