

Disproportionation of Sodium Trimethoxyborohydride in Diglyme.—Both commercial sodium trimethoxyborohydride and freshly synthesized samples were utilized with no significant difference in the results. The apparatus was thoroughly dried. All operations were carried out under nitrogen and the utmost precautions were taken to protect the materials from any contact with oxygen, carbon dioxide or water. Only by careful attention to detail was it possible to realize material balances of 90–95% of the hydride originally introduced.

The samples of sodium trimethoxyborohydride were dissolved rapidly in the samples of diglyme. At appropriate intervals of time a filtered aliquot was removed, and analyzed for sodium, boron and hydride. Typical results are presented in Table III.

Reaction of Diborane with Sodium Tetramethoxyborohydride in Tetrahydrofuran.—In the reaction vessel was placed 2.73 g. (17.3 mmoles) of sodium tetramethoxyborohydride and 30 ml. of tetrahydrofuran. The vessel was

flushed out with nitrogen. Over a period of one hour 12 mmoles of diborane was introduced. When slightly more than one-half the diborane had been introduced, the solution became cloudy. At the end of the reaction there was a finely divided white solid suspended in the tetrahydrofuran. Filtration of the solid offered difficulties. Accordingly, the tetrahydrofuran was distilled off. From the weight of the flask, the product weighed 0.605 g. This material was easily soluble in diglyme. An aliquot of the solution was analyzed for boron and hydride. The ratio, B/H of 3.98, confirmed the formation of NaBH_4 .

In another experiment, 36.6 g. (220 mmoles) of sodium tetramethoxyborohydride was dissolved in 100 ml. of tetrahydrofuran. Into this concentrated solution, 2.2 M, was passed 5.8 mmoles of diborane. No precipitate was observed. Treatment of the clear solution with acid liberated the hydrogen quantitatively.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Prediction of Solubility Product Constants¹

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It is shown that for a large class of species having largely covalent bonds, the degree to which the species separates in aqueous solution into its ions, $\text{A}_x\text{B}_{y(c)} \rightleftharpoons x\text{A}^{+y}_{(aq)} + y\text{B}^{-x}_{(aq)}$, is as a first approximation a function of the difference in electronegativity, Δx , between A and B, when Δx is not large. $pK = a - b\Delta x$. This relationship is followed very closely by the solubility product constants of most of the insoluble sulfides, selenides, tellurides and hydroxides, as well as by insoluble halides, etc. On the other hand, typically ionic species, such as insoluble sulfates, fluorides, etc., or species for which hydration and electrostatic crystal energies are especially large and might be expected to predominate over covalency factors—*e.g.*, $\text{Be}(\text{OH})_2$ —do not obey this relationship. The relationship can be used to predict constants not yet determined or constants for unstable substances, which may appear as reaction intermediates. A thermodynamic explanation is offered, based on the relationship due to Hannay and Smyth between the amount of ionic character of the bond and the difference in electronegativity between the bonded atoms.

The regular trend of the solubilities of the heavy metal sulfides as one crosses the periodic table is one of the striking features of sulfide chemistry. When the trends are examined more closely, however, irregularities are observed which appear to follow closely the irregularities in the trend of electronegativities as can be seen in Table I.

TABLE I

	MnS	FeS	CoS	NiS	CuS	ZnS	CdS	PtS	HgS
pK_{sp}	13.1	16.4	21.3	22.0	35.4	20.0	26.2	72	50
x^a	1.4	1.65	1.7	1.7	1.8	1.5	1.5	2.1	1.9

^a Haïssinsky's electronegativity.³

Thus Cu^{++} , which is more electronegative than either of its neighbors, Ni^{++} and Zn^{++} , produces a sulfide which is more insoluble than either NiS or ZnS . This observation suggests that a relationship may exist between the solubility and the difference in electronegativity between the two elements involved.

The Insoluble Sulfides.—Examination of the pK_{sp} 's of the 1:1 sulfides² versus Δx (taken from Haïssinsky's³ values) revealed a striking degree of correlation. Furthermore the available data for the selenides and tellurides likewise fell into line if the electronegativity of tellurium were taken as 2.3 rather than 2.1 as listed by Haïssinsky. The correlation is shown in Fig. 1.

