

Å. If on the other hand the structure is built upon bromide ions in contact, the Br^- - Br^- distance would be expected to be approximately 3.90 Å., the diameter of the bromide ion,¹⁰ agreeing with the observed position of the second peak.

Conclusion

Application of the rough radial distribution method of these four substances shows in a general way to what extent the method may be relied upon. The results seem to be accurate when there is only one distance involving large atoms near a given value; otherwise resolution is poor. In a large number of cases in which the structure is not known it is impossible to state whether or not this condition is being fulfilled. The use of reflections at large values of $(\sin \theta)/\lambda$ gives increased resolutions; with intense photographs and accurate estimates of intensities of the weak lines being reflected at large angles one could use these important lines to much greater advantage. It is a particularly useful method when applied to large molecules containing a comparatively small number of heavy atoms.

(10) Pauling, *THIS JOURNAL*, **49**, 765 (1927).

I wish to express my gratitude to Professor Linus Pauling for his valuable coöperation, and to Dr. Sidney Weinbaum for his assistance in preparing the curves for presentation.

Summary

The radial distribution method has been applied to orpiment, realgar, sodium sulfantimonate enneahydrate and calcium mercuric bromide. The environment about the atoms in realgar is shown to be remarkably like that in orpiment, and in both cases the distance between arsenic and sulfur atoms agrees within experimental error with the sum of the corresponding covalent radii. A value for the sulfur bond angle is given, and the *b*-axis of the unit cell of orpiment was measured. The sulfur-antimony distance in sodium sulfantimonate enneahydrate was found to be definitely less than the sum of the covalent radii. Application of the method to calcium mercuric bromide led to indefinite results, consistent either with a closest packing of bromide ions, or with a structure consisting of tetrahedral covalent HgBr_4 groups.

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Improvements in Technique for the Determination of Microgram Quantities of Iodine

BY R. H. HAMILTON, JR.¹

Because a small amount of iodine has to be extracted from a large mass of other salts before determination, and because extraction with alcohol, as advocated by von Fellenberg,² requires the iodine to be in the form of iodide, it is necessary to reduce iodates that may be present. Such reduction has been done in the past with sulfites in acid solution. Acidification increases the amount of salts present, and thus increases the difficulty of extraction, because the salt mixture must again be made alkaline before extraction with alcohol.

Harvey³ used hydrazine sulfate to reduce iodate when purifying potassium hydroxide solutions. He did not show how nearly quantitative such reduction was. In the present investigation hydrazine sulfate was found to give quantitative reduction. Hydrazine hydrate was later tried and

found to have the same action. It should be preferable to the sulfate, as the excess is completely volatile when hydrate is used, whereas added sulfate ions remain as potassium sulfate. When an excess of hydrazine sulfate or hydrate has been added, a small drop of carbonate solution produces a dark spot when placed upon paper dipped in a 5% mercuric chloride solution and dried.

The salt mixture from which iodide is to be extracted usually contains much potassium carbonate, since von Fellenberg advocated the use of this substance.² The usual practice has been to evaporate the solution until a solid phase of carbonate appeared. Then the two-phase system was extracted by rubbing with alcohol, which formed a third phase. Occlusion of iodide by crystals becomes marked if there is no aqueous phase present. This fact suggested the use of a two-phase system consisting of saturated potas-

(1) National Research Fellow in the Biological Sciences, 1934-1935.

(2) Th. von Fellenberg, *Biochem. Z.*, **139**, 391 (1923).

(3) C. O. Harvey, *Analyst*, **59**, 479 (1934).

sium carbonate solution and 92% by volume alcohol, without the presence of any solid carbonate. Experiments showed that extraction under these conditions could be made quantitative.

It was noted that when potassium carbonate solutions were boiled for some time in porcelain dishes, silicates dissolved and hindered quantitative extraction of iodides.

Incidentally, it was also noted that sodium fluoride exerted a definite and marked inhibiting action on the re-oxidation of iodide which ordinarily occurs within a few minutes to a few hours if the titration flask is allowed to stand after the end-point is reached. This observation is of theoretical interest, but it will probably not find application in titration methods, as re-oxidation is not a serious factor when they are properly carried out.

