red paper, and air-dried overnight. The material was further dried by placing it in a 1-liter round-bottom flask connected to a water pump and the flask was heated in a water-bath at 80–90° for several hours. The product was a yellow powder weighing 74 g. (94% of the theoretical amount) and melted at 166–171°.

The crude product was dissolved in 350 cc. of boiling glacial acetic acid and the hot solution filtered by suction through a Büchner funnel. If crystals separated in the filtrate, the suction flask was heated to bring all of the material into solution and then left to cool. The small yellow needles that separated were filtered with suction and washed successively with small quantities of alcohol, water, and alcohol. The yield was 59–61 g. (75–78% of the theoretical amount) of 2,4,7-trinitrofluorenone, melting at 175.2–176.0°. Additional material was recovered from the mother liquor by dilution with water; the precipitate was filtered with suction and dried. Crystallization from acetic acid gave about 5 g. of pure material, melting point 175.2–176.0°, which was usually slightly darker than the first crop.

Complex Compound Formation.—Equimolar proportions of the pure T.N.F. and the polynuclear component were dissolved separately in the same solvent (alcohol, benzene or acetic acid) and the two hot, nearly saturated solutions mixed. After separation of the solid, colored complex it was recrystallized from the solvent indicated in the table. In a few instances where acetic acid was used, the complex did not separate until the saturated solution was left at room temperature for six to twelve hours.

Melting Point versus Composition Diagram.—Pure 1,4-diphenylbutadiene and T.N.F. were weighed into small Pyrex test-tubes in various molar proportions. The total weight of the mixture was usually about 200 mg. The test-tubes were sealed, placed in a shaking apparatus, and heated in an oil-bath with shaking until the mixture was completely fluid. The bath was removed, the tubes opened and the solid melt transferred as quantitatively as possible to a small mortar. The mixture was ground and the melting point determined with a capillary tube in the usual fashion.

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The Solubility of Iodine in Concentrated Hydriodic Acid Solutions

BY C. F. POWELL AND I. E. CAMPBELL

This paper presents data on the solubility of iodine in 45 to 67% hydriodic acid. No data are reported in the literature on the solubility of iodine in acid stronger than 10%.

Experimental

Hydriodic acid was prepared in a modified form (Fig. 1) of the synthesis and absorption train described by Caley and Burford.[1] Difficulty experienced with temperature control and sagging of the heated parts in using the original version led to its modification. A 102-hour run, using 435 g. of resublimed iodine (Baker C. P. grade) in the vaporizer and 200 ml. of distilled water in the absorber, produced a 66.7% acid, conversion being better than 90%. Weaker concentrations of acid were prepared when needed by dilution of the 66.7% acid with air-free distilled water.

Three 7-ml. samples of each of five concentrations were

(1) E. R. Caley and M. G. Burford, "Inorganic Syntheses," 1st ed., McGraw-Hill Book Company, Inc., New York, 1939, Vol. 1, pp. 159–162.
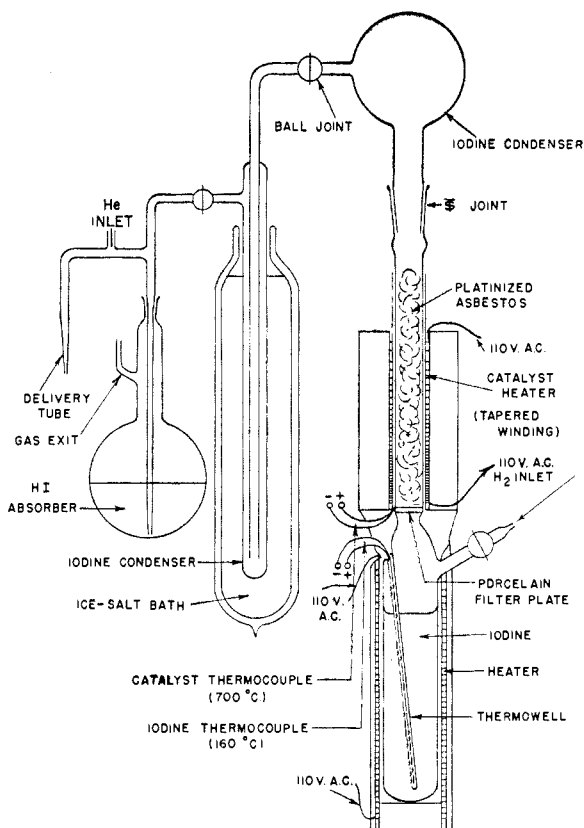

Fig. 1.—Hydrogen iodide preparation apparatus (scale: one sixth).

run into glass ampules containing about 30 g. (an excess) of iodine in a helium atmosphere, and sealed off. The helium used was purified by passing over calcium metal turnings heated to 600°.

After being agitated in a thermostated water-bath at 25.00 ± 0.05° for three days, each ampule was broken in a helium atmosphere and the sample filtered at the equilibrium temperature through a dry asbestos mat into a smaller, weighed ampule holding 3 ml. Two samples were taken from each saturation ampule. These samples, after being sealed off in a helium atmosphere, were reweighed by standard weighing methods, and the weights reduced to vacuum.

