

terials were reduced by method (a) if possible, but most of the products needed the more drastic conditions of method (b). The only substance in which hydrogenation of the aromatic ring interfered seriously was the pulegone-5-*n*-propylresorcinol product, the fractions of which varied from an oily consistency to a very tacky resin. Each product was fractionated and the constants determined on each fraction. The variability of the constants of the fractions is shown in the tables (IV and V). The center fraction was selected for analysis.

### Summary

1. The series of homologs of hexahydrocannabinol of 1-hydroxy-3-*n*-amyl-6,6,9-trimethyl-(7a, 7, 8, 9, 10, 10a)-hexahydro-6-dibenzopyran have been prepared where the 3-*n*-amyl group has been replaced by other *n*-alkyl groups, *n*-propyl through *n*-octyl, inclusive.

The potencies of these compounds, with the exception of the *n*-butyl and *n*-hexyl homologs, are lower than those of the corresponding tetrahydrocannabinol homologs.

2. The series of pulegone-5-*n*-alkylresorcinol

condensation products, *n*-propylresorcinol through *n*-nonylresorcinol, have been prepared and their marihuana potencies determined. A revised value for the potency of the previously reported pulegone-olivetol product is given. Maximum potency occurs in the *n*-octyl condensation product in this series, the region of high potency is broadened to include the *n*-hexyl, *n*-heptyl, and *n*-octyl members, and in the case of these latter two members their potencies exceed those of the corresponding tetrahydrocannabinol analogs made in an unequivocal manner.

3. The series of dihydro reduction products of the members of series 2, with the exception of the *n*-nonyl derivative, have been prepared and their marihuana potencies determined. With the exception of the *n*-amyl member their potencies are all significantly lower than the corresponding members of series 2.

URBANA, ILL.

RECEIVED FEBRUARY 19, 1942

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF STANFORD UNIVERSITY]

## Halogen Addition to Ethylene Derivatives. I. Bromine Additions in the Presence of Bromide Ions

BY KENZIE NOZAKI<sup>1</sup> AND RICHARD A. OGG, JR.

Many workers have noticed that the addition reactions of halogens to ethylene derivatives may be greatly affected by the addition of halide ions to the reaction mixtures. Williams<sup>2</sup> and more recently Robertson and co-workers<sup>3</sup> have reported that hydrogen bromide catalyzed the addition of bromine to several unsaturated compounds. However, others<sup>4</sup> have observed that the addition of halide ions to reaction mixtures caused a retardation in the rate of halogen addition. A study of the existing data showed that all of the workers, whether reporting catalysis or inhibition, found that in the presence of a considerable concentration of halide ions, the reactions were approximately of first order with respect to total halogen concentration and of first order with respect to the ethylene derivative concentration.

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(2) Williams and James, *J. Chem. Soc.*, 343 (1928).

(3) Robertson, Clare, McNaught and Paul, *ibid.*, 335 (1937).

(4) (a) Bartlett and Tarbell, *THIS JOURNAL*, **58**, 486 (1936); (b) James and Sudborough, *J. Chem. Soc.*, 1037 (1907); (c) Berthoud and Mosset, *J. Phys. Chem.*, **33**, 271 (1936).

Thus it appeared probable that all of the addition reactions followed a similar course when the halide ion concentration was high. The purpose of the present investigation was to make a study of several such reactions in order to obtain information concerning the reaction mechanism. Because of their convenience for kinetic measurements, bromine additions to several ethylene derivatives were studied, using glacial acetic acid as the solvent.

**The Equilibrium Constant for the Dissociation of Potassium Tribromide.**—Before empirical rate expressions could be formulated for the reactions under investigation, it was necessary to determine the equilibrium constant for the dissociation of tribromide ion into bromine and bromide ion. This was determined by observing the increase in solubility of potassium bromide in glacial acetic acid accompanying the addition of bromine to solvent. The increase was assumed to be due to tribromide formation. The studies were carried out in solutions whose ionic strength was made up

to two-tenths by the addition of lithium ethane-sulfonate.

