[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Metal Chelate Catalysis of Aqueous Pyrophosphate Hydrolysis[1]

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The influence of various metal salts and chelate compounds on the aqueous hydrolysis of pyrophosphate ions was determined at 70° and $-\log[H]$ of 6.29. Measurable increases in rate were observed for the following substances in order of increasing catalytic activity: Ce(III) salts, MoO_2(VI)-2,4-disulfopyrocatechol < UO_2(VI)-2,4-disulfopyrocatechol < Zr(IV)-EDTA < Zr(IV)-NTA < ZrO(IV)-2,4-disulfopyrocatechol, Zr(IV)-2,4-disulfopyrocatechol < ZrO(IV)-EDTA. Salts and chelates of Cu(II), Mn(II), Pb(II) and Th(IV) showed no catalytic activity under the same experimental conditions.

The aqueous hydrolysis of the pyrophosphate ion and of acid pyrophosphate ions, reported by Campbell and Kilpatrick,[2] is catalyzed by hydrogen ions and to a slight extent by solvent molecules, the rate decreasing markedly with increasing negative charge of the acid phosphate anion. In view of the interest in the role of metal ions in hydrolysis and other reactions of polyphosphates, it seemed of interest to determine if the hydrolysis of pyrophosphate is catalyzed by metal ions. The only previous investigation of this type is a study by Bamann and Meisenheimer[3] of the effect of metal hydroxide gels on the rate of hydrolysis of $HP_2O_7^{-3}$. This investigation is a study of the influence of metal ions on pyrophosphate hydrolysis and is part of a general investigation of the hydrolysis of various types of polyphosphates and polyphosphate esters.

Experimental

Materials.—Reagent grade tetrasodium pyrophosphate obtained from Fisher Scientific Co. was employed for the preparation of a stock solution used in rate determinations. The concentration was checked by complete hydrolysis and colorimetric analysis of the orthophosphate as the phosphomolybdate by the method of Fiske and SubbaRow.[4] The metal salts were Baker analyzed reagents with the exception of Zr(IV) compounds. Metal chelates were prepared at the time of reaction by addition of the metal salt to the ligand solution at low *p*H. The *p*H was then adjusted to a value in the range 3–3.5 in order to bring the final equimolar mixture with tetrasodium pyrophosphate to 6.29. The disodium ethylenediaminetetraacetate (EDTA) and nitrilotriacetic acid (NTA) were obtained through the courtesy of Versenes, Inc. (now the Dow Chemical Company), Framingham, Mass., and were purified by recrystallization from water. Stock solutions were standardized by titration with standard $ZnCl_2$ solution with Eriochromblack T indicator according to the method of Schwarzenbach.[5] The disodium pyrocatechol-3,5-disulfonate (Tiron, PDS) purchased from the LaMotte Chemical Company and disodium 1,8-dihydroxynaphthalene-3,6-disulfonate (DNS), obtained from Fluka, Buchs, Switzerland, were used directly for the preparation of stock solutions which were standardized potentiometrically.

Methods.—Experimental potentiometric titrations were carried out in a jacketed glass vessel maintained at 70° by circulation of water from a constant temperature bath. *p*H meter readings obtained with extension glass and calomel electrodes were converted to hydrogen ion concentration by calibrations based on 1, the titrations of standard acid with standard base and, 2, the *p*H values of standard Beckman buffers divided by mean activity coefficients given by Harned and Owen.[6] These two methods gave points on a straight line having the expected slope of unity for $-\log [H^+]$ *vs.* *p*H meter reading. The ionic strength was maintained at 0.1 by the addition of KNO_3 solution.

In the rate determinations, samples were removed from the reaction mixture from time to time and were analyzed for phosphate by the method of Fiske and SubbaRow.[4] An attempt was made to employ ascorbic acid in place of sulfur dioxide for the development of color in accordance with the procedure of Lowry and Lopez.[7] It was found, however, that ascorbic acid complexes of the metals employed gave interferences, and the low *p*H-SO_2 reduction, which gave more reliable results, therefore was employed.

