Kinetics of the Reactions of Olefins with Halogens in Aqueous Solution. Part II.[1] Reactions of Bromine with Various Olefins, and of Hydrogen Bromide with Some Epoxides

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Kinetic results are reported for the reaction of nine olefins with bromine in aqueous solution. Velocity constants were obtained for reaction with molecular bromine and with tribromide ion, and, for two olefins, also with the ions Br_2Cl^- and $BrCl_2^-$. The relative amounts of bromohydrin and dibromide produced were determined as a function of bromide ion concentration for eight olefins. For most of the reactions studied here and in previous work there is no correlation between the product composition and the kinetics, and it is concluded that an intermediate formed in the rate-determining step then reacts rapidly with either water or bromide ion. The bromination of diethyl fumarate, however, appears to involve simultaneous electrophilic attack by a bromine molecule and nucleophilic attack by water or bromide ion. Both diethyl furmarate and diethyl maleate give the *meso*-form of diethyl dibromosuccinate. Kinetic measurements with three epoxides support a cyclic bromonium ion as the intermediate in the reactions between olefins and bromine, but other formulations are possible. The velocity constants for reaction with bromine or tribromide ion, varying over about eleven powers of ten, show an approximate correlation with Taft's σ^* substituent constants.

Part I explained the advantages of using aqueous solutions for kinetic studies of reactions between olefins and halogens, and reported results for the reaction of bromine with ten olefinic substances. Velocity constants were obtained for the reaction of each substance with molecular bromine and with tribromide ion, and the ratio of the two products formed (dibromide and bromohydrin) was investigated for four substances. It was concluded that the reactions take place in two stages, a rate-determining step to form a reactive intermediate, followed by a rapid reaction of this intermediate with water or bromide ions. No firm conclusion could be reached as to the nature of the intermediate, and some of the results suggested that reaction with bromine and tribromide ion might lead to different intermediates. Some correlation was apparent between the observed velocities and electrophilic substituent constants.

We now report kinetic measurements for the reaction of bromine and tribromide ion with nine olefinic substances, and measurements of product ratios in eight reactions, two previously studied by Atkinson and Bell. A study was made of the reactivity of the ions Br_2Cl^- and $BrCl_2^-$ towards two olefins. Measurements are also reported on the rate of addition of water and hydrogen bromide to three epoxides, in view of the analogy between their protonated forms and the cyclic bromonium ions which have been postulated as intermediates in the reactions with bromine.

EXPERIMENTAL

All measurements of reaction velocity and product ratios were carried out at 25°. Inorganic reagents were of AnalaR grade, and solutions were prepared with water which had been redistilled from alkaline potassium permanganate. The following substances were obtained by drying and fractionally distilling pure commercial specimens: diethyl fumarate (b. p. 99°/20 mm.), diethyl maleate (b. p. 115°/20 mm.), allyl alcohol (b. p. 95°/742 mm.), glycidol (b. p. 64°/12 mm.), propylene oxide (b. p. 34°/756 mm.). Ethylene oxide (B.D.H. Laboratory Reagent Grade) was used without further purification.

The following methods were employed to estimate the purity of the substances whose preparation is described subsequently:

(*a*) An aqueous solution of the olefin was treated with an excess of standard bromine solution, and the bromine remaining after reaction was estimated by adding potassium iodide and titrating the liberated iodine with sodium thiosulphate solution. The time needed for the reaction of one mole of bromine, without complications from subsequent reactions, was estimated from the kinetic measurements.

(*b*) The chlorine in the chloroallyl alcohols was converted into chloride ion and titrated. A solution was treated with potassium permanganate until the purple colour remained after boiling, and a few drops of 10 vol. hydrogen peroxide added to destroy the excess of permanganate. The solution was again boiled to destroy the hydrogen peroxide and to coagulate the manganese dioxide, which was filtered off. The filtrate was acidified with perchloric acid, and its chloride content estimated by titration with silver nitrate solution.

(*c*) The bromide in the quaternary ammonium bromides was estimated by titration with silver nitrate solution.

The values given for the percentage purity of the compounds are designed as (*a*), (*b*), or (*c*) according to the method used. A further criterion of purity is described under the potentiometric method of determining reaction velocities.

2-Chloroallyl alcohol was prepared from allyl chloride by successive conversion into 1,2,3-trichloropropane and 2,3-dichloropropene, which was then converted into the alcohol by refluxing with aqueous sodium carbonate.[2] The structure and purity of the 2,3-dichloropropene (b. p. 91·8—92·0°/748 mm.) were confirmed by its n.m.r. and infrared spectra. The final product was fractionated three times through a Vigreux column [b. p. 132—133°/748 mm., purity (*a*) 98·8%, (*b*) 98·5%].

cis- and *trans*-3-Chloroallyl alcohols were prepared from commercial samples of the corresponding 1,3-dichloropropenes, which were first fractionally distilled (*trans*-1,3-dichloropropene, b. p. 59—60°/125 mm.; *cis*-1,3-dichloropropene, b. p. 54·5—55·5°/125 mm.). Each of these was refluxed for 24 hr. with aqueous sodium carbonate, and the alcohol extracted with ether and twice fractionally distilled [*cis*-3-chloroallyl alcohol, b. p. 93—95°/105 mm.,

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[1] J. R. Atkinson and R. P. Bell, *J. Chem. Soc.*, 1963, 3260, is now considered as Part I of this series.

