CCCCVI.—*The Interaction of Bromine with Acetic Anhydride. Part III. Arrest of the Reaction. A Comparison with the Bromination of Acetone.*

By Herbert Ben Watson.

The powerful negative catalytic effect of quinoline and the less marked influence of certain other basic substances on the bromination of acetic anhydride have been referred to in Part II (this vol., p. 2458). The author finds that the reaction of bromine with acetone can be arrested in a similar manner. When bromine is added to acetone in carbon tetrachloride at 25°, no measurable reaction occurs for a short time; the disappearance of bromine then becomes perceptible, and almost immediately attains great speed, owing to the very powerful catalytic effect (Meyer, *Annalen*, 1911, **380**, 238) of hydrogen bromide upon enolisation in non-ionising solvents. Addition of a trace of quinoline arrests the reaction during a long period, and it seems simplest to suggest that the arrest is due to removal of hydrogen bromide as the hydrobromide (or hydrobromide perbromide, Grimaux, *Bull. Soc. chim.*, 1882, **38**, 124; Trowbridge, *J. Amer. Chem. Soc.*, 1899, **21**, 66) of the base. The well-known inhibition, by certain nitrogen-containing compounds, of gaseous photochemical reactions has been interpreted in terms of the energetics of the system (Chapman and MacMahon, J., 1909, **95**, 1718; 1910, **97**, 847) and of surface phenomena (Norrish, J., 1925, **127**, 2319), but the view here put forward of the influence of quinoline on a reaction which takes place in the liquid phase and in the dark appears to account for the observed facts.

A similar interpretation may be applied to the case of acetic anhydride, and is rendered the more probable by the fact that quinoline is without effect in presence of 1·6 equivalents of sulphuric acid. The reaction of the base with the halogen acid produced in the bromination of the enolised anhydride will prevent the formation of any appreciable quantity of acetyl bromide (or any acetyl bromide formed may be converted into an additive compound with quinoline; Dehn, *J. Amer. Chem. Soc.*, 1912, **34**, 1408); the main series of reactions, involving the bromination of the acid bromide, is thus eliminated until sufficient hydrogen bromide has been formed (in the slow change through the enolised anhydride) to react with the whole of the base. Moreover, removal by the quinoline of the greater part of the hydrogen bromide normally present in the equilibrium $(CH_3{\cdot}CO)_2O + HBr \rightleftharpoons CH_3{\cdot}CO_2H + CH_3{\cdot}COBr$ (Part II, p. 2459) renders the enolisation of the anhydride so slow as to be imperceptible; the values of k' given in Part II refer to the rate of enolisation in presence of this hydrogen bromide. The prolonged period of inertness is thus explained. The shorter duration of this period in presence of pyridine, *iso*quinoline, triethylamine, or dimethylaniline may be attributed to a larger amount of hydrogen bromide present in equilibrium with the base and its hydrobromide, $B,HBr \rightleftharpoons B + HBr$. The relatively feeble effect of aliphatic primary and secondary amines is to be expected, since they can be acetylated by the anhydride, as is also the complete inactivity (and even slight accelerating influence) of aniline and monomethylaniline, which are not only acetylated, but also substituted in the benzene nucleus, hydrogen bromide being evolved.

The effect of acetyl nitrate (Part II) also may be ascribed to the removal of hydrogen bromide (and perhaps of acetyl bromide), with consequent elimination of the main series of reactions and the rendering of the enolisation of the anhydride imperceptibly slow. That the removal is here due to oxidation is indicated by a considerable liberation of bromine when acetyl bromide is added to acetic anhydride containing nitric acid. Addition of 4 mols. of acetyl bromide per mol. of nitric acid completely annuls the effect of the latter, while on further addition of the acid bromide the disappearance of bromine is accelerated in the normal manner. Acetyl nitrate also retards the bromination of acetone, but does not arrest the reaction completely, as quinoline does. Nitric acid, on the other hand, shortens the time needed for the reaction to become perceptible (compare Lapworth, J., 1904, **85**, 31).

The arrests referred to in Part II may be attributed, in general, therefore, to the removal of hydrogen bromide (and perhaps sometimes of acetyl bromide) as a consequence of either the basic or the oxidising quality of the inhibitor.

EXPERIMENTAL.

Bromination of Acetone in Carbon Tetrachloride.—The carbon tetrachloride was shaken with aqueous sodium hydroxide and then with water, dried, and fractionated. Acetone, purified by the sodium iodide method, was dried over calcium chloride and fractionated. The quinoline was dried over solid potassium hydroxide and fractionated, and the nitric acid was distilled from sulphuric acid and freed from nitrous acid by passage of carbon dioxide. The velocity determinations were carried out by withdrawal at intervals of 2 c.c. of the reaction mixture, addition to aqueous potassium iodide, and titration of the iodine. In Table I, titres are expressed as c.c. of *N*/50-thiosulphate.

TABLE I.

Acetone = 0·218*M*.

Time (mins.).	Titre.
0	14·48
9	14·48
10	14·42
10·5	14·32
11	13·98
11·5	0

Acetone = 0·218*M*.
HNO_3 = 0·025*M*.

Time (mins.).	Titre.
0	12·48
5	12·48
7	0

Acetone = 0·109*M*.

Time (mins.).	Titre.
0	13·98
10	13·92
12	13·88
13	13·85
14	13·60
15	0

Acetone = 0·218*M*.
Quinoline = 0·003*M*.

Time (hrs.).	Titre.
0	12·58
164	12·55
222	12·45
232	0

Acetone = 0·218*M*.
HNO_3 = 0·025*M*.
Ac_2O = 0·030*M*.

Time (hrs.).	Titre.
0	12·48
1	12·32
7·5	11·62
22·5	10·05
31	9·32
46	8·05
70	5·95
119	3·75
166	1·62

Bromination of Acetic Anhydride.—Purification of materials and experimental procedure were as described in Part II. Titres in Table II are expressed as c.c. of *N*/10-thiosulphate. Reactions I(d) and II(b) are identical with the reaction of bromine with pure acetic anhydride.

TABLE II.

I. Effect of quinoline and sulphuric acid in conjunction; quinoline = 0·0064*M*.

	Ratio, $\frac{1}{2}H_2SO_4/C_9H_7N$.	Initial titre.	Fall in titre after (mins.) 10.	20.	30.	40.	50.	60.
(a)	1·01	10·35	0	0	0	0	0	0
(b)	1·27	10·15	0	0	0·02	0·60	1·55	3·00
(c)	1·48	9·95	0·05	0·60	1·88	3·30	4·60	5·85
(d)	1·62	10·22	0·20	1·58	2·92	4·38	5·75	7·08
(e)	1·82	10·52	0·82	2·20	3·82	5·45	6·75	8·10

II. Effect of nitric acid and acetyl bromide in conjunction; HNO_3 = 0·0032*M*.

	Ratio, $AcBr/HNO_3$.	Initial titre.	Fall in titre after (mins.) 15.	30.	45.	60.	75.	90.
(a)	2·0	10·75	0	0	0	0	0	0
(b)	4·3	10·70	0·72	2·55	4·68	6·72	8·18	9·10
(c)	7·3	11·15	0·75	4·10	6·60	8·22	9·32	9·95
(d)	13·4	10·75	2·32	5·30	7·30	8·68	9·60	—

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