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Precipitation Boundaries in Calcium–Pyrophosphate and Calcium–Ethane-1-hydroxy-1,1-diphosphonate Systems

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Precipitation boundaries in alkaline calcium–pyrophosphate and calcium–ethane-1-hydroxy-1,1-diphosphonate (EHDP) systems have been determined and an interpretation is given in terms of mass action principles ignoring activity coefficients. It is found experimentally that in systems containing ligand in excess of the stoichiometric amount the ratio of total metal to total ligand is generally less than unity for pyrophosphate, whereas the ratio for EHDP approaches the value of 2. The pyrophosphate boundary is shown to be that of a typical nonpolynucleating ligand, and the EHDP data are interpreted in terms of a "core–links" polynuclear complex model which postulates species of the general form $Ca_{2n-1}L_n^{2-} = CaL(Ca_2L)_{n-1}^{2-}$. From the analyses it is estimated that log $K_{21}(Ca_2P_2O_7) = 2.80$, p$K_{so}(Ca_2P_2O_7) = 12.87$, log K_{11}(CaEHDP) = 5.60, log K_{21}(Ca$_2$EHDP) = 4.18, log $K_{2n-1,n} = 4.83$, and pK_{so}(Ca$_2$EHDP) = 14.60.

Low molecular weight phosphates and phosphonates tend to precipitate from solution when allowed to react with alkaline earth ions, particularly calcium. This is in contrast to the behavior of aminopolycarboxylates, *e.g.*, ethylenediamine-*N*,*N*,*N*,'*N*'-tetraacetic acid (EDTA), whose alkaline earth salts are soluble in amounts approaching 1.0 *M*.[1] The tendency of phosphates and phosphonates to precipitate makes impossible or severely restricts the use of a number of techniques for the determination of soluble complex species. The present work was undertaken for the purpose of determining the extent of these restrictions in calcium–pyrophosphate (PP) and calcium–ethane-1-hydroxy-1,1-diphosphonate (EHDP) systems.

Experimental Section

Chemicals.—Stock solutions of $CaCl_2$ were prepared by weight from "Baker Analyzed" $CaCl_2 \cdot 2H_2O$. Tetramethylammonium hydroxide (TMAOH) solutions were prepared from commercial aqueous solutions (either Eastman Chemicals 10% solution or Matheson Coleman and Bell 25% solution) by passage through a column of Dowex 21K anion exchanger in the hydroxyl form. Tetramethylammonium chloride (TMACl) stock solutions were prepared by weight from Eastman Chemicals TMACl. The source of EHDP was the acid monohydrate prepared by the Brooks method[2] and recrystallized twice from water. This was subsequently neutralized with TMAOH in the preparation of stock solutions. "Baker Analyzed" $Na_4P_2O_7 \cdot 10H_2O$ was converted to $(TMA)_4P_2O_7$ by ion exchange using Dowex 50W-X2 in the TMA^+ form (prepared by repeated alternate washings with TMACl and TMAOH).

Procedures.—All stock solutions were passed through 0.45-μ Millipore filter paper and then kept in a nitrogen atmosphere throughout the sample preparations.

Each point in the right branch of the PP precipitation boundary (points for which $C_L > 2C_M$) and points in the vicinity of the minimum were determined by $CaCl_2$ additions to series of aliquots of each of several stock PP solutions up to the point of precipitation. In these cases precipitation was usually very rapid and voluminous so that end points could be determined visually. The actual point of precipitation was taken to be the midpoint between the last homogeneous and first heterogeneous sample in a series. The left branch of the boundary was determined by PP additions to series of aliquots of stock $CaCl_2$ solutions up to the point of precipitation. In this region heterogeneity was determined turbidimetrically using a GE 88 tungsten light source. Light was passed through a green narrow band pass filter into a sample cell having a light path of 9 cm and then into a cadmium selenide photocell (Type B2M, International Rectifier Corp.). A 5% decrease in transmittance was taken to indicate heterogeneity. Increments were chosen such that each end point had an average deviation between 20 and 40%. The largest uncertainties occurred in the region of low PP and low Ca^{2+}. There was no added electrolyte in any case.

Precipitation boundary points for EHDP were determined similarly but with greater precision by a factor of 2. Also one series of solutions was prepared containing 1.0 *M* TMACl supporting electrolyte in order to determine whether this would shift the boundary appreciably.

