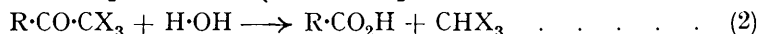


**409.** *An Electrometric Study of Dilute Aqueous Solutions of Halogenated Ketones.*

By E. G. EDWARDS, D. P. EVANS, and H. B. WATSON.

An examination of dilute aqueous solutions of several halogenated acetones, using the glass electrode and a silver-silver halide electrode, has given results which indicate that the acidity of these solutions, first observed by Watson and Yates in 1932, is due to hydrolysis of the ketone. Either the replacement of halogen by hydroxyl or the production of haloform may predominate, or both may occur simultaneously. The structural conditions which facilitate haloform formation are discussed.

Two suggestions have been advanced to interpret the acidic reaction observed by Watson and Yates (J., 1932, 1214) in dilute aqueous solutions of halogenated acetones, ionisation of hydrogen resulting from (a) the change  $>\text{CH}\cdot\overset{\ominus}{\text{C}}\text{O} \longrightarrow >\overset{\oplus}{\text{C}}\cdot\overset{\ominus}{\text{C}}\text{O} + \overset{\oplus}{\text{H}}$  (*loc. cit.*, p. 1209), or (b) the co-ordination of hydroxyl ion at carbonyl carbon (Watson, Nathan, and Laurie, *J. Chem. Physics*, 1935, 3, 170):  $>\text{CH}\cdot\overset{\curvearrowright}{\underset{\text{O}}{\text{C}}} + \text{H}_2\text{O} \longrightarrow >\text{CH}\cdot\overset{\text{O}^{\ominus}}{\underset{\text{OH}}{\text{C}}} + \text{H}^{\oplus}$ . Further investigation, however, has revealed the presence of halide ions in the solutions, and of chloroform in aqueous solutions of hexachloroacetone. These discoveries suggested that the observed acidity was to be ascribed, not to the ionisation of the ketones, but to hydrolysis, either of the "alkyl halide type" (1) or of the "haloform type" (2):



Reaction (1) is reversible as shown by the decrease in concentration of halide ion when sulphuric or nitric acid is added. When water is in excess, the velocity of change is therefore represented by the equation  $dx/dt = k_1(a - x) - k_2x^2$ , but in the cases examined the extent of the hydrolysis was so small that the results were not suited to mathematical treatment. The reaction is characterised, however, by the equality of the concentrations of hydrogen and halide ions.

No halogen acid is produced in reaction (2), but even if this reaction occurs alone in solutions of ketones such as pentachloro-, hexachloro-, or *as*-tetrabromo-acetones, halide ions are likely to appear owing to the further hydrolysis of the halogenated acetic acid. The haloform cleavage takes place readily in presence of bases (*e.g.*, OH', OAc');  $\omega\omega\omega$ -trichloroacetophenone, for example, may be heated with water for 7 hours at 170° without any apparent change, but chloroform is liberated immediately on addition of a drop of potassium hydroxide (Houben and Fischer, *Ber.*, 1931, **64**, 2636). The velocity of reaction (2) may therefore be written  $dx/dt = k[\text{ketone}][\text{OH}'] = k'[\text{ketone}]/[\text{H}'] = k'(a - x)/x$  (complete ionisation of the halogenated acetic acid being assumed in the dilute solutions employed), which gives on integration

$$kt = a \log[a/(a - x)] - x \quad . \quad . \quad . \quad (3)$$

For  $x = a/2$ ,  $t$  is proportional to  $a$ , *i.e.*, the half-period ( $t_{1/2}$ ) varies directly as the initial concentration of ketone.

In our experimental investigation, dilute solutions of the halogenated ketones were prepared in pure water, free from carbon dioxide. The velocity at which hydrogen ions appeared in the solution (at 30°) was then determined by use of the glass electrode (preceding paper), and the development of halide ions was followed by means of a silver-silver halide electrode (see experimental section). The results may be summarised as follows:

(a) In M/500-aqueous solutions of *s*-dichloroacetone the concentration of chloride ion is throughout equal to that of hydrogen ion, within the limits of experimental error; the same applies to  $\omega$ -chloroacetophenone.

