69. *The Kinetics of Bromine Addition to Olefinic Compounds.*

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Recent investigations have established in general terms the mechanism of bromine addition to ethylenic compounds. With effective impact the positive atom of the polarised bromine molecule attaches itself to the negative carbon of the ethylenic system; thereupon the resulting positive charge of the second ethylenic carbon atom is neutralised by the negative bromine ion, which has a momentary existence. Ionising solvents greatly accelerate the change, and, even if themselves only slightly ionised, provide a high local concentration of negative ions which will compete with the bromine ion for the positively charged carbon atom. For instance, in water the bromohydroxy-derivative may be formed almost exclusively (Read and Read, J., 1928, 745), and if an ion such as the nitrate ion is present in the solution, this is added in preference to hydroxyl (Francis, *J. Amer. Chem. Soc.*, 1925, **47**, 2340). Similarly, in methyl alcohol a high yield of the bromomethoxy-compound may be obtained (Jackson, *ibid.*, 1926, **48**, 2166). It appears that the extent to which solvent-ion attachment may take place is a function of the rate of the reaction. In acetic acid solution, bromine only is added in the slow reactions, but with the very rapidly reacting undecenoic acid, as much as 30% of the bromoacetoxy-derivative is formed.

Further evidence that the attack is initiated by a positive bromine atom is furnished by the behaviour of ions containing an ethylenic linkage. The allyl group in neutral molecules adds bromine rapidly, but in a positive ammonium ion it is unreactive. On the other hand, acids such as mesaconic and acrylic in aqueous solution have their rate of bromine addition very largely reduced in the presence of a strong acid, which represses the ionisation, and the mesaconate ion reacts 10^4 times as rapidly as the undissociated acid.
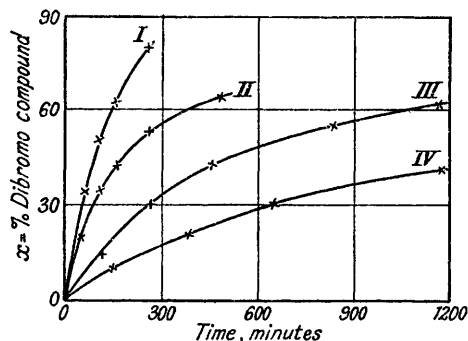
The conclusion of earlier workers that bromine addition is kinetically bimolecular is founded on insufficient evidence : most of the velocities were measured at one concentration only, and even when the initial concentrations were varied (Meyer and Pukall, *Z. physikal. Chem.*, 1929, **145**, 360), no comment was made on the fact that the rate was a function of the concentration. Furthermore, the variation of the bimolecular values of k in a single reaction

has often been considerable. It is now shown that there are three main possibilities : (*a*) unimolecular surface reactions due to impacts of bromine molecules, with rising or falling k_2 (bimolecular coefficient) values according to the conditions, (*b*) homogeneous termolecular reactions, (*c*) homogeneous bimolecular reactions with catalysts but obscured by various disturbing influences.

Reactions in Acetic Acid.—In bromine additions in acetic acid, heterogeneous effects have not been observed, and these reactions are perfectly reproducible and have invariably a positive temperature coefficient; this is unusually small, but this fact is in general accord with the termolecular nature of these processes, which, although unexpected because the reactions are stoicheiometrically bimolecular, has been established as a result of the following considerations. First, the k_2 values fall as the reaction proceeds (*x* is the % absorption of bromine, and the solutions were $M/40$) :

x, %	20	30	40	50	60	70
Allyl acetate, k_2 (25°)	28	25	22	20	18	14
cis-Cinnamic acid, k_2 (25°)	0·13	0·12	0·10	0·087	0·067	0·054

Correspondingly, the values of k_2 at different dilutions for the same fraction of change are different, and calculation of the order of the reaction shows that $n = 3$. To determine the relative participation of the reacting molecules, experiments were carried out in which the proportions of bromine and of ethylenic compound were severally doubled, and it was found that the rate was greater when the bromine was in excess (see figure), showing that two molecules of bromine participate for each molecule of ethylenic compound.

