

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF STANFORD UNIVERSITY]

Halogen Addition to Ethylene Derivatives. III. Bromine and Iodine Additions in Glacial Acetic AcidBY KENZIE NOZAKI¹ AND RICHARD A. OGG, JR.

Reactions between halogens and ethylene derivatives in solution and in the dark have been the subject of many investigations. Some earlier workers claimed that the reactions are of first order with respect to halogen and ethylene derivative concentration² while others stated that the reactions are often autocatalytic.³ More recently Robertson and co-workers⁴ have reported that most reactions are termolecular or heterogeneous, depending upon the solvent used. Since there has been an obvious lack of agreement in the work recorded in the literature, it was believed worth while to study several reactions carefully in an attempt to clarify the kinetics and mechanism of the reactions. The solvent chosen for this study was glacial acetic acid, in which Robertson claimed most reactions are termolecular.

The Action of Bromine on Allyl Chloride

The first reaction which was chosen for study was between bromine and allyl chloride. Preliminary experiments indicated that the reaction was fairly rapid and did not exhibit preliminary inhibition. It was found that exactly one mole of bromine reacted with one mole of allyl chloride in dilute solutions.

Reaction Products.—Analysis of the products of the reaction indicated that a considerable amount of bromide ion was formed. This formation of bromide ion was found to be dependent on the concentration of reactants. Thus, when the initial concentration of bromine and allyl chloride was 0.0080 *M*, 0.45 mole of bromide ion was produced per mole of bromine used. When the reactants were initially 0.040 *M*, 0.25 mole of bromide ion was obtained per mole of bromine. The formation of bromide ion was also found to be dependent on the water content of the solvent. Thus the values of 0.45 and 0.25 mole were in-

creased to 0.50 and 0.35 mole in acetic acid solutions containing 5% of water.

The presence of bromide ions in the reaction products could be explained by substitution reactions of bromine. However, this seems unlikely since more bromide ion was found in the dilute solutions and bromine consumption was quantitative for addition alone. The more probable explanation is that an addition reaction yielding a bromoacetate and hydrobromic acid occurred. This view is supported by the observation⁵ that considerable quantities of chloroacetates are produced in the reaction of chlorine with ethylene in acetic acid solution. Since not all of the bromine was accounted for as bromide ion, it is assumed that the rest reacted with the allyl chloride to form a dibromide.

The Kinetics of the Reaction.—Data from rate measurements could be interpreted best by the expression

$$\frac{-d[\text{Et}]}{dt} = k_a[\text{Br}^-][\text{Et}] + k_b[\text{Br}_2][\text{Et}] + k_c[\text{Br}_2]^y[\text{Et}] \quad (1)$$

where Et represents the ethylene derivative, allyl chloride, and *y* is greater than two. Due to practical difficulties in integration, verification of rate Expression 1 was not carried out by substitution of experimental data into its integrated form. Instead, recourse was taken to indirect methods whereby the terms were considered independently.

The first term on the right in the rate Ex. 1 corresponds to the bromide ion catalyzed bromine addition reaction discussed in a previous communication.⁶ It is obvious that the contribution of this term is dependent on the bromide ion concentration in the reaction mixture.

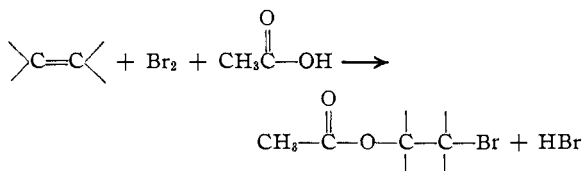
The second term on the right in the rate expression apparently corresponds to the reaction^{6a}

(5) Weber, Hennion and Vogt, *THIS JOURNAL*, **61**, 1457 (1939).(6) Nozaki and Ogg, *ibid.*, **64**, 704 (1942).

(6a) It has been assumed but not proved that the second order reaction gives haloacetate exclusively. It is impossible to obtain experimental verification of this assumption because the other two halogen addition reactions cannot be eliminated. Similarly, it has been assumed but not proved that the higher order reaction gives exclusively dihalide.

