

90. *Acid-Base Catalysis in Non-aqueous Solvents. Part XI. The Halogenation of Acetone by Various N-Halogen Compounds in Chlorobenzene Solution at 50°.*

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Kinetic measurements have been made on the halogenation of acetone by three *N*-halogen compounds in chlorobenzene solution at 50°. The reaction is catalysed by acid and has an order between zero and unity with respect to the halogenating agent. A mechanism is proposed in which the acid catalyses the conversion of acetone into the enol form, and the enol is then halogenated, the two stages having comparable speeds. The experimental results agree quantitatively with this mechanism. It is shown that the reaction cannot involve acyl hypohalite as a halogenating reagent, as has been proposed by Israel, Tuck, and Soper (*J.*, 1945, 547) for some similar reactions.

REACTION with halogens has been widely used as a means of studying the prototropy of ketones and similar substances in aqueous solutions, the reactions being normally of zero order with

respect to halogen and catalysed by acids and bases. It is not possible to extend this method directly to non-dissociating solvents, since the halogen acids produced by halogenation act as immensely powerful catalysts (much more so than the hydrogen ions into which they are converted in aqueous solution). As a result the reaction becomes highly autocatalytic and even explosive in character. It was thought that the use of *N*-halogen compounds as halogenating agents might obviate these difficulties, since they bring about halogenation without the liberation of halogen acid. The present paper deals with the acid-catalysed halogenation of acetone in chlorobenzene solution.

EXPERIMENTAL.

Materials.—Acetone was purified through the sodium iodide compound. Chlorobenzene was dried over phosphoric oxide and redistilled. Monochloroacetic acid was an "AnalaR" product dried over calcium chloride in a desiccator.

It was necessary that the *N*-halogen compounds used should be stable, soluble, and free from basic or acidic groups. The three following compounds were finally selected, the percentage purities given referring to the quantity of iodine liberated from acidified potassium iodide solution. *N*:2:4-Trichlorobenzanilide (I) was recrystallised twice from hexane, m. p. 86°, 99.7% pure; *NN'*-dichloro-*NN'*-di-(2:4:6-trichlorophenyl)urea (II) had m. p. 190° (decomp.), 99.2% pure; *N*-bromophthalimide (III) was recrystallised twice from benzene; m. p. 206°, 98.1% pure.

Kinetic Measurements.—The course of the reaction was followed by running samples of the reaction mixture into acid potassium iodide solution and titrating the liberated iodine. Preliminary experiments showed a fall in titre in solutions containing acetone, monochloroacetic acid, and *N*-halogen compound, but no such fall in solutions containing *N*-halogen compound together with acetone or monochloroacetic acid singly. Since acetone was always present in large excess, it was difficult to identify halogenated acetones, but the fate of the *N*-halogen compound could be determined by pouring into water and examining the solid precipitated. For example, a solution of (I) in excess of acetone gave after complete reaction an almost quantitative yield of white solid, m. p. 115°, undepressed by an authentic specimen of 2:4-dichlorobenzanilide. This confirms the fact that the reaction consists of the halogenation of the acetone rather than its condensation with the *N*-halogen compound.

The measurements were carried out at 50° in reaction vessels of the type previously described (Bell and Levinge, *Proc. Roy. Soc.*, 1935, 151, A, 211) covered with tin-foil. Preliminary experiments showed that the reaction velocity is approximately proportional to the acetone concentration, and all the experiments recorded here refer to a fixed acetone concentration of 1.23M. Weighed samples of about 1 g. were taken, and the liberated iodine titrated with *N*/80-thiosulphate (micro-burette). Saturation of the chlorobenzene solution with water was found to have no effect on the reaction velocities, and no special precautions were therefore taken to exclude moisture.

The plots of titre against time were linear over a considerable part of their course, but approximated to a first-order change towards the end. Examples are given in Fig. 1. The tables below give, for each reaction, x_0 , the initial concentration of *N*-halogen compound (in g.-equiv. of oxidising power per l.); the initial slope *s* (in g.-equiv. l.⁻¹ hr.⁻¹), taken from the linear part of the plot; and $t_{\frac{1}{2}}$, the time (in hours) required to reduce the concentration of *N*-halogen compound to one half. Only a few experiments were done with compound (III): these gave results almost identical with those for (I), and have therefore not been recorded.