I, Br$_2 \dfrac{M}{40}$, A $\dfrac{M}{40}$; II, Br$_2 \dfrac{M}{40}$, A $\dfrac{M}{80}$;

III, Br$_2 \dfrac{M}{80}$, A $\dfrac{M}{40}$; IV, Br$_2 \dfrac{M}{80}$, A $\dfrac{M}{80}$.

Kinetic considerations indicate that the ratio of times for the formation of equal amounts of the dibromophenylpropionic acid should be initially 3 : 1; actually the value as read from the curve at $x = 30\%$ is 3·2 : 1.

With the reactants present in equimolecular amounts (*a*), so that the relative proportions remain constant throughout the reaction, it is in effect the same whether each molecule of bromine contributes one atom or whether the added bromine atoms are derived from a single molecule, so that :

$$dx/dt = k_3 (a - x) (\tfrac{1}{2}a - \tfrac{1}{2}x) (\tfrac{1}{2}a - \tfrac{1}{2}x)$$

and

$$k_3 = (2/t) [1/(a - x)^2 - 1/a^2]$$

With this formula satisfactory termolecular constants are obtained. The following values are for *cis*-cinnamic acid at 25°.

x, %	20	30	40	50	60
k_3 ($M/40$)	22	23	22	22	19
k_3 ($M/80$)	21	20	20	21	20

In Table I are collected the average k_3 values of various compounds in acetic acid solution at concentrations of $M/20$—$M/80$.

TABLE I.

	Allyl acetate.	Allyl chloro-acetate.	Allyl benzoate.	Allyl phenyl-acetate.	*cis*-Cinnamic acid.
$k_3 \times 10^{-2}$ (25°)	48·5	21	42·5	45·5	0·21
$k_3 \times 10^{-2}$ (50°)	69	26	70·5	73	0·47
E, calc.	2700	1600	3900	3600	5800

For the determination of the critical increment of these reactions, the temperature range over which measurements can be made is limited on one hand by the freezing point of the

solvent, and on the other, by the fact that at higher temperatures bromine attacks the acetic acid. Accordingly, observations were made at only two temperatures, 25° and 50°, the relatively small changes in the values of k_3 justifying this somewhat extended range. In accord with the general expectation for a termolecular reaction at the ordinary temperature, the critical increments are small. In applying the formula, rate $= P . Z_3 . e^{-E/RT}$, where Z_3 is the number of termolecular collisions, it is to be noted that the expression for Z_3 (Steiner, *Z. physikal. Chem.*, 1932, *B*, **15**, 249) contains a doubtful term, *viz.*, the time during which the three molecules are within molecular distance. Further, Gerschinowitz and Eyring (*J. Amer. Chem. Soc.*, 1935, **57**, 985) point out that the rotation of the molecules and their internal degrees of freedom must be taken into account as well as the number of collisions. Approximate evaluations for the present reactions indicate that P is of the order unity, *i.e.*, the majority of the termolecular impacts would seem to be effective, at all events in the region $M/40$. At lower concentrations, as is seen by the trend of n from 3 towards 2, the reaction tends to become bimolecular. Ashdown (*ibid.*, 1930, **52**, 268) found that the reaction between butyl alcohol and *p*-nitrobenzoyl chloride was termolecular (two molecules of alcohol to one of acid chloride), with a somewhat higher value of k_3 at infinite dilution.