All PP and EHDP systems were adjusted to pH 11.0 with TMAOH, and in no case was there a difference found due to the order of addition of reagents.

Results

Pyrophosphate (PP).—The $CaCl_2$–$(TMA)_4P_2O_7$ system at pH 11.00 (TMAOH) yielded five different precipitate types, four of which were crystalline in appearance. The one noncrystalline material was gelatinous and appeared immediately in all solutions with concentrations in the region of the left branch but also in the right branch when Ca^{2+} was high. Of the crystalline solids, one appeared only after an induction period of between 4 and 12 hr. The solutions in which this occurred were in the region of the right branch; *i.e.*, the solutions contained a slight molar excess of ligand. This solid had an X-ray powder pattern which matched that of orthorhombic $Ca_2P_2O_7 \cdot 4H_2O$.[3] The other solids were not obtained in sufficient quantity to determine their X-ray diffraction patterns.

The precipitation boundary for Ca^{2+}–PP is shown in Figure 1 together with a theoretical curve derived by assuming a single solid phase to be in equilibrium with the soluble species $CaP_2O_7^{2-}$ and $Ca_2P_2O_7$(aq). At pH 11.0 negligible error is introduced by ignoring protonated species. Thus the equilibria considered are

$$M^{2+} + L^{4-} \rightleftharpoons ML^{2-}, \quad K_{11}$$

and

$$M^{2+} + ML^{2-} \rightleftharpoons M_2L, \quad K_{21}$$

where M^{2+} and L^{4-} are substituted for Ca^{2+} and $P_2O_7^{4-}$, respectively. At the precipitation boundary the species in these equilibria must also satisfy the expression

$$K_{so} = [M^{2+}]^2[L^{4-}]$$

The value of the first constant, K_{11}, is known; the remainder are unknown.

In terms of the defined constants the metal and ligand

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(1) K. V. Astakhov and E. D. Kiseleva, *Zh. Obshch. Khim.*, **20**, 1780 (1950).

(2) B. T. Brooks, *J. Amer. Chem. Soc.*, **34**, 492 (1912); O. T. Quimby, U. S. Patent 3,387,024 (1968).

(3) E. H. Brown, J. R. Lehr, J. P. Smith, and A. W. Frazier, *J. Agr. Food Chem.*, **11**, 214 (1963).

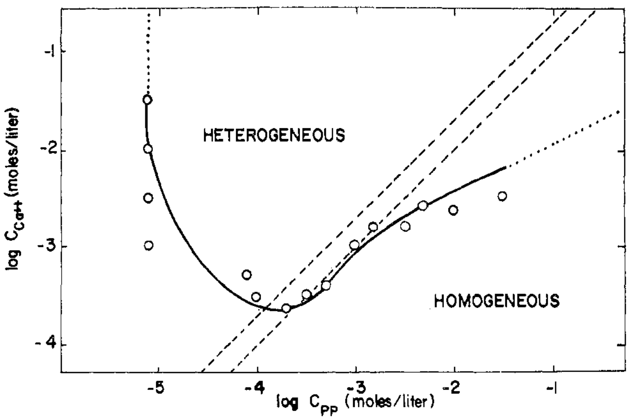

Figure 1.—Calcium–pyrophosphate precipitation boundary in TMACl medium at pH 11: solid curve, theoretical boundary; upper dashed line, stoichiometric equivalence line ($C_M/C_L = 2$); lower dashed line, equimolar line.

mass balance equations, dropping charges for convenience, are

$$C_M = [M] + [ML] + 2[M_2L] = K_{so}^{1/2}[L]^{-1/2} + K_{11}K_{so}^{1/2}[L]^{1/2} + 2K_{11}K_{21}K_{so} \quad (1a)$$

$$C_L = [L] + [ML] + [M_2L] = [L] + K_{11}K_{so}^{1/2}[L]^{1/2} + K_{11}K_{21}K_{so} \quad (1b)$$

