affect the rate of reaction but water has a retarding effect.

3. A study has been made of the reaction of bromine and vinyl bromide in glacial acetic acid. With a high concentration of bromide ions and a low concentration of bromine, the above rate expression is obeyed. The reaction is not affected by the concentration of proton donors or the ionic strength of the solution, indicating that effects observed with maleic and fumaric acids were probably due to the carboxyl group.

4. Lithium bromide and hydrobromic acid have been found to exert the same catalytic effect on the reaction of bromine with allyl chloride but not on the reaction of bromine with allyl acetate. For the latter reaction, hydrobromic acid is a somewhat superior catalyst.

Halogen Addition to Ethylene Derivatives. II. The Mechanism of the Halide Ion Catalyzed Addition Reaction

BY KENZIE NOZAKI AND RICHARD A. OGG, JR.

Although addition reactions of halogens to ethylene derivatives in solution have been the subject of numerous investigations, their mechanism is still a matter of controversy. One reason for this is the complexity of the reactions, which is evident from recent reports in the literature.[1] Depending upon the experimental conditions and the nature of the reactants, one or more of the several processes may be dominant in the mechanism. One such process, which will be referred to as the halide ion catalyzed reaction, is discussed in this paper.

There is considerable evidence for the existence of a halide ion catalyzed addition reaction of halogens to ethylene derivatives. For example, many halogen addition reactions have been reported to be catalyzed by halide ions.[1a,2] Also, the decomposition of 1,2-dihalides is frequently catalyzed by halide ions.[3] Thus there must be a corresponding halide ion catalyzed addition reaction. Finally, halogen additions in the presence of large concentrations of halide ions appear to obey the same empirical rate expression.[4] In the present paper more evidence concerning the halide ion catalyzed reaction is presented. In addition the mechanism of the reaction is discussed in the light of known information concerning it.

Experimental Results

In practically all studies of halogen addition to ethylene derivatives in the presence of halide ions, the halogen molecule and the halide ion were both derived from the same element, e. g., bromine and bromide ions. In the present investigation the effect of the addition of other ions, some of which are not halide ions, has been studied, using glacial acetic acid as the solvent.

The Action of Bromine on Vinyl Bromide in the Presence of Lithium Chloride.—Bromine and vinyl bromide react by an autocatalytic reaction in dilute solutions in acetic acid. The addition of lithium chloride was found to greatly accelerate the rate of consumption of bromine. This lithium chloride catalyzed reaction was studied in this investigation.

It is assumed that the product of the reaction is dibromochloroethane, a chloro-bromo addition product. This is indicated by the presence of a considerable concentration of bromide ions in the reaction product. Also, it has been shown[5] that the product from an analogous reaction, the reaction of bromine with maleic acid in the presence of chloride ion, is a chloro-bromo addition product.

The kinetics were found to fit best the rate expression

$$-d[Et]/dt = k[Br_2][Cl^-][Et] \qquad (1)$$

where Et represents the ethylene derivative, vinyl bromide. Integration yields

(1) (a) Robertson, Clare, McNaught, and Paul, *J. Chem. Soc.*, 335 (1937); (b) Blythell and Robertson, *ibid.*, 179 (1938); (c) White and Robertson, *ibid.*, 1509 (1939); (d) Walker and Robertson, *ibid.*, 1515 (1939).

(2) (a) Williams and James, *ibid.*, 343 (1928); (b) Williams, *ibid.*, 2911 (1932); (c) Hanson and Williams, *ibid.*, 1059 (1930); (d) Berthoud and Mosset, *J. Chem. Phys.*, **33**, 271 (1936).

(3) (a) A. Slator, *J. Chem. Soc.*, **85**, 1697 (1904); (b) van Duin, *Rec. trav. chim.*, **43**, 431 (1924); (c) Biilmann, *ibid.*, **36**, 319 (1916).

(4) Nozaki and Ogg, THIS JOURNAL, **64**, 697 (1942).

(5) Terry and Eichelberger, *ibid.*, **47**, 1067 (1925).

$$k = \frac{1}{(t_2 - t_1)} \left[\frac{1}{(a-b)(c-a)} \ln \frac{a}{a-x} + \right.$$
$$\left. \frac{1}{(a-b)(b-c)} \ln \frac{b}{b-x} + \frac{1}{(b-c)(c-a)} \ln \frac{c}{c-x} \right]$$

$$(2)$$

where a, b, and c represent the $[Br_2]$, $[Cl^-]$, and $[Et]$, respectively, at time t_1, and $(a-x)$, $(b-x)$, and $(c-x)$ represent the $[Br_2]$, $[C^-]$, and $[Et]$ at time t_2. The applicability of Expressions (1) and (2) is illustrated by the typical example shown in Table I. It was assumed in the calculations that all of the bromine was free; *i. e.*, there was no Br_2Cl^- formation.

