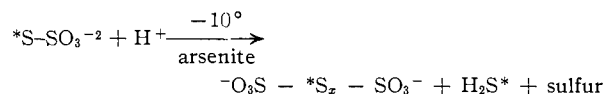


and Eremenko.³³ It was found that the decomposition of $^*SSO_3^{-2}$ in the presence of acid and sodium arsenite gave $^-O_3S-^*S_x-SO_3^-$. The general over-all decomposition was found to be



Estimation of the Rate Constants.—The values reported for the dissociation constants of thiosulfuric acid have been near 0.45 (K_1) and in the range 0.01 to 0.062 for the second dissociation (K_2) in dilute solutions.¹¹ The previous investigators¹¹ used the value of 0.01 for K_2 and calculated the rate constants to be $k = 0.14 \pm 0.02 \text{ min.}^{-1}$ and $k_1 = 0.31 \text{ l. mole}^{-1} \text{ min.}^{-1}$ during the initial stages of the reaction and as $0.29 \text{ l. mole}^{-1} \text{ min.}^{-1}$ from the titrametric data from the latter stages of the reac-

(33) A. I. Brodskii and R. K. Eremenko, *J. Gen. Chem. (U.S.S.R.)*, **24**, 1137 (1954); **25**, 1189 (1955).

tion based upon the gram atom of sulfur. The values of the rate constants are dependent upon the value of K_2 but the values calculated are correct within the order of magnitude of the data. A reasonable assumption can be made concerning the other bimolecular reactions. These reactions are probably somewhat faster than k_1 and probably $k_3 \sim k_4 \sim k_5 \sim \dots$ because of the very similar nature of the intermediates. Assuming $k_3 = k_4 = k_5 \dots$ makes many of the higher terms of (26) and (27) zero, thus simplifying the expression and increasing the importance of the first term. The rates of formation of the various polythionates as equation 38 cannot be obtained from the data but in dilute solution these reactions are much slower and the sulfur is the main product of the decomposition.

The author wishes to thank Professor P. D. Bartlett for helpful discussion and permission to publish this interpretation.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, UNIVERSITY OF LUCKNOW]

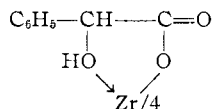
Organic Compounds of Zirconium. V. Studies of Zirconium Mandelates

By R. N. KAPOOR AND R. C. MEHROTRA

RECEIVED DECEMBER 4, 1957

The reaction of zirconyl chloride with mandelic acid in aqueous solution yields mainly zirconium monomandelate which dissolves in one equivalent of alkali. The tetramandelate is formed only in the presence of higher concentrations of hydrochloric acid. The reaction between zirconium isopropoxide and mandelic acid in benzene shows that the carboxyl group is more reactive than the hydroxyl group in replacing isopropyl alcohol; the latter becomes active only when a sufficient concentration of carboxyl groups is not available. The following new compounds of zirconium have been isolated: $Zr(C_8H_6O_3)(OPr-iso)_2$, $Zr(C_8H_6O_3)(C_8H_7O_3)(OPr-iso)$, $Zr(C_8H_7O_3)_2(OPr-iso)_2$ and $Zr(C_8H_6O_3)(C_8H_7O_3)(OBu)$.

The preparation of zirconium alkoxides^{1,2} and tricarboxylates³ has been reported recently. The alkoxides and tricarboxylates are immediately hydrolyzed by water, and even the zirconium salts of the strong acids are appreciably hydrolyzed in solution.⁴ Therefore, the precipitation of pure zirconium tetramandelate from solutions of zirconyl chloride in concentrated hydrochloric acid⁵ is noteworthy in view of the weakly acidic nature of mandelic acid (dissociation constant at $25^\circ = 4.29 \times 10^{-4}$). To explain this, Feigl⁶ postulated the formation of a chelate type structure



This structure explains the solubility of the tetramandelate in dilute alkaline solution as due to the enhanced acidity of the weakly acidic hydroxyl group through coordination.

Hahn and Weber,⁷ in a conductometric titration

(1) D. C. Bradley, R. C. Mehrotra and W. Wardlaw, *J. Chem. Soc.*, 2027, 4204, 5020 (1952); 1634 (1953).

(2) R. C. Mehrotra, *THIS JOURNAL*, **76**, 2266 (1954).

