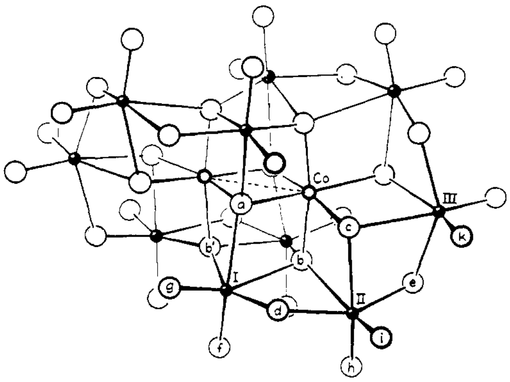

Figure 1. Pictorial view of the decamolybdodicobaltate(III) ion, $[H_4Co_2Mo_{10}O_{38}]^{6-}$.

persion. It was found that the axis of the molecule that is vertical in Figure 1 is tilted away from the pseudo-twofold crystal axis by about 2.5°.

The heteropoly molecule ion, $[H_4Co_2Mo_{10}O_{38}]^{6-}$, conforms closely to an ideal point symmetry 222 (D_2). Thus, the crystal is a raceme, and it may be possible to resolve the complex into optically active components. The structure of the molecule (see Figure 1) may be considered as being derived from the flat, trigonal hexamolybdocobaltate(III) ion (analogous to hexamolybdotellurate ion[5] by removing one MoO_2 group from each of two hexa molecules, turning one 180° around a CoO_6 octahedron diagonal, and joining them so that the two CoO_6 octahedra come together at the center, sharing an edge.

Table I gives the interatomic distances in the decamolybdodicobaltate(III) molecule, averaged over four determinations each, according to the ideal symmetry. The range of individual measurements (standard error of each ± 0.03 Å) is shown, and these are about what would be expected to result from ionic and hydrogen bond interactions with the irregular crystal structure environment. There seems no reason to suppose that D_2 symmetry is not assumed by the free ion in solution. Of particular interest is the Co–Co environment at the center of the molecule. The Co–Co distance (dashed line in Figure 1) is 2.779 ± 0.007 Å and the Co–O_a bond length is 1.889 ± 0.015 Å. These lengths may be compared with those in the dinuclear μ-dihydroxy-bis(tetraammine)dicobalt(III) ion as found by Prout[6] in his crystal structure determination of $[(NH_3)_4Co(OH)_2Co(NH_3)_4]Cl_4 \cdot 4H_2O$, in which the Co–Co length is 2.932 ± 0.005 Å and the Co–OH length is 1.912 ± 0.010 Å.

An outstanding feature of the crystals of both form A and form B is an extreme pleochroism. The optic directions are nearly parallel to the molecular twofold axes, and are blue (vertical in the figure), red (horizontal, normal to the Co–Co axis), and olive yellow (parallel to the Co–Co axis).

Table I. Bond Lengths in the Decamolybdodicobaltate(III) Molecule Ion, Averaged over D_2 Symmetry[a]

Bonded atoms	Max var in crystal, Å	Av bond length, Å
$Co—O_a$	0.025	1.89
O_b	0.045	1.90
O_c	0.051	1.95
$Mo_I—O_a$	0.082	2.31
O_b	0.060	2.26
O'_b	0.035	2.01
O_d	0.039	1.89
O_f	0.074	1.67
O_g	0.021	1.71
$Mo_{II}—O_b$	0.065	2.30
O_c	0.055	2.26
O_d	0.019	1.95
O_e	0.017	1.91
O_h	0.051	1.73
O_i	0.066	1.71
$Mo_{III}—O_c$	0.114	2.28
O_e	0.101	1.97
O_k	0.051	1.71

[a] See Figure 1.

---

(5) H. T. Evans, Jr., *J. Am. Chem. Soc.*, **90**, 3275 (1968).

(6) C. K. Prout, *J. Chem. Soc.*, 4429 (1962).

Howard T. Evans, Jr.
U. S. Geological Survey, Washington, D. C.