Certain compounds, however, appear to give bimolecular constants; *e.g.*, for *trans*-cinnamic acid :

x, %	20	30	40	50
k_2 ($M/40$)	0·035	0·035	0·035	0·035
k_2 ($M/80$)	0·017	0·017	0·016	0·016

but the variation of the velocity constant with the initial concentration, yielding here a value $n = 3·1$, indicates that these reactions are, like those just considered, also termolecular. For some compounds, *e.g.*, *trans*-croton-*p*-bromoanilide, k_2 even rises as the reaction proceeds :

x, %	20	30	40	50	60
k_2 ($M/40$)	0·18	0·22	0·27	0·32	0·38
k_2 ($M/80$)	0·10	0·13	0·17	0·21	0·26

It is found that the compounds which do not show falling values of k_2 have the *trans*-configuration, and their behaviour is caused by stereo-conversion during the reaction. The observed velocity of bromine addition is then dependent on (*a*) the rate of the *trans*- $\longrightarrow$ *cis*-change, (*b*) the rate of addition to the *trans*-form, (*c*) the rate of addition to the *cis*-form. Hydrogen bromide accelerates (*a*), and cinnamic acid, for example, with added hydrogen bromide, has its rate increased to that of the *cis*-isomer.

Reactions in Carbon Tetrachloride.—A marked characteristic of bromine additions in this solvent is the occurrence of certain irregularities, which have been attributed in general to heterogeneous effects, to considerable variations in rate under apparently identical conditions (Sudborough, J., 1910, **97**, 715), to a negative temperature effect (Davis, *J. Amer. Chem. Soc.*, 1928, **50**, 2770), or to a relatively very rapid initial rate of reaction (Herz and Mylius, *Ber.*, 1906, **39**, 3816; Linstead, J., 1927, 356). It is now further established that packing with glass beads may accelerate the reaction very considerably. In certain slow reactions a period of induction has been observed (Williams and James, J., 1928, 343); but this is not necessarily a heterogeneous effect, for it is now found with compounds such as vinyl bromide and acrylic acid in acetic acid solution, where heterogeneous disturbances are absent.

The compounds especially examined in carbon tetrachloride in the present investigation are certain allyl esters and undecenoic acid. At 25° at a concentration of $M/40$, allyl acetate and chloroacetate give rising k_2 values, which are somewhat less at 0°. At 50°, however, there is a very considerable decrease in rate, and the k_2 values now fall as the reaction proceeds (see Table II).

TABLE II.

	Allyl acetate in CCl$_4$.			Allyl chloroacetate in CCl$_4$.		
x, %.	k_2 (0°).	k_2 (25°).	k_2 (50°).	k_2 (0°).	k_2 (25°).	k_2 (50°).
20	1·4	0·70	0·078	0·35	0·28	0·025
60	2·3	1·5	0·050	0·50	0·42	0·016

The rising k_2 values at 0° and 25° indicate a unimolecular reaction due to collisions of bromine molecules on a surface film of unsaturated compound, the film being re-formed as fast as it is depleted. At 50° this film is no longer stable, and the reaction now is homogeneous and is actually termolecular in character (as it is in acetic acid solution). This conclusion with regard to the existence of a reactive surface film is confirmed by the results obtained on keeping the bromine concentration constant, and altering that of the unsaturated compound; *e.g.*, doubling the concentration of allyl acetate gives a fictitious bimolecular value, which is smaller in magnitude; in reality the reaction is to be interpreted as being unimolecular with regard to the bromine, and the k_1 value increases from 0·018 to 0·022, the increase being small because the surface film is already almost saturated. Reducing the allyl acetate concentration to one-half causes a very considerable drop in the rate, as the concentration is now not great enough to cause the formation of a stable film.

This interpretation is in accord with the results obtained for equimolecular proportions at different concentrations :

	$M/20$.	$M/40$.	$M/80$.	$M/160$.
Allyl acetate (k_2)	3·0	0·70	0·014	—
Allyl chloroacetate (k_2)	1·4	0·28	0·008	0·003

The concentration range $M/40$—$M/80$ represents for these compounds a region below which the surface film tends to become unstable. In this region, under apparently identical experimental conditions, the heterogeneous reaction may or may not occur. This is illustrated by reference to allyl chloroacetate at $M/40$. In addition to four values in the vicinity of $k_2 = 0·28$, a fifth was obtained widely different, *viz.*, $k_2 = 0·017$, the heterogeneous reaction apparently not having developed in this case.

