Discussion

The results obtained in this study indicate that titanium tetrabromide crystallizes in the body-centered cubic form with the unit cell dimension $a_0 = 11.300 \pm 0.007$ A. This value can be compared to the reported value[3] of 11.250 Å. which was obtained by averaging five observed a_0 values. This average value was corrected[8] to 11.282 Å. The precision in our powder diffraction data can be seen from the plot of the observed a_0 *versus* $f(\theta)$ and the standard deviation of ±0.007 Å. in the true a_0 value. The additional diffraction lines obtained in this investigation over those reported by Hassel and Kringstad[3] are of relative intensity 40 or less, and can, perhaps, be attributed to a longer time of exposure and/or to the use of a fluorescent filter. Not to be overlooked is the possibility that the observed line at 1.666 Å. could also have been observed by Hassel but was coincident with the CdO (internal standard) line at 1.661 Å. and was, therefore, not reported. The X-ray density of 3.383 g. cc.$^{-1}$, calculated with eight molecules per unit cell, can be compared to the values[9,10] obtained by direct pycnometric measurement, $d_4^{20} = 3.254$ g. cc.$^{-1}$ and $d_4^{25} = 3.37$ g. cc.$^{-1}$, respectively.

Titanium tetraiodide is dimorphic ($-15°$ is the transformation temperature for $TiBr_4$) with the room temperature modification of less symmetry than the high temperature, 100–125°, cubic form. It should be observed that the room temperature form yields a powder pattern with weak and not well-defined back reflections. Also, there is doubt about the existence of two lines at 3.06 and 3.01 Å. This could be the result of sample absorption effects and was apparently eliminated since molybdenum radiation resulted in a single line at 3.04 Å. The observed lines index quite well as hexagonal with $a_0 = 7.978$ Å. and $c_0 = 19.68$ Å. but little credence can be placed in these values until single crystal (we were unable to prepare them) data are available. The cubic form of the tetraiodide has a cell dimension of 12.21 Å. at about 125° which was obtained as an average of ten observed values and not refined by extrapolation techniques. This results in an X-ray density, with eight molecules per unit cell, of 4.01 g. cc.$^{-1}$ and can be compared to the pycnometric value[10] of $d_4^{25} = 4.40$ g. cc.$^{-1}$ and the X-ray density according to Hassel of 4.27 cc.$^{-1}$.

Powder and single crystal X-ray data indicate that acicular titanium triiodide crystallizes in the hexagonal form with the lattice parameters $a_0 = 7.173 \pm 0.003$ Å. and $c_0 = 6.47$ Å. It has an X-ray density of 4.937 g. cc.$^{-1}$ if it is assumed that there are two TiI_3 units per unit cell. Table IV shows that four *d*-spacings can be assigned two different sets of Miller indices. The more probable indices are (111), (221), (222) and (412) rather than (200), (310), (400), and (500), respectively, as determined from a comparison of observed and calculated intensities. The space group d_{3h}^3 can be assumed tentatively.

Acknowledgments.—We wish to thank Dr. Robert E. Gilbert of Oak Ridge and Mr. Neil D. Veigel of Battelle Memorial Institute for their suggestions concerning the preparation of the titanium iodides.

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(9) J. B. Olsen and E. P. Ryan, THIS JOURNAL, **54**, 2215 (1932).

(10) W. Klemm, W. Tilk and S. von Mullenheim, *Z. anorg. Chem.*, **176**, (1928).

[CONTRIBUTION FROM THE NATIONAL LEAD COMPANY, TITANIUM DIVISION, RESEARCH LABORATORY]

A Spectrophotometric Study of the System Titanium(IV)–Peroxide–Fluoride

BY KERMIT HERRINGTON AND DORRIS E. KINGSBURY

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Absorption spectrum measurements are reported for sulfuric acid solutions containing titanium(IV), peroxide and fluoride In the presence of sufficient excess peroxide so that dissociation of the peroxy-titanium(IV) is negligible, the bleaching of the color of this complex by fluoride has been found to be only about 20% in the presence of a hundred-fold excess of fluoride. No evidence was found for any new complex ion in this system in the presence of fluoride. The stability of the peroxy-titanium(IV) complex was found to be unaffected by the presence of fluoride.