[2] G. H. V. Kremer, *Bull. Soc. chim. France*, 1948, 165.

purity (*a*) 100·9%, (*b*) 98·8%; *trans*-3-chloroallyl alcohol 99—101°/115 mm., purity (*a*) 100·9%, (*b*) 99·7%).[3,4] A second sample of *cis*-3-chloroallyl alcohol was prepared from the lower-boiling fraction obtained in the final fractionation of the *trans*-compound. A crystal of iodine was added to this fraction, which was then illuminated by two 100 w electric light bulbs for two days in order to complete isomerisation to the less stable *cis*-compound. After fractionation this led to a product, b. p. 94—96°/115 mm., which was kinetically indistinguishable from the first sample.

The assignment of *cis* and *trans* configurations to the two 1,3-dichloropropenes and 3-chloroallyl alcohols is in some doubt, but the most definitive assignment, adopted here, appears to be that of Hatch and Perry,[5] who converted both isomers of 1,3-dichloropropenes into the corresponding 1-chloropropenes, whose configurations are well established.[6] The two isomers of 3-chloroallyl alcohol show very similar kinetic behaviour (Table 5), so that the assignment (or the contamination of one isomer by the other) is of minor importance in the present context.

3,3-Dichloroallyl alcohol was prepared from *trans*-1,3-dichloropropene (retained from the preparation of 3-chloroallyl alcohol) by a modification of the method described by Kirrmann and Kremer.[7] 1,2,3,3-Tetrachloropropane was first obtained by chlorination, while illuminat-with two 100 w bulbs, until the theoretical increase in weight had been obtained. After excess of chlorine had been removed by passage of air, this substance was converted into 1,3,3-trichloropropene by refluxing with ethanolic potassium hydroxide, adding water, and separating the organic layer. The 1,3,3-trichloropropene was converted into 3,3-dichloroallyl alcohol by refluxing with an aqueous solution of sodium orthophosphate. After extraction with ether and fractional distillation the final product had b. p. 58—60°/13 mm., purity (*b*) 97·7%.

2,3-Dichloroallyl alcohol (probably having the chlorine atoms in the *cis* configuration) was prepared by an analogous procedure from 2,3-dichloropropene, but since it was not possible to obtain reliable kinetic results for this compound details will not be given.

Allyltrimethylammonium bromide was prepared from allyl bromide and an excess of trimethylamine in acetone (cf. Adamson [8]). The mixture was prepared at 0°, and after the excess of trimethylamine had been removed by warming to room temperature, the solid which had separated was recrystallised from ethanol [purity (*a*) 99·4%, (*c*) 100·4%].

trans-3-Phenylallyltrimethylammonium bromide was prepared by an analogous procedure from a commercial specimen of *trans*-cinnamyl bromide. Analysis gave a purity of (*a*) 98·5%, (*c*) 101·0%. The structure and configuration were confirmed by its n.m.r. spectrum, which revealed no impurities.

3,3-Diphenylallyltrimethylammonium bromide was prepared by following closely Adamson's method [8] for the iodide. Ethyl β-dimethylaminopropionate (b. p. 60—61°/14 mm.) was prepared from ethyl acrylate and dimethylamine, and then treated with phenylmagnesium bromide to give (3-hydroxy-3,3-diphenyl-n-propyl)dimethylamine (m. p. 166°). The last product was converted into (3,3-diphenylallyl)dimethylamine hydrochloride by refluxing with a mixture of hydrochloric and acetic acids and the free base (b. p. 187—188°/14 mm.) obtained by treatment with aqueous ammonia followed by ether extraction. Finally the required 3,3-diphenylallyltrimethylammonium bromide was obtained by treating this base with excess of methyl bromide in acetone at 0°. After recrystallisation from ethanol its purity was (*a*) 97·6%, (*c*) 102·7%.

All the quaternary compounds were hygroscopic and were stored in a vacuum desiccator over magnesium perchlorate. The analyses of the last two compounds suggest that they contain small quantities (<3%) of saturated substances containing bromide: this was allowed for in calculating the concentrations of solutions used for kinetic measurements.

The dimethyl esters of *cis*- and *trans*-epoxysuccinic acids were prepared from maleic and fumaric acids, following Payne and Williams [9] method for preparing the epoxy-acids, and Miller's procedure [10] for esterifying the *trans*-acid. Maleic or fumaric acid was oxidised at 65—70° with sodium tungstate and hydrogen peroxide, the pH being kept above 4. The epoxy-acids were precipitated as their barium salts, and the dry salts converted into the esters by refluxing with methanol containing sulphuric acid and anhydrous magnesium sulphate. After recrystallisation from methanol, dimethyl *trans*-epoxysuccinate had m. p. 75°, while the *cis* compound decomposed at about 120°. Neither of these compounds reacted with hydrogen bromide at a rate sufficient for the determination of competition factors.

A solution containing 2,3-epoxy-n-propyltrimethylammonium bromide was prepared by boiling a solution of allyltrimethylammonium bromide with hydrogen peroxide and sodium tungstate until the yellow pertungstate colour had disappeared. Since this solution did not react at an appreciable rate with hydrogen bromide, no attempt was made to isolate the compound.

For those products which reacted rapidly with bromine (the three monochloroallyl alcohols and the three trimethylammonium compounds) the rate was measured by the technique previously described,[1] in which the bromine concentration is followed by measuring the redox potential at a platinum electrode, a glass electrode being used as the reference electrode. The solutions contained perchloric acid, usually 0·1M, in order to fix the potential of the glass electrode. In a typical experiment the concentration of olefin was 10^{-3}M and the initial bromine concentration 10^{-5}M: each reaction therefore followed a first-order course, and the potential decreased linearly with time. The second-order velocity constant is then given by

$$k = -78{\cdot}2\,\frac{\mathrm{d}E}{\mathrm{d}t}\Big/c \qquad (1)$$

where c is the average olefin concentration, differing only slightly from the initial concentration. A linear variation of potential with time was normally observed over at least 50—60 mv, corresponding to 97—99% reaction, after which the potential fell more slowly. The last type of

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[3] L. F. Hatch and A. C. Moore, *J. Amer. Chem. Soc.*, 1944, **66**, 286.