It is further to be noted with reference to the values in the foregoing table that, whereas at $M/40$ the k_2 values rise as the reaction proceeds, yet at $M/20$ k_2 falls. At this higher concentration the surface film is depleted more rapidly than it is re-formed, and this effect is generally found in the rapid heterogeneous reactions, being previously reported as a rapid initial rate of reaction.

Undecenoic acid produces a more stable surface film which persists at as low a concentration as $M/320$. Correspondingly, this compound exhibits a small negative temperature coefficient from 25° to 50°, indicating that even at 50° the heterogeneous reaction is proceeding.

The fact that an ethylenic compound may combine with bromine at a slow termolecular rate, or undergo under modified conditions a rapid heterogeneous change, gives an explanation of the differences observed for ethylene itself in its reaction with bromine in carbon tetrachloride. Whereas Davis (*loc. cit.*) found a low and decreasing k_2 value, D. M. Williams (J., 1932, 2911), as may be calculated from his curves, observed a velocity 50 times as great. It is further to be noted that, with falling temperature, G. Williams (J., 1932, 1747) found in the gas reaction $C_2H_4 + Br_2$ an increase in velocity and a change from a bi- to a unimolecular reaction.

The general conclusion with regard to the rapid reactions in carbon tetrachloride is that they are largely due to bimolecular impacts on an activated surface film, the formation of which is a consequence of the low internal pressure of the solvent (which determines the fugacity of the solute, *i.e.*, its predilection for a second phase). It appears that the attachment of the ethenoid molecules in the surface film renders them in some way more active, for they are susceptible to bimolecular impacts, whereas in solution termolecular collisions are required for chemical change. It is possible that such surface effects occur in other reactions, but usually they are not detected since the homogeneous reactions are also bimolecular. In bromine addition the heterogeneous effect is especially noticeable, as the homogeneous reaction, being termolecular, is relatively slow.

The Influence of Hydrogen Bromide.—In the reaction $C_2H_4 + Br_2$, hydrogen bromide is non-catalytic in the gas phase (G. Williams, *loc. cit.*) and also in dry carbon tetrachloride solution (Davis, *loc. cit.*). In wet carbon tetrachloride, on the other hand, it acts as a powerful catalyst for this reaction (D. M. Williams, *loc. cit.*). Similar results were obtained by Williams and James (*loc. cit.*) for a number of ethylenic compounds in this solvent.

The influence of hydrogen bromide on the rate of addition of bromine in acetic acid solu-

tion has been examined by D. M. Williams (J., 1932, 979) for cinnamic acid. Although the effect here is very much smaller than in carbon tetrachloride, it is attributed to the same cause. A re-examination of this reaction, as well as that of the *cis*-isomer, gave the following results :

Cinnamic acids in acetic acid (M/80) (25°).

		k_2 (trans).			k_2 (cis).			
x, %.	[HBr]/[Br$_2$]	0.	$\frac{1}{8}$.	$\frac{1}{4}$.	0.	$\frac{1}{8}$.	$\frac{1}{4}$.	$\frac{1}{2}$.
20		0·017	0·067	0·068	0·065	0·065	0·067	0·067
50		0·016	0·046	0·045	0·038	0·046	0·049	0·050

It is evident that hydrogen bromide is not a catalyst for the *cis*-acid, and its effect on cinnamic acid is to convert it into the *cis*-isomer, which reacts as such. Allyl acetate was likewise examined in acetic acid, and hydrogen bromide found to be non-catalytic. As, however, some hydrogen bromide is produced in the course of the reaction, the rate was redetermined in the presence of lead acetate, which converts the hydrogen bromide into insoluble lead bromide. Here also for the four allyl esters no alteration in rate was observed during the early stages of the reaction, and after 50% change the lead acetate had a positive effect.