Since work by Bjerrum<sup>5</sup> and Fuoss and Kraus<sup>6</sup> has indicated that, in moderately concentrated solutions in solvents with as low a dielectric constant as acetic acid, practically all of the electrolyte exists in the form of ion pairs, it seemed probable that the amount of dissociated potassium bromide would be small. Thus the equilibrium constant was calculated on the assumption that the total concentration of potassium bromide was the same in all solutions and equal to its solubility in pure acetic acid. With this assumption it was found that satisfactory results were obtained. The method of calculation together with a typical run at 50° is shown below.

$$\begin{aligned} x &= [\text{KBr}_3] + [\text{KBr}] \\ y &= [\text{Br}_2] + [\text{KBr}_3] \\ z &= [\text{KBr}] \text{ in a saturated solution} \\ x - z &= [\text{KBr}_3] \\ K &= \frac{[\text{KBr}][\text{Br}_2]}{[\text{KBr}_3]} = \frac{(z)(y - x + z)}{x - z} \end{aligned}$$

TABLE I

THE EQUILIBRIUM CONSTANT FOR THE DISSOCIATION OF POTASSIUM TRIBROMIDE IN ACETIC ACID AT 50°

$\frac{[\text{KBr}_3] + [\text{KBr}]}{[\text{KBr}_3]}$	$\frac{[\text{Br}_2] + [\text{KBr}_3]}{[\text{LiC}_2\text{H}_5\text{SO}_3]}$	$[\text{KBr}_3]$	$[\text{Br}_2]$	$K \times 10^2$
0.0606	0.1394			
.0845	.1120	0.0384	0.0239	0.0145
.1066	.0900	.0749	.0460	.0289
.1350	.0640	.1229	.0744	.0484
.1734	.0300	.1910	.1128	.0782
.1995	.0000	.2565	.1389	.1176

The increase in the value of  $K$  with bromine concentration is believed to be due to potassium pentabromide formation.

In Table II are listed the results obtained at the three temperatures studied. The constancy of  $\Delta E$ , the energy change in the reaction  $\text{KBr}_3 \rightarrow \text{KBr} + \text{Br}_2$ , indicates that the van't Hoff equation is obeyed. The constants are in good agreement with those obtained by Jones<sup>7</sup> for hydrogen tribromide using an aspiration method. They

TABLE II

THE EQUILIBRIUM CONSTANT FOR THE DISSOCIATION OF POTASSIUM TRIBROMIDE

$T, ^\circ\text{C.}$	$K \times 10^2, \text{ mole/l.}$	$\Delta E, \text{ cal./mole}$
70.49	7.22	7110
50.00	3.67	6910
30.00	1.80	

(5) Bjerrum, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, **7**, No. 9 (1926).

(6) Fuoss and Kraus, *This Journal*, **55**, 1024 (1933).

(7) Jones, *J. Chem. Soc.*, **99**, 402 (1911).

also compare favorably with the value of 0.0024 at 0° in methyl alcohol.<sup>4a</sup>

It has been assumed in the subsequent work that the equilibrium constant obtained for the dissociation of potassium tribromide corresponds to the value of  $[\text{Br}^-][\text{Br}_2]/[\text{Br}_3^-]$  in solutions containing cations other than  $\text{K}^+$ , such as  $\text{H}^+$ ,  $\text{Li}^+$ , and  $\text{Na}^+$ . This may have introduced some error due to specific ion effects, but they are probably small. The rough agreement in the equilibrium constants of potassium and hydrogen tribromides supports this view.

### The Action of Bromine on Maleic and Fumaric Acids

**The Reaction in the Presence of Lithium Bromide.**—Preliminary work indicated that, in dilute solutions of bromine and maleic or fumaric acid, no reaction occurred for an hour or more. At the end of this period, a slow autocatalytic reaction was observed. When similar solutions were made up with added lithium bromide, the initial rate of bromine consumption was relatively high and autocatalysis was not present. In this work these reactions of bromine with maleic and fumaric acids in the presence of added lithium bromide were studied in considerable detail.

The products of the reactions were dibromides, which could only be explained by *trans* addition. Thus, isodibromosuccinic acid, the racemic mixture, was obtained from maleic acid and dibromosuccinic acid, the *meso* form was obtained from fumaric acid. This is in agreement with previous data recorded in the literature.<sup>8</sup>

It was found that the data from rate measurements conformed best to a rate expression

$$-d[\text{Et}]/dt = k_a[\text{Br}_3^-][\text{Et}] \quad (1)$$

where Et represents the ethylene derivative. It was possible to calculate the tribromide ion concentration by using the equation derived below.

$$\begin{aligned} \text{Let } z &= [\text{Br}^-] + [\text{Br}_3^-] \text{ and } b = [\text{Br}_2] + [\text{Br}_3^-] \\ \text{then } K &= \frac{[\text{Br}^-][\text{Br}_2]}{[\text{Br}_3^-]} = \frac{(z - [\text{Br}_3^-])(b - [\text{Br}_3^-])}{[\text{Br}_3^-]} \end{aligned}$$

by solving for tribromide concentration, the resulting equation is

$$[\text{Br}_3^-] = \frac{(z + b + K) \pm \sqrt{(z + b + K)^2 - 4zb}}{2}$$

However, the use of this equation involving many tedious calculations was avoided whenever pos-

