606. *Kinetics of the Reaction of Bromine with Olefins in Aqueous Solution.*

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The rate of the reaction between bromine and ten olefinic substances has been studied in aqueous solution at 25°, and the ratios of dibromide to bromohydrin in the products have been determined for four of these substances. The velocity constants range from 10^{-4} to 6×10^6 l. mole^{-1} sec.$^{-1}$, and in most cases were measured electrometrically. The relative reactivities of molecular bromine and tribromide ion vary with the nature of the olefin and bear no relation either to the reactivity of the olefin or to the product ratio. The mechanism and the effect of olefin structure are discussed.

Most of the kinetic data for the addition of halogens to unsaturated substances relate to organic solvents, for example, acetic acid and carbon tetrachloride.[1] The choice of these has often depended on the solubility of the organic reactant and on the need to obtain a reaction slow enough to follow by conventional means, but there is often doubt about the nature of the halogen species present, especially in solutions containing hydrogen halide, and the dependence of the rate upon halogen concentration is sometimes complex. The study of halogen addition in aqueous solution involves much faster reactions, but has the advantage that the concentration of active halogen species (*e.g.*, Br_2, Br_3^-, and HOBr) is accurately predictable and controllable. In aqueous solution there are also two possible products, dibromide and bromohydrin, the proportions of which may throw light on the reaction mechanism. Kanyaev [2,3] has recently studied the addition of bromine to some olefinic substances in aqueous solution; he claims that the relative reactivity of Br_2 and

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[1] de la Mare, *Quart. Rev.*, 1949, **3**, 126.
[2] Kanyaev, *J. Gen. Chem.* (*U.S.S.R.*), 1959, **29**, 825.
[3] Kanyaev, *J. Gen. Chem.* (*U.S.S.R.*), 1956, **26**, 3037.

Br_3^- varies continuously with the reactivity of the olefin, and also that the proportion of dibromide in the product is equal to the fraction of the reaction effected by the tribromide ion. The olefins studied by Kanyaev all contain strongly electronegative substituents, which was necessary in order to obtain sufficiently slow reactions. We have used the electrometric methods developed in this laboratory for the study of fast halogenation to extend measurements to a much wider range of compounds (including some simple olefins), covering a range of about 10^{11} in velocity constants, and have not been able to substantiate Kanyaev's findings.

EXPERIMENTAL

All solutions were made up with distilled water which had been redistilled from alkaline potassium permanganate in a glass still. Bromine, perchloric acid, potassium bromide, sodium nitrate, and sodium hydroxide were of " AnalaR " grade. Sodium bromide and sodium perchlorate were Laboratory Reagent products, recrystallised from water. The following compounds were purified by fractional distillation: ethyl *trans*-cinnamate (b. p. 127—130°/6 mm.), allyl cyanide (b. p. 117°), allyl alcohol (b. p. 95·5—96°). The following were washed with 5% sodium carbonate solution, then with saturated calcium chloride solution, dried ($CaCl_2$), and distilled: ethyl acrylate (b. p. 99·5°), ethyl *trans*-crotonate (b. p. 137°), diethyl fumarate (b. p. 218°). *trans*-Stilbene (m. p. 124°) was used without further purification. The gaseous olefins were obtained from cylinders (Imperial Chemical Industries Limited) and were examined in the mass spectrometer, with the following results: ethylene, 2—3% of paraffin hydrocarbons, no other olefins present; propene, 3% of propane, no other olefins present; isobutene, no detectable impurities.

All kinetic experiments were carried out at 25°. With the exception of diethyl fumarate, the reaction of bromine with all these compounds was investigated by the method described by Bell and Robinson,[4] in which the fall in bromine concentration is followed by measuring the potential of a platinum redox electrode against a glass electrode. The potential of the latter was fixed by the presence of a known concentration of perchloric acid: this varied from 6×10^{-4}M to 0·1M in different experiments, but was always chosen so that the acid liberated by the formation of bromohydrin would produce a negligible change of potential. Experiments with allyl alcohol (see Table 1) showed no change in velocity when the acid concentration was varied by a factor of 100. In the fastest reactions studied readings were taken at intervals of about 2 sec., and when played back the tape recording could be timed to 0·2 sec.: the time needed for complete mixing of the reactants was estimated at 1—2 sec.

Two different methods were used in treating the results. For four olefins (ethyl cinnamate, ethyl acrylate, ethyl crotonate, and allyl cyanide) the reactivity and solubility made it possible to use an olefin concentration at least twenty times the initial bromine concentration. Each reaction then follows a first-order course, and the e.m.f. falls linearly with time. Accurately linear plots were in fact obtained over at least 60 mv, corresponding to a decrease in bromine concentration by a factor of 100. The second-order velocity constant is given by

$$k = -78{\cdot}2\frac{dE}{dt}\Big/c, \qquad (1)$$

where c is the mean concentration of organic substance, differing little from the final concentration.

