136. *Reaction Kinetics in Films. The Active Agents in the Aqueous Halogenation of Long-chain Phenols.*

By A. E. Alexander.

The use of the monolayer technique of following the course of chemical changes has been extended to reactions between phenols and aqueous halogens which in the bulk phase take place much too rapidly to be measured by ordinary methods. *p*-Hexadecylphenol being used as the film-forming compound, the kinetics of reaction with aqueous iodine, bromine, and chlorine have shown that the active intermediaries are the hypohalous acid and the trihalide ion, the relative activities being HIO > HBrO > HClO, and $I_3' < Br_3' < Cl_3'$. These conclusions have been confirmed by experiments in the bulk phase.

The monolayer method of following reaction kinetics allows reactions to be studied which in bulk occur too rapidly for measurement, and this work opens up a new method of approach to the study of very rapid reactions.

The reactivity of halogens in solution, both for addition reactions to unsaturated compounds and for substitution reactions with aromatic substances such as phenol and aniline, is well known to increase with the polarity of the solvent, being very small in carbon tetrachloride and extremely high in water, which suggests that the active intermediary is not the halogen molecule but one or more of the hydrolysis products formed according to the reaction $X_2 + H_2O \rightleftharpoons HXO + H^{\bullet} + X'$. In agreement with this, most reactions involving aqueous halogens are retarded by hydrogen ions (Baines, J., 1922, **121**, 2810; Moelwyn-Hughes, "Kinetics of Reactions in Solution," p. 203). Cofman (J., 1919, **115**, 1040) and Baines (*loc. cit.*) ascribed the activity entirely to the hypohalous acid, a view which was later rejected by Francis (*J. Amer. Chem. Soc.*, 1925, **47**, 2340), who showed that the reactions of pure aqueous hypobromous acid differed from those of bromine-water. He therefore postulated bromine atoms, probably with positive charges, as the active intermediary, but a simple calculation from the known $Br_2 \rightleftarrows 2Br$ equilibrium (Bodenstein, *Z. Elektrochem.*, 1916, **22**, 327) shows that, unless the aqueous medium has an unexpectedly large effect on this equilibrium, the concentration of free atoms at room temperature is entirely negligible. Soper and Smith's kinetic study of chlorination and iodination of phenols (J., 1926, 1582; 1927, 2757) also showed quite definitely that the halogenating agent could not be the positive halogen ion, but in addition, indicated that some intermediary other than the hypohalous acid was involved. The main reasons why the hypohalous acid cannot be the sole active agent in halogenation are as follows : (*a*) Free chlorine-water reacts more rapidly with phenol than does hypochlorous acid alone (Soper and Smith, *loc. cit.*) ; (*b*) chlorine-water readily chlorinates phenolic ethers, whereas hypochlorous acid is entirely without effect (*idem, ibid.*) ; (*c*) aniline and hypobromous acid give grey and partly colloidal precipitates, whereas slightly acidified bromine-water gives a white precipitate of tribromoaniline (Francis, *loc. cit.*) ; (*d*) bromination by free bromine-water is about 1000 times as rapid as that with hypobromous acid (*idem, ibid.*) ; (*e*) gold leaf is dissolved readily in bromine-water but is unattacked by hypobromous acid (*idem, ibid.*) ; (*f*) mixed halogen addition products of unsaturated compounds are formed in salt solutions (*idem, ibid.*).

From this experimental evidence one is led to conclude that, although the hypohalous acid is without doubt an active halogenating agent, it cannot be the only one, and so, rejecting the positive halogen ion theory, a more probable intermediary has to be found.

The great difficulty in studying reactions with bromine-water has always been the very high velocities encountered, the reactions being complete in a few minutes even in extremely dilute solution. This has been overcome by using a monolayer of a long-chain phenol spread on a substrate of bromine-water of suitable concentration. From the rate of change of the surface pressure and surface potential, the reaction velocity can in general be calculated (Alexander and Rideal, *Proc. Roy. Soc.*, 1937, *A*, **163**, 70), even for reactions with half-life of the order of 40 seconds.

EXPERIMENTAL.

