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. I_2 per liter solvent	Kg. I_2 per 1000-gram solvent
% HI	% I_2	% HI + H_2O	% 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 the last traces of iodine, hence the use of sulfuric acid in the oxidation with iodate.

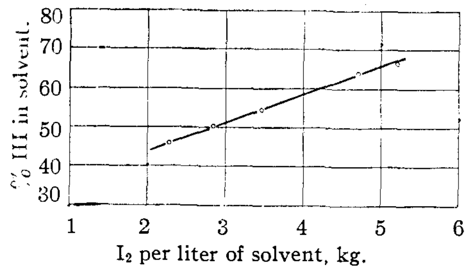

Fig. 2.—Solubility of iodine in hydriodic acid at 25°.

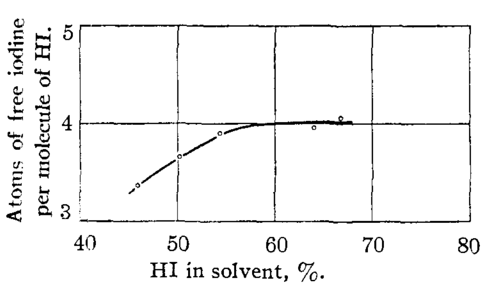

Fig. 3.—Atoms of free iodine per molecule of hydrogen iodide in saturated solution of iodine in hydriodic acid at 25°.

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 HI_5 in the more concentrated solutions.

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

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-

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(1) This note is based entirely on work done for the Office of Scientific Research and Development under Contract OEMsr-790 with Vanderbilt University.

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ture of the complexes of zinc chloride and zinc nitrate with N,N′-diacetylethylenediamine.

Experimental[3]

N,N′-Diacetylethylenediamine Nitrate.—N,N′-Diacetylethylenediamine was prepared by adding 63 cc. (0.66 mole) of acetic anhydride dropwise to 18 g. (0.3 mole) of anhydrous ethylenediamine. To the warm mixture was added 168 cc. (1.8 mole) of acetic anhydride, and this solution (kept homogeneous by warming) was added during eighty minutes to 75 cc. (1.8 mole) of 100% nitric acid which was stirred at 0–5°. After addition was complete the mixture was stirred for two hours at 0–5°. The solid present in the reaction mixture was collected on a sintered glass funnel and washed with acetic acid and ether. The precipitate was stirred with 200 cc. of water. The insoluble material (N,N′-diacetyl-N,N′-dinitroethylenediamine), which was removed by filtration, weighed 11.6 g. and melted at 127.7°. By concentration of the aqueous filtrate to dryness *in vacuo* (bath temperature 50–60°, higher temperatures cause decomposition) there was obtained a residue of white crystalline N,N′-diacetylethylenediamine nitrate weighing 29.5 g. After several recrystallizations from butanone, this substance melted constantly at 120.7–122.6°. It crystallizes in clusters of short heavy needles.

Anal. Calcd. for $C_6H_{13}O_5N_3$: C, 34.78; H, 6.33; NO_3, 29.92. Found: C, 35.05, 34.99; H, 6.57, 6.63; NO_3 (by titration), 29.80.

This nitrate is not hygroscopic, but on standing it decomposes within a few days, as evidenced by a dropping of the m. p.

This salt was also prepared by evaporating to dryness *in vacuo* a mixture of 50 g. of N,N′-diacetylethylenediamine, 75 cc. of water and exactly one equivalent of standardized concentrated nitric acid. The yield of nitrate was 68.8 g. (96%), m. p. 112.5–122.3°. After one crystallization from butanone, this material melted at 120.1–122.6° and gave no depression of m. p. on mixing with the sample isolated from the nitration reaction.

The complex of N,N′-diacetylethylenediamine and zinc chloride was obtained in quantitative yield by mixing equimolar amounts of zinc chloride and N,N′-diacetylethylenediamine in butanone or in acetic anhydride. It is non-hygroscopic and, after crystallization from glacial acetic acid, melts at 185.8–186.6°. The melting point of its mixture with the hygroscopic complex described below is depressed to 164–173.5°.

Anal. Calcd. for $C_6H_{12}O_2N_2{\cdot}ZnCl_2$: C, 25.69; H, 4.31; $ZnCl_2$, 48.59. Found: C, 26.18; H, 4.27; $ZnCl_2$ (by titration of Zn), 48.47.