TABLE I

THE ACTION OF BROMINE ON VINYL BROMIDE

Initial concentrations: vinyl bromide, 0.133 M; lithium chloride, 0.100 M; bromine, 0.015 M; temperature, 40.0°; vol. of samples, 1.97 cc.; $Na_2S_2O_3$, 0.00850 N.

$t \times 10^{-3}$, sec.	$Na_2S_2O_3$, cc.	$k \times 10^3$, (mole/l.)$^{-2}$ sec.$^{-1}$
	7.31	
1.08	6.87	4.58
3.24	6.01	4.59
4.92	5.45	4.50
7.63	4.65	4.56
10.9	3.87	4.59
14.2	3.24	4.50
19.3	2.50	4.47
23.4	2.07	4.44

The fairly constant values of k which were obtained for this run are in part due to the formation of bromide ions during the reaction. These ions can exert two effects, an acceleration of the rate of bromine consumption by the introduction of the bromide ion catalyzed addition reaction, and a retardation in the rate due to the removal of bromine by tribromide ion formation. At low chloride ion concentrations, the first effect is most important, and it was found that the values of k increase somewhat during the final 25% of runs in which the initial lithium chloride concentration is 0.05 M. With high chloride ion concentrations, it would be expected that the second effect would predominate. Experimentally it was found that the values of k fall off rapidly after the first 25% of the reaction for runs in which the initial lithium chloride concentration is 0.40 M.

In Table II are summarized the results of experiments in which the concentrations of the reactants were varied. In addition to the values of k, values of k_1 are listed. These were calculated by assuming that the data fit a rate expression of the form

$$-d[Et]/dt = k_1[Br_2][Et] \qquad (3)$$

Integration of expression (3) gives

$$k_1 = \frac{1}{(t_2 - t_1)(a-c)} \ln \frac{c(a-x)}{a(c-x)} \qquad (4)$$

where the symbols have the same meaning as in Expression (2). Due to the difficulties introduced by bromide ion formation, the constants listed correspond to the initial rate of reaction and were obtained by extrapolation.

TABLE II

THE ACTION OF BROMINE ON VINYL BROMIDE AT 40°

Run	Initial concentrations, mole/l. [LiCl]	[Vinyl bromide]	[Br₂]	$k_1 \times 10^4$, (mole/l.)$^{-1}$ sec.$^{-1}$	$k \times 10^3$, (mole/l.)$^{-2}$ sec.$^{-1}$
1	0	0.133	0.0150	0.55	
2	0.050	.133	.0150	2.70	5.40
3	.100	.133	.0150	4.58	4.58
4	.100	.312	.0150	4.56	4.56
5	.100	.133	.0050	4.58	4.58
6	.200	.133	.0150	8.80	4.40
7	.400	.133	.0150	17.5	4.38

The results of runs 3, 4, and 5 indicate that the reaction is of first order with respect to the concentration of bromine and vinyl bromide. The results of runs 2, 3, 6, and 7 indicate that the reaction is of first order with respect to chloride ion concentration. It is observed that the value of k is greatest for the run in which the lithium chloride concentration is 0.05 M and that k rapidly approaches a constant value at higher lithium chloride concentrations. This is due to the fact that the uncatalyzed reaction between bromine and vinyl bromide, whose initial rate is given in run 1, becomes relatively unimportant at high chloride ion concentrations.

The Effect of Electrolytes on the Halogen Addition Reactions.—Work reported in this and an earlier paper[4] has indicated that bromine additions to ethylene derivatives are catalyzed by bromide and chloride ions. It was thus of interest to determine whether other added substances had any effect on the reactions. The bromine–allyl chloride reaction, which will be discussed thoroughly in a subsequent paper, was chosen for study.

In Table III are summarized the results of experiments in which several different electrolytes were added. The rate constants were calculated using an integrated form of Expression 3, and are for the initial time interval. It is observed that all of the added substances catalyze the reaction. Since runs 6 and 7 indicate that cations have no effect on the reaction, it appears that the catalysis is due to the added anions, of which halide ions are the most effective.