With ethyl cinnamate, c was usually about 2×10^{-4}M and the initial bromine concentration about 10^{-5}M. Stock solutions of the ester near the saturation limit were made by breaking bulbs of ester under the surface of hot water, and making up to a known volume after cooling. If this procedure was not adopted, the ester formed a film on the side of the flask which was difficult to dissolve completely. Potentiometric observations in systems with a slight excess of bromine showed that the stoicheiometry of the reaction was accurately 1 : 1.

With ethyl acrylate typical concentrations were $c = 4 \times 10^{-2}$M, initial bromine 3×10^{-4}M. Several runs were carried out with each reaction solution by adding successive quantities of bromine solution, and tests showed that there was no detectable loss of bromine by evaporation or reaction with impurities during the time required for such a series (about 10 min.). Conditions for ethyl crotonate were similar ($c = 3 \times 10^{-3}$M, initial bromine 3×10^{-4}M), while for

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[4] Bell and Robinson, *Proc. Roy. Soc.*, 1962, *A*, **270**, 411.

allyl cyanide, the most reactive substance in this group, typical initial concentrations were $c = 3 \times 10^{-4}$M, bromine 3×10^{-6}M.

The other olefins studied electrometrically were much more reactive, so that it was no longer possible to work with a large excess of olefin. Measurements were therefore made with comparable and very low initial concentrations of olefin and bromine (average about 5×10^{-7}M for allyl alcohol, ethylene, and stilbene, and about 5×10^{-8}M for propene and isobutene). Such low bromine concentrations could not be reliably obtained by diluting solutions of known concentration, since the doubly distilled water still contained sufficient impurity to react with about 10^{-7}M-bromine. The following procedure was therefore used in experiments with allyl alcohol. The reaction solution was made up without olefin, and approximately the required quantity of dilute bromine solution added. The observed potential at first fell slowly, because of reaction with impurities, but eventually reached a stable value, which was noted. A small volume of relatively concentrated (*ca.* 10^{-4}M) allyl alcohol solution was then added, and the change of potential with time recorded. When reaction had ceased, enough bromine solution was added to the mixture to give a concentration of about 10^{-3}M; the potential was then measured, and the actual bromine concentration determined by withdrawing a sample of the mixture, adding potassium iodide, and titrating the liberated iodine with sodium thiosulphate solution. The last potential can now be used to calculate E_0 in the equation

$$[\mathrm{Br_2^*}]_t = \text{antilog}\,\{(E_t - E_0)/0{\cdot}02958\}, \tag{2}$$

where E_t is the observed e.m.f. at time t, $[\mathrm{Br_2^*}]$ represents the sum of molecular bromine and tribromide ion, and E_0 (though constant during one kinetic experiment) depends upon $[\mathrm{Br^-}]$, $[\mathrm{H^+}]$, and the ionic strength. In calculating E_0 from the potential observed after the final addition of bromine the following factors must be taken into account: (*a*) the proportion of bromine or bromide ion tied up as tribromide ion will differ somewhat from that obtaining during the kinetic observations; (*b*) the hydrogen-ion concentration (and hence the potential of the glass electrode) will be changed a little by the final addition of bromine solution; (*c*) any change in ionic strength caused by this addition will modify the activity coefficients of $\mathrm{H^+}$ and $\mathrm{Br^-}$ which enter the complete expression for the e.m.f. Corrections (*b*) and (*c*) are small, and become negligible if the final addition of bromine is in the form of liquid bromine: correction (*a*) is also reduced by this procedure, which was used in most experiments involving comparable concentrations of bromine and olefin.

E_0 having been obtained, the total bromine concentration at any time is calculated from equation (2), and the concentration of unchanged olefin by difference. A plot against time of $\log([\mathrm{Br_2^*}]/[\text{Olefin}])$ should then be linear, with a slope of $-0{\cdot}434\,([\text{Olefin}]_{\mathrm{i}} - [\mathrm{Br_2^*}]_{\mathrm{i}})k$, where a subscript i indicates that the concentration is the initial one. Fig. 1 shows a typical plot of this kind for the reaction of bromine with allyl alcohol.

The volatility of the gaseous olefins makes it impossible to prepare very dilute solutions of known concentration by dilution, though once the solution was in the reaction vessel, loss by evaporation was relatively slow (half-time about 20 min. for ethylene and 60 min. for propene, compared with 5—30 sec. for reaction with bromine). The same difficulty arises with stilbene because of its low solubility, about 2×10^{-5}M. For these substances it was therefore necessary to determine the initial concentrations of both bromine and olefin from the observed potentials, which is possible by the following procedure if a small excess of bromine remains after reaction. An initial potential E_{i} is measured before the addition of olefin (but after time has been allowed for the bromination of impurities). A small volume of olefin solution is then added, and the fall of potential followed down to a second steady value of E_{f}. It is often convenient to make several kinetic observations in the same solution by the successive addition of bromine solution and olefin solution alternately, and interpretation is simplified if all the solutions used in a given series contain the same concentrations of sodium bromide and perchloric acid. Finally, some liquid bromine is added, and the appropriate value of E_0 for the series determined as described above.