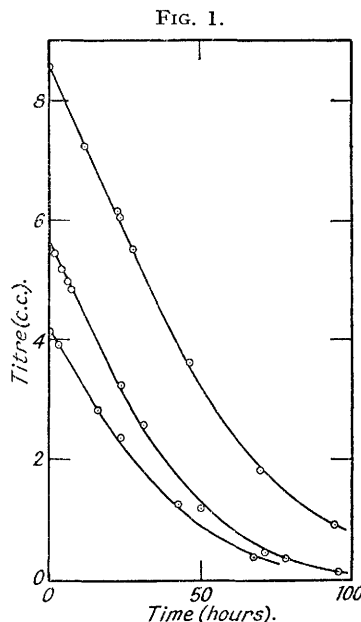


FIG. 1.

Compound (I).

$[CH_2Cl \cdot CO_2H] = 0.0072$.

100 x_0	2.22	5.00	5.68	7.60	10.14	15.12
10 ⁴ <i>s</i>	3.54	6.08	6.39	7.42	7.69	8.66
$t_{\frac{1}{2}}$	32.0	41.0	44.5	51.0	63.0	87.5

$[CH_2Cl \cdot CO_2H] = 0.0138$.

100 x_0	0.85	1.47	3.01	4.58	6.18	7.11	9.47	13.30	15.67
10 ⁴ <i>s</i>	2.83	3.11	6.21	8.71	11.1	9.41	11.4	13.8	14.9
$t_{\frac{1}{2}}$	19.5	23.4	24.2	27.0	28.0	38.2	41.5	48.0	52.5

Compound (II).

$[CH_2Cl \cdot CO_2H] = 0.0072$.

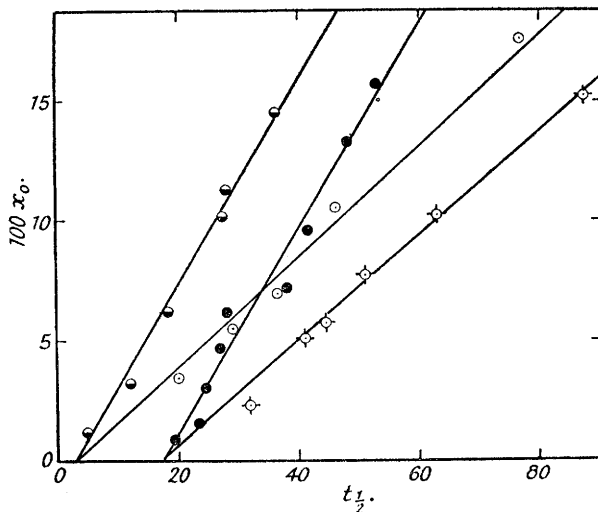
100 x_0	3.37	5.46	6.90	10.45	17.55
10 ⁴ <i>s</i>	7.6	9.4	9.5	11.4	11.7
$t_{\frac{1}{2}}$	20.0	29.0	36.5	46.0	76.0

		[CH ₂ Cl-CO ₂ H] = 0.0138.				
100x ₀	1.28	3.26	6.16	10.11	11.32	14.54
10 ⁴ s	11.6	13.4	16.5	18.4	20.5	20.5
t _{1/2}	4.9	12.2	18.5	27.5	28.0	36.1

DISCUSSION.

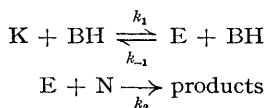
The halogenation of acetone under our conditions is clearly catalysed by acids, but the reaction is not of zero order with respect to the halogenating agent. The shape of the curves in Fig. 1 and the variation of *s* and *t*_{1/2} with the initial concentrations of (I) and (II) suggest a reaction order intermediate between unity and zero. This can be explained by supposing that the acetone is first enolised in presence of the acid catalyst, and the enol then halogenated by the

FIG. 2.



