CLXXIX.—*The Interaction of Bromine with Acetic Anhydride. Part V. Bromination and Chlorination compared* (continued). *Some Properties of Acetic Chloroacetic Anhydride.*

By Herbert Ben Watson and Cecil Edward Gregory.

The results described in Parts II and IV of this series (Orton, Watson, and Hughes, J., 1927, 2458; Watson and Roberts, J., 1928, 2779) indicate that the halogenation of acetic anhydride proceeds by two routes, A and B, as follows :

$$\text{(A)} \qquad CH_3{\cdot}COX + X_2 = CH_2X{\cdot}COX + HX \quad . \quad . \quad (1)$$

$$(CH_3{\cdot}CO)_2O + CH_2X{\cdot}COX \rightleftarrows CH_2X{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 + CH_3{\cdot}COX \quad (2)$$

$$\text{(B)} \qquad (CH_3{\cdot}CO)_2O \rightleftarrows CH_2{:}C(OH){\cdot}O{\cdot}CO{\cdot}CH_3 \quad . \quad . \quad . \quad (3)$$

$$CH_2{:}C(OH){\cdot}O{\cdot}CO{\cdot}CH_3 + X_2 = CH_2X{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 + HX \quad (4)$$

the ultimate products (acyl halide and monohalogenated acid; Gal, *Ann. Chim. Phys.*, 1862, **66**, 187) then being formed by the further reactions

$$(CH_3{\cdot}CO)_2O + HX \rightleftarrows CH_3{\cdot}COX + CH_3{\cdot}CO_2H \quad . \quad (5)$$

$$CH_3{\cdot}CO_2H + CH_2X{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 \rightleftarrows CH_2X{\cdot}CO_2H + (CH_3{\cdot}CO)_2O \quad (6)$$

Section A of this scheme is supported by the results of Brückner (*Z. angew. Chem.*, 1928, **41**, 226), who has isolated, at certain stages of the chlorination of acetic anhydride, fractions having the boiling points of chloroacetyl chloride and acetic chloroacetic anhydride, respectively. Further, the production of acetyl bromide from acetic anhydride and bromoacetyl bromide (equation 2) has already been demonstrated (Part II), and the authors now find that, on distillation of a mixture of acetic anhydride and chloroacetyl chloride, the products are acetyl chloride and either acetic chloroacetic anhydride (b. p. 80—85°/20 mm. Found : Cl, 25·9. Calc. for $CH_2Cl{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3$: Cl, 26%) or chloroacetic anhydride [m. p. 46·5°; compare Bischoff and Walden, *Ber.*, 1894, **27**, 2949. Found : Cl, 41·1. Calc. for $(CH_2Cl{\cdot}CO)_2O$: Cl, 41·5%], depending upon the relative proportions of the reagents.

The halogenation of acetic acid has been shown (Watson, J., 1925, **127**, 2067; 1928, 1137; Part IV of this series) to proceed through the reactions

$$CH_3{\cdot}COX + X_2 = CH_2X{\cdot}COX + HX \quad . \quad . \quad (7)$$

$$CH_2X{\cdot}COX + CH_3{\cdot}CO_2H \rightleftarrows CH_3{\cdot}COX + CH_2X{\cdot}CO_2H \quad (8)$$

any reaction of the halogen with the enolic form of the acid being negligible. In both chlorination and bromination, the introduction of a small quantity of acetic anhydride leads to a rapid reaction *after* an initial period of relatively low but increasing speed; there is no such initial period if an acyl halide is introduced, and the velocity is now proportional to the quantity of acyl halide. These facts leave no doubt that the halogenation proceeds through the halide, and not through the anhydride as suggested by Hentschel (*Ber.*, 1884, **17**, 1286), Shaw (J., 1923, **123**, 2233), and Brückner (*loc. cit.*). The period of increasing velocity clearly represents the time needed for complete conversion of anhydride into acyl halide.