(3) R. N. Kapoor and R. C. Mehrotra, *Chem. & Ind.*, 68 (1958).

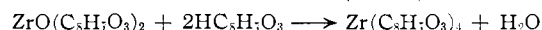
(4) B. A. J. Lister and L. A. Donald, *J. Chem. Soc.*, 4315 (1952).

(5) C. A. Kumins, *Anal. Chem.*, **19**, 376 (1947).

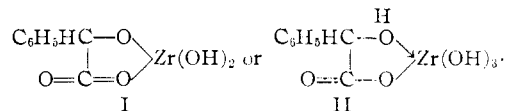
(6) F. Feigl, "Chemistry of Specific, Selective and Sensitive Reactions," Academic Press, Inc., New York, N. Y., 1949, pp. 213-215.

(7) R. B. Hahn and L. Weber, *THIS JOURNAL*, **77**, 4777 (1955).

of zirconyl chloride solution with sodium mandelate, observed a sharp maximum when the ratio of mandelate to zirconium was 2.3:1. To explain their observations, they assumed that the following reactions occur in solution



However, it has been reported recently^{5,9} that zirconium monomandelate preferably is precipitated when zirconyl chloride is treated with mandelic acid or sodium mandelate solution. The monomandelate could have either structure



The easy hydrolysis of the alkoxy oxygen-zirconium linkage suggests that II is probably correct. Furthermore, in the titration of zirconium monomandelate with sodium hydroxide (Fig. 1), we found that that monomandelate dissolves when about 1 mole of alkali has been added; this can be explained by the neutralization of the hydroxyl hydrogen atom which has been made more acidic (dissociation con-

(8) R. B. Hahn and E. S. Baginski, *Anal. Chim. Acta*, **14**, 45 (1956).

(9) R. N. Kapoor and R. C. Mehrotra, *J. Sci. industr. Res.*, **1CB**, 300, 304 (1957).

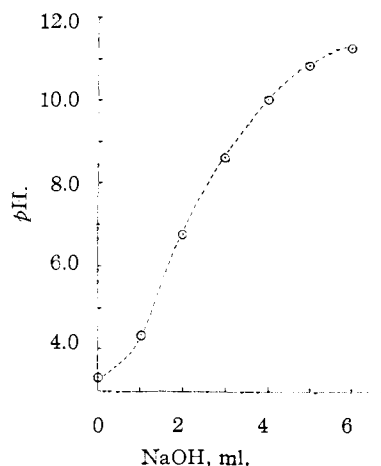


Fig. 1.—Zirconium mono-mandelate (0.1440 g.) titrated with sodium hydroxide (0.1 *N*).

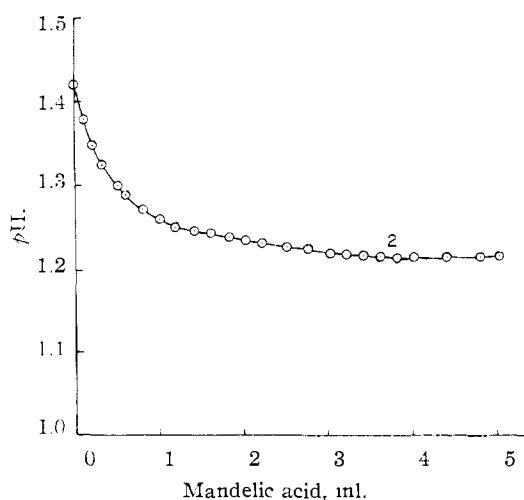


Fig. 2.—Zirconyl chloride (20 ml., *M*/20) titrated with mandelic acid (*M*).

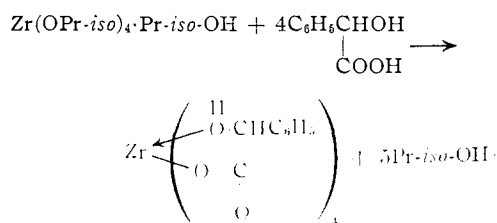
stant from half neutralization point, $10^{-7.8}$) through chelation. Therefore, further study was undertaken of the reaction between zirconyl chloride and mandelic acid as follows. Potentiometric titration of zirconyl chloride with mandelic acid (Fig. 2), with potassium mandelate (Fig. 3) and with potassium hydroxide in the presence of various amounts of potassium mandelate (Fig. 4); the conductometric titration of zirconyl chloride with potassium mandelate (Fig. 6). The results confirmed our preliminary conclusion that zirconium mono-mandelate is formed initially; it behaves as a weak acid which is neutralized by alkali.

