CCCLXVII.—*The Interaction of Bromine with Acetic Anhydride. Part IV. Bromination and Chlorination compared.*

By HERBERT BEN WATSON and EMRYS HADDON ROBERTS.

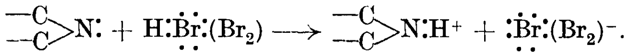
INVESTIGATION of the reactions of chlorine with acetic anhydride, acetyl chloride, and acetic acid has yielded results which indicate that chlorination is in many respects similar to bromination, but nevertheless presents some striking contrasts.

It was shown by Gal (*Ann. Chim. Phys.*, 1862, **66**, 187) that the chlorination of acetic anhydride yields acetyl chloride and monochloroacetic acid, products which are the analogues of those obtained by the action of bromine. The authors now find that the velocity curves resemble in form those obtained by Orton, Watson, and Hughes in bromination experiments (Part II, J., 1927, 2458), and that the reaction is similarly accelerated by acid chlorides, ferric chloride, sulphuric acid, and iodine or iodine chloride. That changes of an identical character take place in the two cases is proved conclusively by the constancy of the values of C obtained by use of the expression $C = 1/t \,.\, \log_e (a + P)/(a + P - x)$, which was deduced by Orton, Watson, and Hughes for bromination. It is clear, therefore, that chlorination, like bromination, proceeds by two routes, involving in the one the halogenation of the acid chloride and in the other the preliminary enolisation of the anhydride.

Chlorine, however, reacts far more slowly than bromine. The values of the constants in Tables II and III leave no doubt that this difference is due entirely to a difference in the speeds of halogenation of the acyl halides, whilst the velocity of enolisation of the anhydride is unaffected.

Quinoline, pyridine, and sodium acetate, which inhibit the bromination of acetic anhydride (Part II), have no similar effect on chlorination; the first-named two, indeed, accelerate somewhat the disappearance of chlorine. The influence of these substances on bromination has been attributed by one of us (Watson, Part III, J., 1927, 3065) to their reaction with a trace of hydrogen bromide produced in the bromination of the enolised anhydride, for by removal of the halogen acid the series of reactions involving the acid bromide will be eliminated, and in addition the speed of enolisation of the anhydride very considerably decreased. The catalytic effect of the base upon the enolisation appears to be but small in comparison with that of halogen acid.

The remarkable difference between bromination and chlorination may find an explanation in the following considerations. Acetic anhydride, in spite of its fairly high dielectric constant, behaves in all respects as a " normal " liquid (compare Jones and Betts, this vol., p. 1178; Jones, *ibid.*, p. 1195). In a medium of this type, the halogen acids are doubtless covalent compounds (compare Sidgwick, " The Electronic Theory of Valency," p. 93), and reaction with the base would consist in the giving up of a proton covalently linked to the halogen. In presence of an excess of bromine, hydrogen bromide exists almost entirely in combination as the perbromide HBr_3; the powerful electron-affinity of the two co-ordinated bromine atoms (Ingold, *Ann. Report*, 1926, 140) will bring about a loosening of the proton, thus enabling its appropriation by the base to take place readily:



$$\begin{matrix}-\mathrm{C}\\-\mathrm{C}\end{matrix}\!>\!\mathrm{N}\!: + \mathrm{H}\!:\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Br}}}\!:\!(\mathrm{Br}_2) \longrightarrow \begin{matrix}-\mathrm{C}\\-\mathrm{C}\end{matrix}\!>\!\mathrm{N}\!:\!\mathrm{H}^{+} + :\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{Br}}}\!:\!(\mathrm{Br}_2)^{-}.$$

An analogy, consisting in the withdrawal of a proton covalently attached to *oxygen*, is found in the production of hydroxo-ammines of cobalt and chromium by the action of pyridine or ammonia on the corresponding aquo-ammines, as exemplified in the reaction $[Cr(NH_3)_2(H_2O)_4]Cl_3 + 2C_5H_5N = [Cr(NH_3)_2(H_2O)_2(OH)_2]Cl + 2C_5H_5N,HCl$ (Werner, *Ber.*, 1907, **40**, 272, 4098, 4113, 4133; Pfeiffer, *ibid.*, p. 3129).