For a given experiment it is easily shown that

$$\left.\begin{aligned} \log\{[\mathrm{Br_2^*}]/[\text{Olefin}]\} &= -\log\left\{1 - \text{antilog}\,\frac{E_{\mathrm{f}} - E_t}{0{\cdot}02958}\right\} = F, \\ \log\{[\mathrm{Br_2^*}]_{\mathrm{i}} - [\text{Olefin}]_{\mathrm{i}}\} &= -(E_0 - E_{\mathrm{f}})/0{\cdot}02958 = F'. \end{aligned}\right\} \tag{3}$$

A plot of F against t should therefore give a straight line of slope $- 0{\cdot}434k$ antilog F', from which k can be calculated: calculation is facilitated by constructing tables of F and F' for all relevant values of the difference in potentials. Typical plots of F against t for propene are shown in Fig. 2. Their linearity is sensitive to the exact value taken for E_f, and occasionally the observed value was adjusted to make the plot linear, though never by more than 0·4 mv.

In the experiments with stilbene the final potential remained constant for 5—10 min., and then fell off with increasing speed, corresponding approximately to a zero-order disappearance of bromine from 3×10^{-7}M down to less than 10^{-9}M. This could be formally accounted for if the product formed in the addition reaction changed in some rate-determining manner into a species which removes bromine very rapidly, but it is difficult to see what this reaction could be. This behaviour does not appear to affect the previous second-order addition of bromine.

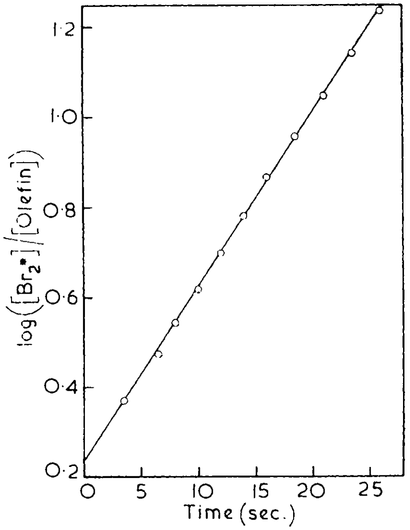

FIG. 1. Bromination of allyl alcohol. Initial concentrations: $[\mathrm{Br_2}^*] = 4{\cdot}41 \times 10^{-7}$, $[\text{Olefin}] = 8{\cdot}41 \times 10^{-7}$M.

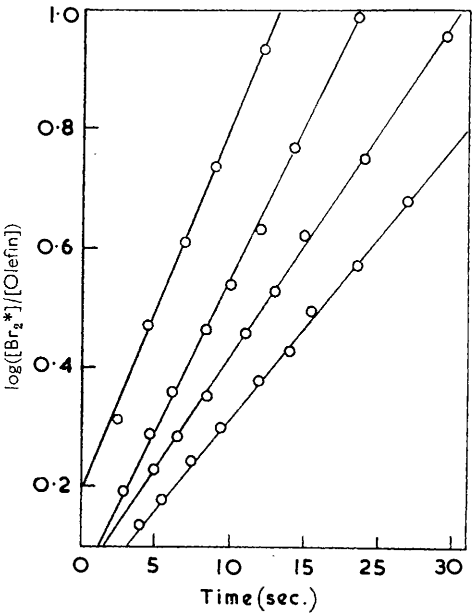

FIG. 2. Bromination of propene. Initial concentrations: $[\mathrm{Br_2}^*] = ca.\ 1 \times 10^{-7}$, $[\text{Olefin}] = ca.\ 7 \times 10^{-8}$M.

The addition of bromine to diethyl fumarate is slow, involving experiments lasting several days with initial concentrations of both reactants about 10^{-2}M. This reaction was therefore followed by removing samples, adding potassium iodide, and titrating the liberated iodine. Blackened vessels were used, and a small correction applied for the loss of bromine by evaporation, determined from blank experiments at each bromide concentration used. The acid concentration was kept low (10^{-3}—10^{-4}M) in order to avoid hydrolysis of the ester: the acid hydrolysis of diethyl fumarate does not appear to have been studied kinetically, but the catalytic constants for dimethyl succinate and methyl acrylate are $2{\cdot}3 \times 10^{-5}$ and $4{\cdot}7 \times 10^{-6}$ l. mole^{-1} sec.$^{-1}$, respectively, at 25°, so that hydrolysis should be negligible. The second-order velocity constants for reaction with bromine were obtained by plotting $\log([\mathrm{Br_2}^*]/[\text{Olefin}])$ against time.

