CXLIV.—*The Reaction of Bromine with Aliphatic Acids. Part II. The Relative Speeds of Bromination of Acetyl Bromide and Acetyl Chloride.*

By Herbert Ben Watson.

The results of the author's investigation of the bromination of aliphatic acids (Part I; J., 1925, **127**, 2067) and anhydrides (Orton, Watson, and Hughes, J., 1927, 2458) have been interpreted by supposing that in both cases the change proceeds mainly through the acid bromide, the speed of bromination of which is assumed to be proportional to the concentration of the halogen. Such proportionality is indicated by the results of Urech (*Ber.*, 1880, **13**, 1688), and has now been confirmed by an examination of the bromination of acetyl bromide at 25° in an apparatus specially designed to avoid contact of the acid bromide with atmospheric moisture. With the acetyl bromide in excess, the values of $k_1 = 1/t \,.\, \log a/(a—x)$ show a progressive decrease, but constants are obtained if allowance is made for the "fixing" of bromine in the equilibrium $HBr + Br_2 \rightleftarrows HBr_3$ (compare Bugarsky, *Z. physikal. Chem.*, 1901, **38**, 561). The proportionality of the velocity to the concentration of bromine is in harmony with the suggestion (Orton, Watson, and Hughes, *loc. cit.*) that rapid enolisation is followed by a comparatively slow reaction with bromine. Small amounts of ferric chloride or sulphuric acid do not accelerate the reaction, but iodine bromide is a catalyst; confirmation is thus obtained of the view previously expressed that the effect of the two first-named substances on the bromination of acetic anhydride is the result of an acceleration of the enolisation of the anhydride itself.

Bromine reacts with acetyl chloride more slowly than with acetyl bromide. At 25°, with the concentrations employed, the velocity is proportional to the concentration of bromine during the first half of the reaction, extensive perbromide formation being prevented by the reaction $HBr + CH_3{\cdot}COCl = CH_3{\cdot}COBr + HCl$ (Staudinger and Anthes, *Ber.*, 1913, **46**, 1417); the values of k_1 increase, however, as would be expected, when the amount of acetyl bromide becomes considerable. The mechanism of the reaction is probably similar to that suggested for the acid bromide, and the different speeds in the two cases may be attributed to the different "polar effects" of bromine and chlorine (Baker and Ingold, J., 1926, 2466; Ingold, *Chem. and Ind.*, 1926, **45**, 357). The comparatively slow rate of bromination of the acid chloride accounts for its inferiority to the acid bromide as an accelerator of the bromination of acids and anhydrides (compare Part I, p. 2074).

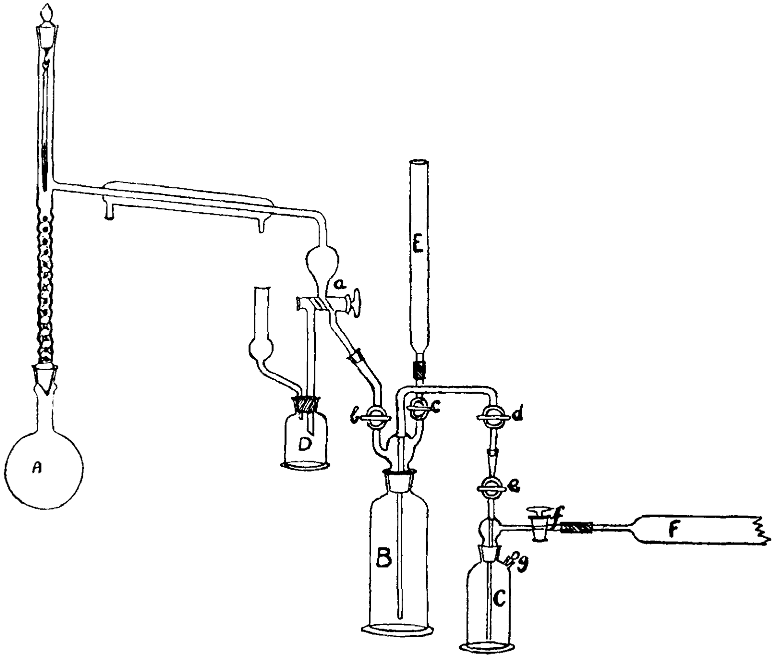
It has now been demonstrated that a carboxylic acid reacts with the bromide of another acid, $R{\cdot}CO_2H + R'{\cdot}COBr = R{\cdot}COBr + R'{\cdot}CO_2H$; on distilling molar quantities of bromoacetyl bromide and acetic acid, the first fraction boiled at 76—78° and gave the analysis of acetyl bromide; further, the freezing point of a solution of the same acid bromide in acetic acid indicated that the greater part had reacted after one hour at 25°.