Introduction

The yellow color produced when peroxide is added to aqueous titanium(IV) is commonly used as an analytical method for titanium(IV).[1] That the color is due to a peroxy–titanium(IV) complex ion has been well established, and Schaeppi and Treadwell[2] have shown, by the method of continuous variations, that this ion has a 1:1 stoichiometry. In his excellent discussion of the limitations of this method, Woldbye[3] concludes that the system titanium(IV)–peroxide is sufficiently uncomplicated so that there should be no reason to doubt the validity of the results obtained by Schaeppi and Treadwell. The absorption spectrum of the ion has a maximum density at 410 mμ and it has been found that Beer's law is followed at titanium(IV) concentrations less than about 10^{-3} molar.[4] Above this concentration, the deviations which occur have been attributed by Reeves and Jonassen to polymerization of the titanium(IV). The color of the ion (both the position of the absorption band and the molar extinction coefficient) has been found to be independent of many common anions; fluoride, however, is reported to

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(1) W. W. Scott, "Standard Methods of Chemical Analysis," 5th Ed., D. Van Nostrand, Inc., New York, N. Y., 1939, p. 987.

(2) Y. Schaeppi and W. D. Treadwell, *Helv. Chim. Acta*, **31**, 577 (1948).

(3) F. Woldbye, *Acta Chem. Scand.*, **9**, 299 (1955).

(4) See for example, R. E. Reeves and H. B. Jonassen, THIS JOURNAL, **76**, 5354 (1954).

bleach the color quantitatively.[5] The bleaching by fluoride has been attributed[6] to the formation of a colorless titanyl fluoride ion. In the absence of fluoride the instability constant of the complex has been determined to be about 10^{-4}.[7] In connection with an investigation in this Laboratory on the constitution of the ions in titanium(IV) solutions, some results were obtained on the system titanium(IV)–peroxide–fluoride which are at variance with those reported by Kleiner. The results are reported here and an alternative explanation is given for the bleaching of peroxy–titanium(IV) by fluoride.

Experimental

The source of titanium(IV) was vacuum-distilled isopropyl titanate. This material was hydrolyzed at room temperature by dropwise addition to vigorously agitated distilled water. The hydrous titania obtained was washed with distilled water on a buchner funnel in order to remove the isopropyl alcohol. After washing, the hydrous oxide was dissolved in strong sulfuric acid and diluted with water to give a solution about 10^{-3} *M* in titanium(IV) and 2 *M* in acid. Concentrations were determined by standard analytical procedures. Peroxide solutions were prepared by dilution of 30% hydrogen peroxide. The peroxide solution was standardized by permanganate titration immediately prior to use. The source of fluoride was reagent grade sodium fluoride, also dissolved in 2 *M* sulfuric acid.

Absorption spectra measurements were made with a Beckman DU spectrophotometer, using calibrated one cm. Corex cells. No attempt was made to control the temperature, which varied between 25 and 30°. Optical density values reported are those read on the instrument, corrected for slight inequality between cells.

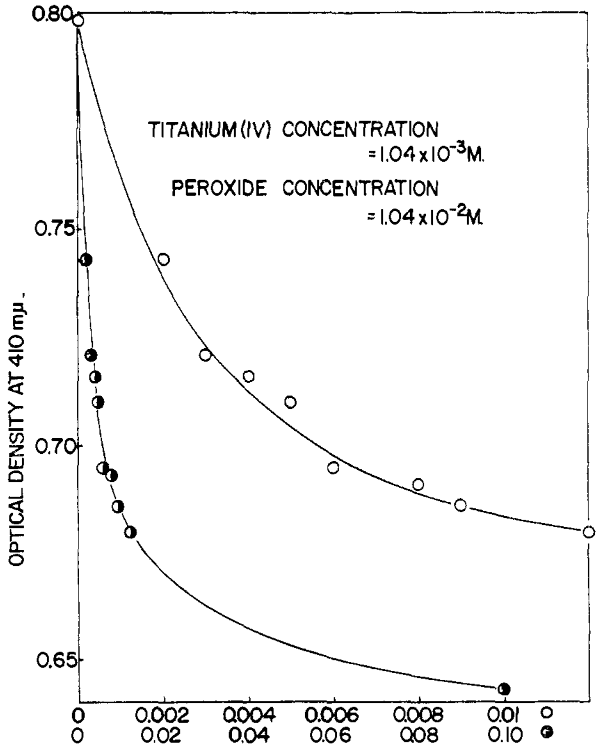

Fig. 1.—Optical density of 1.04×10^{-3} *M* peroxy–titanium (IV) as a function of concentration of added fluoride ion.