Results

Potentiometric titration curves are given in Figs. 1–3 for these various systems: Zr(IV)-PDS, Zr(III)-PDS-pyrophosphate, ZrO(IV)-PDS, ZrO(IV)-PDS-pyrophosphate, Zr(IV)-EDTA, Zr(IV)-EDTA-pyrophosphate, ZrO(IV)-EDTA, ZrO(IV)-EDTA-pyrophosphate, Zr(IV)-NTA, Zr(IV)-H_3X-pyrophosphate, MoO_2(VI)-PDS and MoO_2-PDS-pyrophosphate. The potentiometric titration of pyrophosphoric acid itself, not shown, also was carried out at 70° and 0.10 ionic strength to obtain the dissociation constants which were calculated to be 8.92×10^{-7} for K_3 and 4.07×10^{-9} for K_4. These "concentration" constants apply to solutions of 0.10 ionic strength. At 10^{-3} *M*, the concentration employed in both the titrations and rate studies, the first two dissociations of pyrophosphoric acid were found to be complete.

The results of the rate studies are summarized in Fig. 4 for each of the systems showing catalytic activity with the exception of systems containing uranyl complexes of DNS. In the latter case, the reaction rates were found to be so sensitive to light that a smooth curve *versus* time could not be obtained. However, it was observed qualitatively that the rate of hydrolysis of pyrophosphate was increased by a factor of about three in the presence of visible light and that there was no appreciable catalysis in the dark or in the presence of ultraviolet light. In order to provide a semi-quantitative comparison of the rate studies, the per cent. pyrophosphate hydrolyzed after 60 minutes and after 90 minutes is indicated in Table I. It is believed that the tabulated values present a clear picture of the relative results obtained with different ligands and metals, because the times are short enough that the interfering effects of orthophosphate are largely eliminated.

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[1] This work was supported by a grant from the Esso Education Foundation.

[2] D. O. Campbell and M. L. Kilpatrick, THIS JOURNAL, **76**, 893 (1953).

[3] E. Bamann and M. Meisenheimer, *Ber.*, **71B**, 2233 (1938).

[4] C. H. Fiske and Y. SubbaRow, *J. Biol. Chem.*, **66**, 375 (1925).

[5] G. Schwarzenbach, "Die Komplexímetrische Titration," Ferdinand Enke, Stuttgart, 1955, p. 69.

[6] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 1st Ed., Reinhold Publ. Corp., New York, N. Y., 1943, p. 119.

[7] O. H. Lowry and J. A. Lopez, *J. Biol. Chem.*, **162**, 421 (1946).

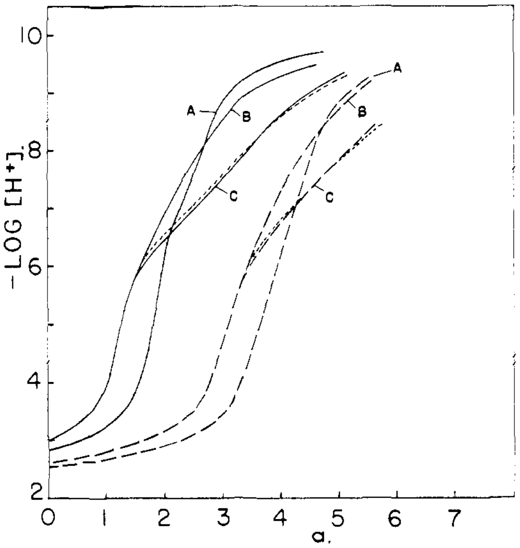

Fig. 1.—Potentiometric titration of Zr(IV) – – – –, and ZrO(IV) ———, in the presence of Tiron and of disodium pyrophosphate: A, metal + Tiron; B, metal + disodium pyrophosphate; C, metal + Tiron + disodium pyrophosphate; . . . . indicates addition of abscissa of B to that of the Tiron titration curve (not shown); a = moles of base added per mole of metal ion or ligand; all reacting substances present at 1.00 × 10^{-3} *M*; *t* = 70.0 ± 0.2°; μ = 0.1 (KNO_3).