The relative amounts of dibromide and bromohydrin formed from allyl alcohol, diethyl fumarate, ethylene, and propene were determined by analysis. The concentration of bromide was varied over the same range as in the kinetic experiments, but the concentrations of bromine and olefin were much greater (usually 0·01—0·1M). The acid produced by bromohydrin formation was estimated by titration with sodium hydroxide solution: Methyl Red was normally used as indicator, but with diethyl fumarate (where the concentrations were low because of limited solubility) a Radiometer automatic pH-titrator was used, and some estimations of acid were also made by adding an excess of iodate and iodide and titrating the iodine liberated (after long storage under nitrogen) with sodium thiosulphate solution. Two series of determinations were carried out with allyl alcohol, with either the alcohol or the bromine in excess. The excess of bromine was removed by a current of nitrogen before titration of the acid. The two series gave concordant results. With ethylene and propene the estimations were checked (cf. de la Mare and Galandauer [5]) by adding a known excess of sodium hydroxide solution and storage overnight, which neutralises the hydrogen bromide formed and also converts the bromohydrins into ethylene oxide or propylene oxide, with the consumption of another mol. of alkali. The excess of alkali is then titrated with acid. The values obtained in this way agreed well with those obtained by direct titration. The results obtained are collected in Table 3: their estimated accuracy is about ±0·03. Attempts were made to extend measurements to the less soluble olefins by measuring the change of pH with a glass electrode, but reliable results could not be obtained.

RESULTS

The second-order velocity constants obtained refer to the total analytical bromine concentration $[Br_2^*]$, and may involve several reactive bromine species. In fact the results can be accounted for in terms of Br_2 and Br_3^-: the absence of any dependence on hydrogen-ion

TABLE 1.

Kinetics of bromine addition at 25°.

k = second-order velocity constant (l. mole^{-1} sec.$^{-1}$); n = number of experiments.

Diethyl fumarate, $[H^+] = 3\cdot2 \times 10^{-3}$M.

		$10^6k(1 + K[Br^-])$	
$[Br^-]$	10^6k	obs.	calc.
0·02	171	225	225
0·04	185	367	370
0·05	202	364	412
0·07	257	545	537
0·10	284	738	724
0·15	305	1037	1036
0·20	323	1360	1350

Ethyl acrylate.

				$10^3k(1 + K[Br^-])$	
$[Br^-]$	$[H^+]$	n	10^3k	obs.	calc.
0·02	0·10	3	97 ± 2	127	127
0·05	0·10	2	88	158	160
0·10	0·10	4	83 ± 1	215	213
0·10	0·05	2	82	213	213
0·15	0·10	2	79	267	267
0·20	0·10	2	77	320	321

Ethyl crotonate, $[H^+] = 0\cdot10$M.

			$10^2k(1 + K[Br^-])$	
$[Br^-]$	n	10^2k	obs.	calc.
0·02	2	228	300	309
0·05	2	203	365	359
0·10	6	169 ± 1	439	442
0·15	3	155 ± 2	528	526
0·20	3	144 ± 4	606	609

Ethyl cinnamate, $[H^+] = 9\cdot0 \times 10^{-4}$M.

Experiments at constant ionic strength $I = 0\cdot2$.

				$k(1 + K[Br^-])$	
$[Br^-]$	Added salt	n	k	obs.	calc.
0·01	$NaClO_4$,NaBr	3	211 ± 2	246	248
0·02	$NaClO_4$,NaBr	2	188	250	250
0·02	$NaNO_3$,KBr	3	187 ± 2	248	250
0·03	$NaClO_4$,NaBr	4	171 ± 1	254	253
0·04	$NaClO_4$,NaBr	2	156	258	256
0·05	$NaNO_3$,KBr	11	148 ± 2	268	258
0·06	$NaClO_4$,NaBr	2	132	260	261
0·09	$NaClO_4$,NaBr	2	112	274	269
0·12	$NaClO_4$,NaBr	2	93	270	275
0·14	$NaClO_4$,NaBr	2	88	286	282
0·15	$NaClO_4$,NaBr	2	83	284	285
0·15	$NaNO_3$,KBr	3	82 ± 1	280	285
0·18	$NaClO_4$,NaBr	4	76 ± 1	294	293
0·20	NaBr	4	70 ± 1	294	298
0·20	KBr	1	70	294	298

Experiments at varying ionic strength.