(1) Presented before the Division of Analytical Chemistry, 131st National A.C.S. meeting, Miami, Florida, April 10, 1957.

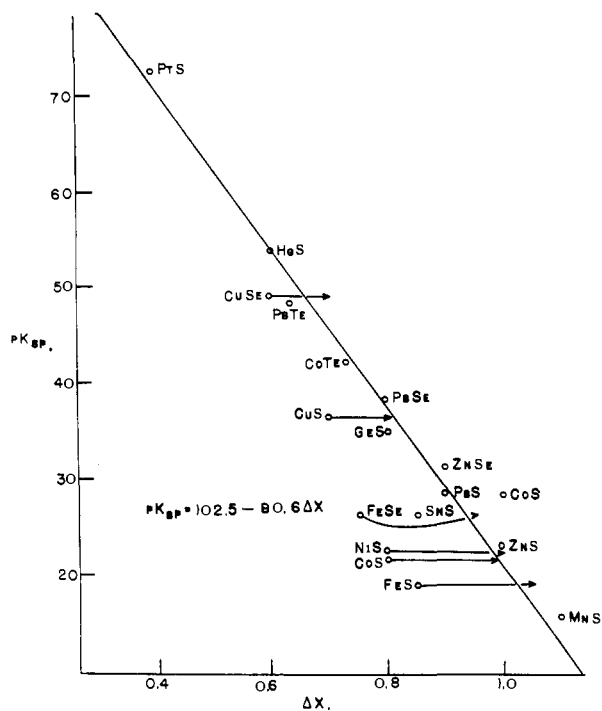
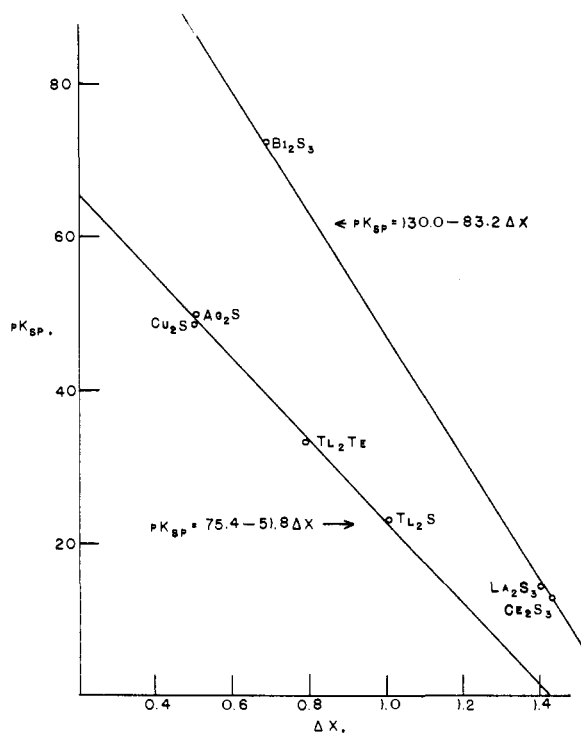
(2) Taken for the most part from W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, New York, N. Y., 1952.

(3) M. Haïssinsky, *J. Phys.*, **7**, 7 (1946).

It will be noted that the correlation is good with the exception of the compounds of Fe, Co and Ni. Several reasons for the lack of agreement for these compounds are possible. The first, that the K_{sp} 's are inaccurate, may be dismissed by noting that all four compounds disagree by the same amount. The second, that the difference is due to the crystal structure (all four compounds have NiAs structure, which is different from those of all the other compounds considered) cannot be dismissed so easily, although it may be noted that among the compounds in good agreement several different structures are represented. The third is that due to the difficulties of determining electronegativities in this part of the periodic table, the values for Fe^{+3} , Co^{+2} and Ni^{+2} are off by a constant amount. That this is probably so is strongly indicated by the fact that FeS and FeSe are off by the same amount. Revision of the electronegativities of these three elements downward by 0.2 unit brings them into harmony with the others. Likewise, if their neighboring element Cu has its electronegativity revised downward by 0.1 both CuS and CuSe fall into line. The revised electronegativities are thus: Fe^{+3} 1.45, Co^{+2} 1.5, Ni^{+2} 1.5, Cu^{+2} 1.7. Further justification for this will be offered below. A least squares analysis of these data yields the relationship

$$pK_{sp} = 102.5 - 80.6\Delta x \quad (1)$$

Correlation of the pK_{sp} vs. Δx relationship for Ag_3S , Cu_3S , Ti_3S and Ti_3Te (Ti_3Se was omitted as