Two compounds have been discovered, however, *viz.*, vinyl bromide and acrylic acid, which differ in a marked degree from *cis*-cinnamic acid and allyl acetate. In the first place these compounds exhibit extended periods of induction, even in an ionising solvent such as acetic acid. Secondly, they are extremely sensitive to mere traces of hydrogen bromide, and in acetic acid solution give rising k_2 values, in all probability owing to the production of small amounts of hydrogen bromide. The reaction between bromine and acrylic acid was examined with various amounts of hydrogen bromide; the results (Table III) were perfectly reproducible and gave no evidence of heterogeneous disturbances.

TABLE III.

Acrylic acid in acetic acid (25°) ; *values of* k_2 (M/80).

x, %.	[HBr]/[Br$_2$]	$\frac{1}{20}$.	$\frac{1}{8}$.	$\frac{1}{4}$.	$\frac{1}{2}$.	1.	2.	3.	4.	5.
20		—	—	0·26	0·33	0·50	0·57	0·46	0·40	0·40
30		0·035	0·14	0·25	0·31	0·48	0·57	0·43	0·38	0·34
40		—	0·14	0·25	0·32	0·49	0·53	0·41	0·37	0·33
50		—	0·14	0·24	0·33	0·44	0·49	0·39	0·35	0·32
60		—	0·14	0·24	0·32	—	0·44	—	0·31	—
70		—	0·14	0·22	0·31	—	0·41	—	0·23	—

This reaction is very sensitive to added water, which reduces the rate; *e.g.*, for $[\text{HBr}]/[\text{Br}_2] = \frac{1}{2}$:

H$_2$O, %	0·15	0·50	1·0	3·0
k_2	0·32	0·11	0·051	0·050

The maximum velocity shown with increasing amounts of hydrogen bromide in pure acetic acid is due to two opposing tendencies : (i) its catalytic influence, and (ii) the removal of bromine as HBr$_3$, which appears to be inactive. With the smaller amounts of hydrogen bromide the k_2 values are approximately constant during the reaction, but this is accidental, being the result of the same two opposing tendencies. As the proportion of hydrogen bromide increases, this equalising effect no longer operates, and k_2 falls as the reaction proceeds. Finally, by doubling and halving the relative proportions of acrylic acid (when $[\text{HBr}]/[\text{Br}_2] = \frac{1}{2}$), and keeping the concentration of bromine unaltered, identical k_2 values were obtained. The conclusion is that the reaction is truly bimolecular, and that the hydrogen bromide activates the bromine and not the ethylenic compound.

It is apparent, then, that bimolecular impacts of HBr$_3$ and ethylenic compounds must be ineffective, just as they are in substitution reactions, *e.g.*, acetaldehyde and bromine in water (Bugarszky, *Z. physikal. Chem.*, 1901, **38**, 561). In the termolecular reactions in the presence of hydrogen bromide there must likewise be a considerable proportion of HBr$_3$ present ($[\text{Br}_2][\text{HBr}]/[\text{HBr}_3] = 0·006$; Jones, J., 1911, **99**, 402). It would seem, therefore, as hydrogen bromide does not alter the rate, that collisions between the ethylenic compound

and two bromine molecules, or two HBr_3 molecules, or one of each, are all approximately equally effective. Such termolecular collisions must also be assumed for acrylic acid, but they must be relatively very much less numerous than the effective bimolecular impacts, and do not perceptibly influence the rate. No explanation is at present offered to account for this difference between cinnamic and acrylic acids, which appears even more marked when the rates in the presence of water are added for comparison :

	HOAc.	HOAc + HBr.	HOAc + 25% H_2O.
Acrylic acid ($M/80$, 25°), k_2	0·005	0·3	0·2
cis-Cinnamic acid ($M/80$, 25°), k_2	0·07	0·07	140

Vinyl bromide behaves similarly to acrylic acid, and of the compounds examined these are the only two that readily polymerise, but there is no evidence of polymerisation as a side reaction.