The acidic nature of the hydroxyl groups in zirconium tetramandelate was studied by Hahn and Weber,⁷ who concluded that a tri-ammonium derivative is formed with ammonium hydroxide.¹⁰ Our electrometric titration of zirconium tetramandelate with dilute ammonia also indicates the formation of a tri-ammonium derivative. The corresponding titration curves with potassium

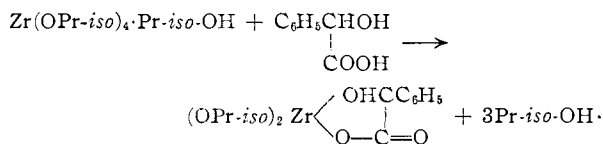
(10) The similar compound, hafnium tetramandelate, gives a tetra-ammonium derivative; R. B. Hahn and P. T. Joseph, *THIS JOURNAL*, **79**, 1208 (1957).

hydroxide are similar, indicating that the reaction is the same; further hydrolytic reactions, however, occur with excess potassium hydroxide (see Fig. 5).

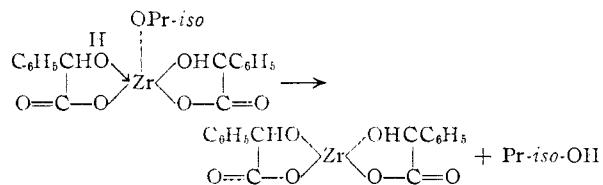
Zirconium tetramandelate was also studied in non-aqueous solution. In the reaction of zirconium isopropoxide, $Zr(OPr\text{-}iso)_4 \cdot Pr\text{-}iso\text{-}OH$, with mandelic acid (more than 4 moles) in anhydrous benzene, all the isopropyl alcohol (5 moles) were displaced and a white crystalline solid, $Zr(C_8H_7O_3)_4$, was precipitated



The reaction shows that the carboxyl groups are more reactive in replacing isopropyl alcohol than the hydroxyl groups. However, with a 1:1 ratio of reactants, 3 moles of isopropyl alcohol were displaced, an observation which indicates that in this case both the hydroxyl and carboxyl groups displaced isopropyl alcohol.



With 1 mole of zirconium isopropoxide to 2 moles of mandelic acid, 4 moles of isopropyl alcohol were easily displaced to give $Zr(C_8H_7O_3)_2 \cdot Pr\text{-}iso\text{-}OH$, which lost isopropyl alcohol when heated under reduced pressure. The difficulty in replacement of



the last isopropoxyl group might be due to a steric effect and has also been reported¹¹ for reactions of zirconium methoxide with *t*-butyl alcohol in which monomethoxyzirconium tributoxide was the end product. This explanation is supported by the replacement of the isopropyl alcohol in $Zr(C_8H_7O_3)_2 \cdot Pr\text{-}iso\text{-}OH$ with 1-butanol in the presence of benzene to give the corresponding monobutoxyzirconium dimandelate. Monobutoxyzirconium dimandelate dissolved in cold benzene in the presence of excess butanol but was reprecipitated on refluxing. The dissolution can be explained on the basis of the formation of a higher butoxy derivative in the cold which dissociated to give the insoluble monobutoxy derivative on heating. This was confirmed in the case of the mono-isopropoxy derivative which was insoluble in benzene but dissolved when isopropyl alcohol was added; removal of the benzene gave $Zr(C_8H_7O_3)_2(OPr\text{-}iso)_2$.

(11) R. C. Mehrotra, *J. Ind. Chem. Soc.*, **31**, 904 (1954).

Experimental

Materials.— $ZrOCl_2 \cdot 8H_2O$ was a Merck G. R. Product. All other reagents employed were of Analar grade and were purified if necessary. Zirconium monomandelate was precipitated by boiling a mixture of dilute solutions of zirconyl chloride ($M/20$) and mandelic acid ($M/20$).

Anal. Calcd. for $O=Zr(OH)(C_8H_7O_3)$: Zr, 33.17; mandelate, 54.90. Found: Zr, 33.00; mandelate, 53.10.