Fig. 1.— pK_{sp} vs. Δx for insoluble monochalcogenides.Fig. 2.— pK_{sp} vs. Δx for hemi- and sesquichalcogenides.

insufficiently accurate) produced an almost perfect straight line (Fig. 2) of equation

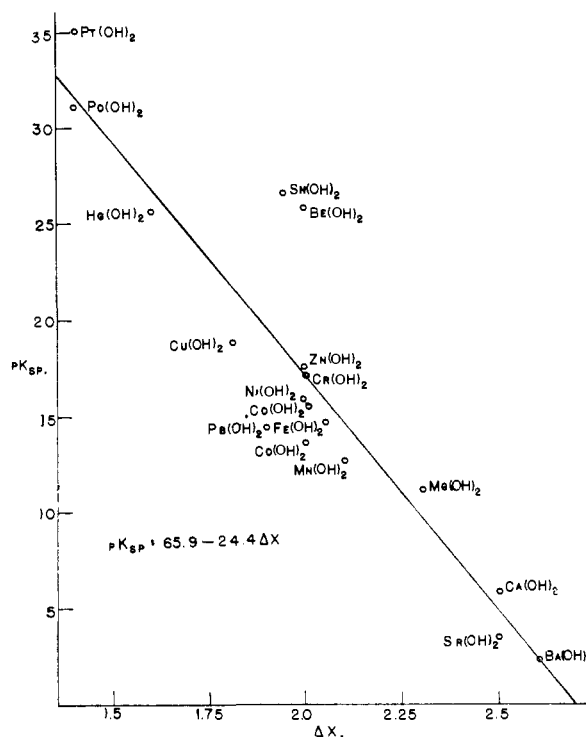
$$pK_{sp} = 75.4 - 51.8\Delta x \quad (2)$$

The data for the sulfides M_2S_3 are fragmentary and open to question. However, a line of equation

$$pK_{sp} = 130 - 83\Delta x \quad (3)$$

seems to describe their relationship reasonably well (Fig. 2).

The Insoluble Hydroxides.—Turning our attention to the insoluble hydroxides, which according to recent studies by Ahrens and Morris⁴ are remarkably covalent in nature, we find there is excellent agreement again for the hydroxides $M(OH)_2$ (Fig. 3). Here we see the justification for the re-

Fig. 3.— pK_{sp} vs. Δx for dihydroxides.

vision of the electronegativity values for Fe^{+2} , Co^{+2} , Ni^{+2} and Cu^{+2} , since assumption of the revised values again brings these (quite different) compounds into line. That this is not a matter of structure is shown by the fact that although FeS , $FeSe$, CoS and NiS have a structure different from all the other chalcogenides considered, $Fe(OH)_2$, $Co(OH)_2$ and $Ni(OH)_2$ (but not $Cu(OH)_2$) have the same structure as $Mg(OH)_2$, $Ca(OH)_2$, $Mn(OH)_2$ and $Cd(OH)_2$, the first three of which agree well with the relationship. The least squares analysis of these data (Fig. 3) gives the relationship

$$pK_{sp} = 65.9 - 24.4\Delta x \quad (4)$$

A notable exception is $Be(OH)_2$, for which the high ionic crystal energy may cause the solubility to be lower than expected.