[4] L. F. Hatch and G. B. Roberts, *J. Amer. Chem. Soc.*, 1946, **68**, 1196.

[5] L. F. Hatch and R. H. Perry, *J. Amer. Chem. Soc.*, 1949, **71**, 3262.

[6] M. S. Kharasch, J. E. Englemann, and F. R. Mayo, *J. Org. Chem.*, 1932, **2**, 288.

[7] A. Kirrmann and G. H. V. Kremer, *Bull. Soc. chim. France*, 1948, 166.

[8] D. W. Adamson, *J. Chem. Soc.*, 1949, *S*144.

[9] G. B. Payne and P. H. Williams, *J. Org. Chem.*, 1959, **24**, 54.

[10] A. I. Miller, *J. Med. Chem.*, 1963, **6**, 233.

behaviour is believed to be due to the return of bromine from the vapour phase into solution, since if the reaction vessel is completely filled with solution linearity persists over 100—120 mv (down to about 10^{-9}M-bromine), or over 140—150 mv (down to about 10^{-10}M-bromine) if de-oxygenated solutions were used. It has been reported [11] that the potential at a platinum electrode does not follow the theoretical dependence on bromine concentration if the latter falls below about 10^{-7}M: this is at variance with our findings. It is probable, however, that the difficulties experienced were due to polarisation at the redox electrode, since the observed behaviour varied with size of electrode, stirring speed, sequence of experiments, and type of potentiometer used. A calomel electrode was used as reference, and the current passing through the redox electrode while balancing the potentiometer was probably 10^{-5} to 10^{-4} A. In our work a glass electrode of resistance about 10^8 ohm was the reference electrode, and the use of a valve potentiometer reduced the imbalance currents to 10^{-12}—10^{-10} A, thus minimising polarisation at the redox electrode. The fact that successive additions of bromine to the same solution gave concordant velocity constants was evidence of the purity of the organic reactants.

For those substances which react slowly with bromine (diethyl maleate, diethyl fumarate, and the dichloroallyl alcohols) the rate of consumption of bromine was followed by titrating aliquot portions removed at intervals. The main problem here is to eliminate or allow for the loss of bromine to the vapour phase when samples are removed. The reactions were carried out in an all-glass apparatus (taps lubricated with silicone grease) in which a calibrated pipette was permanently attached to the reaction vessel. The contents of the pipette were discharged with its tip under the surface of potassium iodide solution. When a sample was removed, the vapour phase replacing its volume was drawn from a subsidiary reaction vessel containing an identical reaction mixture: the vapour phase in the subsidiary vessel was simultaneously replaced by air drawn in from outside the system. Since the vapour phase in both vessels has time to re-establish equilibrium with the solution, the loss of bromine from the first reaction vessel is very small. Calculations show that if the conditions are such that the withdrawal of ten aliquot parts by the normal procedure would cause a decrease of 40% in the bromine concentration in solution (assuming no reaction to take place), the use of the apparatus just described should entail a decrease of only 3·5% in the subsidiary vessel, and only 0·012% in the first reaction vessel. Although this performance was not tested directly, the consistent kinetic behaviour observed in reactions lasting several days suggested that the loss of bromine was in fact very small. The second-order constants were obtained from linear plots of log([olefin]/[bromine]) against time.

Since acid is produced in the formation of bromohydrin, but not in that of dibromide, the ratio of the two products formed can be obtained by titrating the acid produced in the reaction of a known amount of olefin or of bromine. In the measurements of Bell and Atkinson [1] the olefin was present in excess, and the amount of reaction defined by the quantity of bromine added. In view of the difficulties of handling bromine quantitatively we have preferred to use a small excess of bromine, which was removed by a current of air before titrating the acid. For most olefins the bromine was introduced as vapour, either in a current of air, or by diffusion through the vapour phase from a bromine solution in another vessel. The latter method was adopted for trimethylallylammonium bromide, since at the concentrations needed for accurate analysis the presence of any appreciable excess of bromine led to the precipitation of yellow solids, probably the tribromide of the initial substance or the product. The time necessary for complete reaction of the olefin was judged from the kinetic measurements, and after removal of the excess of bromine the acid produced was titrated with borax solution to the methyl-red end-point. The initial reaction solutions contained a small concentration of acid, usually 10^{-3}M-perchloric acid, in order to repress the formation of hypobromous acid, and this initial concentration was allowed for in calculating the amount of bromohydrin formed.

In the case of the chloroallyl alcohols the bromohydrins formed initially react further with the liberation of more acid, giving overall reactions such as

$$\mathrm{CH_2{:}CCl{\cdot}CH_2OH + Br_2 + H_2O \longrightarrow CH_2Br{\cdot}CO{\cdot}CH_2OH + Br^- + Cl^- + 2H^+}$$

$$\mathrm{CCl_2{:}CH{\cdot}CH_2OH + Br_2 + 2H_2O \longrightarrow CO_2^-{\cdot}CHBr{\cdot}CH_2OH + Br^- + 2Cl^- + 4H^+}$$

and this was allowed for in calculating the properties of reaction leading to bromohydrin. The aldehyde or ketone produced in some of these reactions could react slowly with more bromine to produce more acid, but comparison with the known rates of bromination of analogous halogen-substituted ketones [12] shows that it is easy to choose a time which will ensure complete reaction of the olefin without any appreciable subsequent bromination. No determination of product ratio was possible for the two phenyl-substituted allyltrimethylammonium bromides, since it was found that their dibromides (prepared by the addition of bromine in chloroform) are rapidly hydrolysed to bromohydrin in aqueous solution.