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(2) (a) Herz and Mylius, *Ber.*, **39**, 3816 (1906); (b) Sudborough and Thomas, *J. Chem. Soc.*, **97**, 715, 2450 (1910); (c) Bauer and Moser, *Ber.*, **40**, 918 (1907).(3) (a) Williams and James, *J. Chem. Soc.*, 343 (1928); (b) Anantakrishnan and Ingold, *ibid.*, 984 (1935).(4) (a) Robertson, Clare, McNaught and Paul, *ibid.*, 335 (1937); (b) Blythell and Robertson, *ibid.*, 179 (1938); (c) White and Robertson, *ibid.*, 1509 (1939).



It is this term which was responsible for the bromide ions found in the products. Since more bromide ion was produced in dilute solution, dilution must favor this term. If all of the bromine were consumed by the reaction formulated above, the rate Expression 1 would become

$$-d[\text{Et}]/dt = k'_b[\text{Br}_2][\text{Et}] \quad (2)$$

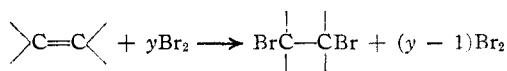
The integrated form of this is

$$k'_b = \frac{1}{(t_2 - t_1)(a - b)} \ln \frac{b(a - x)}{a(b - x)} \quad (3)$$

where a is $[\text{Br}_2]$ at time t_1 , $a - x$ is $[\text{Br}_2]$ at time t_2 , b is $[\text{Et}]$ at time t_1 , and $b - x$ is $[\text{Et}]$ at time t_2 . The integrated form of Expression 2 when $[\text{Br}_2]$ is equal to $[\text{Et}]$ is

$$k'_b = \frac{1}{t_2 - t_1} \frac{x}{a(a - x)} \quad (4)$$

The third term in the rate expression corresponds to the reaction



Since the term is of higher order than the second with respect to bromine, it is favored by a high concentration of the halogen. If bromine addition proceeded only by this reaction, rate Expression 1 would become

$$-d[\text{Et}]/dt = k'_c[\text{Br}_2]^y[\text{Et}] \quad (5)$$

Since the value of y has not been determined, the expression cannot be integrated. In order to permit the calculation of rate constants, it is assumed that y is two. Then Expression 5 becomes

$$-d[\text{Et}]/dt = k'_c[\text{Br}_2]^2[\text{Et}] \quad (6)$$

The integrated form is

$$k'_c = \frac{1}{t_2 - t_1} \left[\frac{1}{(a - b)^2} \log \frac{b(a - x)}{a(b - x)} + \frac{1}{a - b} \left(\frac{1}{a} - \frac{1}{a - x} \right) \right] \quad (7)$$

where the symbols have the same meaning as in Expression 3. When $[\text{Br}_2]$ is equal to $[\text{Et}]$ the integrated form of Expression 6 is

$$k'_c = \frac{1}{2(t_2 - t_1)} \left[\frac{1}{(a - x)^2} - \frac{1}{a^2} \right] \quad (8)$$

Experiments were first carried out at 25°. In order to determine the contribution of the first term on the right in Expression 1, the effect of

a concentration of hydrobromic acid of the same order of magnitude as that produced in most experiments was determined. Two solutions both 0.0080 M in allyl chloride and bromine initially were made up, and sufficient hydrobromic acid was added to one to make the mixture 0.0040 M in the acid. Rate measurements were made on both solutions, and the values of k'_b for the initial interval were calculated using Expression 4. k'_b (initial) for the hydrobromic acid solution was 0.0465 (mole/l.)⁻¹ sec.⁻¹, while the value for the solution without added acid was 0.0200 (mole/l.)⁻¹ sec.⁻¹. These results indicate that the contribution of the first term in Expression 1 is of considerable importance at 25°.