The reaction of acetic acid with one of its halogenated halides (equation 8) has not previously been studied fully, although acetyl bromide has been isolated by one of us (Watson, J., 1928, 1138) by distilling the acid with bromoacetyl bromide. The results described below indicate that reaction 8 occurs in two stages, the mixed anhydride of acetic and halogenated acetic acids being an intermediate product, thus :

$$CH_2X{\cdot}COX + CH_3{\cdot}CO_2H \rightleftarrows CH_2X{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 + HX \quad (9)$$

$$CH_2X{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 + HX \rightleftarrows CH_2X{\cdot}CO_2H + CH_3{\cdot}COX \quad (10)$$

Acetic chloroacetic anhydride was prepared by the method of Anthoine (*Jahresber.*, 1883, 1032), *viz.*, by dropping chloroacetyl chloride into a paste of anhydrous sodium acetate (slight excess) and ether. The reaction mixture was kept cool during the addition, and then refluxed at 100°, and the mixed anhydride was obtained from the ethereal solution as a colourless oil. On heating it decomposed, yielding molecular quantities of acetic anhydride and chloroacetic anhydride (Found : Cl, 41·4%) :

$$2CH_2Cl{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 = (CH_3{\cdot}CO)_2O + (CH_2Cl{\cdot}CO)_2O \quad (11)$$

An analogous decomposition of the corresponding brominated anhydride is reported by Gal (*Z. Chem.*, 1870, 597). When acetic chloroacetic anhydride is refluxed with a molecular proportion of chloroacetic acid, acetic acid and chloroacetic anhydride (Found : Cl, 41·2%) are formed :

$$CH_2Cl{\cdot}CO_2H + CH_2Cl{\cdot}CO{\cdot}O{\cdot}CO{\cdot}CH_3 = CH_3{\cdot}CO_2H + (CH_2Cl{\cdot}CO)_2O \quad (12)$$

Reaction of the mixed anhydride with hydrogen chloride takes place readily at room temperature, the products being acetyl chloride and monochloroacetic acid (Found : Cl, 37·5. Calc. : Cl, 37·6%), as represented in equation 10.

A knowledge of these properties of acetic chloroacetic anhydride renders it easy to understand the reactions which occur when acetic acid and chloroacetyl chloride are heated together. On refluxing molecular quantities of these reagents (120 g. and 225 g.

respectively) at 100°, a considerable amount of hydrogen chloride was evolved (giving a loss in weight of 60 g.), and the following were obtained by fractionation at atmospheric pressure: (*a*) 50 g. of acetyl chloride, distilling at 54°, (*b*) 30 g. at 54—150°, giving on refractionation some acetyl chloride and acetic anhydride but principally acetic acid, (*c*) 70 g. at 150—200°, yielding on redistillation a considerable quantity of acetic acid, and a white solid, m. p. 38—47°, containing 39·6% Cl and consisting of a mixture of chloroacetic acid and its anhydride, (*d*) 135 g. of chloroacetic anhydride (m. p. 45·2°. Found: Cl, 41·3%). The production of large quantities of acetyl chloride, acetic acid, and chloroacetic anhydride, with relatively small amounts of chloroacetic acid and acetic anhydride, may be attributed to the initial formation of acetic chloroacetic anhydride (equation 9), followed by reaction of the mixed anhydride with hydrogen chloride (equation 10) and with chloroacetic acid (equation 12), and to some extent by decomposition into acetic and chloroacetic anhydrides (equation 11). When, after removal of acetyl chloride, the remaining mixture was distilled under reduced pressure, a fraction boiling at 80—85°/20 mm. consisted mainly of acetic chloroacetic anhydride (Found: Cl, 24·9%). It is clear, therefore, that the reaction of chloroacetyl chloride and acetic acid leads, in the first instance, to the formation of acetic chloroacetic anhydride, which may then undergo various other changes according to the experimental conditions. In the chlorination of acetic acid at 100°, the hydrogen chloride present in the system (from reactions 7 and 9) will bring about the conversion of the mixed anhydride into chloroacetic acid and acetyl chloride (equation 10), for this reaction proceeds readily even at room temperature.

The scheme previously put forward to represent the halogenation of acetic acid is thus completely confirmed, with the single modification that reaction (8) may be written in the two stages indicated, for the experimental results lead inevitably to the conclusion that the halogen reacts with the acyl halide, the monohalogenated acid being formed as the result of a reaction between the acid and the substituted halide. This is the only mechanism which is in complete harmony with the results of experiment.

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