

# THE KINETICS OF THE OLEFIN-BROMINE REACTION

## Part I. The Dark Reaction in Acetic Acid Solution

BY S. V. ANANTAKRISHNAN AND R. VENKATARAMAN

(Department of Chemistry, Annamalai University, Annamalainagar)

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THE reaction between olefines and bromine has been the subject of study by several workers but the mechanism of the reaction is still far from clear. While there are numerous instances of close correlation between reactions in the gas phase and reactions in solution, we seem to have here an instance of dissimilarity. Presumably this difference can be attributed to the heterogeneity of the gas reaction as contrasted with the homogeneity of the reaction in solution.\* It is recognised that the course of the reaction is governed by the polarizability of the double bond and the polarization of the bromine molecule. Substituent groups can, therefore, be expected from *a priori* considerations to affect the course of the reaction in so far as these characteristics are affected.

A theory of halogen addition with the development of integral charges on the carbon atoms was put forward by Thiele.<sup>17</sup> Subsequent workers† got apparently bimolecular constants for the reaction and in the competitive method adopted by Ingold and co-workers<sup>1, 8</sup> there is the tacit assumption that the reaction is of the first order with respect to olefin and of the same order with respect to bromine and catalysts. Preliminary investigations with crotonic and tiglic acids<sup>2</sup> showed that irrespective of the solvent there is a distinct induction period which varies with the nature of the olefin. The present work represents a systematic study of the reaction between bromine and monomethyl and dimethyl acrylic acids in acetic acid solution.

Whatever the exact mechanism finally adopted as correctly representing the course of the reaction, it is clear that no simple formulation will result. The reaction shows several of the characteristics of a chain reaction as may be seen by a comparison with the criteria for chain reactions enunciated by Semenov.<sup>15</sup>

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\* *Note.*—Some consider that the reaction in carbon tetrachloride is heterogeneous but this has still to be established. The solvent effect is under investigation by the authors.

† For a full bibliography refer Ingold and Co-workers (1 & 8) and Reference 2.

The reaction has a well-defined period of induction which varies with concentration, solvent, nature of the olefin and temperature (*vide* Tables I, II and III below, and Figs. 1 and 2).<sup>2</sup>

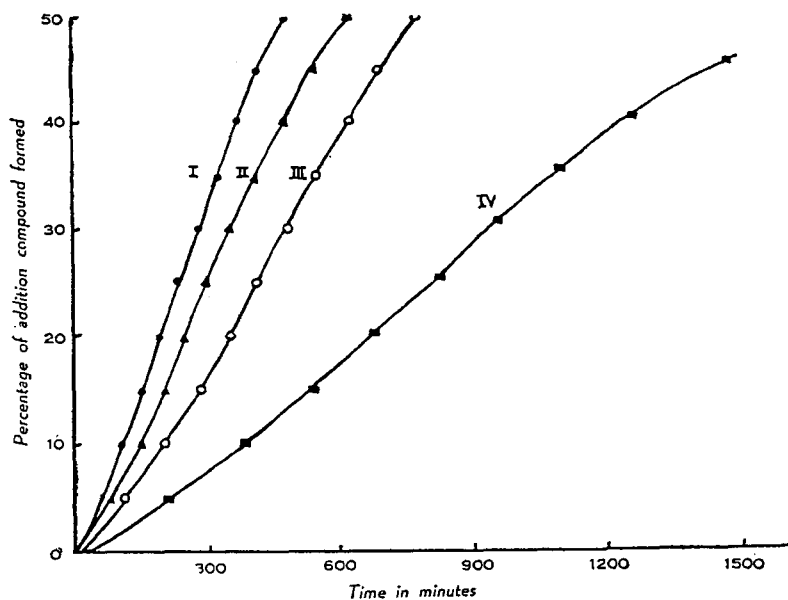


FIG. 1

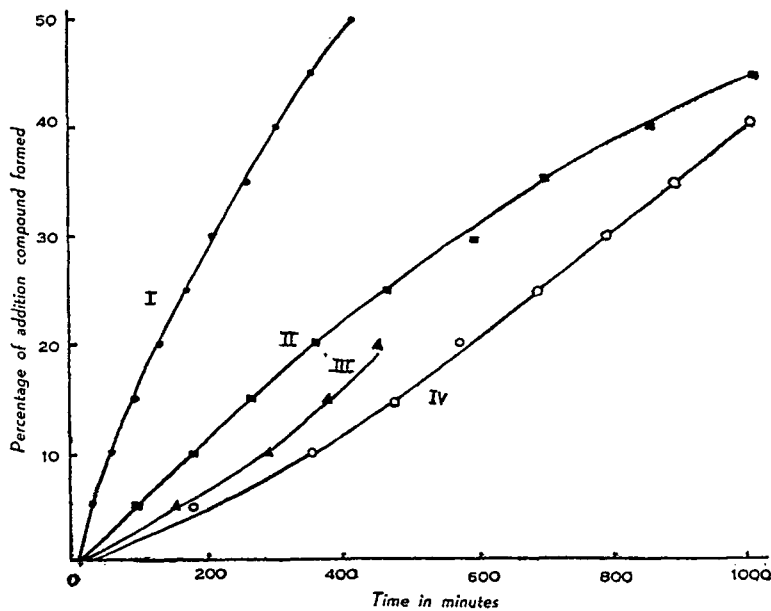


FIG. 2

TABLE I

Substance	Temperature ° C.	Solvent	Induction Period in minutes	Ref.
CH <sub>2</sub> =CH <sub>2</sub> ..	ca 15°	CCl <sub>4</sub>	11 min.	18
CH <sub>2</sub> =CH <sub>2</sub> ..	ca 15°	CH <sub>2</sub> Cl <sub>2</sub>	4 "	1
Crotonic Acid ..	{ 35.5° 42.5 50.0	Glacial Acetic Acid	{ 25 " 13 " 6 "	*
Tiglic Acid ..	{ 35.5° 42.75 49.9	"	{ 4 " 2 " 1 "	*
$\beta\beta$ -Dimethyl acrylic acid	{ 35.5° 42.7	"	{ 1.2 " 1 "	*

\* Present work.