The influence of hydrogen bromide on bromine-addition reactions has also been studied in carbon tetrachloride. The values in Table IV were obtained for allyl chloroacetate.

TABLE IV.

Allyl chloroacetate in CCl_4 (k_2 *values at 25°) with various amounts of* HBr.

		$M/40$.			$M/80$.			$M/160$.	
x, %.	[HBr]/[Br$_2$]	$\frac{1}{6}$.	$\frac{1}{3}$.	$\frac{2}{3}$.	$\frac{1}{3}$.	$\frac{2}{3}$.	2.	4.	2.	4.
10		11	18	44	6	11	59	18	13	18
20		7	18	20	4	7	33	17	8	13
30		5	14	13	3	5	21	14	.7	10
40		4	10	10	3	4	16	10	6	9
50		4	8	7	3	4	12	8	5	8
60		3	7	6	2	3	9	7	4	8
70		3	6	5	—	3	8	6	—	7

The same rise to a maximum velocity with increasing hydrogen bromide concentration as was found for acrylic acid in acetic acid solution is again observed here and is attributed to the same cause, *viz.*, HBr_3 formation. But here the k_2 values fall very rapidly as the reaction proceeds. This cannot be due to removal of bromine as HBr_3 to a relatively greater extent in the later stages of the reaction, since, for acrylic acid under the same conditions, the k_2 values are constant or decrease only slightly. In carbon tetrachloride the reactions are in part heterogeneous, and accordingly, where the reaction is most rapid there is the greatest fall in k_2 value; the surface films are depleted more rapidly than they can be regenerated. Further evidence is that the reactions are more rapid at 0°; with acrylic acid in acetic acid, where the reaction is homogeneous, there is a normal positive temperature effect.

The Influence of Water.—In the reaction between ethylene and bromine in the gas phase, it was found that water had an accelerating influence and changed the order from 2 to 1 (G. Williams, *loc. cit.*). In carbon tetrachloride, drying tends to reduce the rate of the reaction, according to earlier work. The interpretation is that water causes the formation of reactive surface films. In the present experiments the condition of drying was such that added water had merely a slight accelerating effect on existing heterogeneous reactions.

The catalytic influence of water on the addition of bromine to cinnamic acid was shown in acetic acid solution by D. M. Williams (*loc. cit.*), and it is now found for other compounds. Under certain conditions, however, water may even act as a negative catalyst, as in the reaction between bromine and acrylic acid in the presence of hydrogen bromide. Williams's theory that hypobromous acid is the active catalyst is improbable, as it is proved experimentally that the rate of the change, $Br_2 + H_2O \rightarrow HBr + HBrO$, in acetic acid solution is very slow (see p. 342). An explanation can be found, however, from general kinetic considerations. The effect of water on the rate of bromine addition to *cis*-cinnamic acid is to change the order from 3 to 2, whilst at the same time the value of E rises. Normally the effect of catalysts is to decrease the energy of activation, but here another mechanism is in operation. The order of the reaction has been reduced in the presence of water, thereby increasing the rate by more frequent collisions of the reactants to an extent which is not

offset by the increased energy of activation. This would seem to be a type of catalysis not hitherto reported. The influence of water is shown in Tables V and VI.

TABLE V.

cis-*Cinnamic acid in* HOAc; *influence of water* (25°).

x, %	20	30	40	50	60
k_2 (H_2O 10%, $N/10$-H_2SO_4), $M/80$	11·1	9·3	8·3	7·1	5·4
k_2 (H_2O 10%, $N/10$-H_2SO_4), $M/160$	6·9	6·1	5·4	5·0	—
k_2 (H_2O 25%, $N/4$-H_2SO_4), $M/80$	67	68	63	56	50
k_2 (H_2O 25%, $N/4$-H_2SO_4), $M/160$	67	68	64	57	51
k_2 (H_2O 25%), $M/80$	—	138	115	103	—