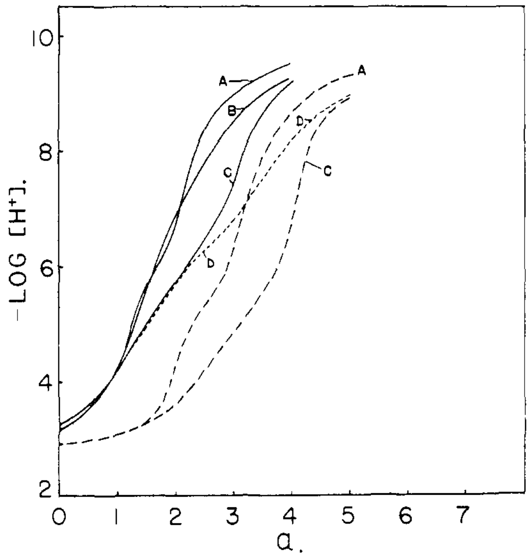

Fig. 2.—Potentiometric titration of Zr(IV) – – – –, and ZrO(IV) ———, in the presence of EDTA and disodium pyrophosphate: A, metal + EDTA; B, metal + disodium pyrophosphate; C, metal + EDTA + disodium pyrophosphate; D (short dashes) indicates addition of abscissa of B to that of the EDTA titration curve (not shown); a = moles of base added per mole of metal ion or ligand; all reacting substances present at 1.00 × 10^{-3} *M*; *t* = 70.0 ± 0.2°; μ = 0.1 (KNO_3).

Discussion

In this investigation, it was first decided to study the catalytic effects of a variety of metal ions and metal chelates over a range of *p*H values. The results indicated no catalysis for divalent metals,

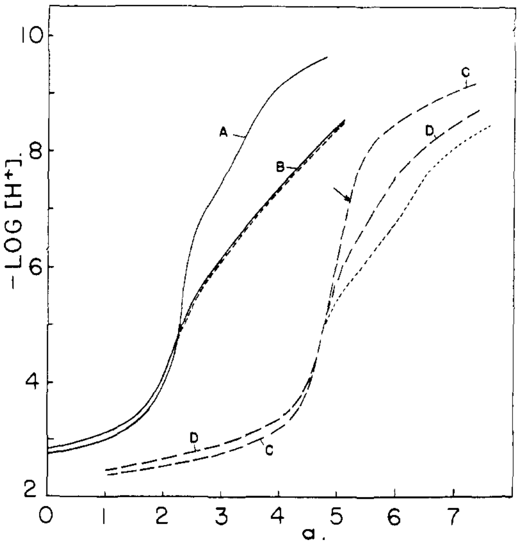

Fig. 3.—Potentiometric titration of MoO_2(VI), ———, in the presence of Tiron and pyrophosphate, and Zr(IV), – – – –, in the presence of nitrilotriacetic acid and pyrophosphate: A, MoO_2(VI) + Tiron; B, MoO_2(VI) + Tiron + pyrophosphate; C, Zr(IV) + nitrilotriacetic acid; D, Zr(IV) + nitrilotriacetic acid + pyrophosphate; . . . . indicates addition of abscissa of A or C to the titration curve of pyrophosphate (not shown); a = moles of base added per mole of metal ion or ligand; all reacting substances at 1.00 × 10^{-3} *M*; *t* = 70.0 ± 0.2°; μ = 0.1 (KNO_3). The arrow on curve C indicates the appearance of a slight amount of precipitate.