Considering (1a) and (1b) to be a set of parametric equations defining the boundary location and taking C_M to be the dependent and C_L the independent variable, it is deduced that a minimum must occur in the precipitation boundary at the point at which $[L] = 1/K_{11}$, *i.e.*, at the point at which

$$(C_M)_{min} = 2K_{11}^{1/2}K_{so}^{1/2} + 2K_{11}K_{21}K_{so} \quad (2a)$$

$$(C_L)_{min} = K_{11}^{-1} + K_{11}^{1/2}K_{so}^{1/2} + K_{11}K_{21}K_{so} \quad (2b)$$

From these relations it is concluded that

$$2(C_L)_{min} - (C_M)_{min} = 2K_{11}^{-1} > 0 \quad (3)$$

This relation indicates that the minimum must occur at a metal to ligand mole ratio less than 2. The parametric mass balance equations (1a) and (1b) also indicate the asymptotic behavior of the precipitation boundary. That is, as $[L] \rightarrow 0$, $C_M \rightarrow \infty$ and $C_L \rightarrow K_{11}K_{21}K_{so}$, while as $[L] \rightarrow \infty$, both C_M and $C_L \rightarrow \infty$. More specifically, as [L] and [ML] become large relative to [M] and [M_2L], the ratio of total concentrations of metal and ligand approaches a limit given by

$$\frac{C_M}{C_L} \simeq \frac{K_{11}K_{so}^{1/2}[L]^{1/2}}{[L] + K_{11}K_{so}^{1/2}[L]^{1/2}} = \frac{1}{[L]^{1/2}/K_{11}K_{so}^{1/2} + 1} \quad (4)$$

By inspection this ratio is limited to values $\lesssim 1$.

To determine the value of K_{so}, $(C_M)_{min}$ was estimated from the experimental data to have the value 2.5×10^{-4} *M*. This was inserted into eq 2a along with the value log $K_{11} = 5.00$[4] and the experimental value for $K_{11}K_{21}K_{so}$, *viz.*, 8.5×10^{-6}. The result is $pK_{so} = 12.87$. From the value for $K_{11}K_{21}K_{so}$ it is then found that log $K_{21} = 2.80$. These data were used in plotting the solid curve shown in Figure 1. It is seen that the right branch points nowhere produce a metal:ligand mole ratio larger than unity (lower dashed line). It is also found that $(C_L)_{min}$ calculated from the derived constants satisfies eq 3 and thus produces a minimum in the theoretical curve with metal:ligand mole ratio less than 2 as required.

Ethane-1-hydroxy-1,1-diphosphonate (EHDP).—EHDP systems yielded two kinds of precipitate. One was a material appearing immediately and the other a material appearing only after weeks to months. The first was a gelatinous, frequently stably dispersed material; the second, a flocculated crystalline material. The former appeared in solutions in which the mole ratio Ca^{2+}:EHDP ≈ 2.0, the latter, when Ca^{2+}:EHDP ≪ 2.0. Seeding the latter samples with previously precipitated material did not hasten precipitation, however. Thus a metastable equilibrium between precipitate precursors and free ions is implied. These precursors were subjected to other physical measurements confirming their existence as stable macromolecular, hence polynuclear, solution species.[5,6]

The two precipitates were characterized by elemental analysis and X-ray powder diffraction. The elemental analysis of the first indicated substantial occlusion of TMACl plus small amounts of $CaCl_2$ but in any case a Ca^{2+}:P mole ratio of unity, to good approximation. The X-ray diffraction pattern was diffuse. Both the elemental analysis and diffraction pattern of a sample which was allowed to age in supernatant for *ca.* 5 months were identical with those for the second type of precipitate. The diffraction pattern was sharp and the elemental analysis produced the following results. *Anal.* Calcd for Ca_2EHDP: C, 8.5; H, 1.4; P, 22.0; Ca, 28.4. Found: C, 7.7; H, 1.6; P, 22.5; Ca, 27.8.

The precipitation boundary points for the first precipitate are shown in Figure 2. The location of the points, within the limits of accuracy of the measurements, is independent of supporting electrolyte concentration. More importantly, the Ca^{2+}:EHDP mole ratio in the region of the right branch approaches a value of 2, in contrast to the limiting value of unity in the PP system. In addition, the minimum in the EHDP precipitation boundary lies at or to the left of the line of stoichiometric equivalence, also in contrast to the PP system where the minimum is to the right of this line.