No appreciable amount of hydrogen bromide or hydrogen chloride is removed by a current of air from aqueous solutions at the concentrations used. There is, however, some loss of allyl alcohol, and in determining the product ratios for this compound the bromine was added as an aqueous solution. One experiment by this method for each of the chloroallyl alcohols served as a check that there was no appreciable loss by volatilisation when the bromine was added in a current of air.

The reactions of bromine with diethyl fumarate, diethyl maleate, and 3,3-dichloroallyl alcohol are so slow that if they are allowed to go to completion there is a danger of subsequent reactions, for example the hydrolysis of the ester group. The product ratios for these substances were therefore determined by an indirect kinetic method, as follows. Consider a reaction between A and B, initially present at equal concentrations a_0, to give products X and Y in constant proportions α and $1 - \alpha$. If a_t and x_t are the concentrations of A and X after time t, the kinetic and stoicheiometric equations give

$$\frac{1}{a_0 - x_t/\alpha} - \frac{1}{a_0} = kt \qquad (2)$$

where k is the second-order velocity constant. This can be written as

$$x_t/t = \alpha a_0^2 k - a_0 k x_t \qquad (3)$$

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[11] W. C. Purdy, E. A. Burns, and L. B. Rogers, *Analyt. Chem.*, 1955, **27**, 1989.

[12] R. P. Bell and J. Hansson, *Proc. Roy. Soc.*, 1960, *A*, **225**, 214.

so that a plot of x_t/t against x_t should give a straight line of slope $-a_0k$ and intercept $\alpha a_0{}^2k$, whence both α and k can be determined from a single experiment. Alternatively, it may be more accurate to use the value of k obtained by one of the other kinetic methods.

In applying this method the rate of production of acid (and therefore of bromohydrin) was determined by means of an automatic titrator (type TTTlc, Radiometer Co., Copenhagen). This instrument automatically adds a reagent, in our case a solution of borax, to maintain the pH at a constant value, usually 3. At the same time the amount of reagent added is recorded on a chart as a function of time. The borax solution contained enough sodium bromide to keep constant the bromide ion concentration in the reaction mixture, allowance being made for the bromide ion formed in the production of the bromohydrin, and for the effect of dilution on the pH of the solution. For 3,3-dichloroallyl alcohol both the product ratios and the rate constants were obtained by this method, the latter being included in Table 1. For diethyl fumarate and diethyl maleate, because of complications due to the hydrolysis of the ester group, the reaction could not be followed over a sufficient range to obtain reliable values of both k and α, and two alternative methods were used to obtain the product ratio. In the first the initial rate of production of acid was determined from the slope of the titrigraph trace, and this was compared with the rate of consumption of bromine, determined independently. In the second a plot of x_t/t against t was constructed, as above, but in determining the intercept the slope was chosen to agree with the independently measured value of k. The results of the two methods agreed closely, and their mean is quoted in Table 3.

TABLE 1

Rates of reaction with bromine in bromide solutions at 25°

k = Second-order velocity constant, M^{-1} sec.$^{-1}$

Diethyl fumarate						
$10^3[Br^-]$	18	58	108	158	208	
$10^6k(1 + 16[Br^-])$ obs.	149	375	650	976	1290	
calc.	141	379	677	974	1272	
Diethyl maleate						
$10^3[Br^-]$	8	58	108	158	208	
$10^6k(1 + 16[Br^-])$ obs.	42	81	128	189	200	
calc.	43	84	125	167	209	
3,3-Dichloroallyl alcohol						
$10^3[Br^-]$	50	100	150	200		
$10^5k(1 + 16[Br^-])$ obs.	653	642	656	649		
calc.	650	650	650	650		
Allyltrimethylammonium bromide						
$10^3[Br^-]$	127	227	327	427		
$10^2k(1 + 16[Br^-])$ obs.	47	61	77	91		
calc.	47	61	76	91		
cis-3-Chloroallyl alcohol						
$10^3[Br^-]$	20	40	60	80	100	
$10^2k(1 + 16[Br^-])$ obs.	306	310	316	317	326	
calc.	306	311	315	321	325	
trans-3-Chloroallyl alcohol						
$10^3[Br^-]$	20	40	60	80	100	
$10^2k(1 + 16[Br^-])$ obs.	320	330	334	345	363	
calc.	318	328	338	348	358	
trans-3-Phenylallyltrimethylammonium bromide						
$10^3[Br^-]$	15	25	45	65	85	105
$10k(1 + 16[Br^-])$ obs.	383	393	404	420	444	449
calc.	383	391	406	422	437	453
2-Chloroallyl alcohol						
$10^3[Br^-]$	21	42	63	85	106	
$k(1 + 16[Br^-])$ obs. ...	68	73	75	78	83	
calc. ...	68	72	75	79	82	
3,3-Diphenylallyltrimethylammonium bromide						
$10^3[Br^-]$	20	40	60	80	100	
$k(1 + 16[Br^-])$ obs. ...	822	815	817	827	820	
calc. ...	818	818	818	818	818	