Discussion

In order to establish that our solutions were equivalent to those used by other investigators, the stoichiometry of the peroxy–titanium(IV) complex was determined by the method of continuous variations and the instability constant was determined with results essentially identical with those previously published. Following this an attempt was made to determine the extent of bleaching of the peroxy–titanium(IV) complex by fluoride, with the results as shown in Fig. 1. It can be seen that the color is bleached incompletely, but by an amount which is almost independent of the fluoride concentration, provided that the fluoride is present in a sufficiently large excess. In the presence of excess fluoride we have established that Beer's law is valid up to a titanium(IV) concentration of about 10^{-3} *M*. An important aspect of these solutions is the kinetics of attainment of equilibrium. Measurements made immediately after mixing the solutions are quite erratic and change with time. After about ten days there is no further change. All experiments reported here are for solutions which have attained equilibrium. Figure 2 shows the change in wave length of maximum density with fluoride concentration. From the curve it is apparent that there is a small but real shift in the position of the absorption band as a function of fluoride concentration. Since the band is rather broad it makes little practical difference whether the density is measured at 410 mμ, or at the wave length of maximum density. A possible explanation for this displacement is discussed below.

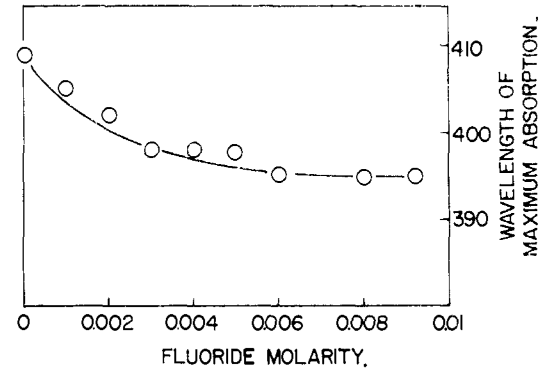

Fig. 2.—Change in position of peroxy–titanium (IV) absorption band as a function of fluoride concentration.

In order to determine the existence of other stoichiometric complexes in this system, a continuous variations experiment was performed using solutions 10^{-3} *M* in titanium(IV)–peroxide and in fluoride. Sufficient peroxide was present to ensure that all the titanium(IV) was complexed, initially. There was no evidence for a complex occurring in this system between titanium(IV) and fluoride as reported by Kleiner.

An examination of the results obtained by Kleiner reveals a number of points which lead us to suspect his postulated existence of an equimolecular complex between titanium(IV) and fluoride in these solutions. In the first case most of his solutions were too concentrated in titanium(IV) for Beer's law to apply. This is important since both the

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[5] A. Weissler, *Ind. Eng. Chem., Anal. Ed.*, **17**, 695 (1945).

[6] K. E. Kleiner, *Zhur. Obshchei Khim.*, **22**, 17 (1952).

[7] E. Gastinger, *Z. anorg. Chem.*, **275**, 335 (1954).

method of Bent and French[8] and the method of continuous variations used by Kleiner are based on Beer's law. From the work of Reeves and Jonassen there is reason to suspect polymerization in solutions with these titanium(IV) concentrations, which would also render the conclusions somewhat invalid. Second, not in all solutions is the peroxide concentration high enough to ensure complete complexing of the titanium(IV). Third, there is no reference to the change with time in the absorption spectra, which we have always observed. Finally, the effective wave length of his filter, 465 mμ, is quite far from the peak of the absorption band (410 mμ).

Using the same procedure employed by Gastinger, we have determined the effect of fluoride on the stability of the peroxy–titanium(IV) complex, with the result that, over the concentration range investigated, the stability of the peroxy–titanium (IV) complex is essentially unaffected by the presence of fluoride.

A possible interpretation of the results reported here can be found in current theories of the absorption spectra of ions in solution recently discussed by Bjerrum and co-workers.[9] The fluoride ion represents a change in the solvent in our case, which alters the crystal field bands slightly by changing the point dipole moment for the second coördination sphere. This brings about the change in the position of the absorption band. The extinction coefficient change is also correct in sign since a change from water to methanol should produce an opposite effect to that obtained in changing the solvent from water to aqueous fluoride. A more quantitative treatment along these lines must be deferred until further refinements are made in these theories.

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[8] H. E. Bent and C. L. French, This Journal, **63**, 568 (1941).