In the case of hydrogen chloride there is but little perhalide formation (compare the relative effects of hydrogen bromide and chloride on the bromination and chlorination, respectively, of acetanilide : Orton and Jones, *Brit. Assoc. Rep.*, 1910, 99); weakening of the covalent bond does not therefore occur, and the base has no opportunity of combining with the proton. The hydrogen chloride is thus free to react with a molar quantity of acetic anhydride : $HCl + (CH_3{\cdot}CO)_2O \rightleftharpoons CH_3{\cdot}COCl + CH_3{\cdot}CO_2H$; the chlorination of the acid chloride then proceeds, and, moreover, the enolisation of the anhydride is catalysed not only by the small quantity of halogen acid present in the above equilibrium but also by the base. Chlorination is therefore not inhibited but accelerated, and the larger the quantity of base introduced the greater is the acceleration.

Acetyl nitrate has been shown to inhibit very powerfully the bromination of acetic anhydride, by oxidation of halogen acid (Parts II and III). As would be expected from the relative indifference of hydrogen chloride to oxidising agents, it does not inhibit chlorination. Addition of a little nitric acid, in fact, accelerates the reaction, an effect which indicates incomplete conversion of the acid into acetyl nitrate.

Chlorination of Acetyl Chloride.—The relatively slow speed of chlorination of acetyl chloride, which is indicated by the experiments described in the foregoing, has been confirmed by an examination of the reaction of chlorine at 25° with the acid chloride itself. Acetyl chloride, in fact, reacts with chlorine more slowly than with bromine (see Table IV). Contrary to expectation, the rate of disappearance of chlorine has been found to *increase* as the reaction proceeds. This peculiarity is not the result of a comparatively rapid substitution of a second hydrogen atom, since chloroacetyl chloride does not react with chlorine appreciably at 25°, but it is due rather to side reactions, which consist, partly at least, in the replacement of the carbonyl oxygen by two atoms of chlorine, followed by further chlorination of the $C_2H_3Cl_3$ to give hexachloroethane, the odour of which is unmistakable in the product (compare the action of phosphorus pentachloride on acetyl chloride : Hübner, *Annalen*, 1861, **120**, 330; Hübner and Müller, *Z. Chem.*, 1870, 328).

Addition of a small quantity of iodine catalyses the production of chloroacetyl chloride so powerfully (compare Jazukowitsch, *Z. Chem.*, 1868, 234) that the side reactions are now imperceptible, and the velocity is proportional to the concentration of chlorine. The side reactions are masked in the same manner when acetyl chloride reacts with chlorine in acetic anhydride medium (preceding section).

Chlorination of Acetic Acid.—A study of the reaction of chlorine with acetic acid at 100° has yielded results resembling those previously obtained by one of us for bromination (Watson, J., 1925, **127**, 2067); the reaction, however, is slower. A powerful acceleration results from the introduction of a small quantity of acetyl chloride, to which the catalytic influence of acetic anhydride (Hentschel, *Ber.*, 1884, **17**, 1286) and also that of phosphorus and phosphorus pentachloride (Brückner, *Z. angew. Chem.*, 1927, **40**, 973) are doubtless to be ascribed (compare the interpretation of the effects of acetic anhydride and phosphorus on bromination: Watson, *loc. cit.*). The velocity is proportional to the quantity of acetyl chloride added, and different acid chlorides have identical effects.