It was shown in an earlier paper⁶ that the reaction corresponding to the term $k_a[\text{Br}_3^-][\text{Et}]$, is most probably a termolecular reaction between the ethylene derivative, bromine, and bromide ion. The reaction corresponding to the term $k_c[\text{Br}_2]^y[\text{Et}]$, is of higher order than the third. Thus the bimolecular term $k_b[\text{Br}_2][\text{Et}]$ in Expression 1 should be favored most by dilution, and the kinetics of this reaction should best conform to Expression 2 in very dilute solutions. The following typical experiment indicates that such is found to be the case experimentally. The values of k'_b and k'_c were calculated using Expressions 4 and 8, respectively. The fact that constant values of k'_b were obtained does not necessarily mean that the consumption of bromine was all due to the second term on the right in Expression 1. The contribution of the higher order term, which may have been important during the first part of the reaction, would have fallen off more rapidly than that of the bimolecular term. However, the contribution of the tribromide ion containing term, which increases as the reaction proceeds, would have just compensated for this fall off, and the net result would have been apparent bimolecular kinetics.

TABLE I

THE REACTION OF BROMINE AND ALLYL CHLORIDE AT 25°

Initial concentrations: bromine, 0.0080; allyl chloride, 0.0080 M ; vol. of samples, 1.97 cc.; $\text{Na}_2\text{S}_2\text{O}_3$, 0.00995 N .

t , sec.	$\text{Na}_2\text{S}_2\text{O}_3$, cc.	k'_b , (mole/l.) ⁻¹ sec. ⁻¹	k'_c , (mole/l.) ⁻² sec. ⁻¹
0	3.03		
600	2.79	0.0190	2.30
1170	2.39	.0203	3.13
2100	1.89	.0206	3.90
3540	1.41	.0203	4.90
3900	1.10	.0203	6.50

Since concentrated solutions of bromine favor the third term on the right in Expression 1, the kinetics of solutions with sufficiently high concentrations of bromine should conform to the Expression 5. This conformity cannot be shown experimentally since the reaction becomes too rapid for rate measurements when this term becomes dominant. However, a definite trend toward a reaction of higher order than the first in bromine in concentrated solutions is indicated by the fact that, with solutions 0.040 *M* or greater in bromine, the values of k'_c are more nearly constant than the values of k'_b within a run.

In Table II the results of several separate experiments using different initial concentrations of reactants are summarized. The constants listed are for the initial time interval and correspond to a termolecular reaction which is of second order with respect to bromine and of first order with respect to allyl chloride. From runs 1 and 2 it is observed that k'_c remained unchanged when the concentration of bromine was kept constant and the allyl chloride concentration was doubled. The same thing is observed from runs 3 and 4. These results indicate that the reaction is of first order with respect to allyl chloride. A comparison of runs 1 and 3 shows that when the allyl chloride concentration was kept constant and the bromine concentration was doubled, the value of k'_c was greater at the higher concentration. The same is true of runs 2 and 4. Since the values of k'_c correspond to a reaction which is of second order with respect to bromine, these results indicate that the reaction is of higher order than the second with respect to halogen. Since the first term on the right in Expression 1 makes no contribution to the initial rate of reaction, the following expression must explain the observed results.

$$-d[\text{Et}]/dt = k_b[\text{Br}_2][\text{Et}] + k_c[\text{Br}_2]^y[\text{Et}] \quad (9)$$

The term $k_b[\text{Br}_2][\text{Et}]$ is of first order with respect to bromine and thus y in the term $k_c[\text{Br}_2]^y[\text{Et}]$ must necessarily be greater than two in order to account for the results summarized in Table II.

TABLE II

THE REACTION OF BROMINE AND ALLYL CHLORIDE AT 25°, VARIATION OF THE INITIAL CONCENTRATION OF REACTANTS

Run	[Br ₂], (mole/l.)	[Allyl chloride], (mole/l.)	k'_c (initial), (mole/l.) ⁻² sec. ⁻¹
1	0.040	0.040	4.58
2	.040	.020	4.50
3	.020	.040	2.95
4	.020	.020	2.90
5	.008	.008	2.25

Temperature Variation.—The results of studies on the kinetics of the reaction at three different temperatures are tabulated in Table III. The first value given is the rate constant for the initial interval while the "final" constant corresponds to an interval after nine-tenths of the reactants have been consumed. The constants were calculated using Expressions 4 and 8.