◇ = Compound I, 0.0072 M-acid. ⊙ = Compound II, 0.0072 M-acid.
 ● = " " 0.0138 M-acid ⊖ = " " 0.0138 M-acid.

N-halogen compound, the two steps being of comparable rates. Schematically if K and E represent the keto- and the enol form of acetone, N the *N*-chloro-compound, and BH the acid, then



giving for a stationary concentration of E

$$-\frac{d[N]}{dt} = \frac{k_1 k_2 [K][BH][N]}{k_{-1}[BH] + k_2[N]} \dots \dots \dots (1)$$

During the course of a given reaction [BH] is constant and [K] sensibly so; hence this equation can be integrated. Writing [N] = *x* this gives

$$t = \alpha \log x_0/x + \beta(x_0 - x) \dots \dots \dots (2)$$

and in particular

$$t_{1/2} = \alpha \log 2 + \frac{1}{2}\beta x_0 \dots \dots \dots (3)$$

where $\alpha = k_{-1}/k_1 k_2 [K]$, $\beta = 1/k_1 [K][BH]$. The value of [K] was the same in all our experiments: hence in a series of experiments with the same *N*-halogen compound and the same acid concentration, the plot of *t*_{1/2} against *x*₀ should give a straight line. Fig. 2 shows four such plots for the four series in the table. Moreover, since k_{-1}/k_1 is independent of the nature or concentration of the catalyst, the intercept $\alpha \log 2$ of these lines on the *t* axis should depend only on the nature of the *N*-halogen compound, and the slopes $\frac{1}{2}\beta$ should depend only on the acid concentration. Both of these points are confirmed by the plots in Fig. 2. Finally, the slopes

should be inversely proportional to the acid concentration; the ratio of the slopes for the two sets of lines in Fig. 2 is 1.93, exactly equal to the inverse ratio of the two acid concentrations.

A similar test may be made in terms of the initial rates. Equation (1) gives

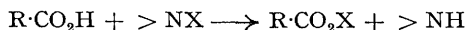
$$1/s = \alpha/x_0 + \beta \quad \dots \quad (4)$$

leading to plots of $1/s$ against $1/x_0$ similar to those in Fig. 2.

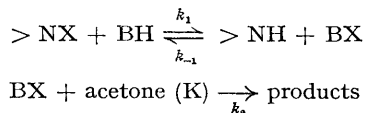
We can also investigate whether the course of individual reactions corresponds to equation (2), using the values of α and β derived from Fig. 2. Fig. 3 shows plots of $\alpha \log x + \beta x$ against t for four typical experiments, with the scales displaced vertically for convenience. The slopes of the lines drawn are 0.98, 0.92, 1.10, and 1.06, compared with the theoretical values of unity.

The experimental data therefore accord well with the reaction scheme proposed, *i.e.*, an acid-catalysed enolization followed by halogenation of the enol. The relative reactivities of the two compounds (I) and (II) are proportional to the corresponding values of k_2 or $1/\alpha$, showing that (II) is about 4.4 times as reactive as (I), after allowing for the fact that (II) has two reactive chlorine atoms. The rate of enolization is measured by $1/\beta$ [*i.e.*, the limiting halogenation rate for an infinitely large value of x_0 : cf. equation (4)], which is of course the same for both *N*-halogen compounds. For 0.0138M-monochloroacetic acid this rate works out at 1.07×10^{-3} mole of acetone/l./hour, in a solution containing 1.23M-acetone. Referred to unit concentrations of acid and acetone, this gives $k_1 = 0.063$ mole/l./hour for the catalytic constant of monochloroacetic acid for the enolization of acetone at 50°. It is of interest to note that this is identical with the value extrapolated from the data of Smith (*J.*, 1934, 1744) at 0° and 25° for the same catalytic constant in aqueous solution. On purely electrostatic grounds the value in chlorobenzene would be expected to be lower than that in water, but the position is likely to be complicated by the association of the carboxylic acid group with itself or with water (cf. Bell, "Acid-Base Catalysis", p. 112, Oxford 1941).