Two methods were used for studying the rate of addition of water and hydrogen bromide to epoxides. In the first (used only for glycidol) the automatic titrator is used to add hydrobromic acid solution at such a rate as to keep the pH constant, and the record of acid consumption serves as a measure of the reaction velocity. Since the concentrations of both hydrogen ion and bromide ion are maintained constant during an experiment, a first-order velocity constant can be obtained directly from the chart record. In a typical experiment the concentration of glycidol was 0·04M, and the syringe contained 1M-hydrobromic acid. In the second method, used for all the epoxides studied, the consumption of hydrogen bromide was followed by the change in the conductivity of the solution. Suppose that the solution contains epoxide at concentration y, initially y_0, hydrobromic acid at concentration x, initially x_0, and that the only reactions contributing appreciably to the observed rate are the acid-catalysed addition of water, with a rate equal to $k_3[H^+][\text{epoxide}]$, and the addition of hydrogen bromide with a rate equal to $k_4[H^+][Br^-][\text{epoxide}]$. The neglect in these solutions of terms proportional to bromide ion concentration only, or independent of both bromide ion concentration and hydrogen ion concentration, is justified by reference to the measurements of Brönsted, Kilpatrick, and Kilpatrick[13] for glycidol at 20°, and by our own measurements by the titrator method. The kinetic equations are then

$$\frac{dx}{dt} = -k_4yx^2;\quad \frac{dy}{dt} = -k_4yx^2 - k_3yx \tag{4}$$

from which it is readily shown that

$$y_0 - y = x_0 - x + \frac{k_3}{k_4}\ln\frac{x_0}{x} \tag{5}$$

and hence

$$\frac{dx}{dt} = -k_4x^2\left(y_0 - x_0 + x - \frac{k_3}{k_4}\ln\frac{x_0}{x}\right) \tag{6}$$

$$\frac{1}{y_0 - x_0 + x}\,\frac{d}{dt}\left(\frac{1}{x}\right) = k_4 - \frac{k_3}{y_0 - x_0 + x}\ln\frac{x_0}{x} \tag{7}$$

In applying equation (7) to the experimental results, the observed resistances were first converted to hydrobromic acid concentrations by means of a calibration curve. A plot of $1/x$ against t was then used to obtain values of $\frac{d}{dt}\left(\frac{1}{x}\right)$ at suitable intervals, and finally a linear plot of $\frac{1}{y_0 - x_0 + x}\,\frac{d}{dt}\left(\frac{1}{x}\right)$ against $\frac{1}{y_0 - x_0 + x}\ln\frac{x_0}{x}$ gave k_3 as the slope and k_4 as the intercept. A typical experiment employed 0·2M-epoxide and 0·1M-hydrobromic acid.

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[13] J. N. Brönsted, M. Kilpatrick, and M. L. Kilpatrick, *J. Amer. Chem. Soc.*, 1929, **51**, 428.

RESULTS

As in Part I,[1] the observed second-order velocity constants k for the reaction of bromine with an olefin in presence of bromide ions has been analysed by the equation

$$k = (k_1[Br_2] + k_1'[Br_3^-])/([Br_2] + [Br_3^-])$$
$$= (k_1 + k_1'K[Br^-])/(1 + K[Br^-]) \quad (8)$$

where $K = [Br_3^-]/[Br_2][Br^-]$. We have assumed $K = 16$ throughout,[14,15] and Table 1 compares the observed values of $k(1 + 16[Br^-])$ with those calculated from equation (8) and the values of k_1 and k_1' in Table 5. The close agreement shows that molecular bromine and tribromide ion are the only bromine species contributing appreciably to the observed rate.

TABLE 2

Rates of reaction with bromine in chloride solutions at 25°

k_2', k_3' are second-order constants for reaction with Br_2Cl^- and $BrCl_2^-$, M^{-1} sec.$^{-1}$

k = Observed second-order constant, M^{-1} sec.$^{-1}$

Diethyl fumarate $k_2' = 6{\cdot}3 \times 10^{-4}$, $k_3' \simeq 0$, $[Cl^-] = 1{\cdot}00$

$10^4[Br^-]$	100	125	167	250	500
10^6k obs.	266	295	291	313	365
calc.	269	285	300	319	342

2-Chloroallyl alcohol $k_2' = 40$, $k_3' = 5{\cdot}4 \times 10^3$, $[Cl^-] = 0{\cdot}20$

$10^4[Br^-]$	100	125	167	250	500
k obs.	154	138	115	86	56
calc.	163	138	112	86	56

TABLE 3

Product ratios at 25°

n = Number of moles of olefin needed to produce one mole of bromohydrin

Diethyl fumarate

$10^3[Br^-]$	10	20	30	40	50
n obs.	3·10	3·62	6·29	8·23	10·00
calc.	2·77	4·54	6·31	8·08	9·85

Diethyl maleate

$10^3[Br^-]$	10	20	30	40	50
n obs.	1·55	2·06	2·28	2·86	3·50
calc.	1·48	1·97	2·45	2·95	3·42

3,3-Dichloroallyl alcohol

$10^3[Br^-]$	50	100	150	200
n obs.	1·40	1·74	1·96	2·47
calc.	1·37	1·74	2·11	2·48

Allyltrimethylammonium bromide

$10^3[Br^-]$	123	223	323	423	523
n obs.	1·27	1·56	1·72	1·99	2·19
calc.	1·28	1·51	1·74	1·97	2·20

cis-3-Chloroallyl alcohol

$10^3[Br^-]$	10	20	30	40	50	60	70
n obs.	1·024	1·046	1·068	1·092	1·113	1·134	1·157
calc.	1·022	1·405	1·067	1·089	1·112	1·134	1·156

trans-3-Chloroallyl alcohol

$10^3[Br^-]$	10	20	30	40	50	60	70
n obs.	1·032	1·046	1·070	1·092	1·106	1·138	1·146
calc.	1·022	1·044	1·066	1·088	1·110	1·132	1·154

2-Chloroallyl alcohol

$10^3[Br^-]$	10	20	30	40	50	60	70
n obs.	1·003	1·010	1·022	1·023	1·033	1·036	1·041
calc.	1·006	1·012	1·019	1·025	1·031	1·037	1·044