(b) The concentration of chloride ion in M/200- to M/2000-aqueous solutions of hexachloroacetone is only about 2% of that of hydrogen ion, and the latter finally becomes approximately equal to the initial concentration of the ketone. Moreover, the experimental figures for hexachloroacetone give fairly good constants when substituted in equation (3), and  $t_{1/2}$  is very nearly proportional to the initial concentration (in g.-mols./l.) of ketone (see below).

*Development of acidity in hexachloroacetone solutions at 30°.*

[ketone] .....	0.005	0.002	0.001
$10^4k$ .....	0.141	0.136	0.137
$t_{1/2}$ (mins.) .....	70.0	27.5	14.5
$10^{-3}t_{1/2}/[\text{ketone}]$ .....	14.0	13.8	14.5

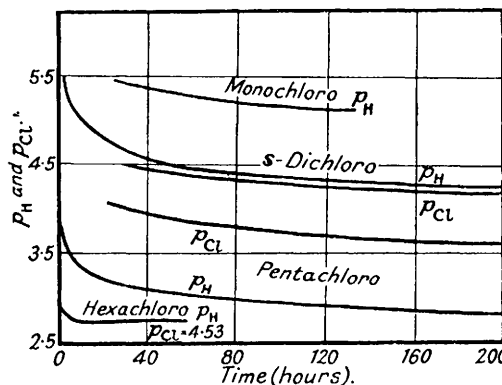
(c) Pentachloro- and *as*-tetrabromo-acetones (both containing the grouping  $-\text{CX}_3$ ) occupy an intermediate position. The concentration of halide ions, although considerable, is much less than that of hydrogen ion.

These results are represented diagrammatically in Figs. 1 and 2. They lead to the conclusions that the acidity of solutions of the lower halogenated acetones (*e.g.*, *s*-dichloro-) is to be ascribed to hydrolysis of the "alkyl halide type," while that of hexachloroacetone solutions is due almost entirely to the haloform cleavage, and that both reactions proceed simultaneously in the case of pentachloro- and *as*-tetrabromo-acetones.

The occurrence of the haloform cleavage in trihalogenated ketones and aldehydes of the type  $\text{R}\cdot\text{CO}\cdot\text{CX}_3$  is clearly to be correlated with other special properties of these compounds, such as the stability of their hydrates and other addition products (*e.g.*, the addition compound of chloral and hydroxylamine isolated by Hantzsch, *Ber.*, 1892, **25**,

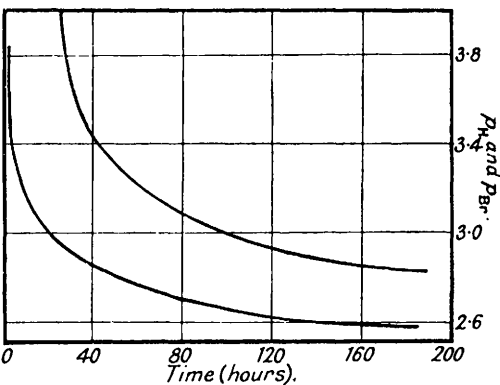
702) and their susceptibility to base-catalysed prototropic change (Watson and Yates, *loc. cit.*, p. 1212). All these phenomena have their origin in the electron-attractive

FIG. 1.



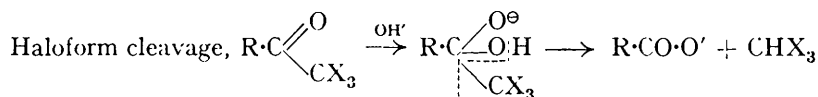
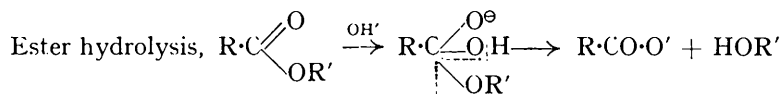
Development of  $p_H$  and  $p_{Cl}$  in  
M/500-chloroacetones.

FIG. 2.