(8) (a) Kirchoff, *Ann.*, **280**, 209 (1904); (b) Kekulé, *Ann. Spl.*, **2**, 87 (1861); **1**, 131 (1860); (c) MacKenzie, *J. Chem. Soc.*, **101**, 120 (1894).

sible. Instead, the tribromide concentration was generally obtained by multiplying the value of the total bromine concentration,  $[\text{Br}_2] + [\text{Br}_3^-]$ , by a constant. The justification for this method is shown below, where  $z$  and  $b$  have the same meaning as in the derivations above

$$[\text{Br}_3^-] = \frac{[\text{Br}_3^-]}{[\text{Br}_2] + [\text{Br}_3^-]} b = \frac{b}{1 + [\text{Br}_2]/[\text{Br}_3^-]}$$

substitution of  $[\text{Br}_2]/[\text{Br}_3^-] = K/[\text{Br}^-]$  gives

$$[\text{Br}_3^-] = \frac{b}{1 + \frac{K}{[\text{Br}^-]}} = \frac{b}{1 + \frac{K}{z - [\text{Br}_3^-]}} = cb$$

In most of the work the total bromine concentration was 0.01  $M$  or less and thus the maximum tribromide ion concentration was 0.01  $M$ . Since the value of  $z$  was in general 0.20  $M$ , the variation of  $z - [\text{Br}_3^-]$  within a run was small and  $1/\{1 + [K/(z - [\text{Br}_3^-])]\}$  was essentially constant.

The integration of expression (1), after making the assumption that  $[\text{Br}_3^-]/([\text{Br}_2] + [\text{Br}_3^-])$  is constant, gives

$$k_a = \frac{1}{(t_2 - t_1)c(a - b)} \ln \frac{b(a - x)}{a(b - x)} \quad (2)$$

where  $a = [\text{Et}]$  at time  $t_1$

$b = [\text{Br}_2] + [\text{Br}_3^-]$  at time  $t_1$

$a - x = [\text{Et}]$  at time  $t_2$

$b - x = [\text{Br}_2] + [\text{Br}_3^-]$  at time  $t_2$

$c = \text{average value of } [\text{Br}_3^-]/([\text{Br}_2] + [\text{Br}_3^-])$

In Table III are presented the results of a typical experiment, illustrating the applicability of expression (2).

TABLE III

THE ACTION OF BROMINE ON MALEIC ACID AT 50°

Initial concentrations: maleic acid, 0.1282  $M$ ; bromine, 0.01075  $M$ ; LiBr, 0.2005  $M$ ; vol. of samples, 1.97 cc.;  $\text{Na}_2\text{S}_2\text{O}_8$ , 0.00951  $N$ .

$t$ , sec.	$\text{Na}_2\text{S}_2\text{O}_8$ , cc.	$k_a \times 10^3$ , (mole/l.) <sup>-1</sup> sec. <sup>-1</sup>
0	4.45	3.05
240	4.12	3.06
480	3.81	3.06
780	3.46	3.07
1200	3.04	3.05
2400	2.09	3.06
4320	1.18	3.06
5520	0.82	3.07

The conformity of the rate measurements to rate expression (1) was indicated by studies in which the lithium bromide concentration was kept constant and the bromine concentration was varied. As is evident from Table IV, the rate constant was unaltered by changes in total bromine concentration. The reason for the depend-

ence of the rate constant on lithium bromide concentration will be discussed later.

TABLE IV

THE EFFECT OF VARIATION OF BROMINE CONCENTRATION ON THE REACTION BETWEEN BROMINE AND MALEIC ACID AT 50°

[LiBr]Initial	[Br <sub>2</sub> ]Initial	$k \times 10^3$ (mole/l.) <sup>-1</sup> sec. <sup>-1</sup>
0.2005	0.0100	3.065
.2005	.191	3.050
.0737 <sup>a</sup>	.0100	3.53
.0618 <sup>a</sup>	.189	3.54

<sup>a</sup> Lithium *p*-toluenesulfonate added to make ionic strength 0.20.