John S. Showell
National Science Foundation, Washington, D. C.

Received July 14, 1969

Degradation of Polyphosphates in Solution. IV. Catalytic Effects of Divalent Metal Ions on Trimetaphosphate Formation

Sir:

It has been shown that the aqueous acid-catalyzed degradation of linear long-chain polyphosphates proceeds *via* four major routes: (1) hydrolytic scission in the interior of the chain to produce two shorter chains; (2) hydrolytic scission of the chain at an end group with the production of orthophosphate; (3) splitting off of trimetaphosphate from an end of the chain; and (4) splitting out of trimetaphosphate from the interior of the chain.[1,2] There have been a number of reports that the formation of the degradation products is significantly accelerated by polyvalent metal ions,[3-7] but very little is known about the pathways of these catalytic processes. Such information is especially desirable for the reactions leading to trimetaphosphate formation because of their biological implications. While trimetaphosphate itself is not known to form in living systems, its production from linear polyphosphates involves the biologically significant formation of a P–O–P linkage, a reaction which in nature appears to need the presence of a divalent metal ion.[8]

We have carried out exploratory studies on the effect of several divalent metal ions on the rate of formation of trimetaphosphate, and our findings may be summarized as follows. (1) The catalytic effects are highly specific and apply only to reactions occurring at the ends of the chains, where rate increases of up to more

---

(1) U. P. Strauss and G. J. Krol, *J. Polym. Sci., Part C*, 2171 (1967).

(2) G. J. Krol, Ph.D. Thesis, Rutgers University, 1968.

(3) B. Toplay, *Quart. Rev.* (London), 3, 345 (1949).

(4) E. Thilo and W. Wieker, *Z. Anorg. Allg. Chem.*, **306**, 48 (1960).

(5) W. Wieker and E. Thilo, *Rev. Chim. Min.*, **6**, 89 (1969).

(6) E. Bamann and M. Meisenheimer, *Chem. Ber.*, **71**, 2233, 2286, (1938).

(7) Y. Moriguchi and M. Miura, *Bull. Chem. Soc. Jap.*, **38**, 678 (1965).

(8) J. M. Lowenstein, *Biochem. J.*, **70**, 222 (1958).

Table I. Metal Ion Catalysis of Trimetaphosphate Formation from Protonated and Unprotonated Polyphosphate End Groups

Metal ion	β_T[a]	k^H, min^{-1} [b]	k, min^{-1} [c]
None	0	2.1	0.3
Mg	0.2	2	14
	0.6	4	21
Ca	0.4	3	52
	0.6	~5	~120
Ni	0.4	9	62

[a] Metal ion to phosphate ratio as described in text. [b] Moles of trimetaphosphate formed per minute from 1 mole of protonated end groups. [c] Moles of trimetaphosphate formed per minute from 1 mole of unprotonated end groups.

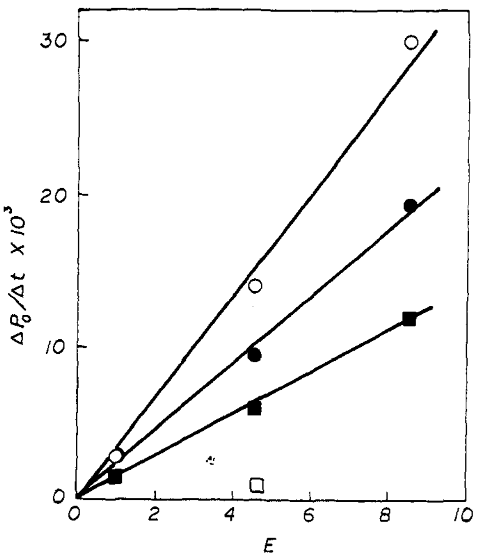

Figure 1. Dependence of the initial rate of formation of trimetaphosphate, $\Delta P_0/\Delta t$, on the per cent end groups. P_0 = moles of trimetaphosphate per 100 g-atoms of total phosphorus. ○: Ca^{2+}, β_T = 0.4, pH 7.0; ■: Mg^{2+}, β_T = 0.4, pH 6.5; ●: Ni^{2+}, β_T = 0.2, pH 7.5; □: no added metal ion, pH 7.0.

than two orders of magnitude are observed. (2) Hydrogen ion, a catalyst itself, inhibits the metal ion catalysis. The evidence on which these conclusions are based is as follows.