It is apparent that the bimolecular term, $k_b[\text{Br}_2][\text{Et}]$, makes a larger contribution to the rate of reaction at the higher temperature. This is suggested from a consideration of the rate constants for the runs with different initial concentrations of reactants. At 25° the "initial" value of k'_c for a solution 0.020 *M* in reactants was greater than the value for a more dilute solution (0.0080 *M*) while at 50 and 70° the initial values of k'_c were greater for the more dilute solution. These results are interpreted as meaning that at higher temperatures the contribution of the bimolecular term is sufficiently great to conceal the true order of the term, $k_c[\text{Br}_2]^y[\text{Et}]$. Further evidence that the bimolecular term becomes increasingly important at higher temperatures is supplied by the observation that the temperature coefficient of the reaction is the greatest for the solutions with the lowest concentrations of reactants. The term $k_b[\text{Br}_2][\text{Et}]$, which makes the largest contribution to the rate of reaction in dilute solutions, must accordingly have a higher energy of activation than the term $k_c[\text{Br}_2]^y[\text{Et}]$.

The data summarized in the table indicate that the contribution of the term $k_a[\text{Br}^-_3][\text{Et}]$ is of considerable importance at the higher temperatures. This is illustrated by the rise of the values of k'_b with time in run 6.

TABLE III

THE REACTION OF BROMINE AND ALLYL CHLORIDE, RATE CONSTANTS AT DIFFERENT TEMPERATURES

Run	<i>T</i> , °C.	[Reactants], (mole/l.)	k'_b , (mole/l.) ⁻¹ sec. ⁻¹		k'_c , (mole/l.) ⁻² sec. ⁻¹	
			Initial	Final	Initial	Final
1	25.0	0.020	0.055	0.030	2.90	10.0
2	25.0	.0080	.020	.020	2.25	11.0
3	50.0	.020	.090	.085	5.40	25.0
4	50.0	.0080	.043	.056	7.30	50.0
5	70.0	.020	.138	.163	8.75	65.0
6	70.0	.0040	.056	.326	18.5	175.0

Different Experimental Conditions.—The reaction of bromine and allyl chloride is extremely sensitive to added water. This is evident from the results summarized in Table IV, where the values of k'_b for the initial time interval are listed.

TABLE IV

THE REACTION OF BROMINE AND ALLYL CHLORIDE AT 25°;
THE EFFECT OF ADDED WATER

[Reactants], (mole/l.)	Initial values of k'_b , (mole/l.) ⁻¹ sec. ⁻¹			
	Anhydrous acetic acid	Acetic acid with 0.2% H ₂ O	Acetic acid with 1% H ₂ O	Acetic acid with 5% H ₂ O
0.040	0.120	0.135	0.220	...
.008	.0180	.020	.0320	0.180

Since Robertson^{4a} had reported that bromine additions in some solvents were heterogeneous, reactions were allowed to proceed in both packed and unpacked reaction flasks. Within experimental error the observed rates were identical. Similarly, runs in oxygen and carbon dioxide atmospheres gave identical rates of reaction.

The Action of Bromine on Allyl Acetate

Among the reactions which Robertson and co-workers^{4a} studied and gave as typical examples of termolecular additions was the reaction of bromine with allyl acetate. As part of the work on halogen additions, it seemed advisable to see if the work could be duplicated.

Reaction Products.—Analysis of the products of the reaction indicated that a considerable amount of bromide ion was formed. It was found that, as with the allyl chloride–bromine reaction, this formation of bromide ions was dependent upon the concentration of the reactants. Thus when the initial concentration of allyl acetate was 0.0040 *M*, 0.68 mole of bromide ion was produced per mole of bromine used. When the reactants were initially 0.020 *M*, this value was reduced to 0.34 mole.