A summary of the results obtained for solutions 0.20  $M$  in lithium bromide is shown in Table V. It should be mentioned that rate expression (1) may be expressed in another form by making the substitution

$$[\text{Br}_3^-] = \frac{[\text{Br}^-][\text{Br}_2]}{K}$$

This gives

$$\frac{-d[\text{Et}]}{dt} = \frac{k_a}{K} [\text{Br}_2][\text{Br}^-][\text{Et}] \quad (3)$$

Rate expression (3) is more satisfactorily explained on the basis of a reaction mechanism than expression (1). Therefore the values of  $k_a/K$  are tabulated together with those of  $k_a$ . The values of  $Q$  refer to  $k_a/K$ .

TABLE V

RATE CONSTANTS FOR LITHIUM BROMIDE CATALYZED BROMINE ADDITION

	$T$ , °C.	$k_a \times 10^3$ , (mole/l.) <sup>-1</sup> sec. <sup>-1</sup>	$k_a/K \times 10^3$ , (mole/l.) <sup>-2</sup> sec. <sup>-1</sup>	$Q$ , cal.
Fumaric	70.49	3.06	4.24	
	50.00	0.609	1.66	9830
	30.00	0.1145	0.635	9370
Maleic	70.49	14.5	20.1	
	50.00	3.045	8.29	9330
	30.00	0.589	3.28	9010

**The Salt Effect.**—It was found that these reactions were rather sensitive to the ionic strength of the solutions. The evidence for this is presented in Table VI, which summarizes results obtained from a study of the maleic acid-bromine reaction at 50°. Although the  $k_a$  values listed were calculated using the dissociation constant of tribromide ion obtained for solutions of 0.20 ionic strength, the error introduced is probably small since, according to the Brönsted<sup>9</sup> view, the dissociation constant of such an ion as tribromide should not be affected appreciably by changes in electrolyte concentration. Also expression (2)

(9) Brönsted, *Chem. Rev.*, **5**, 231 (1928).

and the derivations preceding it indicate that the values of  $k_a$  are not very sensitive to changes in the value of the dissociation constant. Runs 1 to 4 indicate rather conclusively that the reaction rate is higher in solutions of low ionic strength.

TABLE VI  
THE REACTIONS OF MALEIC ACID AND BROMINE AT 50°

Run	[LiBr]	[Added salts]	$k_a \times 10^4$ , (mole/l.) <sup>-1</sup> sec. <sup>-1</sup>
1	0.0737		4.36
2	.1003		3.76
3	.2005		3.07
4	.4010		2.33
5	.0737	0.1263 <sup>a</sup>	3.53
6	.0737	.1263 <sup>b</sup>	3.45
7	.0618	.1382 <sup>a</sup>	3.54
8	.0698 <sup>d</sup>	.1302 <sup>a</sup>	3.42
9	.2005	.1282 <sup>c</sup>	2.80
10	.2005	.2564 <sup>c</sup>	2.35
11	.2005	.5128 <sup>c</sup>	1.88

<sup>a</sup> Lithium *p*-toluenesulfonate. <sup>b</sup> Lithium ethanesulfonate. <sup>c</sup> Sodium acetate. <sup>d</sup> Sodium bromide.

The observation that the addition of salts other than lithium bromide such as lithium *p*-toluenesulfonate, lithium ethanesulfonate, and sodium acetate retard the reaction indicated that the retarding effect was a salt effect.<sup>10</sup> There is evidence for specific ion effects. Thus from runs 3 and 5, it is apparent that lithium bromide exerts a greater salt effect than lithium *p*-toluenesulfonate. Similar comparisons from the table enable an arrangement of the salts in the order of their relative salt effects to be made. It is as follows NaBr > LiBr > NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> > LiC<sub>2</sub>H<sub>3</sub>SO<sub>3</sub> > LiCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>. It is interesting to note that this order is that which would be expected for salting out effects, taking the work of Larsson<sup>11</sup> on the solubility of benzoic acid in aqueous solutions as a criterion. The observation that the reverse of this order is the order of the size of ions in aqueous solutions also agrees with salting out theory.

The results with sodium acetate are of some interest. Since maleic acid is a stronger acid than acetic acid in water, it was believed that the addition of sodium acetate to a solution of maleic acid in glacial acetic acid would give sodium maleate, which would react very rapidly with

(10) In the next paper of this series it will be shown that ions such as nitrate, acetate, and bisulfate are catalysts for halogen addition to ethylene derivatives in the absence of added halide ions. These reactions are, of course, different from the one under consideration. It was found from preliminary experiments that the acetate ion catalyzed addition of bromine to maleic acid was extremely slow in comparison to the bromide ion catalyzed reaction.