The initial rates of formation of trimetaphosphate from three samples of tetramethylammonium polyphosphate (TMAPP) of different chain lengths were determined at 66° in 0.2 *M* TMACl as a function of pH and β_T, the stoichiometric ratio of equivalents of metal ion to gram-atoms of phosphorus. The initial concentration of TMAPP was 0.02 monomole/l. In order to avoid complications known to arise from heterogeneous catalysis,[6] special precautions were taken to prevent conditions which would lead to phase separation. The polyphosphate samples were characterized by potentiometric acid–base titration of the weak acid end groups; their number-average degrees of polymerization were 23, 46, and 200. The degradation products, ortho- and trimetaphosphate, were identified by ion-exchange chromatography and determined quantitatively by an automated technique using Technicon Autoanalyzer components. Figure 1 shows the effects of Mg^{2+}, Ca^{2+}, and Ni^{2+} on the initial rate of trimetaphosphate formation for the three chain lengths. The abscissa is *E*, the concentration of end groups, expressed as mole per cent end group phosphate relative to total phosphate. The results show clearly that the rate of trimetaphosphate formation is directly proportional to the concentration of end groups.

The acid-catalyzed formation of trimethaphosphate has been related directly to the binding of protons to the reactive sites at both interior and end phosphate groups.[2] However, even though the divalent metal ions are bound much more strongly to interior groups than is hydrogen ion,[9] they catalyze only the reaction occurring at the chain end. This conclusion is a departure from the proposal recently made by other workers who infer that, in the presence of divalent metal ions, trimetaphosphate splits out from sites in the chain interior.[5]

Very little has been reported on the effect of pH on the metal ion catalyzed reaction.[3] Our observations show that this reaction is decelerated by decreasing pH exactly in the pH range where the state of protonation of the end groups changes with pH. Over this range of pH, the observed rate can be clearly separated into two contributions, one from the protonated end groups, the other from the unprotonated end groups. (Because the divalent metal ions affect the acid strength of the end groups,[10] the degree of protonation had to be determined from titrations made in the presence of metal ion.) The effects of several metal ions on the specific rate constants for the protonated and unprotonated end groups are listed in Table I. It can be seen that the metal ion catalysis is very pronounced for the unprotonated end groups, but very small for the protonated end groups. It is clear from these data that while hydrogen ion acts as a catalyst in the absence of metal ion, it inhibits the metal ion catalysis.

These findings as well as further results involving the rather complex and specific dependence of the catalysis on the extent of metal ion binding are open to a number of interpretations. The subject will be treated more fully in a future article.

Acknowledgment. This work was supported by Grant GM-12307 from the National Institutes of Health, Public Health Service.

---

(9) See listing of stability constants for various cation complexes of polyphosphate: J. Bjerrum, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, p 199.

(10) J. R. Van Wazer and D. Campanella, *J. Am. Chem. Soc.*, **72**, 655 (1950).

David L. Miller, George J. Krol, Ulrich P. Strauss
School of Chemistry, Rutgers University
The State University of New Jersey
New Brunswick, New Jersey 08903

Received August 7, 1969

The Carbon-13 Nuclear Magnetic Resonance Spectrum at −150° of the 2-Norbornyl Cation and Its Relationship to the 7-Norbornenyl and 7-Norbornadienyl Cations[1]

Sir:

Recently we reported the ^{13}C spectrum of the 2-norbornyl cation at −70° in SbF_5–SO_2 solution.[2] At this

---

(1) Stable Carbonium Ions. XCV. Presented in part at the XXIst National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 1969; part XCIV: G. A. Olah, A. T. Ku, and J. Sommer, submitted for publication.

(2) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3954 (1969).