Zirconium tetramandelate was prepared as described by Hahn and Weber⁷ by the addition of a 15% mandelic acid solution (excess) to zirconyl chloride solution in hydrochloric acid and heating to 80°.

Anal. Calcd. for $Zr(C_8H_7O_3)_4$: Zr, 13.11; mandelate, 86.89. Found: Zr, 13.13; mandelate, 86.3.

Zirconium isopropoxide, prepared by the method of Bradley, Mehrotra and Wardlaw,¹ was purified by repeated crystallization from isopropyl alcohol.

Anal. Calcd. for $Zr(OPr-iso)_4 \cdot Pr-iso-OH$: Zr, 23.53; $OPr-iso$, 76.21. Found: Zr, 23.60; $OPr-iso$, 76.00.

Aqueous solutions were made up in conductivity water. Benzene was dried over metallic sodium and carefully fractionated; isopropyl alcohol was refluxed over solid aluminum isopropoxide and then fractionated.

Analytical Methods.—Zirconium was estimated as the oxide by the direct ignition of the compound. The alcohol content of the benzene-alcohol azeotrope was determined by an oxidimetric method¹⁸ which could be applied directly, as benzene was found not to reduce potassium dichromate at room temperature. Mandelic acid was estimated by oxidation with ceric sulfate.¹³ For the determination of mandelate in the presence of isopropoxy groups, the compound was treated with a boiling solution of caustic soda and then acidified with dilute sulfuric acid prior to the ceric sulfate oxidation.

Titration.—The conductometric titrations were carried out in a thermostat with a bath temperature of $35 \pm 0.05^\circ$. The apparatus consisted of a Leeds and Northrup drum-type bridge (length 470 cm.), a tunable headphone, an audio-oscillator with a tuning fork giving a constant frequency of 1000 c./sec. and an immersion cell of the type G. M. 4221 (Phillips and Co.); the set-up was operated at 110 v.

To 50 ml. of $M/200$ $ZrOCl_2$ solution, the resistance of which had been measured, was added a 0.1 N solution of sodium mandelate in 0.5-ml. portions; the mixture was stirred for about 10 minutes after each addition. The resistances of these solutions were measured and plotted against the volumes of mandelate solution (Fig. 6).

pH measurements were carried out in a thermostatically controlled room (temp. $25 \pm 1^\circ$) with a Phillips pH measuring apparatus G. M. 4491/G. M. 4493. A glass electrode gave readings reproducible to ± 0.005 pH. The instrument was standardized by determination of its asymmetric potential with a 0.05 M solution of potassium hydrogen phthalate (pH 4.005 at 25°).

Studies in Non-aqueous Solvents, Apparatus.—All glass apparatus with standard interchangeable joints was used throughout and special precautions were taken to exclude moisture. Fractionations were carried out in a 60 cm. column packed with Raschig rings and fitted to a total condensation variable takeoff still-head.

Reaction of Zirconium Isopropoxide with Mandelic Acid.

(a) **Molar Ratio 1:4.5.**—The addition of 3.8 g. of mandelic acid to a solution of zirconium isopropoxide (2.15 g.) in benzene (75 g.) gave a gelatinous white product on shaking. The mixture was refluxed in a bath at 110°. The amount of isopropyl alcohol in the distillate was 1.62 g. (1.66 g. required theoretically for the displacement of 5 moles). The residue was washed with ether and dried under reduced pressure to give a light white powder.

Anal. Calcd. for $Zr(C_8H_7O_3)_4$: Zr, 13.11; mandelate, 86.88. Found: Zr, 13.15; mandelate, 86.6.

(b) **Molar Ratio 1:1.**—A mixture of zirconium isopropoxide (1.70 g.) dissolved in benzene (45 g.) and mandelic acid (0.66 g.) was refluxed as above; no precipitation occurred. The distillate contained 0.78 g. of isopropyl alcohol (0.79 g. calculated for the displacement of 3 moles).

(12) R. C. Mehrotra, *J. Ind. Chem. Soc.*, **30**, 588 (1953).

(13) M. R. Verma and S. D. Paul, *J. Sci. industr. Res.*, **13B**, 347 (1954).