These facts lead to the conclusion that chlorination proceeds through a series of reactions analogous to those suggested for bromination (Watson, *loc. cit.*), *viz.*,

$$CH_3{\cdot}COCl + Cl_2 = CH_2Cl{\cdot}COCl + HCl,$$
$$CH_2Cl{\cdot}COCl + CH_3{\cdot}CO_2H = CH_3{\cdot}COCl + CH_2Cl{\cdot}CO_2H,$$

preceded, when the chloride of another acid is added initially, by

$$R{\cdot}COCl + CH_3{\cdot}CO_2H = CH_3{\cdot}COCl + R{\cdot}CO_2H.$$

In presence of an acid bromide, the velocity of *bromination* of acetic acid has been shown to vary directly as the concentration of the halogen, and this is in harmony with the mechanism suggested. A similar relationship is not found in the analogous case of chlorination in presence of an acid chloride, for the velocity of the reaction decreases less rapidly than does the concentration of chlorine. This observation is accounted for, however, by the existence of the side reactions referred to in the preceding section.

Hydrogen chloride accelerates the chlorination of acetic acid, and its influence is probably due to the production of a trace of acid chloride (compare the effect of hydrogen bromide on bromination: Watson, *loc. cit.*). The powerful enolising agents sulphuric acid and ferric chloride, on the other hand, have very little effect, a fact which indicates that reaction of the halogen with the enolic form of acetic acid occurs only to a very small extent. The part played by the enolide, though insignificant, may perhaps contribute to some extent to the absence (noted above) of a simple relation between the fall in concentration of chlorine and the velocity. In bromination, its effect is masked by the relatively great speed of the reaction of bromine with acetyl bromide, or is perhaps to some extent balanced by perbromide formation.

Inactivity of Iodine.—Iodine does not attack acetic anhydride at 25°, nor does introduction of hydrogen iodide or of sulphuric acid lead to reaction. On heating the anhydride with iodine at 100° for several hours there is little fall in iodine concentration but some carbonisation (compare Gal, *loc. cit.*). No reaction takes place when acetic acid is heated with iodine at 100°.

EXPERIMENTAL.

The acetic anhydride was obtained by fractional distillation of "reagent" material. The acid chlorides and other substances employed were purified as described in the earlier papers of this series. Each reaction mixture (25 c.c.) contained 5 c.c. of a solution of chlorine in carbon tetrachloride; in preparing this solution, chlorine from a cylinder was passed through water, permanganate, and sulphuric acid and then into the solvent. The velocity measurements were carried out at 25° in well-stoppered flasks as described previously, 2 c.c. being withdrawn for each titration. The anhydride was used throughout in large excess. Titres are stated in c.c. of *N*/10-thiosulphate.

TABLE I.

Substance added.	Conc., *M*.	Initial titre.	Fall in titre after (hours) 50.	100.	150.	200.	250.	300.	350.
Nil		9·85	0·55	1·60	2·80	3·95	5·00	5·95	6·85*
Nil		4·90	0·25	0·55	1·00	1·40	1·95	2·55	3·10†
CH_3·COCl ...	0·112	11·15	1·20	2·30	3·40	4·60			
CH_3·COCl ...	0·225	11·30	2·15	3·90	5·60				
C_6H_5·COCl ...	0·225	12·05	1·80	3·75	5·60				
C_5H_5N	0·010	9·10	1·80	3·20	4·30	5·10	5·60		
C_9H_7N	0·008	12·80	2·50	4·70	6·75	8·05	8·95		
HNO_3	0·015	8·20	1·50	3·05	3·95	4·65	5·05	5·20	
CH_3·CO_2Na...	0·005	11·35	0·80	1·80	2·75	3·70	4·60	5·45	6·35‡

The fall in titre after 450 hours was 8·05*, 3·85†, and 7·75‡.