With 10% of water (with addition of sulphuric acid to repress ionisation) there is a partial change to a bimolecular reaction ($n = 2·5$); with 25% of water, the identity of the k_2 values at the two concentrations indicates $n = 2$, although there is still a downward trend of k_2. This is attributed to the formation of HBr_3 from hydrogen bromide produced with the greater water content. This fall in the k_2 values makes the determination of E somewhat uncertain; from measurements at 0° for the first part of the reaction, values of 8,500 at $M/80$ and 8,500 at $M/160$ were obtained (in acetic acid, $E = 5,800$). A set of k_2 values obtained in the absence of sulphuric acid is included to show the effect of the acid in retarding the rate by its removal of the rapidly reacting cinnamate ions.

TABLE VI.

Acrylic acid in acetic acid and water (25°).

H_2O, %	25.	50.	100.		100 ($+N/10$-H_2SO_4).	
x, %.	k_2 ($M/80$).	k_2 ($M/80$).	k_2 ($M/80$).	k_2 ($M/160$).	k_2 ($M/80$).	k_2 ($M/160$).
20	0·21	3·2	240	400	—	34
30	0·19	2·9	190	290	34	32
40	0·19	2·8	250	250	29	29
50	0·18	2·1	130	200	25	25
60	0·16	1·3	100	200	23	23

The k_2 values in water show by their downward trend the influence of the hydrogen bromide formed in (*a*) reducing ionisation, and (*b*) forming unreactive HBr_3; the rate in water is greater at $M/160$ owing to greater ionisation. The $N/10$-sulphuric acid represses the ionisation, and the identical k_2 values at each concentration indicate the bimolecular nature of the reaction, although there is still a downward trend of k_2 owing to HBr_3 formation.

In water, bromine addition becomes very rapid, and when the reactants are acids the rates are still further increased by formation of the more reactive anions. To determine the rate of reaction of this ion, *e.g.*, in sodium acrylate, it is necessary to remove the hydrogen bromide formed in the course of the reaction, and this was effected by addition of excess of sodium acetate; sodium acrylate ($M/500$) then gave the following values :

x, %	30	40	50	60	70
k_2 (25°)	8600	8900	8600	9000	9300

It is finally to be noted that these bimolcular reactions in aqueous acetic acid and water are insensitive to light.

EXPERIMENTAL.

The bromine was distilled over potassium bromide, and the middle fraction collected. The acetic acid was purified by Orton and Bradfield's method (J., 1927, 983) and found by f. p. to contain 0·12—0·18% of water, which could be removed only with difficulty. This acid is referred to as acetic acid, and special experiments showed that 0·05% of water (or 0·5% of acetic anhydride) had little effect on the rate; the values in each table are for the same sample of acetic acid. The carbon tetrachloride was washed with dilute potassium dichromate and acid, then dilute sodium hydroxide, and finally with water, left over anhydrous sodium sulphate, refluxed with phosphoric oxide, and finally fractionated; b. p. 76·5°/760 mm. For the very rapid reactions,

special rapid-delivery pipettes were used, and times measured with a stop-watch to half seconds. Either the reaction vessel was broken in a bottle containing potassium iodide solution, or a stream of concentrated iodide solution was blown rapidly into the liquid. For the slower reactions, a small brown-glass bottle was used, which was initially nearly filled with the reaction mixture so as to leave a relatively small air space above the solution; portions were withdrawn by a pipette at the requisite intervals for titration. As the air space above the liquid increases in volume, there is a continual slight loss of bromine by evaporation. Blank tests at 25° with bromine solutions of different concentrations, from which portions were removed at intervals, revealed that under the experimental conditions this loss did not become appreciable until 80% of the bromine was absorbed. At 50° this loss was appreciable at $x = 50\%$, and at this temperature the determinations were carried out in sealed tubes, or small stoppered vessels opened only once.