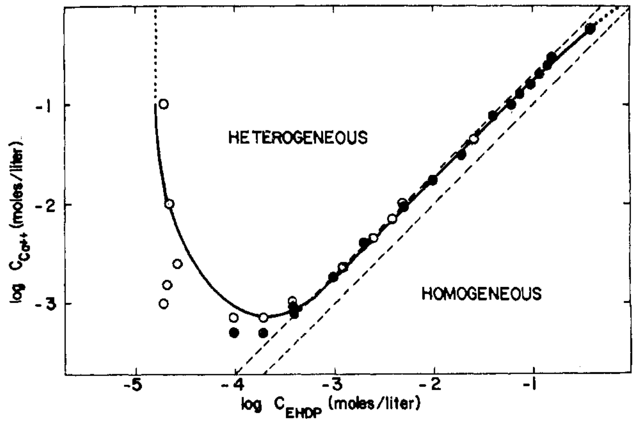

Figure 2.—Calcium–ethane-1-hydroxy-1,1-diphosphonate precipitation boundary in TMACl medium at pH 11: open symbols, no added electrolyte; closed symbols, 1.0 *M* TMACl added; solid curve, theoretical boundary; upper dashed line, stoichiometric equivalence line ($C_M/C_L = 2$); lower dashed line, equimolar line.

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[4] K. B. Yatsimirskii and V. P. Vasil'ev, *Zh. Fiz. Khim.*, **30**, 28 (1956).

[5] R. J. Grabenstetter and W. A. Cilley, *J. Phys. Chem.*, **75**, 676 (1971).

[6] B. H. Wiers, *ibid.*, **75**, 682 (1971).

The gross features of the precipitation boundary for Ca^{2+}–EHDP can be adequately described by an extension of the relations used for the PP system. It is assumed that, in addition to species ML and M_2L, EHDP can form complex ions of general formula $ML(M_2L)_n$, *i.e.*, "core–links" complex ions[7] defined by the equilibria

$$ML^{2-} + M_2L \rightleftarrows M_3L_2^{2-}, \quad K_{32}$$
$$M_3L_2^{2-} + M_2L \rightleftarrows M_5L_3^{2-}, \quad K_{53}$$
$$\text{etc.}$$

The corresponding mass balance equations, again dropping charges, are

$$C_M = [M] + 2[M_2L] + \sum_{n=1} (2n - 1)[M_{2n-1}L_n] \qquad (5a)$$

$$C_L = [L] + [M_2L] + \sum_{n=1} n[M_{2n-1}L_n] \qquad (5b)$$

A reduction of these relations to interpretable form can be achieved by assuming (1) that $K_{32} \cong K_{53} \cong \ldots \cong K_{2n-1,n}$, (2) that $K_{2n-1,n} = (K_{11}K_{21}K_{so})^{-1}$, and (3) that aggregation terminates at some $n = N$. Comparisons with known systems suggest that the first two assumptions might result in overestimates of the effect of polynucleation. For many substances the stepwise equilibrium constants diminish in magnitude as aggregation increases.[8] Moreover, because K_{so} might be expected to be of the order of 10^{-12} and $K_{11}K_{21}$ of the order of 10^7, each constant $K_{2n-1,n}$ would be of the order of 10^5, seemingly too large. However, the effect of the third assumption is precisely to compensate for the first two approximations. It amounts to the replacement of a large number of increasingly weak complexes with a limited number of strong complexes.

Under the first two assumptions, the summations in (5) are reduced to the expressions

$$\sum_{n=1} (2n - 1)[M_{2n-1}L_n] = \sum_{n=1} (2n - 1)[ML] = K_{11}K_{so}^{1/2}[L]^{1/2} \sum_{n=1} (2n - 1) \qquad (6a)$$

$$\sum_{n=1} n[M_{2n-1}L_n] = \sum_{n=1} n[ML] = K_{11}K_{so}^{1/2}[L]^{1/2} \sum_{n=1} n \qquad (6b)$$

The truncation of the sums at $n = N$ then leads to the expressions

$$C_M = K_{so}^{1/2}[L]^{-1/2} + K_{11}N^2K_{so}^{1/2}[L]^{1/2} + 2K_{11}K_{21}K_{so} \qquad (7a)$$

$$C_L = [L] + K_{11}\left(\frac{N^2 + N}{2}\right)K_{so}^{1/2}[L]^{1/2} + K_{11}K_{21}K_{so} \qquad (7b)$$