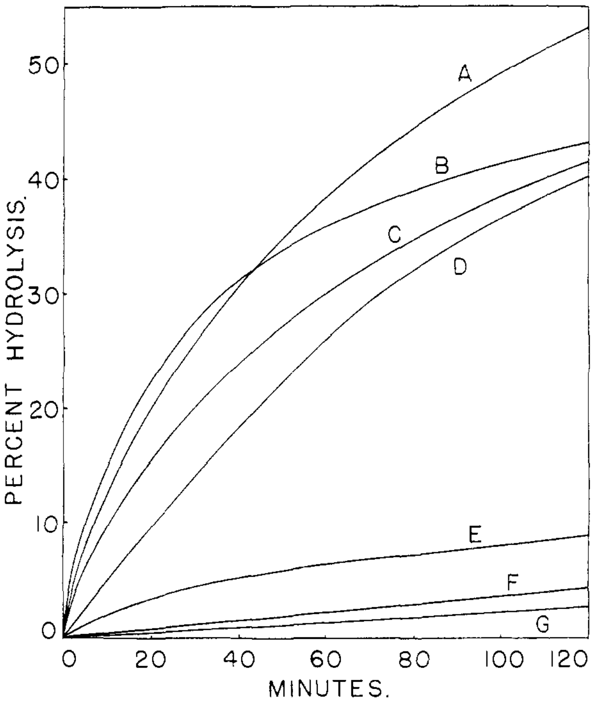

Fig. 4.—Metal-catalyzed pyrophosphate hydrolysis at 70° in systems containing equivalent initial concentrations of ligand, metal ion and pyrophosphate: A, ZrO(IV)-EDTA; B, Zr(IV)-PDS; C, ZrO(IV)-PDS; D, Zr(IV)-NTA; E, Zr(IV)-EDTA; F, MoO_2(VI)-PDS; G, no metal chelate; all reacting substances 0.00100 *M*; μ = 0.10 (KNO_3); $-\log[H^+]$ = 6.29.

such as Cu(II) and Zn(II) aquo ions or complexes. Similar negative results were obtained with molybdate(VI) and Th(IV). The aquo Ce(III) ion, probably complexed by pyrophosphate, was found to be slightly catalytic. These results led to the study of heavier elements of higher oxidation number, in the form of water-soluble chelates. Since the greatest activity was found in complexes of Zr(IV), UO_2(VI) and MoO_2(VI), it was decided to investigate these particular metals in some detail. A relatively high *p*H ($-\log[H^+] = 6.29$) was selected to minimize the spontaneous hydrolysis of the pyrophosphate; however, it was sufficiently low to prevent serious disproportionation reactions and decomposition of the metal chelates of these readily hydrolyzed metal species. Maintaining the *p*H in the second buffer region of pyrophosphoric acid ($pK_3 = 6.05$ at 70°) served to increase somewhat the buffer capacity of the solution. This procedure was an advantage in this particular case since the addition of buffers was not possible in the presence of the metals being investigated.

The plots of the kinetic data of Fig. 4 indicate that ZrO(IV) and Zr(IV) chelates are by far the most active catalysts, while some activity is shown by the UO_2(VI)–Tiron chelate in the presence of visible light. The Ce(III) nitrate and MoO_2(VI)–Tiron chelate showed definite but only very slight activity. The data in Fig. 4 do not follow any specific rate law, the rates falling off rapidly as the reaction proceeds beyond 30%, and dropping close to zero at 60–70% of completion. This effect probably is due to further complexing of the metal by the phosphate anion produced in the reaction; in fact in a few cases the latter reaction resulted in disproportioning of the metal chelate formed to give a precipitate of the phosphate. When such precipitation was observed, the measurements were stopped. The data of Fig. 4 therefore correspond only to homogeneous systems.

Influence of Metal Ion.—The evident superiority of Zr(IV) and ZrO(IV) chelates over those of other metal ions as catalysts for pyrophosphate hydrolysis suggests some unique characteristic in these complexes not found in the other metals tried. Since it is known that aqueous Zr(IV) chelates and complexes are extensively hydrolyzed and polymerized,[8,9] it appears that this property is the one which also determines to a large extent the observed catalytic activity. This suggestion is further supported by the interesting contrast in catalytic activity of the Zr(IV)–EDTA and ZrO(IV)–EDTA chelates. Apparently the most significant difference between these two systems is that the ZrO(IV) chelates were formed from the aged metal salt, which was already in a highly hydrolyzed and polymerized condition. This interpretation of the differences in the zirconium(IV) and zirconyl(IV) catalysts in the presence of EDTA is supported by the potentiometric titration data described below.

Potentiometric Measurements.—The potentiometric measurements illustrated in Figs. 1–3 may be used to indicate the nature of the interactions between the metal and the various ligands present in the experimental solutions.