TABLE III

THE ACTION OF BROMINE ON ALLYL CHLORIDE AT 25°

Initial concentrations: allyl chloride, 0.00800 M; bromine, 0.00800 M; added electrolytes, 0.100 M.

Run	Added electrolyte	k_1 (initial), (mole/l.)$^{-1}$ sec.$^{-1}$
1		0.200
2	Sodium acetate	.275
3	Sulfuric acid	.320
4	Sodium nitrate	.580
5	Lithium chloride	1.44
6	Lithium bromide	0.695
7	Hydrogen bromide	.695

Since it was desirable to know if iodine additions to ethylene derivatives were also affected by added electrolytes, a study was made of the allyl acetate–iodine reaction. It was found that allyl acetate and iodine react slowly in acetic acid solutions and that the reaction is catalyzed considerably by the addition of electrolytes. This is illustrated by the results shown in Table IV. The rate constants were calculated using Expression 4 and are for the initial time interval.

TABLE IV

THE ACTION OF IODINE ON ALLYL ACETATE AT 25°

Added electrolyte	Initial concentrations, (mole/l.) [Electrolyte]	[I_2]	[Allyl acetate]	k_1 (initial) × 10⁵, (mole/l.)$^{-1}$ sec.$^{-1}$
		0.0180	0.416	2.57
Sodium acetate	0.100	.0186	.370	5.39
Lithium chloride	.100	.0182	.388	9.35
Hydrogen iodide	.100	.0180	.410	10.50

The Mechanism of the Reaction

The data from our studies of bromine addition to ethylene derivatives in the presence of added bromine and chloride ions have been found to fit best a rate expression of the form

$$-d[Et]/dt = k_a[X_3^-][Et] = k[X_2][X^-][Et] \quad (5)$$

where the halogen atoms, represented by X, are not necessarily the same. An analogous rate expression has been found to fit the iodide ion catalyzed addition of iodine to acetylene derivatives.[6] Indeed, it is possible that the kinetics of all halogen additions to ethylene and acetylene derivatives in the presence of a sufficiently high concentration of halide ions will fit a similar rate expression. Thus it is of interest to understand the mechanism of the reaction.

There are two mechanisms of halogen addition which will give the empirical rate expression.[6a]

(6) Moelwyn-Hughes and Ligard, *J. Chem. Soc.*, 424 (1933).

(6a) Other mechanisms suggested in the literature will not satisfy the kinetics of the reaction. For example, the Robinson and Ingold[5] mechanism predicts a rate expression of the form $-d[Et]/dt = k[X_2][Et]$.

(7) Robinson, "Outline of an Electrochemical Theory of the

Each will be discussed below on the basis of available experimental evidence.

Mechanism I.—The first mechanism which will satisfy the empirical rate expression may be formulated as
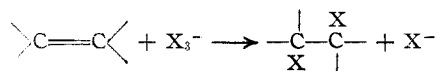
The trihalide ion is assumed to be the active agent which reacts in some manner with the unsaturated compound to give the dihalide.

This mechanism is not satisfactory because it fails to predict several of the experimental results which we have obtained from studies of the reaction. For example, no simple reason is apparent why tribromide ions should add bromine to maleic acid when bromine itself will not add.[4] This is especially difficult to explain if it is assumed that halogen addition proceeds through the formation of an intermediate positively charged carbonium ion.[7,8] Another result which could not be predicted by this mechanism is the catalysis of halogen addition by anions such as acetate, nitrate, and bisulfate which probably do not form complex ions with the halogens.

Mechanism II.—The second mechanism, which gives a much better explanation of the experimental observations, will now be considered. It may be formulated as
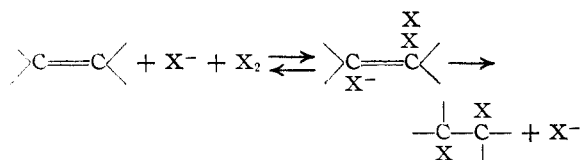
It is a termolecular reaction between unsaturated compound, halide ion, and halogen molecule.

This mechanism explains the catalytic effect of added halide ions by the fact that they are involved in the rate determining step. The catalysis by other added electrolytes is readily understood since any anion, whether it forms a complex ion with halogen or not, may be substituted for the halide ions shown in the formulation. The addition of foreign salts would be expected to lead to the formation of mixed addition products, several of which have been reported in the literature.[5,9] *trans* addition, which seems to be the rule in halo-

Course of the Organic Reactions," Institute of Chemistry of Great Britain and Ireland, London (1932).