Development of  $p_H$  and  $p_{Br}$  in  
M/500-as-tetrabromoacetone.

character of the halogen substituents, which promote the combination of carbonyl carbon with nucleophilic reagents (compare also the effect of electron-attractive groups upon the alkaline hydrolysis of esters and the base-catalysed prototropy of acetophenones). The halogen atoms of  $R\cdot CO\cdot CX_3$  therefore render the carbonyl group very reactive towards hydroxyl and other bases (*e.g.*, acetate ion, alkoxyl ion). There is, however, an additional factor which contributes to the facility with which the haloform cleavage can occur. This change may be compared with the alkaline hydrolysis of esters, as indicated in the following schemes:



In the former case the alkoxyl group  $OR'$  is eliminated (Polanyi and Szabo, *Trans. Faraday Soc.*, 1934, **30**, 508), and  $CX_3$ , when linked to carbonyl (a necessary condition for the occurrence of the haloform cleavage; see summary by Fuson and Bull, *Chem. Reviews*, 1934, **15**, 275), behaves similarly. Like alkoxyl, it can form a stable compound by the addition of a single proton, and the electron-attraction of the three halogen atoms enables it to break away with the electron pair by which it was linked to carbonyl carbon. The comparison may be extended to include  $-CX_3$ ,  $-OR$  (in esters),  $-NR_2$  (in acid amides), and  $-X$  (in acyl halides).

Our results are therefore in accordance with expectation. Whereas *s*-dichloroacetone is attacked by a nucleophilic reagent at the  $\alpha$ -carbon atom, Cl being replaced by OH (reaction 1), the haloform cleavage (reaction 2), which involves the attack of the reagent upon carbonyl carbon, becomes prominent in ketones which have three halogens linked to the same  $\alpha$ -carbon atom, and in hexachloroacetone the carbonyl group is so activated that this change occurs to the almost complete exclusion of reaction 1.

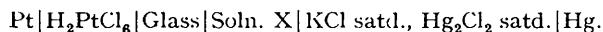
#### EXPERIMENTAL.

*Halogenated Ketones.*—Monochloroacetone was purified by three distillations at atmospheric pressure, followed by one at low pressure; b. p.  $119^\circ/763$  mm. *s*-Dichloroacetone (m. p.  $42.5^\circ$ ) and *as*-tetrabromoacetone (m. p.  $36.3^\circ$ ; Found: Br, 87.5. Calc. for  $C_2H_2Br_4O$ : Br, 87.6%) were recrystallised to constant m. p. from light petroleum. Penta- and hexa-chloroacetones were prepared by prolonged chlorination of acetone. Chlorine was passed into acetone

dissolved in 90% acetic acid in presence of a little hydrochloric acid for 12 hours at room temperature, and then, after addition of sodium acetate (since bases catalyse the halogenation of the higher halogenated acetones more powerfully than do acids), for a further 40 hours in boiling solution. The resulting liquid was poured into twice its volume of water, and the oil removed. The aqueous solution was extracted three times with chloroform, and extract and oil dried over anhydrous sodium sulphate. After repeated fractionation under low pressure in a Claisen flask fitted with a 12-pear column, hexachloroacetone was obtained by freezing out the fraction of b. p.  $> 103^{\circ}/40$  mm.; it was purified by freezing, and finally by distillation under low pressure. It was a colourless liquid, b. p.  $110^{\circ}/40$  mm., m. p.  $-3^{\circ}$  to  $-4^{\circ}$  (Found: Cl, 80.4. Calc. for  $C_3Cl_6O$ : Cl, 80.36%). Continued fractionation of the liquid of b. p.  $< 103^{\circ}/40$  mm. led to a fraction of b. p.  $97.5-99.5^{\circ}/40$  mm., and on cooling below  $0^{\circ}$  pentachloroacetone separated as a solid. It was purified by freezing and finally by distillation under low pressure; b. p.  $97.5-98.5^{\circ}/40$  mm., m. p.  $2.1^{\circ}$  (Found: Cl, 77.0. Calc. for  $C_3HCl_5O$ : Cl, 77.0%).  $\omega$ -Chloroacetophenone, obtained by chlorination of acetophenone in glacial acetic acid, was recrystallised from alcohol; m. p.  $54.5^{\circ}$ .