The Kinetics of the Reaction.—The data from rate measurements were found to conform to rate Expression 1. However, the kinetics of the reaction were somewhat different from those for the allyl chloride–bromine reaction because the relative contribution of each term in the rate expression was different.

The contribution of the first term, $k_a[\text{Et}][\text{Br}_3^-]$, at 25° was shown to be slight by the following experiments. Rate studies were made on two solutions, both of which were initially 0.0125 *M* in allyl acetate and bromine. One solution was 0.050 *M* in lithium bromide while the other contained no added halide ion. The "initial" value of k'_b for the solution containing lithium bromide was 0.220 (mole/l.)⁻¹ sec.⁻¹ while k'_b for the other solution was 0.233 (mole/l.)⁻¹ sec.⁻¹. It will be recalled that, for the allyl chloride–bromine

reaction, the addition of a small amount of bromide ion had a much greater effect.

Dilute solutions were found to favor the term, $k_b[\text{Et}][\text{Br}_2]$. This was indicated by the fact that data from rate measurements gave constant values of k'_b when substituted into Expressions 3 and 4. Likewise concentrated solutions were found to favor the term $k_c[\text{Et}][\text{Br}_2]^y$, and to give fairly constant values of k'_c .

In Table V are summarized the results of separate experiments using different initial concentrations of reactants. Only the values of k'_b and k'_c for the initial interval are listed. It is observed that, as with the allyl chloride–bromine reaction, the values of k'_b fall with decreasing bromine concentration. However, the values of k'_c increase with decreasing bromine concentration for this reaction. This indicates that either *y* is 2 in the term, $k_c[\text{Et}][\text{Br}_2]^y$, or that the contribution of the term, $k_b[\text{Et}][\text{Br}_2]$, is sufficiently great to conceal the true value of *y*. The latter explanation is more likely since *y* was found to be greater than 2 for the other three reactions studied in this investigation. Also analysis of the products of this reaction showed that for the highest concentration of reactants which could be used for kinetic measurements, not more than 66% of the reaction was due to the term $k_c[\text{Et}][\text{Br}_2]^y$.

TABLE V

THE REACTION OF BROMINE AND ALLYL ACETATE AT 25°;
VARIATION OF THE INITIAL CONCENTRATION OF REACTANTS

[Br ₂], (mole/l.)	[Allyl acetate], (mole/l.)	k'_b , (mole/l.) ⁻¹ sec. ⁻¹	k'_c , (mole/l.) ⁻² sec. ⁻¹
0.0255	0.0184	0.318	17.5
.0200	.0200	.265	21.5
.0168	.0061	.230	22.0
.0134	.0106	.200	22.5
.0090	.0121	.158	30.5
.0040	.0040	.113	36.0

Temperature Variation.—Results of studies on the addition of bromine to allyl acetate at three different temperatures are summarized in Table VI. The constants are given for both the initial interval and an interval after nine-tenths of the reactants have been consumed.

It is apparent, especially from the variation of "initial" values of rate constants with concentration, that the term, $k_b[\text{Et}][\text{Br}_2]$, is becoming increasingly important at higher temperatures. Also, since the values of k'_b increase with time at 70° whereas they decrease at 25°, the contribution of the term, $k_a[\text{Et}][\text{Br}_3^-]$, must be greater at higher temperatures. Thus the term, $k_c[\text{Et}]$ -

TABLE VI

THE REACTION OF BROMINE AND ALLYL ACETATE, RATE CONSTANTS AT DIFFERENT TEMPERATURES

T, °C.	[Reactants], (mole/l.)	k_b , (mole/l.) ⁻¹ sec. ⁻¹		k'_b , (mole/l.) ⁻² sec. ⁻¹	
		Initial	Final	Initial	Final
25.0	0.0200	0.265	0.130	22.3	50.0
25.0	.0040	.113	.100	36.0	150
50.0	.0200	.480	.450	46.0	182
50.0	.0080	.413	.450	74.0	350
50.0	.0040	.292	.405	111	680
70.0	.0080	.690	.728	124	463
70.0	.0040	.656	1.090	250	6060

$[\text{Br}_2]^y$, appears to have the smallest temperature coefficient of the three terms in the rate expression.