			$k(1 + K[Br^-])$	
$[Br^-]$	Added salt	k	obs.	calc.
0·04	KBr	143	227	222
0·04	NaBr	132	217	222
0·06	KBr	116	228	232
0·06	NaBr	120	236	232
0·08	KBr	108	247	241
0·08	NaBr	106	236	241
0·12	KBr	88	259	260
0·12	NaBr	87	256	260
0·16	KBr	77	276	279
0·16	NaBr	80	284	279
0·20	KBr	70	294	298
0·20	NaBr	70	294	298

[5] de la Mare and Glandauer, *J.*, 1958, 36.

TABLE 1. (*Continued.*)

Allyl cyanide, $[H^+] = 0{\cdot}1$M.

$[Br^-]$	n	k	$k(1 + K[Br^-])$ obs.	calc.
0·05	7	288 ± 3	519	520
0·10	7	231 ± 2	601	600

Ethylene, $[H^+] = 3{\cdot}2 \times 10^{-3}$M.

$[Br^-]$	n	$10^{-3}k$	$10^{-3}k(1 + K[Br^-])$ obs.	calc.
0·10	5	165 ± 2	429	428
0·20	5	110 ± 1	460	460
0·40	5	71 ± 2	523	524

Stilbene, $[H^+] = 0{\cdot}10$M.

$[Br^-]$	n	$10^{-4}k$	$10^{-4}k(1 + K[Br^-])$ obs.	calc.
0·10	32	30 ± 1	77	78
0·20	11	18 ± 1	78	78

Propene, $[H^+] = 3{\cdot}2 \times 10^{-3}$M.

$[Br^-]$	n	$10^{-5}k$	$10^{-5}k(1 + K[Br^-])$ obs.	calc.
0·10	6	39 ± 1	101	96
0·15	7	34 ± 1	118	122
0·20	5	42 ± 2	175	147
0·25	3	36 ± 2	180	173
0·30	2	31	179	199
0·40	4	30 ± 2	223	250
0·50	10	39 ± 2	350	301

Isobutene, $[H^+] = 3{\cdot}2 \times 10^{-3}$M.

$[Br^-]$	n	$10^{-5}k$	$10^{-6}k(1 + K[Br^-])$ obs.	calc.
0·05	5	28 ± 3	5·1	4·8
0·30	4	52 ± 2	30	29
0·50	7	53 ± 2	48	48

Allyl alcohol, experiments at constant ionic strength $I = 0{\cdot}2$, $NaClO_4$ added, $[H^+] = 6{\cdot}0 \times 10^{-4}$M.

$[Br^-]$	$10^{-3}k$	$10^{-4}k(1 + K[Br^-])$ obs.	calc.
0·08	391	89	75
0·10	309	80	78
0·12	281	82	80
0·14	247	80	82
0·15	268	91	84
0·18	209	81	87
0·20	226	95	89

Experiments at varying ionic strength.

$[Br^-]$	$[H^+]$	n	$10^{-3}k$	$10^{-4}k(1 + K[Br^-])$ obs.	calc.
0·05	$6{\cdot}0 \times 10^{-4}$	1	344	62	72
0·08	$6{\cdot}0 \times 10^{-4}$	1	316	72	76
0·10	$6{\cdot}0 \times 10^{-4}$	2	305	79	78
0·12	$6{\cdot}0 \times 10^{-4}$	1	303	88	80
0·16	$6{\cdot}0 \times 10^{-4}$	1	222	79	85
0·20	$6{\cdot}0 \times 10^{-4}$	2	226	95	89
0·25	$5{\cdot}4 \times 10^{-3}$	2	192	96	95
0·35	$8{\cdot}9 \times 10^{-4}$	1	155	102	106
0·35	$8{\cdot}9 \times 10^{-4}$	2	154 *	101	106
0·40	$1{\cdot}8 \times 10^{-2}$	1	151	112	111
0·45	$1{\cdot}8 \times 10^{-3}$	1	145	119	117
0·45	$1{\cdot}8 \times 10^{-2}$	1	141	116	117
0·50	$3{\cdot}2 \times 10^{-4}$	2	136	122	122
0·50	$3{\cdot}2 \times 10^{-3}$	2	140	126	122
0·50	$5{\cdot}4 \times 10^{-3}$	1	121	109	122
0·50	$1{\cdot}8 \times 10^{-2}$	1	138	124	122

* 0·15M-$NaClO_4$ added.

concentration excludes the participation of hypobromous acid, and no significant concentrations of bromine cations can be present at the relatively high bromide concentrations employed. The observed velocity constant is therefore given by

$$k = (k_1[Br_2] + k_1'[Br_3^-])/[Br_2^*], \tag{4}$$

and hence

$$k(1 + K[Br^-]) = k_1 + k_1'K[Br^-], \tag{5}$$

where $K = [Br_3^-]/[Br_2][Br^-]$. All calculations have been made with the value [6,7] $K = 16$. Values of k_1 and k_1' can be obtained by plotting $k(1 + K[Br^-])$ against $[Br^-]$: Table 1 gives the observed values of $k(1 + K[Br^-])$ and also those calculated from equation (5) with the values of k_1 and k_1' given in Table 2.