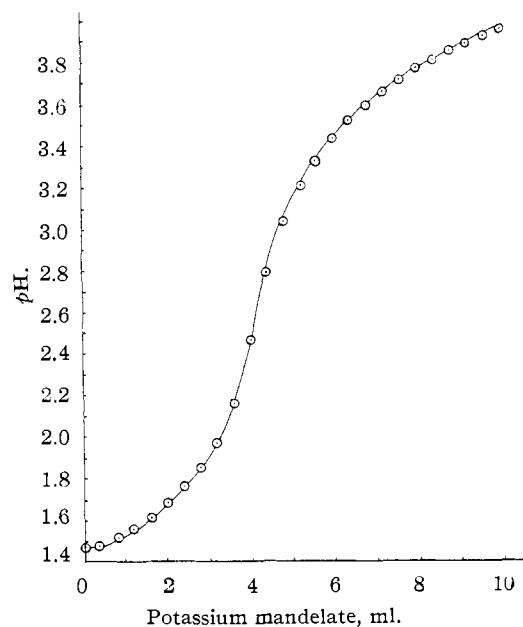


Fig. 3.—Zirconyl chloride (20 ml., $M/20$) titrated with potassium mandelate (0.5 M).

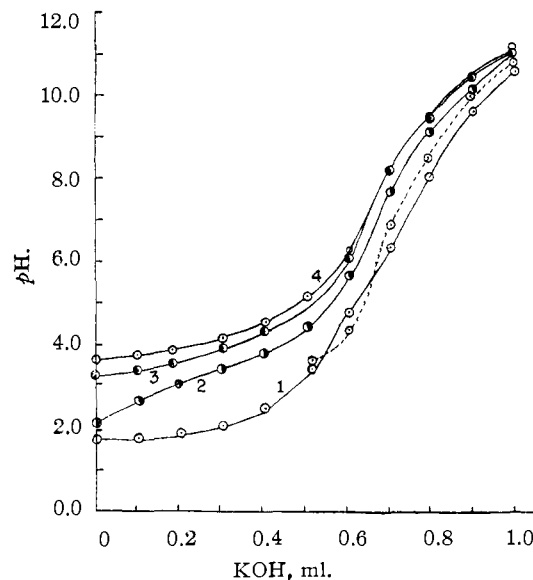


Fig. 4.—Zirconyl chloride (20 ml., $M/20$) titrated with potassium hydroxide (2 M) in the presence of 1 (curve 1), 2 (curve 2), 3 (curve 3), 4 (curve 4) ml. of potassium mandelate (M).

The remaining benzene was removed under a high reflux ratio. The volatile fractions were distilled *in vacuo* from the resulting solution in a bath at 30° in the course of 2 hours. The end-product (1.6 g.) was a glassy powder.

Anal. Calcd. for $Zr(OPr-iso)_2(C_8H_7O_3)_2$: Zr, 25.35; mandelate, 41.7. Found: Zr, 25.44; mandelate, 42.0.

(c) **Molar Ratio 1:2.**—When a mixture of zirconium isopropoxide (1.88 g.) in benzene (62 g.) and mandelic acid (1.48 g.) was refluxed as above, a white mass precipitated. The distillate collected in 1 hour (about 20 ml.) contained 1.1 g. of isopropyl alcohol (1.4 g. calculated for the replacement of isopropyl alcohol). Removal of the remaining benzene under a high reflux ratio gave a white solid product, which was washed with benzene and dried under reduced pressure (2 mm.) for 2 hours at 50°.

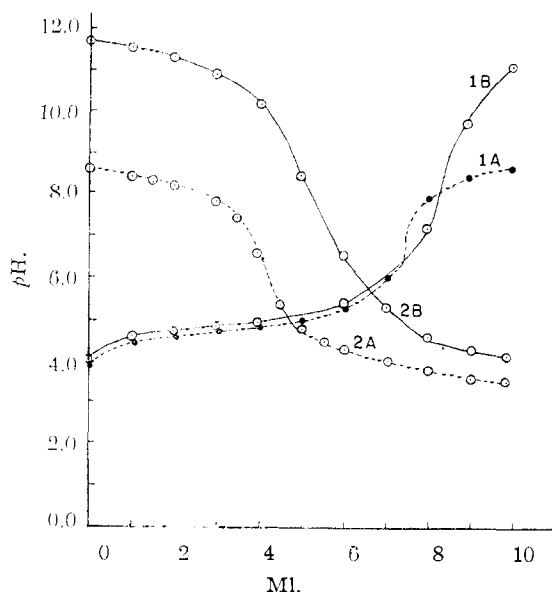


Fig. 5.— $Zr(C_8H_7O_3)_4$ (0.35 g.) suspended in 20 ml. of water: curve 1A, titrated with 0.2 *N* NH_4OH ; curve 1B, titrated with 0.2 *N* KOH . $Zr(C_8H_7O_3)_4$ (0.35 g.): curve 2A, dissolved in 10 ml. of 0.5 *N* NH_4OH and titrated with 0.1 *N* HCl ; curve 2B, dissolved in 12 ml. of 0.5 *N* KOH and titrated with 0.1 *N* HCl .