(11) (a) Larsson, *Z. physik. Chem.*, **153**, 306 (1931); (b) P. Gross, *Chem. Rev.*, **13**, 91 (1933).

bromine.<sup>12</sup> However, the experimental observation that only the salt effect was present indicates that maleic acid is a weaker acid than acetic acid in glacial acetic acid solution.

**The Reaction in the Presence of Added Hydrobromic Acid.**—It was found from preliminary studies that hydrobromic acid was a much better catalyst than lithium bromide for the addition of bromine to maleic and fumaric acids. However, due to the rapid isomerization of maleic acid to fumaric acid catalyzed by hydrobromic acid, it was found that the addition of bromine to maleic acid could not be studied. Thus, all of the studies in which hydrobromic acid was used as a catalyst for bromine addition were made with fumaric acid.

The product of the fumaric acid–bromine reaction was found to be largely dibromosuccinic acid, the *meso* form. This was the same product which was obtained in the lithium bromide catalyzed reaction. A small amount of bromosuccinic acid was also isolated, indicating that some hydrobromic acid had added to the double bond.

It was found that the data from rate measurements conformed best, as with the lithium bromide catalyzed reaction, to a rate expression

$$-\frac{d[\text{Et}]}{dt} = k_a[\text{Br}_3^-][\text{Et}] = \frac{k_a}{K}[\text{Br}_2][\text{Br}^-][\text{Et}]$$

when the concentration of catalyst was kept constant. Rate constants were calculated using the expressions developed previously for the lithium bromide catalyzed reactions. The constants within a run fell off somewhat with time, but this was shown to be due to the addition of hydrobromic acid to fumaric acid. Studies on the rate of hydrobromic acid addition to fumaric acid indicated that the rate of this reaction, although slower than bromine addition, was of appreciable magnitude at the temperature and concentration used. The results of a study in which the concentration of hydrobromic acid was kept constant (0.188 *M*) are summarized in Table VII.

TABLE VII  
THE REACTION OF BROMINE AND FUMARIC ACID WITH 0.188 *M* HYDROBROMIC ACID CATALYST

<i>T</i> , °C.	$k_a \times 10^4$ , (mole/l.) <sup>-1</sup> sec. <sup>-1</sup>	$k_a/K \times 10$ , (mole/l.) <sup>-2</sup> sec. <sup>-1</sup>	<i>Q</i> , cal.
70.49	34.6	4.80	11,350
50.00	5.95	1.62	11,750
30.00	0.873	0.485	

Variation of the initial concentration of cata-

(12) Berthoud and Mosset, *J. Chem. Phys.*, **33**, 271 (1936).

lyst showed that the kinetics of this reaction were somewhat different from the kinetics of the reactions in which lithium bromide was used as a catalyst. The rate of the reaction was found to be dependent on the concentration of proton donors in the reaction mixture. This is evident from an inspection of Table VIII. It is observed that the value of  $k_a$  is roughly proportional to the concentration of proton donors but is independent of the concentration of bromide ion.

TABLE VIII

THE REACTION OF FUMARIC ACID AND BROMINE AT 50°

Catalyst	$k_a \times 10^3$ , (mole/l.) <sup>-1</sup> sec. <sup>-1</sup>
0.188 M HBr	5.95
.100 M LiBr + 0.094 M HBr	2.91
.100 M H <sub>2</sub> SO <sub>4</sub> + .099 M HBr	5.62
.094 M HBr	2.78

The catalysis by proton donors was further illustrated by a study of bromine addition to maleic acid and fumaric acid without the addition of a halide ion catalyst. It was found that for these reactions, which are autocatalytic, the addition of 0.20 M sulfuric acid was accompanied by a tenfold increase in the rate of reaction.

**The Effect of Added Water.**—The effect of water on the lithium bromide and hydrobromic acid catalyzed reactions was studied and the results are shown in Table IX. The constants were calculated using expression (2). If parallel effects are assumed for maleic and fumaric acids, it is evident that the hydrobromic acid catalyzed reaction is retarded much more by water than the lithium bromide reaction. The effect of water on the hydrobromic acid catalyzed reaction is probably largely due to its basic action. Water undoubtedly competes for protons in the solution, leaving less available for a catalytic role.