Experimental

In all cases, the method of determination of iodine present, after separation from salt masses, was that described by Reith.⁴ In no case did the amount of iodide ion in the aliquot taken for analysis exceed 5 micrograms.

Quantitative Reduction of Iodate in Alkaline Solution by Means of Hydrazine Sulfate.—To 2 cc. of saturated potassium carbonate solution (expt. A, Table I) was added 50 micrograms of iodine as potassium iodate, in 5 cc. of water. The solution was boiled for thirty minutes, water being added to maintain the volume, and was then evaporated to dryness, moistened, and extracted by trituration with 94% alcohol, three 5-cc. portions of alcohol being used.

TABLE I
REDUCTION OF IODATE BY HYDRAZINE SULFATE

Expt.	Satd. K_2CO_3 , cc.	Iodine as iodate, γ	Hydrazine sulfate, mg.	Time of boiling before starting evaporation, min.	Total iodine extracted, γ
A	2	50	..	30	1.6
B	2	50	10	30	48.8
C	2	50	10	30	50.5
D	2	1	10	30	1.16
E	2	50	10	..	49.1
F	2	1	10	..	1.04

In expts. B, C and D, a similar procedure was followed, except that each time 10 mg. of hydrazine sulfate was added before the carbonate-iodate solution was boiled for thirty minutes. In expts. E and F, the thirty-minute boiling period was omitted, and extraction was carried out as described below.

Two-phase Extraction of Iodide from Potassium Carbonate Solution.—In expts. E to J, inclusive, a glass-stoppered test-tube was used for the extraction. In expts. G and H, the tube, containing iodide, saturated carbonate solution, and 92% (by volume) alcohol, was stoppered and shaken vigorously 200 times, and laid on its side until the emulsion settled out.

TABLE II

TWO-PHASE EXTRACTION OF IODIDE								
Expt.	Satd. K_2CO_3 , cc.	Iodine as KI, γ	Extraction no.	Alcohol used, cc.	Residue, mg.	Iodine in aliquot, γ	Iodine in whole extract, γ	Total iodine found, γ
G	2	50	1	10	6.3	4.76	47.6	
			2	10	6.8	0.3	1.5	49.1
H	2	50	1	10	5.7	4.91	49.1	
			2	10	6.5	0.66	1.6	50.7
I	1	50	1 and 2	10 + 10		4.96		49.6
J	2 ^a	50	1	10	21.7	4.48	44.8	
			2	10	21.6		3.0	
			3	10	18.6		..	47.8

^a See text.

Separation of the layers was effected by means of a pipet shaped like, and about the dimensions of, a 10-cc. graduated pipet. The tubing at the top of the pipet should have a small lumen (about 2 mm.), to prevent alcohol from wetting the finger upon inversion, and should be 5 or 6 cm. long. The pipet was wet inside with alcohol before use; otherwise the additional partial pressure of alcohol vapor would cause some of the contents to be spilled upon inversion. The alcoholic layer was sucked up into the pipet along with some of the aqueous layer. The latter was allowed to run back into the extraction tube, and the pipet was inverted, the alcoholic contents being allowed to run into an evaporating dish through the top of the pipet. By this procedure, admixture of aqueous phase was avoided. A second extraction was made similarly, without rinsing of the pipet between extractions of the same sample.

In expt. I, 1 cc. of carbonate solution was used, and the two extracts were analyzed together.

A test of this method of extraction was made when other ions than carbonate were present (expt. J). In a platinum dish were placed, in solution, 100 mg. each of potassium nitrate, potassium sulfate and potassium chloride, 50 micrograms of iodine as potassium iodide, and 2 cc. of saturated potassium carbonate, containing about 1.46 g. of the anhydrous salt. The solution was heated gently on an asbestos-covered wire gauze until crepitation ceased, and the salt mixture was transferred mechanically to a glass-stoppered test-tube. The platinum dish was rinsed several times with water, the rinsings being added to the test-tube until the volume of salt solution was slightly over 2 cc. This material was extracted as above with alcohol. Two more extractions were made, no iodine being found in the third extract.

Discussion

After hydrazine sulfate or hydrate is added to the carbonate solution, the latter should be evaporated to dryness over a low flame in order to drive off excess hydrazine, which will otherwise reduce bromine at a later step.