Allyl alcohol

$10^3[Br^-]$	100	200	300	400	500	600
n obs.	1·056	1·099	1·139	1·168	1·230	1·251
calc.	1·044	1·088	1·132	1·176	1·220	1·264

Kinetic measurements were also made with diethyl fumarate and 2-chloroallyl alcohol in the presence of 1M- and 0·2M-chloride ions. These solutions will contain, in addition to molecular bromine and tribromide ions, appreciable quantities of the ions Br_2Cl^- and $BrCl_2^{2-}$, and the observed velocity constant should now be given by

$$k(1 + K[Br^-] + K_1[Cl^-] + K_2[Cl^-]^2/[Br^-])$$
$$= k_1 + k_1'K[Br^-] + k_2'K_1[Cl^-] + k_3'K_2[Cl^-]^2/[Br^-] \quad (9)$$

where $K_1 = [Br_2Cl^-]/[Br_2][Cl^-]$, $K_2 = [BrCl_2^-][Br^-]/[Br_2][Cl^-]^2$, and k_2' and k_3' are the velocity constants for the reactions of Br_2Cl^- and $BrCl_2^-$ with olefin. Recent measurements in this laboratory[16] have given $K_1 = 1{\cdot}14$, $K_2 = 7{\cdot}2 \times 10^{-3}$. Table 2 contains the observed velocity constants, together with values calculated from the above values of K_1 and K_2, k_2' and k_3' from Table 2, and k_1 and k_1' from Table 5.

TABLE 4

Reactions of epoxides at 25°

k = Observed first-order velocity constant (sec.$^{-1}$)
k_0' in sec.$^{-1}$, k_3 in M^{-1} sec.$^{-1}$, k_4 in M^{-2} sec.$^{-1}$ [cf. eqn. (11)]

Glycidol. (*a*) Titrator method

$k_0' = 5 \times 10^{-5}$, $k_3 = 4{\cdot}0 \times 10^{-3}$, $k_4 = 1{\cdot}30 \times 10^{-2}$

$[Br^-] = 0{\cdot}100$

$10^4[H^+]$ …	41	64	92	105	115	151	200	251
10^6k obs. …	30	34	52	62	68	82	102	125
calc.…	27	39	54	61	66	85	111	142

$[Br^-] = 0{\cdot}200$

$10^4[H^+]$ …	40	63	79	100	126	159	200	229	254
10^6k obs. …	43	57	62	75	95	123	141	163	181
calc.…	36	52	62	76	93	115	142	161	178

$[Br^-] = 0{\cdot}300$

$10^4[H^+]$ …	36	68	105	145	178	207	251
10^6k obs. …	40	73	93	130	152	180	219
calc.…	43	69	98	130	163	179	214

$[Br^-] = 0{\cdot}400$

$10^4[H^+]$ …	34	78	106	126	174	209	251
10^6k obs. …	48	86	117	141	184	219	253
calc.…	51	92	117	136	180	212	251

(*b*) Conductimetric method

10^3[glycidol]	10^4k_3	10^3k_4
200	55	32
243	52	33
257	50	32
312	56	32
Mean	53	32

Propylene oxide. Conductimetric method

10^3k_3 = 40, 40, 41, 40; mean 40
10^2k_4 = 38, 39, 39, 39; mean 39

Ethylene oxide. Conductimetric method

10^4k_3 = 99, 100, 100, 99; mean 100
10^3k_4 = 114. 117, 118, 120; mean 117

The product ratios determined are given in Table 3. If the proportions of bromohydrin and dibromide are determined by the competition of water and bromide ions for a single intermediate (see Discussion section), then

$$n = 1 + \beta[Br^-] \quad (10)$$

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[14] G. Jones and S. Baeckström, *J. Amer. Chem. Soc.*, 1934, **56**, 1517.

[15] D. B. Scaife and H. J. V. Tyrrell, *J. Chem. Soc.*, 1958, 386.

[16] R. P. Bell and M. Pring, *J. Chem. Soc.* (*A*), 1966, 1607.

where n is the number of molecules of olefin required to produce one mole of bromohydrin and β is a competition factor characteristic of the olefin. The values of n(calc.) in Table **3** are obtained from equation (10) and the values of β in Table 5.

The kinetic results for reactions of epoxides are given in Table 4. The total rate of reaction is given by

$$-\mathrm{d}[\text{epoxide}]/\mathrm{d}t = (k_0'[\mathrm{Br}^-] + k_3[\mathrm{H}^+] + k_4[\mathrm{H}^+][\mathrm{Br}^-])[\text{epoxide}] \quad (11)$$

The conductivity method gives the values of k_3 and k_4 directly, while in the titrator method the observed first-order velocity constants are compared with those calculated from equation (11) and the values of k_0', k_3, and k_4 given in the Table. The contribution of the term in k_0' is small, and this constant is not given reliably by our experiments. For glycidol there is a considerable discrepancy in the results obtained by the two methods: this is explicable by the large kinetic salt effects observed in this reaction.[13]

TABLE 5

Summary for reactions of olefins with bromine at 25°

k_1 and k_1' in M^{-1} sec.$^{-1}$; β = competition factor, M^{-1}
Values marked with an asterisk are from ref. 1