*Detection of the Haloform Reaction in Aqueous Solutions of Hexachloroacetone.*—Small quantities of chloroform are removed completely from aqueous solution by passage of air for an hour at  $30^{\circ}$ . The chloroform can be collected in a glass spiral immersed in solid carbon dioxide-ether. This method was used in the detection of chloroform in aqueous solutions of hexachloroacetone. 2 L. of a M/200-solution stood at  $30^{\circ}$  for 2 hours. Purified air was passed through half of this solution and then through the cooled spiral for 2 hours. At the end of this period the  $p_H$  values of the two portions of the solution were identical (2.48). Chloroform was detected in the spiral (odour and b. p.). Similar aeration of 1 l. of a solution M/200 with respect to both trichloroacetic acid and chloroform gave a similar quantity of chloroform. It appears justifiable to suppose that the hexachloroacetone had been completely, or almost completely, converted into trichloroacetic acid and chloroform, and this is in harmony with the results of the electrometric measurements.

*Electrometric Measurements.*—During the initial stages of the reaction between halogenated ketones and water, the development of hydrogen-ion concentration was rapid, but became slow after 1–2 hours. A constant  $p_H$  was then approached after an interval of 3–10 days according to the ketone studied. The rapid change in  $p_H$  was followed in the glass electrode assembly (figure, previous paper) immersed in an oil-bath at  $30^{\circ}$ . A measured volume of pure water, previously boiled to remove carbon dioxide, was placed in the electrode vessel *P*, the rubber stopper carrying an S. glass electrode and a small stoppered glass tube was placed tightly in the mouth of the vessel, and a current of purified air passed through the liquid to remove traces of carbon dioxide. Previous tests had shown that this procedure yielded water of  $p_H$  6.9–7.2, and addition of 1–2 ml. of absolute alcohol did not affect the measured  $p_H$ . A solution of ketone in absolute alcohol was made in a 5-ml. stoppered flask, and 1 ml. of this solution was added quickly from a small pipette through the stoppered glass tube in the rubber bung to the water of  $p_H$  about 7. Aeration was continued throughout the experiment. This procedure ensured the rapid solution of the ketone in water. One minute was allowed for thorough mixing of the solution by the air current, and the liquid junction between the saturated calomel and the test solution was made in the tap *T* (figure, previous paper). *E.M.F.* Readings were then taken at short intervals, zero time being the instant of half delivery of the ketone solution into the water. The constancy of the liquid-junction potential was shown as follows: (a) on quickly refilling the liquids through the tap *T*, during the later (slow) changes in  $p_H$  no alteration was caused in the *E.M.F.* of the cell, and (b) experiments with solutions of the same concentration of a given ketone were reproducible to within 0.01  $p_H$  unit as indicated in the following table, in which  $E_n$  represents the *E.M.F.* of the cell (1):



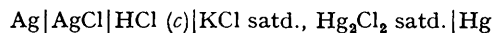
*Initial Development of  $p_H$  in M/200-Hexachloroacetone.*

Time (mins.).	$E_g$ (mv.).		Mean $p_H$ .	Time (mins.).	$E_g$ (mv.).		Mean $p_H$ .	Time (mins.).	$E_g$ (mv.).		Mean $p_H$ .
	A.	B.			A.	B.			A.	B.	
3	238	238	3.23	8	252	252.3	2.99	16	260	260	2.85
4	243	243.5	3.14	9	253.8	253.5	2.97	18	261	261	2.84
5	247	246.5	3.09	10	254.8	254.8	2.95	20	262	262	2.83
6	249	249	3.05	12	256.6	256.9	2.91	26	265	265.5	2.78
7	251	250.9	3.03	14	258.6	259	2.87	30	266.4	266.6	2.75

The glass electrodes, which were calibrated in buffer solutions, exhibited a linear relation between  $p_{\text{H}}$  and  $E.M.F.$  over the range  $p_{\text{H}}$  1—9, and were checked after each series of measurements by using an acid buffer of known  $p_{\text{H}}$  as solution X in cell (1). The latter  $E.M.F.$ 's served for the calculation of the  $p_{\text{H}}$  of the ketone solutions by use of the formula  $E_{\text{X}} - E_{\text{B}} = 0.0601(p_{\text{HX}} - p_{\text{HB}})$  (compare preceding paper, p. 1940).