The first of each sample pair was analyzed for free iodine by breaking the ampule in a flask containing 100 ml. of distilled water, 20 g. of Baker C. P. potassium iodide, and 5 g. (an excess) of Baker C. P. sodium bicarbonate, and titrating with 1 N sodium thiosulfate using 1 ml. of a 0.25% starch solution as indicator. The 1 N thiosulfate solution was standardized against resublimed iodine.[2]

The second ampule of each pair was broken in a flask containing 100 ml. of distilled water, 2 or 3 ml. of 12 N sulfuric acid, and 25.00 ml. of 1 N potassium iodate solution made up with Baker C. P. potassium iodate and standardized against the 1 N thiosulfate solution described above. After boiling off all free iodine (addition of a small marble chip facilitated complete removal) the hydrogen iodide content of the sample was obtained by determining the excess iodate in the cooled solution by adding an excess of Baker C. P. potassium iodide and titrating with 1 N thiosulfate solution.[3]

(2) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, 8th ed., John Wiley & Sons, Inc., New York, N. Y., 1935, p. 599.

(3) H. Dietz and B. M. Margosches, Chem.-Ztg., II, 1191 (1904).

Table I summarizes the experimental results, the averages of three samples of each acid concentration being given. The percentages of hydrogen iodide in the original solvents were calculated from the relative concentrations of hydrogen iodide and water in the saturated solutions. Iodine solubilities in kilograms per liter of solvent were calculated using data on hydriodic acid specific gravities available in the literature.[1,4] The probable error of the results is about 1%.

TABLE I

THE SOLUBILITY OF IODINE IN HYDRIODIC ACID AT 25°

┌───Saturated solution───┐			Original solvent		Kg. I₂ per liter solvent	Kg. I₂ per 1000- gram solvent
% HI	% I₂	% HI + H₂O	% HI	Sp. gr., 25°/4°		
18.1	72.85	27.15	66.7	1.946	5.22	2.68
18.2	71.55	28.45	64.0	1.877	4.72	2.52
17.5	67.8	32.2	54.4	1.644	3.47	2.11
17.8	64.6	35.4	50.2	1.557	2.84	1.825
18.1	60.5	39.5	45.9	1.486	2.28	1.532

Discussion

The iodine–saturated hydriodic acid solutions were dense black liquids from which iodine precipitated upon dilution with water. Specific gravity determinations of these solutions gave 3.22 and 3.28, respectively, for the iodine solutions made from 64.0 and 66.7% acid.

Analysis of the solutions was complicated by the high concentrations of iodine and hydrogen iodide present. In the determination of hydrogen iodide, the method described here was the only one of three procedures tried which gave reasonably accurate and consistent results. In this method the presence of hydrochloric acid prevents removal of
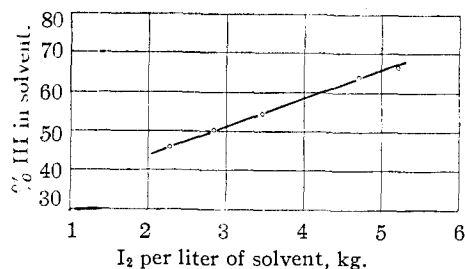

Fig. 2.—Solubility of iodine in hydriodic acid at 25°.
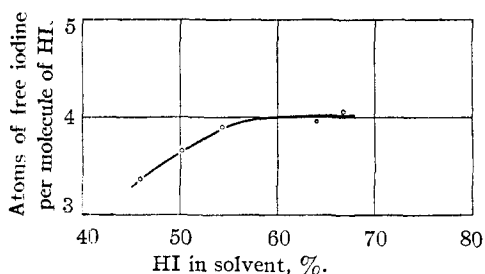

Fig. 3.—Atoms of free iodine per molecule of hydrogen iodide in saturated solution of iodine in hydriodic acid at 25°.

(4) E. W. Washburn, editor, "International Critical Tables," 1st ed., Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 55.

the last traces of iodine, hence the use of sulfuric acid in the oxidation with iodate.

Figure 2 shows the solubility of iodine in 45 to 67% hydriodic acid, and Fig. 3 the number of atoms of free iodine associated with one molecule of hydrogen iodide in the five concentrations of saturated solutions analyzed. The latter plot shows that the composition approaches that of HI₅ in the more concentrated solutions.

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N,N'-Diacetylethylenediamine Nitrate[1]

BY FRANKLIN S. PROUT AND JAMES CASON[2]

If N,N'-diacetylethylenediamine is treated with nitric acid in acetic anhydride under appropriate conditions, the amide is converted to the corresponding N,N'-dinitro derivative; however, if this reaction is carried out at about 0° in a mixture containing equimolar amounts of acetic anhydride and nitric acid the yield of the dinitro compound is poor. The principal product of such a reaction is a water-soluble compound which has been characterized as the salt of nitric acid and N,N'-diacetylethylenediamine. The same compound is obtained if an aqueous solution of exactly equimolar quantities of N,N'-diacetylethylenediamine and nitric acid is concentrated to dryness at low temperature in vacuo.

This nitrate is unaltered by heating with acetic anhydride at 45–55°; however, if anhydrous zinc chloride is added to the acetic anhydride solution an exothermic reaction takes place, and the reaction product crystallizes from the cooled solution. This product is not a nitramide but a highly hygroscopic substance which contains zinc and halogen. Since it was considered probable that the substance is a molecular complex between zinc chloride and N,N'-diacetylethylenediamine, this complex was prepared by mixing equimolar amounts of the two constituents in acetic anhydride or butanone. The complex so obtained was non-hygroscopic and differed in several other properties from the substance obtained from N,N'-diacetylethylenediamine nitrate. Subsequent investigation has shown that the latter complex contains N,N'-diacetylethylenediamine, zinc, chloride and nitrate. The ratio between these constituents cannot be expressed as small numbers, however; and it seems probable that this substance is not a definite compound but a mix-