Different Experimental Conditions.—The reaction of bromine with allyl acetate, like the allyl chloride-bromine reaction, is extremely sensitive to water. The addition of 1% of water to the solvent is accompanied by about an 80% increase in the rate of reaction. Oxygen and carbon dioxide have no effect on the rate of reaction.

The Action of Iodine on Allyl Acetate

It was expected that the addition of all of the halogens to ethylene derivatives would proceed by related mechanisms. Since bromine additions had been studied quite carefully, it was now desirable to study iodine additions. The reaction of allyl acetate and iodine, which Blythell and Robertson^{4b} had previously investigated and reported as a termolecular reaction, was chosen for study.

Reaction Products.—Analysis of the products of the reaction showed that considerable iodide ion was present. Only a qualitative analysis was carried out since the reverse reaction prevented a more accurate determination.

The Kinetics of the Reaction.—The kinetics of the reaction were found to be analogous to those for the bromine addition reactions. That is, the rate measurements were interpreted best by the expression

$$-d[\text{Et}]/dt = k_a[\text{I}_3^-][\text{Et}] + k_b[\text{I}_2][\text{Et}] + k_c[\text{I}_2]^y[\text{Et}] \quad (10)$$

where y is greater than 2.

At 25° the values of k'_b calculated using Expression 3 were found to be relatively constant within a run. This indicated that either the term $k_b[\text{I}_2][\text{Et}]$ in Expression 10 was dominant or that the contribution of the two other terms compensated and gave bimolecular kinetics. Sub-

sequent studies showed that the latter alternative was most probable.

The effect of using different initial concentrations of reactants was carefully studied, and the results are shown in Table VII, where the constants for the initial interval and an interval after 50% of the iodine had been consumed are given. It is evident that, analogous to the allyl chloride-bromine reaction, the values of k'_c increase with increasing iodine concentration, indicating that this reaction is of first order with respect to the ethylene derivative and of higher order than the second with respect to halogen.

TABLE VII

THE REACTION OF IODINE AND ALLYL ACETATE AT 25°

Run	[I ₂], (mole/l.)	[Allylacetate], (mole/l.)	$k'_c \times 10^3$, (mole/l.) ⁻² sec. ⁻¹	
			Initial	At 50% completion
1	0.0160	1.48	1.21	1.46
2	.0162	1.48	1.27	1.69
3	.0180	0.416	1.39	2.62
4	.057	1.48	1.81	3.53
5	.060	0.371	2.39	3.33
6	.075	.371	2.74	3.38
7	.0829	.016	3.68	2.70
8 ^a	.062	.371	2.93	3.92
9 ^b	.061	.371	4.34	2.54

^a Solvent contained 0.20% H₂O. ^b Solvent contained 0.20% H₂O and was 0.014 M in HI.

Different Experimental Conditions.—It has been found that both water and hydriodic acid are good catalysts for the reaction. This is apparent from runs 5, 8 and 9 in Table VII. Since the concentration of hydriodic acid used was of the same order of magnitude as the amount which might be produced in a reaction, it is obvious that the strong catalytic effect of the acid would easily explain the rise in the values of k'_c with time in a given run.

The rate of this reaction was not affected by the use of either oxygen or carbon dioxide atmospheres.

The Action of Iodine on Allyl Alcohol

Blythell and Robertson^{4b} reported that iodine addition to allyl alcohol proceeded by a termolecular reaction. Again it was considered desirable to repeat their work.

It was found that within a run the kinetics were very similar to those for the allyl acetate-iodine reaction. However, the results obtained from experiments using different initial concentrations of reactants were somewhat different.