Israel, Tuck, and Soper (*J.*, 1945, 547) have recently investigated the halogenation of anisole and its derivatives by various *N*-bromo-compounds. They find that bromination does not take place unless acetic acid is added to the solution, whereupon the reaction velocity is found to be independent of the nature and concentration of the anisole, but depends on the concentrations of acid and of *N*-bromo-compound. This is interpreted by supposing that the halogenating agent is the acyl hypohalite, the rate-determining step being the reaction



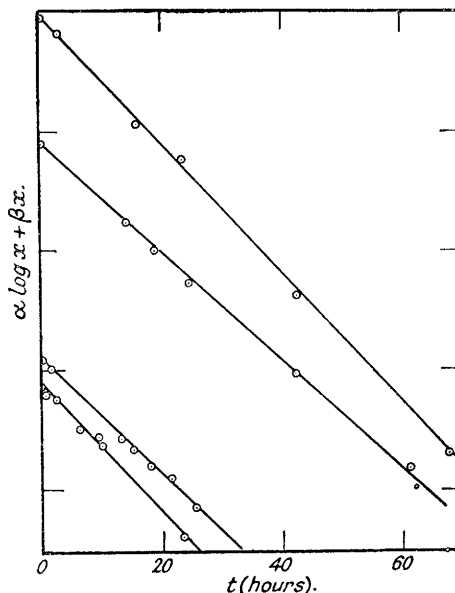
This step cannot be solely rate-determining in our work, since the reaction velocity was found to depend on the acetone concentration. It might, however, be suggested that the rôle of the acid is to form acyl hypohalite, and not to catalyse the formation of enol from the acetone. The reaction scheme then becomes



BX is the acyl hypohalite, which may be assumed to react either with the keto-form of acetone, or with the enol in equilibrium with it. The condition for a stationary concentration of BX gives

$$-\frac{dx}{dt} = \frac{k_1 k_2 x [BH][K]}{k_{-1}(x_0 - x) + k_2 [K]} \quad \dots \quad (5)$$

FIG. 3.



and on integration

$$t = (\alpha x_0 + \beta) \log x_0/x - \alpha(x_0 - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$t_{\frac{1}{2}} = (\alpha x_0 + \beta) \log 2 - \frac{1}{2}\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where

$$\alpha = k_{-1}/k_1 k_2 [\text{BH}][\text{K}], \quad \beta = 1/k_1 [\text{BH}].$$

Like equation (3), (7) predicts that for a given *N*-halogen compound and a given acid concentration the plot of $t_{\frac{1}{2}}$ against x_0 should give a straight line of slope inversely proportional to the acid concentration. However, since k_1 , k_{-1} , and k_2 now all depend on the nature of $> \text{NX}$, different halogenating agents should give different slopes, in contradiction to equation (3) and to experiment. Moreover, equation (7) predicts an intercept $\alpha \log 2 - \frac{1}{2}\beta$ inversely proportional to the acid concentration, while experiment gives intercepts independent of acid concentration, as demanded by equation (3). It is clear, therefore, that our results are not consistent with a reaction scheme in which the acid serves solely as a source of acyl hypohalite. There still remains the possibility that it acts both as an acid catalyst for enolisation and as a source of acyl hypohalite. However, if this were so, the velocity for low concentrations of *N*-halogen compound $> \text{NX}$ (where the halogenation rate largely determines the observed velocity) should be decreased by adding an excess of the compound $> \text{NH}$, owing to repression of the reaction $> \text{NX} + \text{R}\cdot\text{CO}_2\text{H} \rightleftharpoons \text{R}\cdot\text{CO}_2\text{X} + > \text{NH}$. In order to test this, a 20-fold excess of 2:4-dichlorobenzanilide was added in an experiment with 0.007*N-N*:2:4-trichlorobenzanilide. The result was to increase the velocity threefold, probably because of basic catalysis by the $> \text{NH}$ group. It therefore seems very improbable that acyl hypohalite plays any part in the reaction.

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