Olefin	k_1	k_1'	$16k_1'/k_1$	β	$\Sigma\sigma$ *
Diethyl fumarate	$3{\cdot}40 \times 10^{-5}$	$3{\cdot}72 \times 10^{-4}$	175	177	(4·98)
Diethyl maleate	$3{\cdot}60 \times 10^{-5}$	$5{\cdot}20 \times 10^{-5}$	23	48	4·98
3,3-Dichloroallyl alcohol	$6{\cdot}5 \times 10^{-3}$	—	—	7·4	4·97
Ethyl acrylate	* $1{\cdot}06 \times 10^{-1}$	* $6{\cdot}7 \times 10^{-2}$	10	—	3·47
Allyltrimethylammonium bromide	$2{\cdot}84 \times 10^{-1}$	$9{\cdot}1 \times 10^{-2}$	0·51	2·30	3·37
Ethyl crotonate	* 2·76	* 1·04	6·0	—	2·98
cis-3-Chloroallyl alcohol	3·01	0·15	0·80	2·23	3·50
trans-3-Chloroallyl alcohol	3·08	0·31	1·62	2·20	3·50
trans-3-Phenylallyltrimethylammonium bromide	37	4·8	2·08	—	3·48
2-Chloroallyl alcohol	65	9·9	2·43	0·62	3·50
Ethyl cinnamate	* 220	* 23	1·67	—	3·58
Allyl cyanide	* 440	* 100	3·4	—	2·77
3,3-Diphenylallyltrimethylammonium bromide	818	—	—	—	3·59
Ethylene	* $3{\cdot}9 \times 10^{5}$	* $2{\cdot}0 \times 10^{4}$	0·80	* 0·60	1·96
Allyl alcohol	* $6{\cdot}7 \times 10^{5}$	* $6{\cdot}9 \times 10^{4}$	1·60	0·44	2·03
Propene	* $4{\cdot}5 \times 10^{6}$	* $3{\cdot}2 \times 10^{5}$	1·14	* 0·59	1·47

DISCUSSION

The main kinetic results and the product ratios are collected in Table 5, which also includes some of the values from ref. 1. The results for isobutene have not been included, since recent measurements[17] have given somewhat different values. Our velocity constants for diethyl fumarate are all a few per cent. lower than those of Bell and Atkinson,[1] who probably underestimated the loss of bromine by volatilisation. In determining the product ratio for this compound we observed a considerably smaller liberation of acid than reported in ref. 1, probably because of hydrolysis of the ester in the more strongly acid solutions used in the earlier work. Our observed product ratios with allyl alcohol are consistent with those reported by Bell and Atkinson,[1] but show much less scatter.

The velocity constants obtained for the reactions of glycidol and ethylene oxide at 25° (Table 4) are consistent with those reported by Brönsted *et al.*[13] and by Virtanen[18] at other temperatures.

It has been suggested by Kanyaev[19] that in aqueous solution olefins react with tribromide ion to give dibromide, and with molecular bromine to give bromohydrin. If this were so, the quantity $16k_1'/k_1$ (representing the ratio of the two reaction velocities in 1M-bromide solution) should have the same value as the factor β defined in equation (10). Table 5 shows that there is no correspondence between these two quantities. As previously suggested,[1] Kanyaev's hypothesis cannot therefore be generally valid: it has also been shown by Hine[20] that a kinetically equivalent hypothesis fails to account for the results of Bartlett and Tarbell[21] for the reaction of styrene with bromine in methanol. Our results strongly support the usually accepted scheme in which a reactive intermediate is formed by electrophilic attack on the olefin by either Br_2 or Br_3^-, and the product ratio is determined by a subsequent rapid competition for this intermediate by bromide ions and water. It is simplest to assume that both Br_2 and Br_3^- lead to the same intermediate, but, as pointed out by Bell and Atkinson,[1] this makes it difficult to explain the fact that $k_1' > k_1$ for diethyl fumarate (and perhaps for some of the compounds studied by Kanyaev[19]), since tribromide ion can hardly be a more powerful electrophilic reagent than bromine. For this reason Bell and Atkinson suggested a more complicated kinetic scheme involving two different intermediates: however, no direct evidence was produced for this scheme, and it is difficult to envisage what the two intermediates could be.

It seems more probable that the rate-determining step in the reaction of bromine with diethyl fumarate is not a simple electrophilic attack, but also involves nucleophilic attack by water or by bromide ion; the

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[17] J. E. Dubois and E. Barbier, *Tetrahedron Letters*, 1965, 1217.

[18] S. Virtanen, *Ann. Acad. Sci. Fennicae*, 1963, *AII*, 124.

[19] N. P. Kanyaev, *J. Gen. Chem. U.S.S.R.*, 1956, **26**, 3037; 1959, **29**, 825.

[20] J. Hine, " Physical Organic Chemistry," McGraw-Hill, New York, 1956, p. 207.

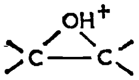
[21] P. D. Bartlett and D. S. Tarbell, *J. Amer. Chem. Soc.*, 1936, **58**, 466.

latter is kinetically equivalent to reaction with tribromide ion. This would explain the observation that $k_1' > k_1$ for diethyl fumarate, and also that the quantities $16k_1'/k_1$ and β are equal for this compound. An electrophilic–nucleophilic mechanism is the most probable explanation of the high kinetic orders sometimes observed for the reaction of bromine with olefins in non-aqueous solvents, and Shilov[22] has recently shown that in some solvents various nucleophilic catalysts are incorporated in the product to the extent that they catalyse the reaction. The suggested mechanistic differentiation between the reaction of diethyl furmarate and those of the remaining olefins is supported by the results obtained in chloride solutions (Table 2). For 2-chloroallyl alcohol the velocity constants for reaction with Br_3^-, Br_2Cl^-, and $BrCl_2^-$ are 9·9, 40, and 5·4 × 10^3 M^{-1} sec.$^{-1}$, which is the order expected for simple electrophilic attack, while for diethyl fumarate the corresponding figures are 3·7 × 10^{-4}, 6·3 × 10^{-4}, and *ca.* 0, which do not form a logical sequence. The results for diethyl fumarate can be re-interpreted in terms of third-order reactions involving both a bromine molecule and a nucleophil by using the appropriate equilibrium constants and taking $[H_2O] = 55$. This gives $k(Br_2,H_2O) = 6{\cdot}1 \times 10^{-7}$, $k(Br_2,Cl^-) = 7{\cdot}2 \times 10^{-4}$, $k(Br_2,Br^-) = 6{\cdot}0 \times 10^{-3}$, which are in the expected order of nucleophilicity.