TABLE IX

THE EFFECT OF ADDED WATER AT 50°

Acid	Catalyst	$k_a \times 10^3$ , (mole/l.) <sup>-1</sup> sec. <sup>-1</sup>	$k_a \times 10^3$ , (mole/l.) <sup>-1</sup> sec. <sup>-1</sup>
		without H <sub>2</sub> O	1% H <sub>2</sub> O
Fumaric	0.188 M HBr	5.95	1.43
Maleic	0.2005 M LiBr	3.045	2.45

**The Effect of Light and Oxygen.**—The lithium bromide and hydrobromic acid catalyzed addition reactions of bromine to maleic and fumaric acids were found to be indifferent to oxygen and light. No difference in rate was observed in two runs, one in a carbon dioxide atmosphere and the other in an oxygen atmosphere. The substitution

of unpainted vessels for blackened ones had no effect on the rate of the reaction.

### The Action of Bromine on Vinyl Bromide

The study of the bromide ion catalyzed addition of bromine to maleic and fumaric acids, although convenient because it was not accompanied by side reactions, suffered two complications. These were (1) the catalysis by proton donors and (2) the salt effect. It seemed probable that these effects were due to the carboxyl group in the unsaturated acids. To prove that such was actually the case, a kinetic study of bromine addition to vinyl bromide was undertaken. Vinyl bromide was chosen because it contains no oxygen.

**The Reaction in the Presence of Added Lithium Bromide.**—Preliminary experiments indicated that at very low bromine concentrations bromine and vinyl bromide react by a slow autocatalytic reaction. The addition of lithium bromide accelerated the reaction, indicating that bromine addition to vinyl bromide is catalyzed by bromide ion. This bromide ion catalyzed reaction was subjected to considerable study.

The product of this reaction, although not isolated, was presumably tribromoethane. It was expected that the reaction would be analogous to the lithium bromide catalyzed bromine additions to maleic and fumaric acids. Accordingly, rate constants were calculated by substitution into expression (2), which was derived for the maleic and fumaric acid reactions. The results of a study in which a moderate concentration of bromine (0.015 M) was used are in Table X. Smaller concentrations were avoided due to the extreme slowness of this reaction. In the table and in subsequent tabulations,  $k$  (Final) refers to the rate constants for an interval when the reaction was 90–95% completed.

TABLE X

THE ACTION OF BROMINE ON VINYL BROMIDE

Run	T, °C.	[LiBr] Initial [Br <sub>2</sub> ] = 0.015 M	Initial [Vinyl bromide] = 0.10 M	
			$k_a \times 10^4$ , (mole/l.) <sup>-1</sup> sec. <sup>-1</sup> Initial	Final
1	25.00	0.050	3.10	2.67
2	25.00	.100	2.90	2.67
3	25.00	.400	2.75	2.70
4 <sup>a</sup>	25.00	.400	7.10	2.67
5	40.00	.050	11.70	9.17
6	40.00	.100	10.30	9.17
7	40.00	.200	9.50	9.00
8	40.00	.400	9.35	9.17

<sup>a</sup> Initial bromine concentration was 0.18 M.

It is to be noted from Table X that the final rate constants at a given temperature have practically the same value, regardless of the lithium bromide concentration. Also, it should be pointed out that in runs 3 and 8, where the lithium bromide concentration was 0.400 *M*, the initial and final rate constants are practically equal. These observations indicate that, when the bromide ion concentration is much greater than the bromine concentration, rate expressions (1), (2) and (3) are obeyed.

It is observed from the table that the initial rate is the greatest for the runs with the lowest lithium bromide concentration. This initial rate drops off with increasing bromide concentration until at 0.400 *M* the initial and final rates are almost equal. The large initial rate is due to uncatalyzed addition reactions which will be discussed in a subsequent communication. The importance of these contributions at higher bromine concentrations is illustrated by runs 3 and 4. It is observed that the initial rate constant was much larger for the run in which the initial bromine concentration was 0.18 *M*. A further illustration is the observation that a 0.18 *M* solution of bromine without added lithium bromide reacted five to ten times as rapidly with vinyl bromide as the solution 0.18 *M* in bromine and 0.400 *M* in lithium bromide.

It was mentioned that, regardless of the lithium bromide concentration, the final reaction rate constant reached a constant value at a given temperature. This indicates that the bromide ion catalyzed addition of bromine to vinyl bromide differs from the maleic and fumaric acid reactions by not being affected by the salt concentration in the reaction solution. The average values of the reaction rate constant at two temperatures are given in Table XI.