The apparatus employed was identical with that previously described (Alexander and Rideal, *loc. cit.*). The chlorine- or bromine-water was made up shortly before use, and standardised against sodium thiosulphate after addition of potassium iodide. The substrate concentration was generally about 10^{-4}M with respect to the total halogen and N/100 with respect to sulphuric acid. The latter ensured that both the phenol and the hypohalous acid were in the un-ionised form, so that there was no possibility of reactions involving either the phenoxide or the hypohalite ions. The hypohalous acid was prepared by Francis' method (*loc. cit.*, p. 2342), and standardised with potassium iodide and thiosulphate before and after use.

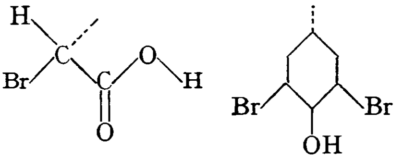
The phenol used, *viz.*, *p*-hexadecylphenol, was very kindly given by Professor N. K. Adam.

Results.—The films of the phenol were solid and stable up to quite high pressures (*ca.* 20 dynes/cm.), the *F–A* measurements and the hysteresis phenomena being in accord with the early measurements of Adam (*Proc. Roy. Soc.*, 1923, *A*, **103**, 676). The moment of the phenol (*ca.* 2·5 milli-Debyes) is somewhat greater than that of the alcohols (*ca.* 2·2 milli-Debyes), as would be expected owing to the presence of the benzene nucleus.

On injecting a few drops of saturated bromine-water beneath a film of the phenol at a constant surface pressure (2 dynes/cm. in all the experiments described below), a very rapid expansion was noticed, the apparent moment (μ) increased very considerably, and the state of the film changed from solid to liquid, showing that bromination had taken place. The final area and moment were about 37 A.^{2} and 3·55 milli-Debyes, as compared with the initial values of about 23·5 A.^{2} and 2·5 milli-Debyes.

By analogy with the bulk bromination of *p*-cresol, it would be anticipated that substitution affords 2 : 6-dibromo-*p*-hexadecylphenol. This is substantiated by the dipole moment, which can be calculated very approximately from the effect of the introduction of bromine into other long-chain compounds. A comparison of the unsubstituted with the α-bromo-acids (author's unpublished results) shows that the effect of the α-bromine atom is to increase μ by about 0·6 milli-Debye. Although the configuration of the acid dipole is still unsettled, yet, as will be seen from Fig. 1, it is very probable that the C–Br linkages are inclined at approximately the same angle with respect to the surface in both cases, and on this assumption the moment of the dibromophenol should be about 3·7 milli-Debyes, in fair agreement with the experimental value previously quoted.

FIG. 1.



Suggested probable configurations for the α-bromo-acid and dibromophenol dipoles.

When the phenol was spread on a dilute bromine-water substrate (10^{-3} to 10^{-4}M), the area–time curve was found to be unimolecular in shape, and the pseudo-unimolecular velocity constant (k_{uni}) was calculated from this curve by Guggenheim's method (*Phil. Mag.*, 1926, **2**, 538).

On addition of potassium bromide to the dilute bromine-water substrate, a very pronounced increase in the reaction velocity was noted, which suggested that the Br_3' ion was active in bringing about bromination. A series of experiments was therefore carried out in which a definite concentration of bromine ($0·96 \times 10^{-4}$M) and various concentrations of potassium bromide were used. From the known values of the equilibrium constants of the two reactions

$$Br_3' \rightleftharpoons Br_2 + Br' \qquad K_1 = [Br_2][Br']/[Br_3'] \quad . \ . \ . \ . \quad (1)$$

$$Br_2 + H_2O \rightleftharpoons H^{\bullet} + Br' + HOBr \qquad K_2 = [H^{\bullet}][Br'][HBrO]/[Br_2] \quad . \quad (2)$$

it is possible to calculate the concentrations of the various components (Br_2, Br_3', Br', and HOBr). If the total concentrations of bromine and of potassium bromide are respectively c_1 and c_2, then for the concentrations of bromide used in these experiments ($2·5 \times 10^{-3}$—0·9M), the following relations hold :