The effect of substituents on the values of k_1 and k_1' shows an approximate correlation with Taft's σ^* constants. The values of $\Sigma\sigma^*$ in the last column of Table 5 derive mainly from standard compilations.[23,24] Values of σ^* for –Cl and –OH cannot be obtained directly, and we have derived σ^* (Cl) = 2·00, σ^* (OH) = 0·85 from the equation $\sigma^* = 4{\cdot}47\ \sigma$ (*meta*) + 0·34 which is found to hold for many substituents. No exact correlation with σ^* would be expected since resonance is possible in several of the compounds and steric effects must also play a part, but the results show the very strong dependence on electron density expected for a simple electrophilic attack. Relations between substituent constants and addition reaction to olefins over a much smaller range of velocities have been recently reported by Dubois and his co-workers.[25]

The nature of the reactive intermediate formed by the action of bromine or tribromide ion is still uncertain, but our results provide some further evidence that the cyclic bromomium ion proposed by Roberts and Kimball[26] is to be preferred to a carbonium ion. It is unlikely that bromide ion at low concentrations could compete successfully with water for the unstable primary and secondary carbonium ions corresponding to some of the olefins in Table 5, since for the much more stable t-butyl cation the competition factor is only 2M^{-1}.[27] Moreover, the results obtained here for the chloroallyl alcohols are difficult to reconcile with the carbonium ion hypothesis. As already mentioned, the amounts of acid liberated in the bromination of these compounds at low concentrations of bromine ions show that the attack by water takes place at the carbon atom bearing the chlorine, with subsequent hydrolysis and liberation of more acid. If a cyclic bromonium ion is formed, this is readily explained by the preference of the water molecule for the carbon atom bearing the higher positive charge, but in terms of carbonium ions it would imply the preferential formation of improbable carbonium ions such as $CH_2OH{\cdot}CHBr{\cdot}C^+Cl_2$.

It was hoped to test the bromonium ion hypothesis by a study of the reasons of analogous epoxides. There is good evidence from the entropies[18] and volumes[28] of activation that the reactions of epoxides with aqueous hydrogen halides involve the pre-equilibium formation of the cation (I) which is then competed for by halide ions and water molecules. These cations are analogous to the cyclic bromonium ions, and the competition factors should be affected similarly by substituents in the two cases. Unfortunately it was found possible to prepare only three relevant epoxides which reacted at a convenient rate. For these three the ratios k_4/k_3 (Table 4) are ethylene oxide 11·7M^{-1}, propylene oxide 9·8M^{-1}, glycidol 4·6M^{-1}. The corresponding competition factors β in the bromination of the analogous olefins (Table 5) are ethylenes 0·60M^{-1}, propylene 0·59, allyl alcohol 0·44. The trend is similar in the two series, but much more extensive results would be needed to provide a real test of the bromonium ion mechanism.



(I)

Finally it should be mentioned that the facts are equally well accounted for by the type of intermediate suggested by Williams,[29] in which one end of the bromine molecule is attached to the π-electrons of the double bond. This is analogous to the formulation of the tribromide ion in terms of pure *p*-bonding,[30] which is supported by the observed force-constants[31] and nuclear quadrupole coupling.[32] The main evidence adduced to support the bromonium ion hypothesis is the preponderance of *trans*-addition, though an exception has to be made for addition to the doubly charged maleate ion. We have found that the reaction of bromine with diethyl fumarate and diethyl maleate in aqueous 1M-sodium bromide (under which conditions the dibromide is formed almost exclusively) gave white

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[24] J. Hine, "Physical Organic Chemistry," 2nd edn., p. 97, McGraw-Hill, New York, 1962.

[25] J. E. Dubois and G. Mouvier, *Compt. rend.*, 1964, **259**, 2101; J. E. Dubois and E. Goetz, *Tetrahedron Letters*, 1965, 303.

[26] I. Roberts and G. E. Kimball, *J. Amer. Chem. Soc.*, 1937, **59**, 947.

[27] L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 1940, 979.

[28] J. Koskikallio and E. Whalley, *Trans. Faraday Soc.*, 1959, **55**, 815.

[29] G. Williams, *Trans. Faraday Soc.*, 1941, **37**, 749.

[30] G. C. Pimentel, *J. Chem. Phys.*, 1951, **19**, 446.

[31] W. B. Person, G. R. Anderson, J. N. Fordemwalt, H. Stammreich, and R. Forneris, *J. Chem. Phys.*, 1961, **35**, 908.

[32] R. S. Yamasaki and C. D. Cornwell, *J. Chem. Phys.*, 1959, **30**, 1265.

solids, m. p. 58°, singly and when mixed. Schulek and Burger[33] find 58° for the m. p. of diethyl *meso*-dibromosuccinate, while the (—)-isomer is a liquid at room temperatures. The formation of the *meso*-isomer in both cases implies that diethyl fumarate and maleate undergo *trans*- and *cis*-addition, respectively. The electrophilic–nucleophilic mechanism which we have suggested for diethyl fumarate predicts *trans*-addition, but the occurrence of *cis*-addition with diethyl maleate is the reverse of what would be expected from a bromonium ion. In the Williams intermediate the migration of charge from the double bond into the bromine molecule should lower the barrier to rotation, so that there is more latitude in the stereochemical course of the reaction.

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