If $k_1' \ll k_1$ it may be difficult to establish even its approximate value because of uncertainties due to salt effects on either the velocity constants or the equilibrium constant K. Such salt effects will be specific, as previously shown in the bromination of anisoles,[8] and the problem is not solved by working at a constant ionic strength. Fig. 3 shows the results of two sets of experiments with ethyl cinnamate: in the first set the ionic strength was kept constant at $I = 0{\cdot}2$ by the addition of sodium perchlorate or sodium nitrate, while in the second it was allowed to vary with the added sodium or potassium bromide. The two series clearly lead to considerably different values of k_1 and (especially) k_1', both of which are given in Table 2. However, in corresponding experiments with allyl alcohol, shown in Fig. 4, there is no apparent

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[6] Jones and Baeckström, *J. Amer. Chem. Soc.*, 1934, **56**, 1517.

[7] Scaife and Tyrrell, *J.*, 1958, 386.

[8] Bell and Rawlinson, *J.*, 1961, 63.

TABLE 2.

Collected velocity constants at 25°.

k_1, k_1' = second-order velocity constants (l. mole^{-1} sec.$^{-1}$).

Olefin	k_1	k_1'	k_1'/k_1
Diethyl fumarate	$1{\cdot}00 \times 10^{-4}$	$3{\cdot}90 \times 10^{-4}$	3·9
Ethyl acrylate	$1{\cdot}06 \times 10^{-1}$	$6{\cdot}7 \times 10^{-2}$	0·63
Ethyl crotonate	2·76	1·04	0·38
Ethyl cinnamate	(*a*) 245, (*b*) 203	(*a*) 17, (*b*) 30	(*a*) 0·07, (*b*) 0·15
Allyl cyanide	440	100	0·23
Ethylene	$3{\cdot}94 \times 10^{5}$	$2{\cdot}0 \times 10^{4}$	0·05
Allyl alcohol	$6{\cdot}7 \times 10^{5}$	$6{\cdot}9 \times 10^{4}$	0·10
Stilbene	$7{\cdot}8 \times 10^{5}$	—	(Small)
Propene	$4{\cdot}5 \times 10^{6}$	$3{\cdot}2 \times 10^{6}$	0·7
Isobutene	—	$6{\cdot}0 \times 10^{6}$	(Large)

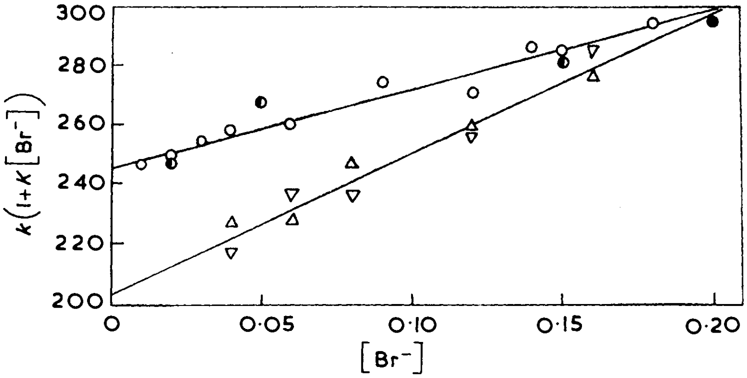

FIG. 3. Bromination of ethyl cinnamate: effect of bromide.
○ I = 0·20 (NaBr + NaClO$_4$). ◐ I = 0·20 (KBr + NaNO$_3$). △ I variable (KBr). ▽ I variable (NaBr). ● point common to both lines.

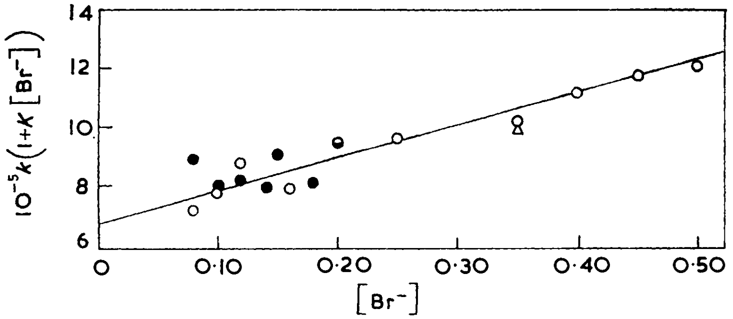

FIG. 4. Bromination of allyl alcohol: effect of bromide.
● I = 0·20 (NaBr + NaClO$_4$). △ I = 0·50 (NaBr + NaClO$_4$). ○ I variable (NaBr).

distinction between the two sets, perhaps because the experimental accuracy is lower. With all the other olefins the ionic strength was allowed to vary with the added sodium bromide.