This is illustrated by the data summarized in Table VIII, where the constants listed are for the initial interval. It appears that the reaction is of higher order than the second with respect to iodine concentration and of higher order than the first with respect to allyl alcohol concentration. Thus from runs 2, 4 and 6, in which the allyl alcohol concentrations were similar, it is observed that an increase in iodine concentration caused a considerable increase in the termolecular rate constants. This is analogous to the results obtained for the allyl chloride-bromine and allyl acetate-iodine reactions. In runs 1, 3, 5 and 7, in which the iodine concentrations were similar, an increase in the allyl alcohol concentration was accompanied by a considerable increase in the termolecular rate constants. This unusual dependence of the rate of reaction on the concentration of ethylene derivative had not been observed previously. The reason for it will be discussed later.

TABLE VIII

Run	[I ₂], (mole/l.)	[Allyl alcohol], (mole/l.)	$k'_c \times 10^3$, (mole/l.) ⁻² sec. ⁻¹
1	0.0287	0.283	3.93
2	.0155	.647	5.00
3	.0270	.577	6.80
4	.0296	.518	7.23
5	.0260	1.130	11.3
6	.0562	0.518	12.1
7	.0245	2.352	17.2

Discussion

The results of this investigation indicate that halogen addition reactions may proceed by rather complex mechanisms. This is evidenced by the empirical rate expressions which have been found to fit best halogen addition data. Each of the three terms on the right in the typical rate expression

$$-d[\text{Et}]/dt = k_a[\text{X}_2^-][\text{Et}] + k_b[\text{X}_2][\text{Et}] + k_c[\text{X}_2]^2[\text{Et}] \quad (11)$$

is assumed to correspond to a different addition process and in subsequent discussions each will be treated separately. The reaction corresponding to the first term will be referred to as the halide ion catalyzed reaction, the second as the second order reaction, and the third as the higher order reaction.

The knowledge that the rate expression for halogen addition may consist of three terms enables one to offer an explanation of many ap-

parently conflicting results found in the literature. For example, the effect of added halide ion on halogen addition reactions has been the subject of much controversy. There have been claims that added halide ion catalyzes the reactions,^{3,7} has no effect,^{2a,8} and retards the reactions.⁹ It is evident from the rate expressions that the addition of halide ion can exert two effects on the reaction rate. These are an acceleration due to the increased importance of the term containing the trihalide ion concentration and a retardation due to the decreased contribution to the rate by the other two terms (because of the lowering of the halogen concentration by trihalide ion formation). Depending on the relative importance of these two effects, added halide ion may accelerate, not affect, or retard the addition.

The observation that some unsaturated compounds add bromine by an autocatalytic reaction while others add with a high initial rate^{8a} may be readily explained. It is to be expected that different compounds would have different values for the constants in the rate expression. For compounds such as maleic and fumaric acids,¹⁰ k_a is much larger than k_b or k_c and an autocatalytic reaction is observed. For compounds such as allyl chloride and allyl acetate, k_b and k_c are relatively large and a high initial rate of reaction is observed. Vinyl bromide is intermediate between the two types of compounds.¹⁰ For low concentrations of bromine, the addition reaction is autocatalytic, while for high concentrations the initial rate is very great and autocatalysis is not observed.

The Halide Ion Catalyzed Reaction.—The reaction corresponding to the first term in the rate Expression 11 has been discussed thoroughly in an earlier publication.⁶ It was concluded that the most probable mechanism involves a termolecular reaction between ethylene derivative, halide ion and halogen.