Substance added.	Conc., *M*.	Initial titre.	Fall in titre after (mins.) 15.	30.	45.	60.	90.	120.	240.
C_5H_5N	0·118	11·50	3·90	5·75	6·65	7·25	8·00	8·30	8·85
C_9H_7N	0·100	11·00	1·35	2·25	2·80	3·15	3·65	4·00	4·90
H_2SO_4	0·001	11·05	0·40	0·80	1·25	1·75	2·60	3·55	7·05
H_2SO_4	0·002	11·05	0·60	1·35	2·15	2·85	4·25	5·65	10·55
Iodine	0·003	9·85	0·35	0·80	1·60	2·50	4·65	8·25	
Iodine	0·006	9·75	0·60	1·60	3·40	5·20	9·10		

Substance added.	Conc., *M*.	Initial titre.	Fall in titre after (mins.) 5.	10.	15.	20.
ICl	0·003	10·55	2·00	5·05	7·05	9·00
ICl	0·006	9·20	3·30	5·70	7·05	
$FeCl_3$	0·003	9·85	0·40	1·90	3·50	5·50
$FeCl_3$	0·007	9·90	2·05	6·35	Gone	

The reaction of bromine with acetic anhydride at 25°, when carried out under the same conditions as the above (5 c.c. of carbon tetrachloride in 25 c.c. of reaction mixture), gave the following:

Initial titre.	Fall in titre after (hours) 1.	2.	3.	4.	5.
11·60	0·75	3·10	6·05	8·40	10·50

Comparison with the figures recorded in Part II for the bromination of pure acetic anhydride shows the very marked retardation produced by the carbon tetrachloride (compare Watson, this vol., p. 1138).

Reaction of Halogens with Acetic Anhydride and Excess of Acyl Halide.—As in the above experiments, 25 c.c. of reaction mixture contained 5 c.c. of a solution of the halogen in carbon tetrachloride. Titres are stated in c.c. of $N/50$-thiosulphate, and time in minutes. The constants are calculated from the formula $C = 1/t \,.\, \log_e (a + P)/(a + P - x)$ (Part II), where $C = k$[acyl halide] and $C' = k'[Ac_2O]$, k and k' being the velocity coefficients for the halogenation of the acyl halide and the enolisation of the anhydride, respectively, and $P = C'/C$.

TABLE II.

Chlorine and Excess of Acetic Anhydride and Acetyl Chloride.

$[Ac_2O] = 6{\cdot}376M$, $[AcCl] = 2{\cdot}915M$, $P = 1{\cdot}10$.

$a = 0{\cdot}1215M$.			$a = 0{\cdot}0344M$.		
Time.	Titre.	C.	Time.	Titre.	C.
0	24·30		0	6·88	
120	21·10	0·000106	60	5·48	0·000097
200	19·40	0·000104	125	3·92	0·000102
395	14·50	0·000104	152	3·20	0·000106
600	9·50	0·000104	185	2·45	0·000106
660	8·10	0·000104	240	1·18	0·000106
	Mean	0·000104		Mean	0·000104

$k = 0{\cdot}0000357$, $C' = 0{\cdot}0001144$, $k' = 0{\cdot}0000179$.

TABLE III.

Bromine and Excess of Acetic Anhydride and Acetyl Bromide.

(These experiments differ from those of Orton, Watson, and Hughes in Part II, in that 5 c.c. of carbon tetrachloride were present in each 25 c.c. of reaction mixture.)

$[Ac_2O] = 6{\cdot}245M$, $[AcBr] = 2{\cdot}932M$, $P = 0{\cdot}0029$.

$a = 0{\cdot}1138M$.			$a = 0{\cdot}0454M$.		
Time.	Titre.	C.	Time.	Titre.	C.
0	22·75		0	9·08	
20	10·25	0·0384	10	6·08	0·0373
32	6·28	0·0382	15	4·78	0·0391
40	4·05	0·0403	20	3·82	0·0391
	Mean	0·0390		Mean	0·0385

$k = 0{\cdot}0132$, $C' = 0{\cdot}0001125$, $k' = 0{\cdot}0000180$.

The values of k' are in excellent agreement in the two sets of experiments.