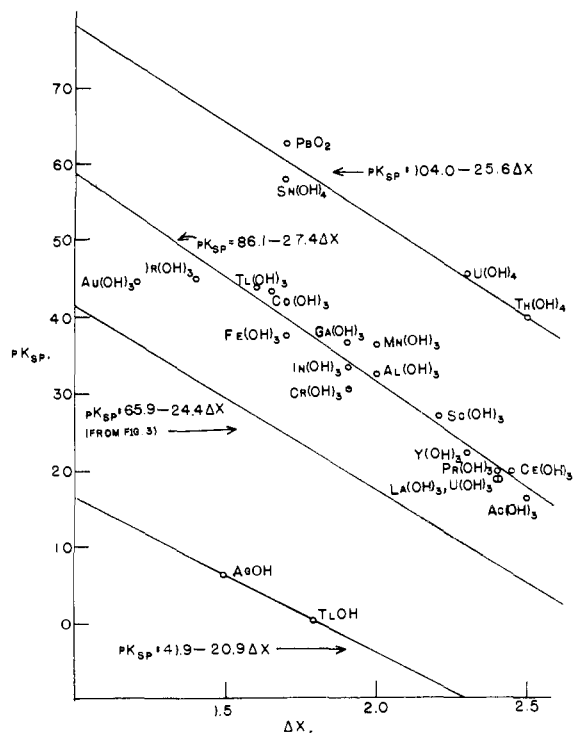
The hydroxides $M(OH)_3$ are likewise susceptible to this treatment, as indicated in Fig. 4. Here the relationship

$$pK_{sp} = 86.1 - 27.4\Delta x \quad (5)$$

is obeyed, with gold the only serious exception. (The reported K_{sp} of $Au(OH)_3$, however, is open to question.)

The data on the hydroxides $M(OH)_4$ are limited, and for the most part unreliable. However, if one takes the pK values for the best of these ($Th(OH)_4$, 39; $U(OH)_4$, 45) and the average of the values for

(4) L. H. Ahrens and D. F. C. Morris, *J. Inorg. Nucl. Chem.*, **3**, 263, 270 (1956).

Fig. 4.— pK_{sp} vs. Δx for hydroxides.

$\text{Sn}(\text{OH})_4$, 57 and PbO_2 , 64, the straight line through these three points (Fig. 4) has the equation

$$pK_{sp} = 104.0 - 25.6\Delta x \quad (6)$$

The data for the hydroxides MOH is likewise quite fragmentary. The only MOH 's sufficiently covalent to be considered are TlOH , AgOH and CuOH , only the first of which is actually known as the hydroxide. The estimation of the data for AgOH from that for Ag_2O may be accomplished by applying available information on the acid and basic ionization constants. Since the acid ionization constant of Cu_2O is not known, however, no reasonable estimate can be made of how unstable CuOH is with respect to dehydration to the oxide. Consequently only the data for TlOH and AgOH may be used (Fig. 4). The equation for the straight line through these two points is

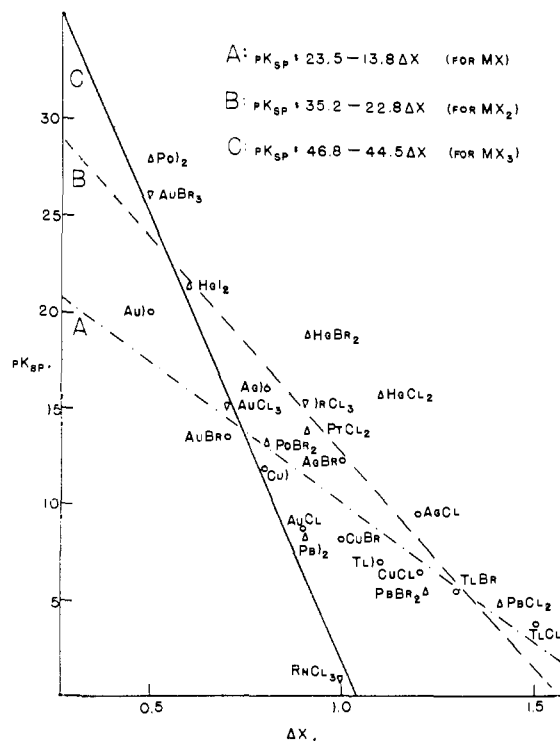
$$pK_{sp} = 41.9 - 20.9\Delta x \quad (7)$$

(Some data are available for the substances $\text{CH}_3\text{-HgOH}$, $(\text{C}_6\text{H}_5)_2\text{TlOH}$ and $(\text{CH}_3)_3\text{SnOH}$. However, it is difficult to know how to assign electronegativity values for these cases.)