The olefins in Table 1 are listed in order of increasing reactivity. When the number of experiments warrants it the probable error in the mean velocity constant is given.

DISCUSSION

Only one of our results can be compared directly with a published value. Kanyaev [2] gave k_1 = 200 l. mole^{-1} min.$^{-1}$, k_1' = 2·02 l. mole^{-1} min.$^{-1}$, for the addition of bromine to stilbene in aqueous solution at 0°, differing widely from our results in Table 2. However, Kanyaev's figures are identical with those found by Bartlett and Tarbell[9] for the addition of bromine to stilbene in methanol at 0°, and the same is true for the values which he gives for the proportion of dibromide formed at two different concentrations of bromide ion: Kanyaev's results must therefore be viewed with suspicion.

The relative reactivities of tribromide ion and molecular bromine vary considerably from one olefin to another, and Kanyaev linked this with the proportions of dibromide and bromohydrin in the product, supposing that the former was produced by reaction with tribromide ion, and the latter by reaction with bromine. This assumption is kinetically equivalent to a reaction scheme proposed by Hine[10] in which an addition complex of bromine and olefin is formed in an equilibrium step, and then reacts with either bromide ion or water in the rate-determining stage. According to either scheme the dibromide : bromohydrin ratio should be $k_1'[Br_3^-]/k_1[Br_2] = Kk_1'[Br^-]/k_1$. Kanyaev showed that this was approximately true for alkyltrimethylammonium perchlorate, and also pointed out that for the olefins which he investigated the dibromide : bromohydrin ratio changes in the same sequence as k_1'/k_1. However, the expression $Kk_1'[Br^-]/k_1$ does not represent the product ratios for the other three olefins studied by Kanyaev, the discrepancy amounting to a factor of 2—5, while Hine[10] found a similar discrepancy in applying this reaction scheme to the results of Bartlett and Tarbell[9] for the reaction of bromine with stilbene in methanol. Our own results (Table 3) lead to the same conclusion. Although the product ratios for ethylene are approximately equal to $Kk_1'[Br^-]/k_1$, this is not so for the other three olefins: in particular, although the product distributions are similar for ethylene, propene, and allyl alcohol, the values of k_1'/k_1 varies by a factor of 14.

TABLE 3.

Ratios of dibromide to bromohydrin in product.

Figures in parentheses represent $k_1'[Br_3^-]/k_1[Br_2] = K[Br^-]k_1'/k_1$.

$[Br^-]$	Et_2 fumarate	Ethylene	Allyl alcohol	Propene
0·01	—	0·03 (0·01)	—	0·02 (0·11)
0·02	0·37 (1·2)	0·06 (0·02)	—	0·06 (0·22)
0·04	0·43 (2·5)	—	0·04 (0·06)	—
0·05	1·54 (3·3)	0·08 (0·04)	—	0·08 (0·9)
0·07	1·86 (4·4)	—	—	—
0·10	1·92 (6·2)	0·10 (0·08)	0·05 (0·16)	0·09 (1·1)
0·12	—	—	0·07 (0·19)	—
0·15	3·77 (9·4)	—	0·08 (0·24)	—
0·20	5·65 (12·5)	0·13 (0·16)	0·09 (0·32)	0·15 (2·2)
0·24	—	—	0·16 (0·38)	—
0·30	—	0·20 (0·24)	0·14 (0·48)	0·22 (3·4)
0·36	—	—	0·22 (0·58)	—
0·40	—	0·25 (0·32)	0·18 (0·64)	0·25 (4·5)
0·50	—	0·34 (0·40)	—	0·31 (5·6)
1·0	—	—	—	0·33 (11)
7·0	—	—	—	6·7 (79)

The above facts appear to favour the usually accepted scheme for halogen addition, in which a reactive intermediate, usually taken to be a carbonium ion, is formed in a rate-determining step by the reaction of olefin with either Br_2 or Br_3^-, followed by a rapid reaction of the intermediate with either water or a bromide ion. According to this scheme the product ratio is not related to the relative reactivities of Br_2 and Br_3^-, but depends upon the competition of bromide and water for the intermediate. However, this view leads to some difficulty in interpreting the observed values of k_1'/k_1. It has previously been supposed that tribromide ion will always be a less effective electrophilic agent than

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[9] Bartlett and Tarbell, *J. Amer. Chem. Soc.*, 1937, **59**, 407.