Comparison with eq 1a and 1b reveals no essential difference in character as $[L] \rightarrow 0$. There is an important difference as [L] increases, however. The ratio of total concentrations approaches the limit

$$\frac{C_M}{C_L} = \frac{2K_{11}N^2K_{so}^{1/2}[L]^{1/2}}{2[L] + (N^2 + N)K_{11}K_{so}^{1/2}[L]^{1/2}} = \frac{2N^2}{2[L]^{1/2}/K_{11}K_{so}^{1/2} + (N^2 + N)} \qquad (8)$$

As $N \rightarrow \infty$, this ratio has a value of 2.0.

The predicted position of the boundary minimum is also different in the present case. By differentiation it is found that the minimum occurs when $[L] = N^{-2}K_{11}^{-1}$ *i.e.*, at

$$(C_M)_{min} = 2NK_{11}^{1/2}K_{so}^{1/2} + 2K_{11}K_{21}K_{so} \qquad (9a)$$

$$(C_L)_{min} = N^{-2}K_{11}^{-1} + {}^1/_2(N + 1)K_{11}^{1/2}K_{so}^{1/2} + K_{11}K_{21}K_{so} \qquad (9b)$$

From these relations it is concluded that, neglecting $[L] = N^{-2}K_{11}^{-1}$

$$\frac{(C_L)_{min} - K_{11}K_{21}K_{so}}{(C_M)_{min} - 2K_{11}K_{21}K_{so}} > \frac{N + 1}{4N}$$

or that, for large N

$$2(C_L)_{min} - (C_M)_{min} > 2(K_{11}K_{21}K_{so} - (C_L)_{min}) \qquad (10)$$

indicating that the experimental minimum can lie either to the right or to the left of the line of stoichiometric equivalence.

The fit of the Ca^{2+}–EHDP data is shown in Figure 2. Polynuclear complexes up to $Ca_{11}L_6^{2-}$ were included and the fitting was clearly excellent in the region of the right branch, where the data are most abundant and least uncertain. The values of the parameters employed are $\log K_{11} = 5.60$, $\log K_{21} = 4.18$, $\log K_{32} = \log K_{53} = \ldots = \log K_{2n-1,n} = 4.83$, and $pK_{so} = 14.60$. Except for K_{so} these values were obtained by trial and error using visual-fit criteria. K_{so} was taken from the point of intersection of the line of stoichiometric equivalence and the experimental precipitation boundary.

It was found that all constants were insensitive to changes in N above about $N = 6$.

Discussion

For both of the systems examined in this work qualitative agreement between theory and experiment has been very satisfactory. That is, the data have been fit quite acceptably in spite of the assumption of a single solid phase in equilibrium with homogeneous solution and in spite of the neglect of activity coefficients. Concerning the phase assumption, one might infer either that there is in fact only one or that, if there are several phases, then the differences in chemical potential that exist among them are small. The latter inference is supported by data for anhydrous dicalcium phosphate, $CaHPO_4$, and its dihydrate, $CaHPO_4 \cdot 2H_2O$. The solubility product constants for these two substances differ from one another by less than 2%.[9] Thus it would appear to be justifiable in the present approximation to neglect differences between the various possible solid phases. Furthermore, the agreement between the EHDP data with 1.0 *M* added electrolyte and the data with no added electrolyte is taken to indicate that the neglect of activity coefficients also does not introduce a substantial error.

Beyond this, it was noted that the EHDP boundary data could not be fit even approximately by assuming a very strong Ca_2EHDP complex in addition to the expected CaEHDP complex. The reason this fails can be seen by reference to the mass balance equations (1a) and (1b). In order for a 2:1 boundary limit to be approached the last terms in each of these equations would be required to be the dominant terms over wide variations in [L]. In other words, $[M_2L]$ would be required to be the principal contributor to C_M and C_L. However, $[M_2L]$ is constant, since the species is in equilibrium with the solid

$$M_2L(s) \rightleftarrows M_2L(aq), \quad K_{eq} = K_{11}K_{21}K_{so}$$

This being the case, C_M/C_L can neither equal nor approach the value 2, except at one point.

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(8) J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry, Principles and Methods," Interscience, New York, N. Y., 1960, p 34.