The insoluble halides (except fluorides) also are susceptible to this treatment. However, because of the lower valences and greater ionic character of these compounds, agreement with the simple electronegativity principle is less good than with the previous classes of compounds. Nevertheless the data for the copper family and thallium monohalides has fairly good internal consistency (Fig. 5), the least squares treatment giving the equation

$$pK_{sp} = 23.5 - 13.8\Delta x \quad (8)$$

Data on the insoluble divalent halides is of about the same consistency (Fig. 5). The least squares

Fig. 5.— pK_{sp} vs. Δx for insoluble halides.

line for the halides of $\text{Hg}(\text{II})$, $\text{Pb}(\text{II})$, PdI_2 and PtCl_2 has the equation

$$pK_{sp} = 35.2 - 22.8\Delta x \quad (9)$$

Reliable data on the K_{sp} 's of insoluble trihalides are very few. The relationship for AuCl_3 , AuBr_3 , IrCl_3 and RhCl_3 (Fig. 5) is

$$pK_{sp} = 46.8 - 44.5\Delta x \quad (10)$$

Comparison of the Relationships.—Examination of the four hydroxide relationships shows that the slopes of all are essentially the same: 20.9 (MOH), 24.4 ($\text{M}(\text{OH})_2$), 27.4 ($\text{M}(\text{OH})_3$), 25.6 ($\text{M}(\text{OH})_4$), weighted average, 25.1. For the chalcogenides, two of the three are essentially the same: 80.6 for MS and 83.2 for M_2S_3 , whereas that for M_2S is 51.8. For the halides the slopes are 13.8 (MX), 22.8 (MX_2) and 44.5 (MX_3).

The intercepts of these curves ($\Delta x = 0$), when divided by the sum of the charges of the cation and anion (or the sum of the valences of metal and non-metal) again show considerable similarity. For the hydroxides we have $50.5/2 = 25.3$ (MOH), $65.9/3 = 23.0$ ($\text{M}(\text{OH})_2$), $86.1/4 = 21.5$ ($\text{M}(\text{OH})_3$), $104.0/5 = 20.8$ ($\text{M}(\text{OH})_4$). For the chalcogenides, $76.6/3 = 25.5$ (M_2S), $102.5/4 = 25.6$ (MS), $130.0/5 = 26.0$ (M_2S_3). For the halides, $23.5/2 = 11.8$ (MX), $35.2/3 = 11.7$ (MX_2) and $46.8/4 = 11.7$ (MX_3). The weighted average of the hydroxide values is 22.33, that for the chalcogenides, 25.63, and the weighted average of both is 23.55. The weighted average for the halides is 11.7.

Since the intercepts are the pK_{sp} values for $\Delta x = 0$, it can be seen that the higher the charges on the ions to be put into solution the larger the pK_{sp} for $\Delta x = 0 - pK_{sp}$ being, in fact, proportional to the sum of the charges on the ions formed.

The Prediction of K_{sp} 's.—These relationships can be used to predict the K_{sp} 's of unknown substances or substances for which the K_{sp} 's are not known. For example from (1) we calculate the pK_{sp} for AuS to be 78. The upper limit of the oxidation potential for the Au-Au⁺⁺ couple calculated from this agrees well with the potential estimated from Taube's⁵ values for the chloro complexes. Some other calculated values are shown in Table II.

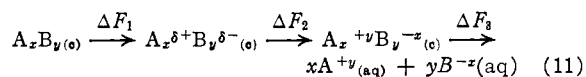
TABLE II
CALCULATED pK_{sp} 's

AuS	78	Au ₂ S ₃	113	Ag(OH) ₃	50
AgS	62	Mn ₂ S ₃	47	Cu(OH) ₃	48
TiS	38	Cr ₂ S ₃	55	Au(OH) ₂	39
CrS	14	V ₂ S ₃	39	Ag(OH) ₂	36
VS	-2	Ti ₂ S ₃	35	InI	8
TiS	-10	Sc ₂ S ₃	30	InCl	1

Discussion

A justification for this relationship may be developed as follows.