[9] J. Bjerrum, A. W. Adamson and O. Bostrup, *Acta Chem. Scand.*, **10**, 329 (1956).

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[Contribution from the Chemistry Department of Cornell University]

Fluoride Complexes of Indium(III)[1]

By John E. Roberts[2] and A. W. Laubengayer

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Aqueous systems of indium(III) fluoride with each of 15 cations have been studied. Only the ammonium ion and the cobalt(II) ion produced identifiable fluoroindate complexes. Thermal analysis of the system lithium fluoride–indium(III) fluoride showed that only the compound Li_3InF_6 is stable in this system.

Introduction

Ammonium hexafluoroindate, $(NH_4)_3InF_6$, has been prepared and characterized by Huysse[3] and by Hannebohn and Klemm.[4] The latter could not prepare sodium hexafluoroindate, Na_3InF_6, although Ensslin and Dreyer[5] reported this compound and Sunden[6] isolated a precipitate of this composition. Polarographic[6,7] and potentiometric[8] measurements have identified InF^{++}, InF_2^+ and InF_4^- ions in solution although no solids containing these ions have been isolated.

In view of the large number of fluoro-complexes known for related elements, particularly gallium,[9] it is reasonable to expect similar compounds for indium. The formation of indium fluoride complexes will be complicated, however, by the hydrolysis of indium fluoride.[10]

If the value 1.3 is assumed for the electronegativity of indium, the indium–fluorine bond may be expected to be about 90% ionic,[11] and the radius ratio gives a maximum coördination number of indium toward fluorine of eight. Such highly coördinated complexes should be stabilized by the triple charge on the indium ion but mutual repulsion between adjacent fluorine atoms could decrease the maximum coördination number.

Experimental

Preparation of Materials.—Anhydrous indium trichloride was prepared from spectrographically pure indium metal by the method of Baxter and Alter,[12] purified by triple sublimation in dry nitrogen and converted to the anhydrous trifluoride by heating in a stream of dry hydrogen fluoride at 700° for three hours. *Anal.* Calcd. for InF_3: In, 66.8; F, 33.2. Found: In, 66.5; F, 33.4. All attempts to prepare InF_3 by dehydrating $InF_3 \cdot 3H_2O$, even in an HF atmosphere led to hydrolyzed products of variable composition.[10]

Hydrated indium trifluoride was prepared by dissolving spectrographically pure indium metal in strong nitric acid and repeatedly evaporating the solution to dryness with 40% hydrofluoric acid. The residue was dissolved in hot dilute hydrofluoric acid, the solution evaporated to incipient crystallization and allowed to cool. The colorless crystals were separated by decantation, washed with 40% hydrofluoric acid and dried over soda lime. *Anal.* Calcd. for $InF_3 \cdot 3H_2O$: In, 50.8; F, 25.2. Found: In, 50.3; F, 25.9. Microscopic examination showed the crystals to be tetragonal, the common view being rectangular prisms showing negative elongation. An occasional square basal pinacoid showing a negative uniaxial optic axis figure was observed. Refractive indices for white light at room temperature: $\epsilon = 1.43 \pm 0.01$ and $\omega = 1.47 \pm 0.01$.

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[1] Taken from the Ph.D. thesis of John E. Roberts, Cornell Univ., June, 1947. Presented at the 111th meeting of the American Chemical Society, Atlantic City, N. J., April 15, 1947.

[2] Department of Chemistry, Univ. of Mass., Amherst, Mass.

[3] A. C. Huysse, *Z. anal. Chem.*, **39**, 9 (1900).

[4] O. Hannebohn and W. Klemm, *Z. anorg. allgem. Chem.*, **229**, 337 (1936).

[5] F. Ensslin and H. Dreyer, *ibid.*, **249**, 119 (1942).

[6] L. G. Hepler, J. W. Kury and Z. Z. Hugus, *J. Phys. Chem.*, **58**, 26 (1954).

[7] J. A. Schufle and H. M. Eiland, This Journal, **76**, 960 (1954).

[8] N. Sunden, *Svensk. Kem. Tidskr.*, **66**, 50 (1954).

[9] W. Pugh, *J. Chem. Soc.*, 1046, 1959 (1937).

[10] J. E. Roberts and A. W. Laubengayer, unpublished research.

[11] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, pp. 69–75.

[12] G. P. Baxter and C. M. Alter, This Journal, **55**, 1944 (1933).