TABLE I

RELATIVE RATES OF PYROPHOSPHATE HYDROLYSIS IN THE PRESENCE OF METAL CHELATE COMPOUNDS[a]

Metal	Ligand	After 60 min. % hydrolyzed	After 60 min. Rel. rate[c]	After 90 min. % hydrolyzed	After 90 min. Rel. rate[c]
MoO_2(VI)	PDS	2.0	1.3	2.8	1.3
Ce(III)	...	2.0	1.3	2.8	1.3
UO_2(VI)[b]	DNS	4.5	3.0	6.5	3.0
ZrO(IV)	PDS	30.0	20	36.5	17
ZrO(IV)	EDTA	38.0	25	47.0	21
Zr(IV)	EDTA	6.4	4.3	7.6	3.5
Zr(IV)	NTA	26.0	17	34.5	16
Zr(IV)	PDS	36.0	24	40.0	18

[a] $t = 70 \pm 0.2°$; $\mu = 0.1$ (KNO_3); $-\log[H^+] = 6.29$. [b] Average value. [c] Rate relative to non-catalytic rate of pyrophosphate hydrolysis under the same conditions.

The Zr(IV) and ZrO(IV) titration curves in the presence of Tiron and pyrophosphate, illustrated in Fig. 1, indicate two very similar families of curves separated in the abscissa by two moles of base per mole of ligand. It thus seems that the same interactions occur regardless of whether zirconium(IV) or zirconyl(IV) is used in the experimental solution. These curves indicate that 1, the interaction of one mole of Tiron per mole of Zr(IV) or ZrO(IV) is sufficiently strong to maintain a homogeneous solution over the whole *p*H range, and 2, the interaction with disodium pyrophosphate is similar to that of Tiron; 3, both the Tiron and pyrophosphate complexes contain hydroxo or oxo groups bound to the metal to give chelates which may be polynuclear; and, 4, in the presence of both disodium pyrophosphate and Tiron, chelate formation takes place *exclusively* with the pyrophosphate.

The Zr(IV) and ZrO(IV) titration curves in the presence of the disodium salt of EDTA and disodium pyrophosphate, illustrated in Fig. 2, show a striking contrast to the analogous titration curves of Fig. 1, in that there is considerable difference between the reactions of zirconium(IV) and zirconyl(IV) with EDTA. In the zirconyl(IV)–EDTA titration, there was initially a very slight precipitate which redissolved at $-\log[H]$ of 7 and remained in solution at higher *p*H. The fact that the interaction of ZrO(IV) with EDTA is considerable is indicated by comparison of the curves of Fig. 2 with curve B of Fig. 1. It is apparent that the interaction of ZrO(IV) with pyrophosphate alone is sufficiently strong to displace (or exclude) Tiron. The left-hand dotted line of Fig. 2, however, indicates that pyrophosphate and EDTA are both bound to the metal, since the titration curves of the ZrO(IV)–EDTA and the ZrO(IV)–pyrophosphate systems, added in the abscissa to the titration curve of pyrophosphoric acid and EDTA, respectively, do not reproduce the experimental curve obtained with both ligands present simultaneously.

For Zr(IV), however, the potentiometric data indicate that the interactions with EDTA and with EDTA and pyrophosphate together are considerably stronger than for the hydrolyzed ZrO(IV) compounds. The right-hand dashed line indicates

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[8] S. Chaberek, Jr., R. L. Gustafson, R. C. Courtney and A. E. Martell, THIS JOURNAL, **81**, 515 (1959).

[9] B. Intorre and A. E. Martell, *ibid.*, in press.

further that a relatively stable double complex with both EDTA and pyrophosphate is formed. The shift of the ordinate between the Zr(IV) and ZrO(IV) curves corresponds to about one mole of base per gram-ion of metal, indicating that the former complexes probably contain fewer bridging hydroxo groups, very likely as a consequence of more extensive reaction with the two ligands present. Apparently the highly polymeric zirconyl(IV) system cannot combine as readily with these ligands as does the less hydrolyzed Zr(IV) solution.

The titration curves for the MoO_2(VI) system illustrated in Fig. 3 indicate that the 1:1 MoO_2(VI)–Tiron chelate compound previously described[9] does not react with pyrophosphate and that the latter anion is present in the same state as in the absence of the metal chelate.

The potentiometric data for the Zr(IV)–NTA–pyrophosphate systems illustrated in Fig. 3 clearly show that 1, the interaction of Zr(IV) with NTA is sufficient to keep the metal from precipitating below $-\log[H^+]$ of 7.5; and 2, in the presence of pyrophosphate, the normal pyrophosphate–Zr(IV) chelate only is formed, and the NTA behaves as if it is present in the free state in solution.

