Inorganica Chimica Acta, 46 (1980) L109–L110
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The Effect of Cobalt(III) Complexes on the Rate of Hydrolysis of Triphosphate Ion

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Received May 27, 1980

Introduction

The coordination of metal ions to phosphates can accelerate the rate of phosphate hydrolysis by at least three means [1]: a) charge neutralization or electron withdrawal from the phosphorus atom, b) inducement of strain in the ground state, and c) simultaneous coordination of attacking water molecule (or hydroxide ion) and of the phosphate moiety. Experiments in this laboratory have been designed to examine each of these factors independently by making use of triphosphato complexes of the substitution-inert metal ion cobalt(III). Charge neutralization alone has been shown for $Co(NH_3)_4H_2P_3O_{10}$ [2] not to be greatly more effective for the metal ion than for hydrogen ion. Investigation of the extent to which strain is important is currently under investigation using the linkage isomers of $Co(NH_3)_4H_2P_3O_{10}$ [3] which differ in the size of the chelate ring (six or eight members) formed by the bidentate triphosphate ligand.

Hubner and Milburn [4] have shown the dramatic effect that the condition of a 2:1 (or higher) metal: phosphate stoichiometry can have upon the rate of hydrolysis of pyrophosphate ion. In the present report, results are presented which make use of the higher stoichiometry and which show the importance of the third contributing factor, simultaneous coordination of phosphate and attacking nucleophile.

Experimental

The cobalt(III) compoexes β,γ-$Co(NH_3)_4H_2P_3O_{10}$ [2, 5], $[Co(NH_3)_4CO_3]NO_3$ [6], and $[Co(NH_3)_5CO_3]NO_3$ [7] were prepared by methods previously described. Purified $Na_5P_3O_{10}$ was obtained from Fisher Scientific. Analyses for total orthophosphate ion (free plus metal bound) used a spectrophotometric phosphomolybdate method [8] modified for the phosphatocobalt(III) systems [2]. Constant pH (6.00 ± 0.02) was maintained by additions of 5 *M* NaOH using a screw driven glass syringe capable of delivering solution in less than 1 μl increments. Capillary polyethylene tubing (i.d. <0.3 mm) was used to deliver the NaOH solution under the surface of the stirred 0.010 *M* phosphate solution. Temperature was maintained using a water bath held at 40.0 ± 0.1 °C, and $(CH_3)_4NCl$ was used to establish 1.0 *M* ioni strength.

Results and Discussion

The experiments reported here make use of the complex* β,γ-$Co(NH_3)_4H_2P_3O_{10}$ which has been characterized both by phosphorus-31 NMR in solution [5] and by X-ray crystallography in the solid state [9]. The triphosphate ligand is bound to the cobalt through the center phosphate and one terminal phosphate group. Initial rate measurements were performed to determine the rate of hydrolysis of triphosphate ion as the free ion, as a ligand in the complex $[Co(NH_3)_4P_3O_{10}]^{2-}$, and as a ligand in the same complex, but in the presence of different +3 cobalt complexes, $[Co(NH_3)_5H_2O]^{3+}$ or $[Co(NH_3)_4(H_2O)_2]^{3+}$, at a concentration equal to 80% that of the triphosphato complex. At pH 6 and 40 °C the rate constant determined for the hydrolysis of free triphosphate ion is 2.3×10^{-7} sec^{-1}. The relative rates for all four of the reaction solutions are given in Table I.

The faster relative rate of phosphate hydrolysis for $[Co(NH_3)_4P_3O_{10}]^{2-}$ than for $P_3O_{10}^{5-}$ under the conditions used here contrasts with the slightly slower relative rate in solutions of 0.1 to 1.0 *M* hydrochloric acid [2]. The difference between the results in acidic solution and those at pH 6 can be attributed to the difference in the state of protonation of the triphosphate ion. In solutions of 1.0 *M* ionic strength maintained by tetramethylammonium salts pK values [11, 12] are 8.6, 5.7, 2.0, 1.0, and *ca.* 0.5 for triphosphate ion, and the values [2] for

TABLE I. Relative Rate of Hydrolysis of Triphosphate Ion in the Presence of Different Cobalt(III) Complexes.

Species	Relative Rate
$P_3O_{10}^{5-}$	1
$Co(NH_3)_4P_3O_{10}^{2-}$	7
$Co(NH_3)_4P_3O_{10}^{2-} + Co(NH_3)_5H_2O^{3+}$	26
$Co(NH_3)_4P_3O_{10}^{2-} + Co(NH_3)_4(H_2O)_2^{3+}$	700

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*This complex in which the center phosphate group and one terminal phosphate group are coordinated is labeled β,γ- by analogy with the ATP complex from which crystals for the structure determination were prepared (refs. 5 and 9). We have also reported the α,β,γ-tridentate binding of triphosphate ion to form two six-membered chelate rings in $Co(NH_3)_3H_2P_3O_{10}$. See ref. 5 and 10.

$[Co(NH_3)_4P_3O_{10}]^{2-}$ are 5.7 and 2.2. These values are such that at pH 6 coordination of cobalt(III) to triphosphate ion can be effective in charge neutralization because only one proton is released** in the substitution of triphosphate ion into the coordination sphere of the cobalt complex:

$$HP_3O_{10}^{4-} + [Co(NH_3)_4(H_2O)_2]^{3+} \rightarrow [Co(NH_3)_4P_3O_{10}]^{2-} + H^+ + 2H_2O \qquad (1)$$

The negative charge on the phosphate species is therefore decreased by two. At pH 0, on the other hand, 3 hydrogen ions are released and the charge on the phosphate species is unchanged upon substitution:

$$H_5P_3O_{10} + [Co(NH_3)_4(H_2O)_2]^{3+} \rightarrow [Co(NH_3)_4H_2P_3O_{10}] + 3H^+ + 2H_2O \qquad (2)$$

Thus in highly acidic solutions the coordination of cobalt(III) to triphosphate ion causes hardly any change in the rate of hydrolysis, while at pH 6 the coordination increases the rate of hydrolysis by a factor of 7.

The largest increase in the rate of the hydrolysis of triphosphate ion is caused by the introduction of the ion $[Co(NH_3)_4(H_2O)_2]^{3+}$ into solutions containing triphosphate coordinated as $[Co(NH_3)_4P_3O_{10}]^{2-}$. Charge neutralization alone is an insufficient explanation for the increase because the presence of $[Co(NH_3)_5H_2O]^{3+}$ causes a much smaller increase in rate. A plausible explanation lies in the ability of the tetraammine to simultaneously coordinate both a water molecule and the phosphate to be hydrolized. The pentaamine must lose its only water molecule in order to coordinate to the single free phosphate group of $[Co(NH_3)_4P_3O_{10}]^{2-}$. The tetraamine can lose one molecule of water as it binds to the free phosphate group and still have one coordinated water molecule poised for nucleophilic attack on the phosphorus. The simultaneous coordination of a phosphate moiety and attacking nucleophile by a metal ion, shown here to be an important factor in determining the rate of phosphate hydrolysis, is a possible role for a metal ion at the active sites of enzymes that catalyze phosphoryl transfer reactions.

Acknowledgements

This research was supported by Research Corporation and by the National Science Foundation, Grant No. CHE-7809301. The author appreciates helpful discussions with Professor Gilbert P. Haight of the University of Illinois at Urbana-Champaing.

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**The pK values at 5.7 result in the presence of species which are protonated to a greater extent than shown in eqn. 1, but the net change in the negative charge is unchanged because both $H_2P_3O_{10}^{3-}$ and $[Co(NH_3)_4HP_3O_{10}]^-$ have the same pK.