(9) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience, New York, N. Y., 1958, p 520.

Qualitative agreement between experiment and theory is the principal achievement of this work, but it is also noteworthy that the derived equilibrium constants are acceptably close to previously determined values. Thus for EHDP log $K_{11} = 5.60$ compares well with the values 6.04,[10] 5.74,[11] and 5.52,[5] and log $\beta_{21} = 9.78$ compares well with 9.67.[10] For the higher complexes, it is found that log $\beta_{32} = 20.2$ and log $\beta_{74} = 49.4$. These values are to be compared with 18.78 and 48.23, respectively.[5] Some differences in the values for the higher complexes are in fact expected because the "core-links" model assumed here is known to be slightly inadequate to describe the full range of species found in Ca^{2+}–EHDP systems.[5] The value for $K_{so}(Ca_2EHDP)$, the most uncertain of the derived quantities, probably errs on the high side because the method of estimation neglects the (presumably) low level of soluble species in equilibrium with the solid.[12]

The value of log $K_{21}(Ca_2P_2O_7) = 2.80$ compares well with values commonly observed for other 2–2 electrolyte pairs such as $CaSO_4$, *viz.*, log $K_{21} \cong 2.70$,[13] and with the order of magnitude expected based on data for $Mg_2P_2O_7$, for which log $K_{21} = 2.33$.[14] The value pK_{so} = 12.87 found here compares poorly with pK_{so} = 14.7, previously determined by Wolhoff and Overbeek.[15] This latter value is perhaps too high by at least an order of magnitude, however, since its derivation depends on the authors' value of log $K_{11} = 6.8$, which is out of the range of accepted values for this quantity. This range is from 4.41 to 5.60 for media of 1.0 ionic strength down to infinite dilution.[16,17]

Conclusions

The most significant result of this work is that a formulation is provided for distinguishing polynucleating from nonpolynucleating systems by precipitation boundary measurements alone. Although aggregate charges are identical with the mononuclear precursor's charge and hence would not be distinguishable from the mononuclear complex in the conventional formalism,[7,18] the present formalism reveals two points of contrast at which systems of the two types can be seen to differ, without placing severe demands on experimental precision.

With respect to the derivation of thermodynamic parameters from the experimental precipitation boundaries the present method is greatly preferred over the method of tangents as employed with AgBr and other compounds.[19] This latter method becomes increasingly imprecise as species existence domains overlap. The present method overcomes this shortcoming by looking at all species effects simultaneously.

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Molecular Structure of Phosphorus Tribromide as Studied by Gas Electron Diffraction and Microwave Spectroscopy

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The internuclear distances and the mean vibrational amplitudes for PBr_3 have been determined by gas electron diffraction: r_g(P–Br) = 2.2204 ± 0.003 Å, r_g(Br–Br) = 3.424 ± 0.006 Å, θ_α(Br–P–Br) = 101.0 ± 0.4°, l(P–Br) = 0.053 ± 0.005 Å, and l(Br–Br) = 0.098 ± 0.007 Å, where the uncertainties represent estimated limits of error. The microwave spectra for $P^{79}Br_3$ and $P^{81}Br_3$ have given the rotational constants, B_0, 1035.24 ± 0.04 and 1010.96 ± 0.04 MHz, respectively, and the centrifugal distortion constant, D_J, $(2.2 \pm 0.9) \times 10^{-4}$ MHz. The average structure for the ground vibrational state, calculated from the r_g distances with corrections for vibrational and centrifugal effects, is consistent with the rotational constants B_z calculated from the above B_0. The experimental D_J constant and mean amplitudes agree with those estimated from the quadratic force constants.

Introduction

The internuclear distances in phosphorus tribromide were first determined by Lister and Sutton[2] to be r(P–Br) = 2.23 ± 0.04 Å and θ(Br–P–Br) = 100 ± 2° by means of the visual method of electron diffraction. Swingle[3] also reported the structure to have r = 2.18 ± 0.03 Å and θ = 101.5 ± 1.5° by the same method. On the other hand, the rotational constants of $P^{79}Br_3$ and $P^{81}Br_3$ measured by microwave spectroscopy[4] gave another set of estimates for the P–Br distance (r_0),

(1) Microwave spectra were measured by this author at the Government Chemical Industrial Research Institute, Tokyo.

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