Let the process of dissolution of a completely covalent substance A_xB_y to give ions $A^{+v}(aq)$ and $B^{-x}(aq)$ be represented as



where $(\Delta F_1 + \Delta F_2)$ is the total ΔF required for transition from the completely covalent crystalline state to the completely ionic crystalline state, and where $A_x^{\delta+}B_y^{\delta-}(c)$ represents the actual state of a substance for which the electronegativities of A and B are not the same. Let us further note that the free energy of dissolution of the completely covalent substance

$$\Delta F_0 = \Delta F_1 + \Delta F_2 + \Delta F_3 \quad (12)$$

(5) R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 6 (1954).

and that the free energy of dissolution of the actual substance

$$\Delta F_{sp} = \Delta F_2 + \Delta F_3 \quad (13)$$

and

$$\Delta F_0 = \Delta F_1 + \Delta F_{sp} \quad (14)$$

It easily can be seen that the degree of ionic nature of A_xB_y is

$$I = \frac{\Delta F_1}{\Delta F_1 + \Delta F_2} \quad (15)$$

or for single covalent bonds, according to Hannay and Smyth⁶

$$I = 0.16\Delta x + 0.035(\Delta x)^2 \quad (16)$$

or

$$I \approx 0.16\Delta x \text{ for } \Delta x < 0.5 \quad (16')$$

Let us now consider the cases of highly covalent substances, for which $\Delta x < 0.5$. For these cases it will also be true that $\Delta F_2 \gg \Delta F_1$ and, therefore

$$I \approx \frac{\Delta F_1}{\Delta F_2} \quad (15')$$

Combining (15') and (16') and substituting an indefinite constant a for the coefficient 0.16 because of the many bonds involved

$$a\Delta F_2\Delta x = \Delta F_1 \quad (17)$$

Now combining (14) and (17)

$$\Delta F_0 = a\Delta F_2\Delta x + \Delta F_{sp} \quad (18)$$

Now noting that when $\Delta F_2 \gg \Delta F_1$, the percentage change in Δx will be much greater than the percentage change in ΔF_2 , it can be seen that ΔF_2 is relatively constant, and, therefore

$$\Delta F_0 = b\Delta x + \Delta F_{sp} \quad (19)$$

or

$$\Delta F_{sp} = \Delta F_0 - b\Delta x$$

Since $\Delta F = 1.364 pK$, then

$$pK_{sp} = pK_0 - C\Delta x_0 \quad (20)$$

(6) N. B. Hannay and C. P. Smyth, *THIS JOURNAL*, **68**, 171 (1946).
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[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

Preparation of Highly Purified TiO₂ (Anatase)

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Spectroscopically pure TiO₂ has been prepared by dissolving silica-free titanium metal in an ammoniacal solution of 90% H₂O₂. Common impurities, such as Fe, Mn, Mg, Sn, Ni, Al, Ag were quantitatively removed by filtration. Care was taken to avoid contamination with Si, which could not be removed by this procedure. Upon driving off the peroxide, titania gel formed, from which crystals of TiO₂ 3 mm. on each edge were obtained by heating to 200°. The sample composition was established by titration of Ti³⁺ ion with ferric ammonium sulfate. X-Ray diffraction results showed that samples prepared in this manner were of the anatase structure.

Introductory Comments

In the course of research on properties of TiO₂, it became necessary to prepare this material in highly pure form. Several preparative methods have been described in the literature. Work up to 1950 has been summarized in Gmelin.¹ Since then, some additional work has been described.²⁻⁴ The meth-

(1) "Gmelins Handbuch der Anorganischen Chemie," 8th Ed., Vol. 41, Gmelin Institut; Verlag Chemie, Weinheim, Germany, 1951, pp. 226-232.

(2) S. Teichner, *Compt. rend.*, **237**, 900 (1953).

ods of procedure may be classified broadly as follows: (1) direct combination of titanium and oxygen; (2) treatment of titanium salts in aqueous solution; (3) reaction of volatile, inorganic titanium compounds with oxygen; (4) oxidation or hydrolysis of organic compounds of titanium.

Regarding method 1, the stoichiometry of the final product is likely to be indefinite and non-uni-

(3) F. Trombe and M. Foëx, *ibid.*, **238**, 1419 (1954).

(4) S. Taki and M. Kunitomi, *J. Chem. Soc. Japan; Ind. Chem. Sect.*, **57**, 534 (1954).