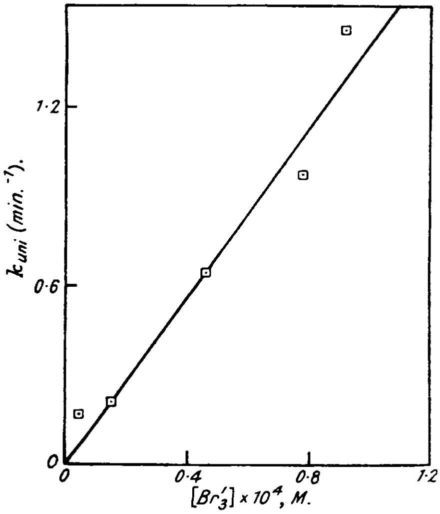
$$[Br_3'] = \tfrac{1}{2}\left\{(c_1 + c_2 + K_1) - \sqrt{(c_1 + c_2 + K_1)^2 - 4c_1c_2}\right\} \quad . \ . \ . \ . \quad (3)$$

$$[Br'] = c_2 - [Br_3'] \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

$$[Br_2] = c_1 - [Br_3'] \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

Taking K_1 from the data of Griffith, McKeown, and Winn (*Trans. Faraday Soc.*, 1932, **28**, 101) and $K_2 = 5·2 \times 10^{-9}$ (Bray and Connolly, *J. Amer. Chem. Soc.*, 1911, **33**, 1485), we calculate the values shown in Table I. The highest concentration of potassium bromide (0·9M) was chosen such that, for the concentration of bromine used ($0·96 \times 10^{-4}$M), the concentration of free bromine was very small and that of hypobromous acid negligible, so that any activity of this solution has to be ascribed solely to the tribromide ion. The variation in the reaction velocity constant (k_{uni}) with bromide concentration is given in Table I, and with tribromide-ion concentration in Fig. 2. If the reaction occurs between the phenol molecule and the tribromide ion then, according to Brönsted's theory, the velocity should be proportional to the concentration of this ion, and the linear relationship found between k_{uni} and $[Br_3']$ shows that this is so, the free bromine and bromide ion being without influence except in so far as they determine the concentration of the tribromide ion. From the slope of the line the bimolecular velocity constant for the latter, $k_{\text{bi}}^{Br_3'}$, was calculated to be $1·4 \times 10^4$ l./g.-mol.-min.

FIG. 2.



If now for the reaction on bromine-water alone it be assumed that only the tribromide ion and hypobromous acid are active, *i.e.*, $k_{\text{uni}} = k_{\text{bi}}^{Br_3'}[Br_3'] + k_{\text{bi}}^{HOBr}[HOBr]$, then k_{bi}^{HOBr} can be determined, and hence the activity of the two brominating agents compared. From Table I we have

$$0·023 = 1·4 \times 10^4 \times 1·068 \times 10^{-8} + k_{\text{bi}}^{HOBr} \times 6·82 \times 10^{-6}$$

TABLE I.

Total bromine = c_1 = 0·96 × 10^{-4}M; total KBr = c_2; temp. = 22·0°.

c_2.	[Br′$_3$].	[Br].	[Br$_2$].	[HBrO].	k_{uni}, min.$^{-1}$.
0	1·068 × 10^{-8}	6·797 × 10^{-6}	0·892 × 10^{-4}	6·82 × 10^{-6}	*ca.* 0·023
2·5 × 10^{-3}	0·045 × 10^{-4}	2·5 × 10^{-3} (nearly)	0·91 × 10^{-4}	1·9 × 10^{-8}	0·174
1·0 × 10^{-2}	0·15 × 10^{-4}	0·01 ,,	0·66 × 10^{-4}	3·4 × 10^{-9}	0·21
5·0 × 10^{-2}	0·46 × 10^{-4}	0·05 ,,	0·50 × 10^{-4}	5·2 × 10^{-10}	0·64
0·25	0·78 × 10^{-4}	0·25 ,,	0·18 × 10^{-4}	3·7 × 10^{-11}	0·97
0·9	0·92 × 10^{-4}	0·90 ,,	0·04 × 10^{-4}	2·3 × 10^{-12}	*ca.* 1·46

which gives $k_{\text{bi}}^{\text{HOBr}}$ = 0·34 × 10^4 l./g.-mol.-min., so that on this view the tribromide ion is some four times as effective as the hypobromous acid molecule.

This conclusion is capable of experimental verification, since by using pure hypobromous acid solution it should be possible to work out an independent value of $k_{\text{bi}}^{\text{HOBr}}$. On a substrate of 1·42 × 10^{-4}M-hypobromous acid in N/100-sulphuric acid at 22·0°, two velocity measurements gave k_{uni} as 0·75 and 0·77 min.$^{-1}$ (mean, 0·76 min.$^{-1}$), whence $k_{\text{bi}}^{\text{HOBr}}$ = 0·53 × 10^4, as compared with the above value of 0·34 × 10^4 l./g.-mol.-min. Considering the experimental difficulties and the approximations involved, the agreement is satisfactory, and we are led to conclude that the active agents in free bromine-water are the tribromide ion and the hypobromous acid molecule.