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

molecular bromine, although there might be little difference between them with organic species of high reactivity, on the principle that selectivity will generally decrease with increasing reactivity.[11,12] Some support for this view was obtained in a study of the bromination of anilines,[13] enols,[14,15] and phenols,[16,8] including the anions of the last two classes of compound. On the other hand, Kanyaev [2] reports that k_1'/k_1 decreases steadily with increasing reactivity of the olefin, having values of 2 and 4 for the two least reactive compounds studied. Our own results (Table 2) show no general relation between k_1'/k_1 and reactivity, but we find a value of 4·9 for diethyl fumarate the least reactive compound studied, and $k_1' > k_1$ for isobutene, the most reactive. It is difficult to see how the tribromide ion can be a stronger electrophilic reagent than molecular bromine, especially for olefins of low reactivity, if both reagents produce the same intermediate.

All the experimental facts can be accounted for by the following reaction scheme:

$$\mathrm{S} + \mathrm{Br_2} \xrightarrow{k_1} \mathrm{R} \xrightarrow{\text{Fast}} \mathrm{S(OH)Br}$$

$$\mathrm{S} + \mathrm{Br_3^-} \xrightarrow{k_1'} \mathrm{R'} \xrightarrow{\text{Fast}} \alpha\mathrm{SBr_2} + (1 - \alpha)\mathrm{S(OH)Br}$$

where S is the olefin, R and R′ are two ***different*** intermediates, and α is a fraction which depends upon the olefin but is independent of the concentration of bromide ion. The observed velocity constant will still be given by equations (4) or (5), and the product distribution is now

$$\frac{[\mathrm{SBr_2}]}{[\mathrm{S(OH)Br}]} = \frac{\alpha k_1' K[\mathrm{Br^-}]}{k_1 + (1 - \alpha)k_1'\mathrm{K}[\mathrm{Br^-}]}. \qquad (6)$$

There is now no reason why k_1' should not be greater than k_1, since they relate to different reactions. Equation (6) predicts that the ratio $[\mathrm{SBr_2}] : [\mathrm{S(OH)Br}]$ should be less than $k_1'\mathrm{K}[\mathrm{Br^-}]/k_1$, and this is in fact the case (cf. Table 3), except perhaps for ethylene at low bromide concentrations, where the experimental error is high. The intermediates R and R′ cannot be definitely identified, but it is reasonable to suppose that R′ is derived from R by addition of a bromide ion, since it is assumed to produce dibromide without requiring further reaction with bromide. Possibilities are thus $\mathrm{R} = \mathrm{SBr^+}$, $\mathrm{R'} = \mathrm{SBr_2}$, or $\mathrm{R} = \mathrm{SBr_2}$, $\mathrm{R'} = \mathrm{SBr_3^-}$. More elaborate schemes are possible, in which the product distribution from R′ depends upon bromide concentration, or in which both intermediates yield both products; the essential point is that two different intermediates are involved, of which R′ yields a greater proportion of dibromide. In principle, it should be possible to distinguish between some of these alternatives from the form of the relation between product ratio and bromide concentration, but the present results are not sufficiently accurate for this purpose.

The effect of olefin structure upon reactivity can be discussed without reference to the problems so far considered, since k_1 and k_1' vary in approximately the same way and are not connected with the product ratio. The velocity constants in Table 2 vary by a factor of more than 10^{10}, and confirm the retarding effect of electron-attracting substituents and the accelerating effect of methyl groups, previously pointed out.[1,17] Our results do not embrace enough compounds to warrant a quantitative treatment; but in each of the following series, $\mathrm{R{\cdot}CH{:}CH_2}$ ($\mathrm{R} = \mathrm{H}$, Me, $\mathrm{CH_2{\cdot}OH}$, $\mathrm{CH_2{\cdot}CN}$, $\mathrm{CO_2Et}$), $\mathrm{R{\cdot}CH_2{\cdot}CH{:}CH_2}$ ($\mathrm{R} = \mathrm{H}$, OH, CN), $\mathrm{R{\cdot}CH{:}CH{\cdot}CO_2Et}$ ($\mathrm{R} = \mathrm{H}$, Me, Ph, $\mathrm{CO_2Et}$), there is an approximate

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[11] Stock and Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 3233, and earlier papers.

[12] Shatenshtein, *Zhur. fiz. Khim.*, 1960, **34**, 594.

[13] Bell and Ramsden, *J.*, 1958, 161.

[14] Bell and Spiro, *J.*, 1953, 429.

[15] Bell and Rawlinson, *J.*, 1961, 726.

[16] Bell and Spencer, *J.*, 1959, 1156.

[17] Ingold and Ingold, *J.*, 1931, 2354; Anantakrishnan and Ingold, *J.*, 1935, 984, 1396.

correlation of the rate with appropriate electrophilic substituent constants, for example the σ^*-values of Taft.[18]

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[18] Taft, Chapter 13 in "Steric Effects in Organic Chemistry," ed. M. S. Newman, Wiley and Sons Inc., New York, 1956.