The Second Order Reaction.—The second term in the rate expression for halogen addition has been assumed to correspond to a reaction in which a haloacetate and a hydrogen halide are produced. This, together with the knowledge that the reaction is of first order with respect to halogen and ethylene derivative concentrations,

(7) Berthoud and Mosset, *J. Chem. Phys.*, **33**, 271 (1936).(8) Davis, *THIS JOURNAL*, **50**, 2769 (1928).(9) (a) Bartlett and Tarbell, *ibid.*, **58**, 466 (1936); (b) James and Sudborough, *J. Chem. Soc.*, **91**, 1037 (1907).(10) Nozaki and Ogg, *THIS JOURNAL*, **64**, 704 (1942).

very few examples of termolecular reactions, the probability of a fourth order reaction seems rather small. However, there is a bit of evidence for this view. The two previously discussed reactions for halogen addition, both of which may be termolecular, have positive temperature coefficients while this reaction appears to have a negative coefficient.^{4a,13} This suggests that it is of higher order than the other reactions.

Experimental Part

Materials.—The acetic acid was Merck "99.5% Acetic Acid"; m. p. 16.2°. Anhydrous acetic acid was prepared by the acetic anhydride method of Orton and Bradfield.¹⁴ The bromine was washed with potassium bromide solution and was distilled from concentrated sulfuric acid. The iodine, J. T. Baker c. p., was sublimed from potassium iodide and was dried over calcium chloride.

The ethylene derivatives were all carefully fractionated through a 100-cm. Vigreux column. They possess the following boiling points: allyl chloride, 44.4–44.6°; allyl acetate, 104.5–104.8°; allyl alcohol, 97.0–97.1°.

Analytical Procedures.—Most procedures were carried out as described in an earlier communication.¹⁰ For studies with iodine addition reactions, precautions were taken to avoid the decomposition of the diiodide during analysis; *i. e.*, samples were chilled and titrated rapidly.

It was necessary to determine the amount of halide ion produced during the course of a reaction. These determinations were carried out in the following manner. Equivalent known quantities of bromine and unsaturated compound were allowed to react to completion in acetic acid. The mixture was then poured into an aqueous solution of sodium carbonate, and the solution was extracted with three 25-cc. portions of carbon tetrachloride. The aqueous solution was then analyzed for bromide ion concentration by the regular procedure.

Procedure for Rate Studies.—The reactions were allowed to proceed in blackened volumetric flasks. For the rapid bromine reactions, standardized solutions of bromine and of ethylene derivative were made up. Known volumes of these solutions were then added to the reaction vessel, the vessel was well shaken, and samples were re-

moved from it at appropriate intervals. The samples were analyzed for bromine content. For the slower iodine reactions, samples of the reactants were weighed directly into the volumetric flasks. The unsaturated compound was generally kept in great excess in an attempt to avoid the reverse reaction. Even under these conditions, the back reaction became important after about half the iodine had been consumed.

All runs in which oxygen was excluded were made in a closed, all glass vessel equipped with two stopcocks. A carbon dioxide atmosphere was used and samples were removed by gas pressure. Oxygen was removed from the solvent by boiling and repeated evacuation.

Summary

1. The reaction between bromine and allyl chloride has been studied, using glacial acetic acid as the solvent. The reaction is complex. This is indicated by a mixture of products and the rate expression

$$-d[\text{Et}]/dt = k_a[\text{Br}_3^-][\text{Et}] + k_b[\text{Br}_2][\text{Et}] + k_c[\text{Br}_2]^\nu[\text{Et}]$$

to which rate measurements conform best. The reaction rate has been found to be greatly affected by the addition of small amounts of water to the solvent but to be unaffected by oxygen or packed reaction vessels.

2. The bromine–allyl acetate and iodine–allyl acetate reactions are similar to the bromine–allyl chloride reaction; *i. e.*, mixed products are obtained, an analogous rate expression is required, and water strongly catalyzes the reactions.

3. The iodine–allyl alcohol reaction has been studied and shown to be even more complex than the other three reactions.

4. Many apparently conflicting results in the literature are explained on the basis of the complex rate expression.

5. Mechanisms for the reactions corresponding to the terms in the rate expression are discussed.

(13) Davis, *THIS JOURNAL*, **50**, 2769 (1928).

(14) Orton and Bradfield, *J. Chem. Soc.*, 983 (1927).