The values of x were plotted against the time, and from the resultant smoothed curves, the values of k were calculated in g.-mol./l.-min. The results for the reactions described as homogeneous are perfectly reproducible, and were frequently checked by separate observers. The heterogeneous reactions, on the other hand, are not perfectly reproducible, but when an adjustment is made graphically for the short inhibition periods that frequently occur, the variations in the rate are inconsiderable.

A source of error in the heterogeneous reactions is due to the change in the ratio of volume to surface as portions are removed from the reaction vessel. It was estimated that under the experimental conditions this variation over the range $x = 10$—60% would be of the order 20%. No correction is applied, and such a variation is small in comparison with the changes in rate at different temperatures and concentrations.

When the ethylenic compound and bromine are present in equivalent proportion, the k_2 values are presented, even when the reactions are not bimolecular, as they offer a convenient means of comparing the nature of the velocity changes occurring with alterations in temperature or concentration. Unless otherwise specified, all the k_2 values quoted in the text are for $x = 20\%$.

The following compounds have been used in the investigation : allyl acetate, b. p. 103·5—104·5°/760 mm., from allyl alcohol and acetic acid; allyl chloroacetate, b. p. 162—163·5°/766 mm., from allyl alcohol and chloroacetyl chloride; allyl benzoate, b. p. 226—227°/748 mm., from allyl alcohol and benzoyl chloride; allyl phenylacetate, b. p. 239—240·5°/761 mm., from allyl alcohol and phenylacetyl chloride; cinnamic acid, m. p. 134°; *cis*-cinnamic acid, m. p. 68°, from phenylpropiolic acid; cinnamo-*p*-chloroanilide, m. p. 182°, from cinnamyl chloride and *p*-chloroaniline; cinnamo-*p*-bromoanilide, m. p. 192°, cinnamo-2 : 5-dichloroanilide, m. p. 174°, crotono-*p*-chloroanilide, m. p. 169°, all similarly prepared; crotonic acid, m. p. 72°; acrylic acid, b. p. 138·5—139·5°/760 mm.; undecenoic acid, m. p. 24°.

The experimental results are largely quoted in the course of the discussion. In addition to these compounds there were also examined the following : allyl benzoate and phenylacetate in carbon tetrachloride; in general, the results were similar to those obtained for allyl acetate, although the heterogeneous effects here were less marked. This is indicated by the following comparative figures :

	Acetate.	Chloroacetate.	Phenylacetate.	Benzoate.
k_2 (CCl$_4$, 0°)	1·4	0·35	0·057	0·013
k_2 (HOAc, 25°)	28	15	28	26

Undecenoic acid showed in acetic acid solution a very rapid termolecular rate with a small heat of activation ($E = ca.$ 3000 cals.), as for the other termolecular reactions. In carbon tetrachloride, it gave heterogeneous reactions even at 50° : k_2 ($M/320$, 25°) $= 1\cdot6$; k_2 ($M/320$, 50°) $= 0\cdot73$.

Cinnamo- and crotono-*p*-bromo (and chloro) anilides were also examined in acetic acid, and gave results corresponding with those obtained for cinnamic acid.

Vinyl bromide in acetic acid was similar in its behaviour to acrylic acid, giving a marked period of induction, and being sensitive to hydrogen bromide.

D. M. Williams's theory (see p. 340) that the catalytic activity of water in bromine addition is due to the formation of hypobromous acid was tested by examining the equilibrium, $Br_2 + H_2O \rightleftharpoons HBr + HBrO$, in acetic acid solution. A solution containing 5% of water and lead acetate, and saturated with lead bromide at 25°, was found to be sensitive to added hydrogen bromide (deposit of lead bromide) in a concentration of $M/2000$. On the other hand, when bromine vapour was added until the concentration reached $M/40$, and the solution was kept in the dark at 25° and examined at intervals, only after 4 days (duplicate experiments) had a faint deposit of

lead bromide become perceptible. The amount of hypobromous acid formed in the relatively short half-reaction times of the reactions investigated must therefore be very small.