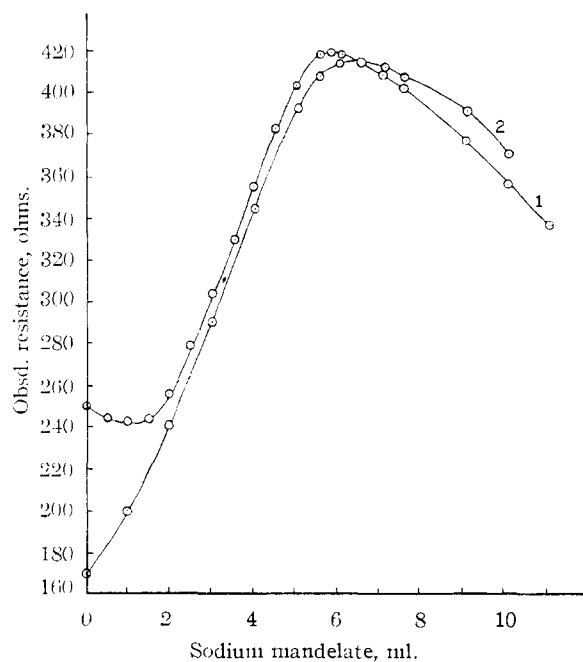


Fig. 6.—Curve 1, zirconyl chloride (50 ml., 0.005 *M*) vs. 0.1 *N* sodium mandelate; curve 2, HCl (50 ml., 0.001 *N*) vs. 0.1 *N* sodium mandelate.

Anal. Calcd. for $Zr(C_8H_6O_3)_2 \cdot Pr\text{-}iso\text{-}OH$: Zr, 20.20; mandelate, 66.50. Found: Zr, 20.06; mandelate, 66.75.

When this product was heated to about 150° under reduced pressure (1–2 mm.) for an hour, it appeared to lose a molecule of isopropyl alcohol.

Anal. Calcd. for $Zr(C_8H_6O_3)_2$: Zr, 23.30; mandelate, 76.70. Found: Zr, 23.28; mandelate, 76.52.

Reaction of $Zr(C_8H_6O_3)_2 \cdot Pr\text{-}iso\text{-}OH$ with 1-Butanol.—1-Butanol (about 4 ml.) was added to a suspension of $Zr(C_8H_6O_3)_2 \cdot Pr\text{-}iso\text{-}OH$ (about 1.8 g.) in benzene (30 g.).

When the clear solution obtained after shaking for 5 minutes was refluxed, a white mass separated which redissolved on cooling. The reaction mixture was refluxed for an hour at 110° and about 5 ml. of distillate containing the alcohol was collected at 75–80°. The remaining benzene was removed under a high reflux ratio, and the product was dried under reduced pressure.

Anal. Calcd. for $Zr(C_8H_6O_3)_2 \cdot BuOH$: Zr, 19.41. Found: Zr, 18.98.

Reaction of $Zr(C_8H_6O_3)_2 \cdot Pr\text{-}iso\text{-}OH$ with Isopropyl Alcohol in Benzene.—Isopropyl alcohol (1.08 g.) was added to $Zr(C_8H_6O_3)_2 \cdot Pr\text{-}iso\text{-}OH$ (1.62 g.) suspended in benzene (40 ml.). The volatile fractions were removed from the resulting clear solution by distillation under reduced pressure (1 mm.) in a bath at 20°; a white solid (1.8 g.) was obtained.

Anal. Calcd. for $Zr(C_8H_6O_3)_2 \cdot 2Pr\text{-}iso\text{-}OH$: Zr, 17.83; mandelate, 59.08. Found: Zr, 18.01; mandelate, 60.4.