Correlation of Rates with Metal Chelates Formed.—A comparison of the kinetic data in Table I and Fig. 4, with the results of the potentiometric measurements in Figs. 1–3, indicates that the observed rates are probably the result of two opposing tendencies: 1, catalytic activity of the metal ion which increases as the number of uncoördinated positions on the metal increases, and 2, tendency of a polydentate chelating agent to lower the activity of the metal through coördination. Thus, high catalytic activity is seen in Table I for the Zr(IV) chelates with relatively few donor groups, such as PDS and NTA. In the case of EDTA, which forms a much more stable Zr(IV) chelate compound, the catalytic activity is greatly reduced.

The remarkably high catalytic activity of the ZrO(IV) chelate of EDTA is unique and, as suggested above, probably is due to a polymeric and highly olated or oxolated structure for this particular substance. In any case it is seen that the primary function of the chelating agent is to hold the metal in soluble form. Of the metal chelates with sufficient stability to maintain a homogeneous solution, those with the lowest stability seem to be the best catalysts.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. XXIV. Cobalt Stilbenediamine Complexes[1]

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A number of previously unreported cobalt(III) coördination complexes of active and *meso*-stilbenediamine have been prepared and their properties studied. Attempts to isomerize *trans*-dichloro-bis-*active*-stilbenediamine-cobalt(III) chloride to the *cis*-isomer failed. What is believed to be the *cis*-isomer was obtained by interaction of gaseous hydrogen chloride and solid carbonato-bis-*active*-stilbenediamine-cobalt(III) nitrate 1-hydrate. Efforts to obtain positive proof of the configuration by X-ray diffraction were unsuccessful due to the amorphous nature of the material. Reaction of *racemic*-stilbenediamine and carbonatotetrammine-cobalt(III) nitrate $^1/_2$-hydrate gave two carbonato bis-stilbenediamine complexes differing in composition only in that one was a monohydrate and the other a dihydrate. The two materials, however, differed greatly in their chemical and physical characteristics. Tartrato-bis-*active*-stilbene-cobalt(III) complexes prepared by reaction of *trans*-dichloro-bis-*active*-stilbenediamine-cobalt(III) nitrate with silver tartrate gave indication that the tartrate group was not behaving as a bidentate ligand. Unsuccessful attempts were made to resolve *racemic*-tartaric acid by reaction of its silver salt with *trans*-dichloro-bis-*levo*-stilbenediamine-cobalt(III) nitrate. Cobalt(III) complexes containing *meso*-stilbenediamine were found to be more difficult to prepare and to be considerably less stable than complexes containing the active amine.

The stereochemistry of coördination complexes containing the bidentate asymmetric propylenediamine has been studied extensively, and the propylenediamine-cobalt(III) complexes have been used to effect partial resolution of racemic organic compounds.[2,3] The possibility that a bidentate diamine containing two asymmetric centers might reenforce coördinative selectivity of optical antipodes and make possible complete resolution of organic racemates was considered an intriguing problem worthy of the present investigation.

Stilbenediamine was selected as the diamine to be used because it satisfies the stereochemical prerequisite of having vicinal amino groups attached to asymmetric carbon atoms; it exists in both *racemic*- and *meso*-forms.

The first extensive study of the metal complexes of stilbenediamine was conducted by Lifschitz and Bos.[4] In the present investigation their work on the cobalt complexes has been extended and a number of previously unreported complexes have been prepared and studied. Difficulties encountered in the synthetic work and the anomalous behavior of some of the complexes limited the extent of the stereochemical investigations. Further stereochemical studies of the complexes are under way.

The *trans*-dichloro-bis-stilbenediamine-cobalt(III) complexes containing *active*- and *meso*-amine were prepared by a modification of the procedure re-

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(1) Taken in part from the Doctoral Dissertation of O. F. Williams, University of Illinois, 1951.

(2) H. B. Jonassen, J. C. Bailar, Jr., and A. Gott, THIS JOURNAL, **74**, 3131 (1952).

(3) A. D. Gott and J. C. Bailar, Jr., *ibid.*, **74**, 4820 (1952).

(4) I. Lifschitz and J. G. Bos, *Rec. trav. chim.*, **59**, 173 (1940).