The proposed method of extraction is not usable unless the salt mass is mostly potassium carbonate, as so much water is required to dissolve other salts that the alcohol used is diluted, and interfering ions will be extracted by the dilute alcohol. As

(4) J. F. Reith, *Biochem. Z.*, **216**, 249 (1929).

will be noted in Table II, the salt extracted by alcohol when carbonate alone is present amounts to only 0.6 to 0.7 mg. per cc. of alcohol. After careful trituration of crystals of potassium carbonate and saturated solution with 94% alcohol, the amount of carbonate extracted was found, as an average of nine determinations, to be about 1.09 mg. per cc. of alcohol.

Much of this work was done in the Rijksinstituut voor de Volksgezondheid, Utrecht, Holland. The author's sincere thanks are due Dr. J. F. Reith, Head of the Chemical Division there, who demonstrated his methods, and offered valuable suggestions and criticisms.

Summary

1. Iodate can be quantitatively reduced in hot alkaline solution by means of hydrazine sulfate.
2. Efficient extraction of iodide can be made with alcohol from a saturated solution of potassium carbonate, without danger of occlusion by crystals.
3. Alkaline solutions containing iodide should not be boiled in porcelain dishes before extraction of the iodide.
4. Fluoride delays the re-oxidation of iodide which takes place after a titrimetric determination of iodine.

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

The Reduction of Aromatic Compounds with Hydrogen and a Platinum Oxide-Platinum Black Catalyst in the Presence of Halogen Acid

By J. H. BROWN, H. W. DURAND AND C. S. MARVEL

While reducing hot alcoholic solutions of some bromophenylelefins to the corresponding paraffins by hydrogen in the presence of Adams, Voorhees and Shriver's platinum catalyst,¹ we observed that in some runs more than the expected amount of hydrogen was absorbed, and hydrogen bromide was formed. Further investigation showed that this reaction involved not only removal of bromine from the benzene ring, but also reduction of the benzene ring to a hexahydro derivative. Since Adams and Marshall² have found that, in general, aromatic compounds are very slowly reduced in alcohol and only with moderate rapidity in glacial acetic acid, with platinum oxide-platinum black as a catalyst, it has seemed worth while to investigate our chance observation in greater detail.

When bromobenzene was dissolved in alcohol at about 55° and shaken with the catalyst in the presence of hydrogen, rapid absorption of hydrogen occurred, and cyclohexane was formed. By interrupting the reduction when one equivalent of hydrogen per molecule of bromobenzene had been absorbed, the product obtained was an impure sample of benzene, but the reaction did not seem to offer a satisfactory scheme for removal of halogen from a benzene derivative. Other aryl halides, such as *o*-, *m*- and *p*-bromotoluene, *p*-dibromo-

benzene, chlorobenzene and *p*-dichlorobenzene, were also readily reduced to halogen acid and the cyclohexane derivative. However, not all aryl halides could be reduced readily, as shown by the fact that iodobenzene, *o*-bromobenzoic acid, α -chloronaphthalene and α -bromonaphthalene were not affected in our experiments.

Since the reduction of an aryl halide apparently was taking place in two steps—first, removal of halogen acid, and then reduction of the ring—and more rapidly than the usual reduction of the ring alone, it seemed probable that the liberated halogen acid must be an activator for the platinum catalyst for reduction of aromatic compounds. This was verified by reducing various aromatic compounds in alcoholic solution in the presence of various concentrations of hydrogen chloride and bromide. Some of the first reductions were carried out after preheating the solutions to 50–70°, but later it was found that this was not necessary, as reduction took place rapidly, and the temperature of the mixture soon rose to this point without outside heating. Benzene, toluene, xylene, mesitylene, ethylbenzene, cymene, diphenyl and anthracene were readily reduced, whereas naphthalene and phenanthrene were not affected. There seemed to be no choice between hydrogen chloride and hydrogen bromide as an activator.

When functional groups are present in the aro-

(1) Adams, Voorhees and Shriver, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, 1932, p. 452.

(2) Adams and Marshall, *THIS JOURNAL*, 50, 1970 (1928).