Discussion of Physico-chemical Studies

Our observations on the reaction of zirconyl chloride and mandelic acid in aqueous solution can be explained as follows. The low *pH* (1.4–1.5) of zirconyl chloride solution indicates that even in 0.05 molar solution, it is appreciably hydrolyzed

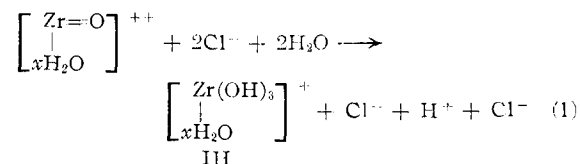
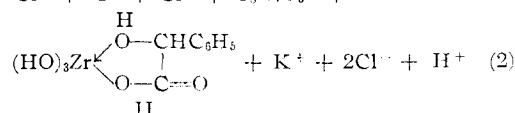
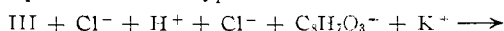
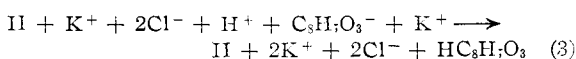


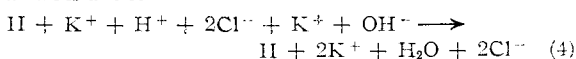
Figure 3, in which zirconyl chloride was titrated with potassium mandelate, shows a slow initial rise in *pH* followed by a more rapid increase. The slow initial rise indicates an equilibrium of the type



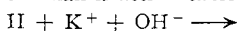
The rapid rise with the further addition of potassium mandelate is due to



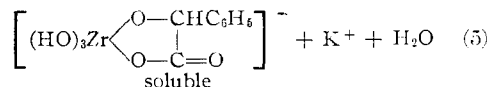
In curve 1 (Fig. 4) an equimolecular mixture of zirconyl chloride and potassium mandelate, represented by equilibrium 2, was titrated with potassium hydroxide. The initial slow rise in *pH* which occurs up to the addition of 1 mole of alkali is due to



The subsequent rapid rise with dissolution at about 2 moles of alkali is attributable to



insoluble

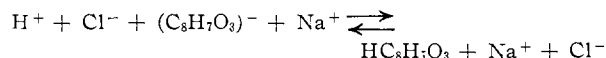


Reaction 5 is confirmed by the fact that the curve obtained for the titration of zirconium monomandlate with sodium hydroxide (Fig. 1) is almost identical with the corresponding part of curve 1, Fig. 4; Fig. 1 is shown by the dotted line in Fig. 4.

Titration curves 2, 3 and 4 (Fig. 4) are similar to curve 1 but higher in *pH* due to the presence of excess potassium mandelate.

On the basis of these results, the conductometric titration curve of zirconyl chloride with sodium mandelate (curve 1, Fig. 6; cf. Hahn and Weber)⁷ is explained easily. Up to the addition of one mole of sodium mandelate (system represented by equation 2), the conductivity rises slightly due to the replacement of heavy III by Na^+ ions. With the second mole of sodium mandelate (system 3), the conductivity falls due to the replacement of H^+ by Na^+ ions. This con-

tinues up to the addition of 2.3 moles of sodium mandelate due to the reversible nature of the equilibrium.



The correctness of this interpretation was demonstrated by the titration of an equivalent amount of hydrochloric acid with sodium mandelate (curve 2, Fig. 6); a maximum in the curve occurs in the same region (2.4 moles of sodium mandelate).

Acknowledgment.—The authors are grateful to the Council of Scientific and Industrial Research for a research grant and assistantship awarded to R.N.K.. Thanks are due to Prof. A. C. Chatterji for providing laboratory facilities and to Magnesium Elektron, Ltd., London, for zirconium tetrachloride.

LUCKNOW, INDIA

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Diboron Tetrafluoride

BY ARTHUR FINCH AND H. I. SCHLESINGER

RECEIVED JANUARY 24, 1958

The preparation and properties of the new compound, diboron tetrafluoride, B_2F_4 , are described.

The preparation of diboron tetrachloride, B_2Cl_4 , was accomplished by passing boron trichloride through an electric discharge between mercury electrodes.^{1,2} The corresponding treatment of boron trifluoride leaves the latter unchanged. We have, however, succeeded in preparing the tetrafluoride in excellent yield and purity by treating diboron tetrachloride with antimony trifluoride, as will be described below.