The measurements on solutions in which the  $p_{\text{H}}$  was changing slowly (see below) indicated that with the exception of hexachloroacetone the  $p_{\text{Cl}}$  or  $p_{\text{Br}}$  developed by hydrolysis (equation 1) during the first 2 hours was smaller than could be detected with a silver chloride or silver bromide electrode. The halide ion attained its equilibrium concentration in 3 minutes when hexachloroacetone was dissolved in water. In order to ascertain whether the pure ketones contained free halide ion, 0.1M-sulphuric acid (halide free) was placed in the electrode vessel P, and a silver chloride electrode immersed in the solution. The  $E.M.F.$  of the saturated calomel-silver chloride cell was then measured. On adding 1 ml. of the alcoholic solution of the ketone, containing sufficient of the latter to make the acid M/500 with respect to ketone, no change was observed in the  $E.M.F.$ , a fall in which would have indicated presence of halide ions, since the sulphuric acid prevented hydrolysis of the "alkyl halide type."

In the slower stages of the reaction between water and halogenated ketones the changes in  $p_{\text{H}}$  and  $p_{\text{Cl}}$  were studied. Pyrex 250-ml. graduated flasks were steamed out and filled to within 1 ml. of the mark at 30° with carbon dioxide-free pure water. 1 Ml. of the alcoholic solution of ketone was added quickly, the flask securely stoppered, and the solution well shaken and stored in a thermostat at 30°. At known times, samples of the solution were poured into the glass-electrode vessel and the  $p_{\text{H}}$  and  $p_{\text{Cl}}$  determined by means of a glass and a silver chloride electrode respectively. The glass electrodes were checked after each measurement, a buffer solution of approximately the same  $p_{\text{H}}$  as the ketone solution being used. The silver halide electrodes were prepared according to Keston (*J. Amer. Chem. Soc.*, 1935, 57, 1671) and Rule and LaMer (*ibid.*, 1936, 58, 2339) and were protected from daylight. The silver chloride electrodes were calibrated in the cell (2)



various concentrations of hydrochloric acid from 0.1M to 0.00001M being used. Between the limits  $p_{\text{Cl}}$  1—4 a straight line was obtained on plotting the  $E.M.F.$ 's of cell (2) against the  $p_{\text{Cl}}$  calculated from the equation  $p_{\text{Cl}} = -\log_{10} a_{\text{Cl}}$ , Lewis and Randall's activity coefficients of chloride ion ("Thermodynamics," p. 382) being used together with the concentrations of hydrochloric acid. At  $p_{\text{Cl}} > 4$  the  $E.M.F.$  of the cell is less than theoretical, and at  $p_{\text{Cl}}$  5 it is almost independent of the  $p_{\text{Cl}}$  owing to the solubility effect of the silver chloride. This indicates the limiting concentration of chloride ion which can be measured directly with the silver chloride electrode. Different electrodes gave results agreeing to within 1 mv. at  $p_{\text{Cl}} < 4$ , but as  $p_{\text{Cl}}$  5 was approached the experimental error increased. The silver bromide electrodes were calibrated in dilute solutions of potassium bromide and exhibited theoretical behaviour up to  $p_{\text{Br}}$  5. Above this the solubility effect of the silver bromide became evident. The  $p_{\text{Cl}}$  values of the ketone solutions were obtained from the calibration curve after determination of the  $E.M.F.$  of the cell (2) with the ketone solution replacing the hydrochloric acid. The following tables indicate the type of results obtained for the slower stages of the reactions.

M/500-Hexachloroacetone.			M/500-Pentachloroacetone.		
Time (hrs.).	$p_{\text{H}}$ .	$p_{\text{Cl}}$ .	Time (hrs.).	$p_{\text{H}}$ .	$p_{\text{Cl}}$ .
28	2.76	4.53 (approx.)	7.75	3.41	4.30
56	2.75	4.60 "	30	3.14	3.99
			79	2.97	3.85
			103	2.94	3.76
M/500- $\omega$ -Chloroacetophenone.					
48	4.58	—	126	2.91	3.70
150	4.30	4.30	150	2.86	3.66
			247	2.84	3.56

The remaining results are given in the graphs in Figs. 1 and 2.

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