Francis' objections against hypobromous acid (see p. 729) have now to be considered in the light of the above conclusions. His bulk bromination experiments were repeated, bromine-water, hypobromous acid, and bromine-water saturated with potassium bromide being used. The concentration of the bromine water (*ca.* 10^{-2}M) was such that, when it was saturated with potassium bromide (*ca.* 3·5M), the bromine existed practically entirely as the tribromide ion. In this connexion it is of interest that the original reddish-orange colour of the bromine-water changes to a clear yellow on saturation with the bromide. The hypobromous acid solution was prepared as indicated above from the same solution of bromine-water, so its concentration would also be about 10^{-2}M.

Aniline, as the sulphate, hydrochloride, or free base, gave with bromine-water a white colloidal precipitate which slowly settled out. A precisely similar behaviour was found with the potassium tribromide solution, whereas the hypobromous acid gave coloured colloidal precipitates, as noted by Francis (*loc. cit.*). The hydrochloride and sulphate gave a purple colour and a greenish-blue precipitate, the free base a deep brown colour and a greyish-brown precipitate. With phenol, all three solutions appeared to have an identical effect, *viz.*, formation of a small white precipitate on standing, but with the gold leaf a very marked difference was noted, the rate of attack being followed by means of the " purple of Cassius " test with stannous chloride. Bromine-water alone gave a positive, but very faint reaction after 10 minutes; with hypobromous acid after a similar interval the test was negative, but with the potassium tribromide solution the gold leaf could actually be seen to dissolve, giving an immediate positive reaction with the stannous chloride.

The last objection raised by Francis, concerning the formation, in salt solutions, of mixed halogen addition products, can be overcome by assuming the formation of mixed ions such as [Br_2Cl]′ which are active for halogenation. Such ions have been shown to exist in solution by Winkler (J., 1907, **91**, 996; 1908, **93**, 1611). Further evidence was given by a comparison of the properties of the above solution of bromine-water saturated with potassium chloride or bromide, since the colour and the reactivity with aniline and gold leaf appeared to be the same in both cases. Using ethylene, bromine, and a saturated solution of sodium chloride (*ca.* 4·5M) Francis obtained about 45% of α-chloro-β-bromoethane, the remainder being ethylene dibromide. If it be assumed that addition occurs solely through the intermediary of the Br_2Cl′ ions, that the addition complex involves one such ion per double bond, and that the probability of the loss of a bromide or a chloride ion from this complex is the same, then the product should contain 50% C_2H_4ClBr, 50% $C_2H_4Br_2$, and no $C_2H_4Cl_2$, which is in agreement with experiment. The other mixed addition products found by Francis can be similarly accounted for, and also the observations of Terry and Eichelberger (*J. Amer. Chem. Soc.*, 1925, **47**, 1067), who showed that with sodium maleate and fumarate bromohydrin formation could be prevented by a high concentration of sodium bromide, and that bromine, potassium chloride, and sodium maleate gave the chlorobromo- but no dichloro-compound.

The evidence which has been put forward therefore indicates that, for aqueous bromination at any rate, the activity is due solely to the negative tribromide ion and the hypobromous acid molecule. Whether in all aqueous halogenations a similar explanation is tenable, is discussed below.

A few experiments with the long-chain phenol using iodine as the substituting agent showed that iodination was extremely slow, on a substrate of 0·85 × 10^{-4}M-iodine in N/100-sulphuric acid only about 15% having reacted in 2 hours. This slight activity would appear to be mainly due to the hypoiodous acid molecule, as the velocity on a substrate of 0·1M-iodine in 0·5M-potassium iodide, where the iodine exists largely as I_3', was even slower. This agrees with the conclusions of Cofman (*loc. cit.*) and of Soper and Smith (*loc. cit.*), that for the bulk iodination of phenols the activity is due solely to the hypoiodous acid molecule. From the kinetics of the addition of aqueous iodine to β-phenylpropiolic acid, Moelwyn-Hughes and Legard (J., 1933, 424) have shown that both the tri-iodide ion and the hypoiodous acid molecule are effective in bringing about reaction, the latter being by some 1000 times the more active.