TABLE XI

THE LITHIUM BROMIDE CATALYZED BROMINE ADDITION TO VINYL BROMIDE

<i>T</i> , °C.	$k_a \times 10^4$ , (mole/l.) <sup>-1</sup> sec. <sup>-1</sup>	$k_a/K \times 10^3$ , (mole/l.) <sup>-2</sup> sec. <sup>-1</sup>	<i>Q</i> , cal.
25.00	2.68	1.78	8650
40.00	9.15	3.58	

**The Relative Catalytic Effects of Lithium Bromide and Hydrobromic Acid.**—The catalytic effects of lithium bromide and hydrobromic acid on the addition of bromine to vinyl bromide were studied. The results are shown in Table XII, and they indicate that within experimental error the

catalytic effects of lithium bromide and hydrobromic acid are identical. It will be recalled that, with maleic and fumaric acids, hydrobromic acid was by far the better catalyst.

TABLE XII

THE ACTION OF BROMINE ON VINYL BROMIDE  
THE CATALYTIC EFFECTS OF LITHIUM BROMIDE AND  
HYDROBROMIC ACID

Run	<i>T</i> , °C.	Catalyst	[Catalyst]	$k_a \times 10^4$ , (mole/l.) <sup>-1</sup> sec. <sup>-1</sup> Initial	Final
1	25.00	LiBr	0.100	2.90	2.67
2	25.00	HBr	.100	2.92	2.75
3	40.00	LiBr	.100	10.3	9.17
4	40.00	HBr	.100	10.2	9.17
5	40.00	LiBr	.200	9.5	9.00
6	40.00	HBr	.200	9.4	9.00

### The Action of Bromine on Allyl Chloride and Allyl Acetate

Both allyl chloride and allyl acetate were found to react rapidly with bromine in the absence of bromide ion. These reactions, which are of higher order than the first with respect to bromine concentration, will be discussed in a subsequent paper. Upon the addition of a large concentration of bromide ion, the reactions followed normal second order kinetics; *i. e.*, rate expressions (1), (2) and (3), were obeyed. This seemed to indicate that the bromide ion catalyzed reactions had replaced the non-catalyzed reactions.

The reactions of bromine with allyl chloride and allyl acetate were studied in order to compare the effect of the addition of lithium bromide and hydrobromic acid. It was found that, in agreement with the vinyl bromide-bromine reaction, both had the same effect on the allyl chloride reaction. However, such was not the case with allyl acetate, which contains oxygen. Experiments showed that, under otherwise identical conditions,  $k_a$  in the presence of 0.20 *M* hydrobromic acid was 0.210 while in the presence of 0.20 *M* lithium bromide  $k_a$  was 0.174. Thus hydrobromic acid is somewhat superior to lithium bromide. Although the superiority is not nearly as marked as with maleic and fumaric acids, the results suggest that the catalytic effect of protons on halogen addition is due to association of the protons with oxygen atoms in the ethylene derivatives.

### Experimental

**Materials.**—The solvent was Merck "99.5% Acetic Acid," which possessed a melting point of 16.2°. Merck bromine was washed with saturated aqueous potassium

bromide solution and was then distilled from sulfuric acid in an all glass apparatus. The lithium bromide, a Merck product, was dried before use. Anhydrous hydrobromic acid was prepared by dropping bromine on boiling tetralin and was purified by passing through naphthalene towers.

Lithium *p*-toluenesulfonate was prepared by heating equivalent quantities of lithium carbonate and *p*-toluenesulfonic acid. Lithium ethanesulfonate was prepared by mixing equivalent quantities of lithium perchlorate and potassium ethanesulfonate in glacial acetic acid. The insoluble potassium perchlorate was filtered off and the solution was concentrated.

The maleic acid was obtained by hydrolysis of Eastman Kodak Co. maleic anhydride; m. p. 138–139°. The fumaric acid was obtained from the maleic acid by rearrangement; m. p. 287°. The vinyl bromide was prepared by treating ethylene dibromide with alcoholic potassium hydroxide; b. p. 16.4°. The allyl acetate was prepared from allyl alcohol and acetyl chloride; b. p. 104.5–104.8°. The allyl chloride, an Eastman product, was carefully fractionated; b. p. 44.4–44.6°.

**Analytical Procedures.**—The determination of the halogen concentration in reaction mixtures was carried out in the familiar manner. A sample of the solution to be analyzed was pipetted out into an aqueous potassium iodide solution, and the liberated iodine was titrated with standard thiosulfate solution, starch indicator being used.

The determination of the halide ion concentration in various solutions was often necessary. It was carried out by pipetting samples into beakers, evaporating to dryness, and titrating the remaining halide ion with standard silver nitrate, chromate indicator being used. For determinations of the concentration of hydrobromic acid, the samples were pipetted into aqueous solutions of sodium carbonate, and the resulting solution was evaporated and treated as above.