In contrast to diboron tetrachloride, which undergoes partial slow decomposition at 0° , the corresponding tetrafluoride suffers very little if any change at room temperature. A sample of it heated at 100° for 20 minutes liberated a trace of what appeared to be boron trifluoride but underwent no other noticeable change; even at 200° only about 40% of the compound was lost by decomposition in several hours. The products were boron trifluoride and a yellow, non-volatile solid not further investigated. The tetrafluoride is considerably more volatile than the tetrachloride, but its melting point is higher.

The chemical behavior of the tetrafluoride closely resembles that of the tetrachloride, as is illustrated in the experimental part by its hydrolysis and by its reactions with diethyl ether and with trimethylamine. Its reactions with ethylene, with butene-2 and with acetylene also follow the pattern of the reactions of tetrachloride; description of this aspect of its behavior will be included in a subsequent paper covering the behavior of both the tetrachloride and the tetrafluoride in this respect. It is of interest in this connection to mention that the tetrafluoride exerts a more decided catalytic effect on the polymerization of the unsaturated compounds than does the tetrachloride.

Experimental

Materials and Procedure.—The preparation and purification of diboron tetrachloride were as described in the earlier paper² already referred to, which also described the methods employed for the purification of the diethyl ether and trimethylamine. Antimony trifluoride was a commercial sample sublimed into the reaction vessel by electrically

heating an evacuated tube containing the sample. Standard type vacuum lines³ equipped with mercury float valves were used throughout.

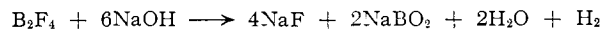
Preparation of Diboron Tetrafluoride.—Diboron tetrachloride was transferred by distillation into a reaction vessel containing freshly sublimed antimony trifluoride. After the mixture had stood overnight at -80° , the volatile portion of the mixture was transferred to a storage bulb (or U-tube) attached to the line. The reaction vessel, which was designed to make this possible without exposure to air, was then charged with a fresh supply of antimony trifluoride, and the volatile material previously removed from the reaction vessel was returned to it. After the mixture had once more stood at -80° for several hours, the volatile material was once more removed and was fractionated. By this procedure 2.23 mmoles of the tetrafluoride was obtained from 2.86 mmoles of the tetrachloride, a yield of 78%. The purity of the product is shown by the sharpness of its melting point, by its molecular weight and by its analysis as is described below.

Although good yields were obtained at -80° , the preparation may be accelerated by raising the temperature to -45° after the mixture had stood for some length of time at -80° . On the other hand, when the second treatment of the volatile material with antimony trifluoride was omitted, the yield was poor and the purity unsatisfactory.

Physical Properties and Analysis of Diboron Tetrafluoride.—Three determinations of the melting point gave the values: -55.4 , -56.2 and -56.4 , average -56.0 . Temperatures were measured with a liquid ammonia vapor tension thermometer.³ A Stock melting point apparatus was used.³

A 0.1004-g. sample of the compound exerted a pressure of 304.7 mm. at 27.5° in a volume of 63.7 cc. The corresponding molecular weight is 97.0 (calcd. for B_2F_4 is 97.6).

For the analysis, a 0.894 mmole sample of the compound was heated with an excess of chloride-free sodium hydroxide solution (15%) for two hours at from 60 to 80° in the vacuum line, producing 538.1 cc. of hydrogen at 24° and 30.7 mm. This quantity represents 0.891 mmole, in excellent agreement with the 0.894 mmole demanded by the equation



A fluorine determination by the thorium nitrate method showed that the 0.894 mmole sample contained 3.55 mmoles of fluoride and an only insignificant amount of chloride. The theoretical fluorine content for 0.894 mmole of B_2F_4 is 3.57 mmoles.

The following data were obtained for the vapor tensions of the solid and of the liquid diboron tetrafluoride. The values in the last row were calculated from the equation $\log_{10} p_{(\text{mm.})} = 10.82 - 1856/T$. For the calculated values of the vapor tension of the liquid the equation $\log_{10} p_{(\text{mm.})} = 9.009 - 1466/T$ was used. The equation leads to the values

(3) See, for example, R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

(1) Thomas Wartik, R. E. Moore and H. I. Schlesinger, THIS JOURNAL, **71**, 3265 (1949).

(2) Grant Urry, Thomas Wartik, R. E. Moore and H. I. Schlesinger, *ibid.*, **76**, 5293 (1954).