Now, since it has been shown that hypoiodous acid is very much more active than the tri-iodide ion, whereas hypobromous acid and the tribromide ion are of approximately the same order, it would be anticipated that the activity of hypochlorous acid would be very much less than that of the trichloride ion (if, indeed, this exists; see Sidgwick, *Ann. Reports*, 1933, **30**, 127). As a preliminary, bulk chlorination experiments were carried out on the lines of those previously described with bromine. Chlorine-water (*ca.* 0·01M), a similar solution saturated with potassium chloride (*ca.* 3·5M), and hypochlorous acid (also *ca.* 0·01M) were compared in their reactions with aniline, phenol, anisole, and gold leaf. With phenol, none of the above solutions gave a precipitate; with anisole, hypochlorous acid appeared to have little effect, whereas the other two gave white colloidal solutions, although this experiment was inconclusive owing to the insolubility of the anisole. Aniline (as free base or sulphate) gave with hypochlorous acid almost black colloidal precipitates, whereas the other two solutions gave light brown colloidal solutions, the difference being very marked.

The most striking difference, however, was found with the gold leaf experiments, the solution of which was followed by the " purple of Cassius " test as before. With free chlorine water there was no apparent solution and no positive reaction after 8 minutes, hypochlorous acid behaved similarly after an interval of 30 minutes, but with the chlorine-saturated potassium chloride solution all the gold had disappeared in less than a minute and a positive reaction was shown immediately. A blank experiment using saturated potassium chloride solution alone gave a negative test after 24 hours. These bulk experiments indicated that the trichloride ion existed and that it was an extremely active halogenating agent, and the velocity measurements fully substantiated this.

With the same long-chain phenol at the same surface pressure (2 dynes/cm.) as in the bromination experiments, the variation in the velocity with potassium chloride concentration was studied. The effect was just as pronounced as that of potassium bromide in the bromination, the half-life of the reaction on a substrate of 1·15 × 10^{-4}M-chlorine in N/100-sulphuric acid decreasing from about 20 minutes (no chloride added) to about 25 seconds in the presence of 2·67M-potassium chloride. The experimental velocities are shown in Table II.

TABLE II.

Substrate, 1·15 × 10^{-4}M-Cl_2 in N/100-H_2SO_4. Temp. = 20·0°.

Concn. of KCl, M	0	0·01	0·04	0·20	1·5	2·67
k_{uni} (min.$^{-1}$)	*ca.* 0·034	0·066	0·245	0·83	1·42	1·64
$K = [Cl_2][Cl']/[Cl_3']$ (calc.)		0·240	0·231	0·197	0·237	—

Assuming that at the highest concentration of potassium chloride used all the chlorine existed as trichloride ions, we find that $k_{bi}^{Cl_3'} = 1{\cdot}43 \times 10^4$ l./g.-mol.-min. It is now possible to calculate the equilibrium constant for the reaction $Cl_2 + Cl' \rightleftarrows Cl_3'$ from the velocity measurements at lower concentrations by ascribing all the activity to the trichloride ion. The results are given in Table II, and indicate a reasonable value of about 0·23 for this constant, since the corresponding values for bromine and iodine are 5·7 × 10^{-2} and 1·4 × 10^{-3} respectively. The work of Sherrill and Izard (*J. Amer. Chem. Soc.*, 1931, **53**, 1667) appears to be the only previous attempt to measure this equilibrium constant, their results on the comparison of the solubilities of chlorine and oxygen in aqueous solutions of chlorides giving a value of about 5·8.

The activities of the trichloride ion and the hypochlorous acid molecule were compared after determining that of a pure solution of the latter. Owing to its much slower reaction a much more concentrated solution than with hypobromous acid had to be used. The unimolecular velocity constant on a substrate of 9·23 × 10^{-3}M-hypochlorous acid in N/100-sulphuric acid at 20·0° was 0·181 min.$^{-1}$, giving k_{bi}^{HOCl} = 19·6 l./g.-mol.-min., so that the hypochlorous acid molecule is about 10^3 times less active than the trichloride ion, as previously anticipated.

These experiments indicate that for substitution reactions involving aqueous halogens both the hypohalous acid and the trihalide ion are the active intermediaries, the activity of the hypohalous acid increasing, and that of the trihalide ion decreasing, with increasing atomic weight of the halogen. The activities thus run inversely as their chemical stability.

Although the above conclusions have direct reference only to substitution reactions, they may well prove to be helpful principles in the study of addition reactions also.

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