The concentration of the ethylene derivative in a solution was often checked by halogen addition, the bromide-bromate method of Francis<sup>13</sup> being used.

**The Equilibrium Constant for the Dissociation of Potassium Tribromide in Acetic Acid.**—The procedure used for determining the equilibrium constant, involving the determination of the solubility of potassium bromide in acetic acid solution of bromine, was as follows. About a gram of coarsely powdered potassium bromide and 25 cc. of acetic acid were placed in each of six 30 cc. glass stoppered bottles. A roughly known amount of bromine, different for each bottle, was added to all except one. Sufficient lithium ethanesulfonate was added to each bottle to make a total ionic strength of two-tenths after equilibrium had been established. The amount to be added was determined by preliminary experiments on the solubility of potassium bromide in acetic acid solutions of bromine. After being kept in a thermostat at the desired temperature for one hour, the bottles were sealed with wire and paraffin. They were then placed in a thermostat, equipped with a shaking device, for twelve hours. At the end of this time the bottles were opened and four 5-cc. portions were pipetted out from each, precautions being taken to avoid the inclusion of solid potassium bromide. One portion was used for the determination of the bromine

concentration, and the other three were analyzed for total halide ion concentration. The previously discussed procedures were used for the analyses.

**The Products of the Addition Reactions.**—An analysis of the products from the addition of bromine to maleic acid was made in the following manner: 1 g. of lithium bromide, 2.0 g. of maleic acid and 1 cc. of bromine were dissolved in 20 cc. of acetic acid, and the mixture was heated for forty hours at 50°. The solution was then evaporated to dryness leaving a solid which was very soluble in water. After recrystallization from water its melting point was 163°. These properties agree with those of isodibromosuccinic acid, which is very soluble in water and melts at 166°. Partial neutralization of a solution of the acid with ammonium hydroxide, followed by the addition of barium chloride, gave no precipitate, indicating that bromomaleic acid was absent.

The product from the addition of bromine to fumaric acid was determined by a similar procedure: 0.1 g. of lithium bromide, 1.00 g. of fumaric acid and 15 cc. of bromine were dissolved in 50 cc. of acetic acid, and the mixture was heated at 50° for seventy-five hours. The fumaric acid gradually dissolved. The solution was evaporated to dryness, and the remaining solid was recrystallized from water. The material was slightly soluble in water and sublimed at 240°. These properties are in accord with those of dibromosuccinic acid. A solution of the acid treated with barium chloride gave no precipitate, indicating the absence of bromofumaric acid. An experiment similar to the one described here indicated that the same product was obtained when hydrobromic acid was substituted for the lithium bromide.

**The Procedure for the Rate Studies on the Addition Reactions.**—The halide catalyzed reactions were allowed to proceed in blackened volumetric flasks. A solution containing known amounts of unsaturated compound and catalyst was made up to volume with acetic acid at 25°. After the mixture had reached the desired temperature in the thermostat, a few drops of bromine were added. Samples were removed at appropriate intervals and were analyzed for bromine content.

## Summary

1. The equilibrium constant for the dissociation of potassium tribromide in glacial acetic acid has been determined at three different temperatures.
2. The reaction of bromine with maleic and fumaric acids has been studied, using glacial acetic acid as the solvent. In the presence of added lithium bromide, *trans* addition products are obtained, and the data from rate measurements conform best to the rate expression

$$-\frac{d[\text{Et}]}{dt} = k_a [\text{Br}_3^-][\text{Et}] = \frac{k_a}{K} [\text{Br}_2][\text{Br}^-][\text{Et}]$$

These reactions are sensitive to both the concentration of proton donors and the ionic strength of the reaction solution. Light and oxygen do not

(13) Francis, *Ind. Eng. Chem.*, **18**, 821 (1926).

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.

STANFORD UNIVERSITY, CALIF. RECEIVED AUGUST 8, 1941

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA, AND THE CHEMISTRY DEPARTMENT OF STANFORD UNIVERSITY]

## 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.<sup>1</sup> 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.<sup>1a,2</sup> Also, the decomposition of 1,2-dihalides is frequently catalyzed by halide ions.<sup>3</sup> 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.<sup>4</sup> 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.

(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).

### 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<sup>5</sup> 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

$$-d[\text{Et}]/dt = k[\text{Br}_2][\text{Cl}^-][\text{Et}] \quad (1)$$

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

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