Chlorination of Acetyl Chloride.—The distillation of the acid chloride and the velocity measurements (for which 5 c.c. of the solution of chlorine in carbon tetrachloride were added to 25 c.c. of acetyl chloride) were carried out in the apparatus described by one of us (Watson, this vol., p. 1139). The acetyl chloride was throughout in large excess. The velocity of bromination under identical conditions is given for comparison. Titres are expressed in c.c. of $N/10$-thiosulphate.

TABLE IV.

25 c.c. AcCl + 5 c.c. soln. of Cl in CCl_4.		25 c.c. AcCl + 5 c.c. soln. of Br in CCl_4.		25 c.c. AcCl + 5 c.c. soln. of Cl in CCl_4 + 0·03M-iodine.		
Time (hrs.).	Titre.	Time (hrs.).	Titre.	Time (mins.).	Titre.	k_1.
0	12·25	0	12·00	0	7·95	
12	10·10	6	9·85	30	5·65	0·0114
24	7·55	12	7·85	60	4·05	0·0112
36	4·60	18	5·85	90	2·85	0·0114
48	1·45	24	4·40			
		30	2·70			

Chlorination of Acetic Acid.—The acetic acid was purified by the method of Orton and Bradfield (J., 1927, 983). It melted at 16·45°, was stable to halogens at the ordinary temperature, and gave results identical with those obtained by use of the best Kahlbaum acid. A solution of chlorine in this acid was used in making up the reaction mixtures, which were heated in sealed tubes at 100° in portions of 2 c.c. The acetic acid was throughout in large excess. Titres are stated in c.c. of $N/10$-thiosulphate.

TABLE V.

	Titre of 2 c.c.			
Time (hrs.).	Pure $CH_3{\cdot}CO_2H$.	Pure $CH_3{\cdot}CO_2H$.	$CH_3{\cdot}CO_2H$ + 0·19M-H_2SO_4.	$CH_3{\cdot}CO_2H$ + 0·045M-$FeCl_3$.
0	17·95	9·68	9·38	8·02
2	15·42	7·70	6·90	5·82
4	14·08	5·88	4·25	3·52
6	12·12	3·68	2·00	1·85
8	8·62	1·72	0·70	0·50
10	4·20	0·38		

	Titre of 2 c.c.	
Time (mins.).	$CH_3{\cdot}CO_2H$ + 0·24M-HCl.	$CH_3{\cdot}CO_2H$ + 0·56M-HCl.
0	8·82	8·80
45	7·05	6·42
90	5·65	4·42
180	3·00	1·65
240	1·48	0·60

Substance added.	Conc., M (=C).	Titre after (mins.)						First value of k_1.	k_1/C.
		0.	5.	10.	15.	20.	30.		
$CH_3{\cdot}COCl$ ...	0·093	8·98	7·05	4·98	3·20	1·42		0·048	0·51
$CH_2Cl{\cdot}COCl$	0·070	8·40	7·00	5·82	4·58	3·20		0·035	0·50
$C_6H_5{\cdot}COCl$ ...	0·079	8·32	6·90	5·50	3·92	2·48		0·037	0·47
$CH_3{\cdot}COCl$ ...	0·052	8·80		6·75		5·22	2·92*	0·026	0·50
$CH_2Cl{\cdot}COCl$	0·054	10·15		7·70		5·45	2·95†	0·027	0·51
$C_6H_5{\cdot}COCl$ ...	0·052	10·52		8·22		5·82	3·21‡	0·025	0·48

The titre after 40 mins. was 1·00*, 1·15†, and 2·10‡.

Our best thanks are due to Professor Orton, F.R.S., for his continued interest in the work, and to the Chemical Society for a grant by which the cost of the materials has been largely defrayed.

UNIVERSITY COLLEGE OF NORTH WALES,
BANGOR.

[*Received, September* 11*th*, 1928.]