The hygroscopic complex obtained when N,N′-diacetylethylenediamine nitrate was warmed in acetic anhydride with zinc chloride, crystallized from butanone–alcohol as heavy prisms. Samples recrystallized until the melting point became constant at 187–189° (varying with rate of heating) were analyzed, and the values were C, 27.88; H, 4.72; Zn (by titration), 16.86, 17.02, 16.75; Cl, 7.89, 8.08; NO_3 (with nitron), 18.70, 18.73. The zinc is equivalent to the sum of nitrate and chloride, and the organic portion of the substance, by difference, amounts to 56.4%. This was shown to be N,N′-diacetylethylenediamine by cleavage of the complex with sodium hydroxide and isolation of a quantity of the amide amounting to 54% of the complex. The amide was identified by analysis and by a mixed m. p. with an authentic sample. A complex containing one molecule of amide and one molecule of the mixed salt, $ClZnNO_3$, would contain about 47% amide, and if the ratio of amide to mixed salt were 2:1 the amide content would be about 63%. No other simple combination of amide, zinc, chloride and nitrate gives values in agreement with the values found.

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(3) All melting points are corrected.

Preparation of Cacodyl Chloride

BY BENJAMIN WITTEN

Bunsen[1] prepared cacodyl chloride by treating Cadet's liquid, which is composed chiefly of a mixture of cacodyl and cacodyl oxide,[2] with mercuric chloride and hydrochloric acid. Steinkopf and Mieg[3] prepared cacodyl chloride by reduction of cacodylic acid with hypophosphite in the presence of concentrated hydrochloric acid. They report the boiling point as 106.5–107°. Skinner and Sutton,[4] who prepared cacodyl chloride by this method, report the boiling point as 106–107°. Valeur and Gailliot[5] prepared it by reduction of cacodylic acid with stannous chloride and hydrochloric acid, and list the boiling point as 107°. Lee, Thing and Dehn,[6] who prepared it by Bunsen's method, list the boiling point as 109°.

The advantage of the method of Steinkopf and Mieg or of Valeur and Gailliot, over Bunsen's method is that it eliminates the handling of spontaneously inflammable Cadet's liquid. The method, however, requires oxidation of Cadet's liquid to cacodylic acid and subsequent reduction to cacodyl chloride.

In this paper, there is reported a procedure for preparing cacodyl chloride from potassium acetate and arsenic trioxide without the necessity of isolating the spontaneously inflammable Cadet's liquid, as is required by Bunsen's method, and without the necessity of oxidation to cacodylic acid and subsequent reduction to cacodyl chloride, as is required by the method of Steinkopf and Mieg or of Valeur and Gailliot. It was found that ferric chloride could be substituted for the mercuric chloride used by Bunsen.

Experimental

Cacodyl Chloride.—Into a 2-quart cast-iron retort was placed a mixture of 750 g. of potassium acetate and 750 g. of arsenic trioxide. The retort was connected to a condenser, and then to a receiver consisting of a 2-liter balloon flask into which was introduced a solution of 1000 g. of hydrated ferric chloride dissolved in 500 ml. of concentrated hydrochloric acid. The receiver was cooled in an ice-bath during the run. The distillation was carried out on a sand-bath. Distillation began at a bath temperature of about 300° and was complete after six hours, at which time the bath temperature reached 350–400°. Cadet's liquid which formed during the distillation reacted with the ferric chloride and hydrochloric acid in the receiver to form cacodyl chloride. The resulting ferric chloride mixture in the receiver consisted of a lower brownish-green paste and an upper red liquid layer. After the distillation, the receiver was disconnected from the system, was stoppered, and was allowed to stand overnight.

The residue in the iron pot was disposed of by dissolving it in water which was added slowly to the retort while it was still hot. If the retort were allowed to cool before removing the residue, difficulty was encountered in removing the solid cake which formed.

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(1) Bunsen, *Ann.*, **37**, 1 (1841); Baeyer, *ibid.*, **107**, 257 (1858).

(2) Dehn and Wilcox, *Am. Chem. J.*, **35**, 1 (1906).

(3) Steinkopf and Mieg, *Ber.*, **53**, 1016 (1920); Augur, *Compt. rend.*, **142**, 1152 (1906).

(4) Skinner and Sutton, *Trans. Faraday Soc.*, **40**, 164 (1944).

(5) Valeur and Gailliot, *Bull. Soc. Chim.*, **41**, 1485 (1927).

(6) Dehn, THIS JOURNAL, **45**, 2993 (1923).