The observations described above provide further evidence in favour of the scheme put forward in Part I to represent the bromination of acetic acid and its homologues. The possibility of a reaction of bromine with the enolic form of the acid is not excluded, however, but, if such reaction occurs, the slowness of enolisation (compare Orton, Watson, and Hughes, *loc. cit.*) renders it imperceptible when even a small quantity of acid bromide is present (hence constant values of k_1; Part I, p. 2081). In presence of only a trace of the acid bromide, however, such as is probably produced by the introduction of hydrogen bromide (which will also accelerate the enolisation of the acid), the reaction may proceed to an appreciable extent through the enolide.

The vast difference in the speeds of bromination of acids and anhydrides is due mainly to the effect of the medium on the velocity of bromination of the acid bromide; for example, addition of only 1 c.c. of acetic anhydride to 30 c.c. of acetyl bromide results in a great increase in the speed of bromination, whereas at 25° the acid bromide reacts with bromine only slowly in acetic acid solution, and not perceptibly in tetrachloroethane or carbon tetrachloride (compare Ingold and Shoppee, this vol., p. 384). There is thus a complete analogy between the bromination of carboxylic acids and their anhydrides.

EXPERIMENTAL.

The purification and bromination of the acid halides were carried out in the apparatus shown in the figure, which consists of a flask, *A*,



with fractionating column and condenser, a bubbler *B* for collection of the pure halide, and a reaction vessel, *C*, all connexions being made of glass; *a* is a three-way tap, by means of which the distillate may be admitted either to the bubbler, *B*, or to the vessel *D*; when the three-way tap *e* is " closed " the reaction vessel, *C*, is shut off, and liquid allowed to drain away from the tube above *e*. Entry of moisture through the taps *c* and *f* is prevented by the phosphoric oxide tubes *E* and *F*. The thermometer is suspended from a glass hook fused on the glass stopper at the top of the column. The taps may conveniently be lubricated by liquid paraffin. Before the apparatus is used, the flask, *A*, is replaced by a phosphoric oxide tube, and a slow current of air drawn through; the acyl halide is then distilled from *A*, the early and late fractions being delivered into *D* and the pure material into *B*. The desired quantity of liquid is transferred to the reaction vessel, *C*, by blowing dried air through *c*, and the reaction vessel is then disconnected from the remainder of the apparatus and placed in a thermostat at 25°. Bromine is introduced rapidly at *g*. For the purpose of withdrawing measured volumes of the reaction mixture, a ground-in pipette (capacity, 2·01 c.c.) is fitted in the aperture above the tap *e*, this tap is opened, and dried air blown in at *f*; *e* is then closed, the liquid in the pipette is allowed to fall to the mark and then delivered into an excess of aqueous potassium iodide, and the iodine is titrated with *N*/10-thiosulphate. In the tables which follow, time is expressed in minutes and titres in c.c. of *N*/10-thiosulphate.