(8) (a) Burton and Ingold, *J. Chem. Soc.*, 912 (1928); (b) Ingold, *Chem. Rev.*, **15**, 225 (1934).

(9) Francis, THIS JOURNAL, **47**, 2340 (1925).

gen addition,[10] is explained since the carbon to which the anion becomes attached undergoes a Walden inversion.

The proposed reaction, interpreted in terms of the collision theory of third order reactions,[11] gives reasonable results. If it is assumed that the "effective collision diameters" and the "distances at which collisions persist" are of the order of 10^{-8} cm., the calculated rate constant for the maleic acid–lithium bromide–bromine reaction is $6.67 \times 10^{12}T^{1/2}e^{-9170/RT}$ (mole/cc.)$^{-2}$ sec.$^{-1}$. The experimental value[4] expressed in the same form is $4.37 \times 10^{9}T^{1/2}e^{-9170/RT}$ (mole/cc.)$^{-2}$ sec.$^{-1}$. The difference of over a thousand-fold may be attributed to an expected steric or orientation factor. For application of the activated complex theory, the empirical rate expression may be expressed as $2.25 \times 10^{16}T^{-2}e^{-(9170 + 1/2RT)/RT}$(mole/cc.)$^{-2}$ sec.$^{-1}$. The calculated value, assuming that only translational entropy is involved and that the transmission coefficient is unity, is $7.80 \times 10^{11}T^{-2}e^{-(9170 + 1/2RT)/RT}$(mole/cc.)$^{-2}$ sec.$^{-1}$. The difference corresponds to an increase in vibrational and rotational entropy of 20.6 calories per degree in the formation of the activated complex from the reactants.

The reaction need not be a simultaneous termolecular reaction. That is, association of either the halogen molecule or halide ion with the ethylene derivative may precede the rate determining step. Both possibilities will now be considered.

If preliminary complex formation between halogen and ethylene derivative occurs, the association would probably involve the double bond acting as an electron donor and the halogen molecule acting as an electron acceptor. Such complexes have been discussed by White and Robertson.[1c] It would be expected that factors which would favor electron donation by the ethylene derivative would favor complex formation and a greater over-all rate of halogen addition. There is experimental evidence which is in agreement with this expectation. For example, studies on the effect of substituent groups on the rate of halogen addition[12] have shown that groups which tend to repulse electrons (e. g., CH_3) are accompanied by high rate constants while groups which attract electrons (e. g., CO—OH) are accompanied by low rate constants. Also, it is well known

that salts of unsaturated organic acids add halogens at a greater rate than the acids themselves.[1a,2d,13] Electrons should be more readily available in the salt because of the presence of the negative charge on the molecule.[14] If, on the other hand, preliminary complex formation between the halide ion and the ethylene derivative occurs, the association should involve the ethylene carbons acting as the electron acceptor and the halide ion acting as the electron donor. As evidence in favor of such a complex may be cited our work on catalyzed cis–trans isomerizations, in which intermediates such as
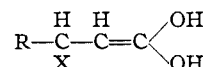
were proposed.[15] Further evidence is supplied by the experimental observation that proton donors catalyze halogen addition to oxygen-containing compounds such as maleic acid, fumaric acid, allyl acetate,[4] and unsaturated aldehydes[1c] but not to compounds such as vinyl bromide and allyl chloride. The catalytic effect of protons is probably due to the formation of complexes in which the protons are attached to a carbonyl oxygen. The formation of such complexes would favor the initial addition of halide ion due to both electrostatic attraction and tendencies for electronic displacements such as
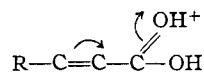
From the evidence, it appears that preliminary complex formation of either type may occur. On the basis of this, the view is taken that in general it is through the joint and simultaneous action of the halide ion and halogen molecule that addition to the double bond occurs. However, in some cases association between the ethylene derivative and either the halide ion or the halogen molecule may precede reaction with the other reactant. Thus the hydrobromic acid catalyzed addition of bromine to maleic acid is looked upon as involving preliminary association between the
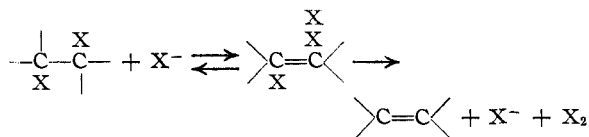
(10) Ogg, THIS JOURNAL, 57, 2727 (1935).

(11) Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, N. Y., p. 78.

