CXXXVII.—*The Purification of Acetic Acid. The Estimation of Acetic Anhydride in Acetic Acid.*

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Though the purity of commercial acetic acids has undergone considerable improvement within the last three or four years, it is still found to be necessary to distil from 2% of chromic oxide, as described by Orton and Bradfield (J., 1924, **125**, 960), in order to obtain an acid free from reactive impurities suitable for a medium for the delicate halogenation experiments which are in progress in this laboratory. The resulting stable acetic acid melts, however, some 0·5° lower than the original acid, owing to the formation of water by oxidation of the impurities, and to obtain an acid melting above 16°, the rather tedious and wasteful process of fractionation was resorted to. It is now found that when acetic anhydride equivalent to the water present is added together with the chromic acid, by simple distillation some 85% of a commercial acid melting at, say, 14·5—15·5° can be converted into a stable acid melting at 16·2—16·4°.

It was shown by Orton and M. Jones (J., 1912, **101**, 1708) that, unless a catalyst be present, the hydrolysis of acetic anhydride in glacial acetic acid is a slow process, but that strong acids have a powerful catalytic effect. The chromic acid used in the above process acts as the necessary catalyst so effectively that the distillate contains not more than 5 parts of acetic anhydride per 100,000, an amount which is generally negligible, and gradually falls to zero on keeping.

The following illustrates the method. A commercial acetic acid melted at 14·2°. If distilled from chromic oxide alone, a main fraction melting 0·5° lower, *i.e.*, at 13·7°, would be obtained. If the melting point of the anhydrous acid be taken as 16·6°, and the lowering of the melting point as 0·2° for each 0·1% of water present (de Visser, *Rec. trav. chim.*, 1893, **12**, 101), this would correspond to 1·45 g. of water per 100 g. of acid. To each 100 g. of acid were therefore added 1·45 × 102/18 = 8·22 g. of acetic anhydride, and 2 g. of chromic oxide. The mixture was heated to just below the boiling point for ½ hour, and then distilled, a short still-head being used to prevent traces of chromic acid being carried over as spray. A first fraction of 10—15% was neglected; the remainder, collected as one fraction, melted at 16·2°, had a bromine absorption number of 1·1 (Orton and Bradfield, *loc. cit.*), and, tested as described below, was found to contain 0·0047 g. per cent. of acetic anhydride. An acid purified in this manner which had been standing for 3 months contained no trace of acetic anhydride. It should be noted that if halogen is present in the original acetic acid, chromium will appear in the distillate.

For the rectification of an acid previously distilled from chromic acid alone, distillation in a similar way of a mixture with the theoretical amount of acetic anhydride (no further lowering of melting point of 0·5° being allowed for in this case) together with 0·2 g. per cent. of β-naphthalenesulphonic acid as a catalyst, is equally effective.

A further examination of the effect of possible impurities on the “ absorption ” of chlorine and bromine by acetic acid indicates that the high “ absorption number ” for bromine shown by commercial acids is probably due mainly to formic acid, whilst the presence of 0·15 g. per cent. of acetone causes an appreciable absorption of chlorine. The presence of a manganese salt or of ethyl alcohol has little effect.

The Estimation of Acetic Anhydride in Acetic Acid.—In 1911, Orton and Edwards (J., **99**, 1181) developed a method of estimation of acetic anhydride in acetic acid based on the knowledge that 2 : 4-dichloroaniline is rapidly and completely acetylated by acetic anhydride, whilst, at the ordinary temperature, acetic acid is without action. The method has been modified by Spencer (*J. Assoc. Offic. Agric. Chem.*, 1923, **6**, 493), who used ordinary aniline in place of the 2 : 4-dichloroaniline, and after separation of the aniline and anilide by a method similar to that employed by Orton and Edwards, titrated the anilide, after hydrolysis, with a bromate–bromide solution; and by Calcott, English, and Wilbur (*Ind. Eng. Chem.*, 1925, **17**, 942), who used the dichloroaniline, and titrated the excess with nitrous acid.

In the present modification, 2 : 4-dichloroaniline is added to the acetic acid, containing anhydride, and the excess aniline estimated by titration with bromate–bromide solution, without separation from the anilide formed. To 75 c.c. of the acid to be tested, 10 c.c. of a solution of 2 : 4-dichloroaniline in acetic acid (containing approximately 3 g. in 250 c.c.) were added. Next morning, the solution was diluted with 85 c.c. of water, 10 c.c. of 10% hydrochloric acid were added, and then 10 c.c. of $1{\cdot}862N/10$-bromate–bromide solution. The flask was corked, and potassium iodide added after 5 minutes. 9·60 C.c. of $1{\cdot}005N/20$-thiosulphate were required. In a control, in which 75 c.c. of an acid known to contain no anhydride were used, and the other quantities and the procedure were the same, the titre was 8·43 c.c. of $1{\cdot}005N/20$-thiosulphate. Hence the aniline acetylated is equivalent to $(9{\cdot}60 - 8{\cdot}43) \times 1{\cdot}005$ c.c. of $N/20$-bromine, and the acetic anhydride = 0·004 g. per 100 c.c. (Br_2 equivalent $C_6H_3Cl_2{\cdot}NH_2$).

The method was tested by the titration of the aniline in the presence and the absence of 2 : 4-dichloroacetanilide, and more rigorously by the addition of known quantities of acetic anhydride to acetic acid, and actual estimation thereof. The following results were obtained :

Anhydride (g.) added to 75 c.c. of acid.	Anhydride found.	
	(a).	(b).
0·0955	0·0936	—
0·0478	0·0479	0·0470
0·00955	0·00951	0·00942

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