Acetyl Bromide and Bromine.—The constants are calculated by a method similar to that employed by Bugarsky (*loc. cit.*). If $\{Br_2\}$ and $\{HBr\}$ represent total concentrations, and $[Br_2]$ and $[HBr]$ the concentrations of " unfixed " bromine and hydrogen bromide, then

$$K[HBr_3] = [Br_2][HBr] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\{Br_2\} = [Br_2] + [HBr_3] \quad . \; . \; . \; . \; . \quad (2)$$

$$\{HBr\} = [HBr] + [HBr_3] \quad . \; . \; . \; . \; . \quad (3)$$

With the acetyl bromide in large excess, if a be the initial concentration of bromine, and x the amount of bromine which reacts with the acid bromide in time t, then, from the above equations, the concentration of " unfixed " bromine at time t will be

$$[Br_2] = \tfrac{1}{2}\{\sqrt{(K + 2x - a)^2 + 4K(a - x)} - (K + 2x - a)\},$$

$$\text{and } dx/dt = \frac{k}{2}\left\{\sqrt{(K + 2x - a)^2 + 4K(a - x)} - (K + 2x - a)\right\},$$

which, on integration, becomes

$$k = \frac{1}{2t}\left\{\frac{2(a + K)}{K} \cdot \log_e \frac{2a}{p} - \frac{2a + K}{K} \cdot \log_e \frac{2a + K}{p + K} - \frac{2a - p}{p + K}\right\}$$

$$\text{where } p = \sqrt{(K + 2x - a)^2 - 2K(K + 2x - a) + 2K(a + K)} - (K + 2x - a).$$

Pure AcBr.			AcBr + 0·035*M*-$FeCl_3$.			AcBr + 0·035*M*-H_2SO_4.		
t.	Titre.	*k*.	*t*.	Titre.	*k*.	*t*.	Titre.	*k*.
0	10·00		0	10·90		0	10·30	
60	8·75	0·0023	60	9·60	0·0022	60	9·00	0·0024
120	7·65	0·0024	120	8·40	0·0023	120	7·65	0·0027
240	5·95	0·0023	240	6·80	0·0021	240	6·85	0·0019
360	4·95	0·0024	360	5·60	0·0022	360	5·70	0·0019
540	3·90	0·0023	540	4·55	0·0021	540	4·05	0·0022

The somewhat irregular values of *k* when sulphuric acid is present are doubtless due to side reactions (compare Part I, p. 2070).

AcBr + 0·035*M*-IBr.

t.	Titre.	*k*.
0	10·10	
30	9·10	0·0037
60	8·30	0·0036
120	7·05	0·0033
240	5·50	0·0030
360	4·30	0·0030

AcBr (30 c.c.) + Ac_2O (1 c.c.).

t.	Titre.	*k*.
0	10·35	
60	6·60	0·0085
180	3·20	0·0089
240	2·60	0·0082

Acetyl Chloride and Bromine.—Values of $k_1 = 1/t \,.\, \log a/(a - x)$.

t.	Titre.	*k*.	*t*.	Titre.	*k*.
0	10·45		540	6·55	0·00086
120	9·40	0·00089	720	5·40	0·00092
240	8·50	0·00086	1380	1·20	0·00157
360	7·70	0·00085			

Freezing Point of a Solution of Bromoacetyl Bromide in Acetic Acid.—0·9822 G. of the acid bromide was dissolved in 17·2668 g. of acetic acid of f. p. 16·5°. The theoretical f. p. of the solution if no reaction took place would be 15·4°, and if the acid bromide reacted completely ($CH_2Br\cdot COBr + CH_3\cdot CO_2H = CH_3\cdot COBr + CH_2Br\cdot CO_2H$) it would be 14·4°. Observed f. p.'s were 15·05°, 14·80°, and 14·60° after 15, 30, and 60 minutes, respectively, at 25°. Hence, proportion of acid bromide changed after 60 minutes = 80%.

In conclusion, the author wishes to express his appreciation of Professor Orton's interest in the work, and of a grant from the Chemical Society Research Fund which has largely defrayed the cost.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

[*Received, March* 15*th*, 1928.]