(12) Ingold and Ingold, J. Chem. Soc., 2354 (1931).

(13) Barrett and Lapworth, J. Chem. Soc., Proc., 23, 18 (1907).

(14) An alternative explanation for the rapid addition reaction of salts of unsaturated acids involves the initial formation of lactone-like complexes. For example, the complex for acid maleate ion

would be –CH—CH—COOH. This complex could react with a halogen to give a halolactone, which could then react with a halide ion to yield a dihalide. This mechanism is considered to be unlikely since it predicts a cis addition product whereas an analysis of the product from the addition of bromine to sodium crotonate showed that only the trans addition product was obtained.

(15) Nozaki and Ogg, THIS JOURNAL, 63, 2583 (1941).

ethylene derivative and the catalyst while the addition of halogens to salts of unsaturated acids is considered to involve preliminary complex formation between the unsaturate and the halogen molecule.

The Reverse Reaction.—From thermodynamic considerations it is necessary that the mechanism of the halide ion catalyzed decomposition of dihalides[10,16] be the reverse of the halide ion catalyzed addition reaction. Since a termolecular reaction is favored for addition, the mechanism for the decomposition must be formulated as follows

$$-\overset{|}{\underset{X}{C}}-\overset{X}{\underset{|}{C}}- + X^- \rightleftharpoons \overset{X}{\underset{X}{\diagdown}C=C\diagup} \longrightarrow$$
$$\diagup C=C\diagdown + X^- + X_2$$

where the halide ion and the halogen molecule fall away practically simultaneously from the ethylene derivative.

Experimental Part

Materials.—The iodine, J. T. Baker C. P., was sublimed from potassium iodide and dried over calcium chloride. The sodium acetate, sodium nitrate, lithium chloride, lithium bromide, and sulfuric acid were all C. P. materials. The salts were fused before use. Hydriodic acid solutions in acetic acid were prepared by mixing the correct amounts of aqueous hydriodic acid and acetic anhydride. All other materials were the same as described in an earlier communication.[4]

Procedure.—Most procedures were as described in an earlier paper.[4] For iodine reactions, the samples were chilled and titrated rapidly to avoid decomposition of the addition products.

Analysis of the Product of the Vinyl Bromide–Bromine–Lithium Chloride Reaction.—It was expected that bromide ions would be a product of this reaction. The following qualitative experiment was carried out to show that this expectation was realized: 0.106 g. of lithium chloride, 15 cc. of 0.227 *M* vinyl bromide solution and 10 cc. of acetic

(16) Winstein, Pressman and Young, THIS JOURNAL, **61**, 1645 (1939).

acid were mixed, and 0.060 g. of bromine was added. The solution was kept at 40° for six hours and was then poured into 25 cc. of an aqueous solution of sodium carbonate. The mixture was extracted with three 25-cc. portions of carbon tetrachloride to remove organic matter. More carbon tetrachloride was added, followed by 2 cc. of 6 *N* nitric acid and a few cc. of dilute permanganate solution. A colorimetric comparison of the orange carbon tetrachloride solution with solutions containing known concentrations of bromine indicated that about 90% of the bromine had reacted to yield bromide ion as one of the products.

The Product from the Addition of Bromine to Sodium Crotonate.—It was desirable to know whether the reactions of halogens with salts of unsaturated acids gave *cis* or *trans* addition products. The following experiment indicated that a *trans* addition product was obtained: 8.6 g. of crotonic acid, 12 g. of potassium bromide and 4.0 g. of sodium hydroxide were dissolved in 50 cc. of water, and 16 g. of bromine was added slowly. After the addition of the bromine the solution was evaporated at room temperature, and the remaining solid was recrystallized from water. The material melted at 85°. This agrees very well with the melting point of the dibromide from crotonic acid, the *trans* addition product. There was no evidence of any *cis* addition product, which melts at 59°.

Summary

1. The reaction between bromine and vinyl bromide in the presence of added lithium chloride has been studied, using glacial acetic acid as the solvent. The data conform best to the rate expression $d[Et]/dt = k[Br_2][Cl^-][Et]$.

2. It has been found that the allyl chloride–bromine reaction and the allyl acetate–iodine reaction are catalyzed not only by halide ions but by other ions such as acetate, nitrate, and bisulfate.

3. The mechanism of the halide ion catalyzed addition of halogen to ethylene derivatives has been discussed. The most probable mechanism involves a termolecular reaction between ethylene derivative, halide ion, and halogen molecule.

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