TABLE II

*Both Reactants same Concentration*

Substance	Concentration of reactants	Induction period in minutes
Crotonic acid .. ..	M/30	25
	M/15	4
Tiglic acid .. ..	M/60	10
	M/30	4
	M/15	1
$\beta\beta$ -Dimethyl acrylic acid ..	M/240	16
	M/60	3
	M/30	1

TABLE III

*Concentrations of Both Reactants Varied Independently*

Acid concentration	Bromine concentration	Induction period
Tiglic acid { M/30 .. M/30 .. M/60 ..	M/60	9
	M/120	25
	M/120	24
Crotonic acid { M/15 .. M/30 ..	M/30	14
	M/15	5

An examination of the tables indicates the dominating importance of bromine concentration. This feature coupled with the known catalytic activity of hydrogen bromide<sup>1, 2, 18</sup> leads one naturally to the conclusion that the formation of hydrogen bromide is an important and necessary step in

the series of reactions that ultimately lead to the formation of a dibromide. At the same time, as will be indicated later on, one has to bear in mind that group influences activating the double bond may render the 'catalytic' influence of hydrogen bromide negligible especially in a polar solvent. It is also relevant to point out here that there is no direct proportionality between the concentration of the hydrogen bromide and the velocity constant.

Besides the existence of an induction period, it is interesting to notice that the course pursued by the reaction, in the absence of a catalyst, obeys Semenoff's  $e^{\phi t}$  law for reactions of the "degenerate explosion" type. Fig. 3

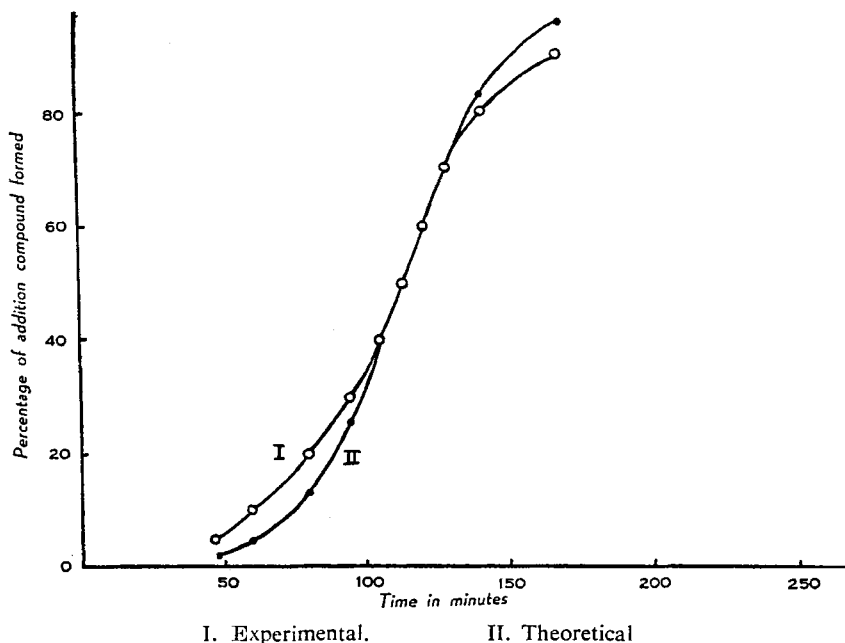


FIG. 3

shows the experimental curve of Williams<sup>18</sup> and the calculated theoretical curve, using the relation

$$W_{max} = \frac{1}{4} (x\phi),$$

where  $\phi$  is a parameter determined by the properties of the initial reacting mixtures. If  $W_{max}$  is expressed as the percentage reacting per second,  $x$ , the total amount reacted, becomes 100. From the slope of the curve,  $\phi$  can be calculated. Making use of this value of  $\phi$  and substituting in

$$x = \frac{100}{1 + e^{-\phi\theta}}$$

where  $\theta = t - t_{max}$  ( $t_{max}$  = time for maximum velocity) the necessary data for the theoretical curve were obtained.

In our own measurements in acetic acid solution, while an exact curve of this type is not observed, the nature of the curve approximates to that indicated by Semenoff<sup>15</sup> for higher concentrations. With very dilute solutions, however, even in acetic acid, the curve tends to this theoretical expectation. The deviations noticed in this connection is attributable partly to this concentration factor and partly also to the complications of a hydroxylic solvent. It has been shown by Hennion, Vogt and Weber<sup>6</sup> that in the reaction between ethylene and chlorine in acetic acid solution, the solvent takes part in the reaction and the same may hold good for bromine-olefin reactions too. Some of our preliminary studies indicate this as well.

It is generally accepted that the existence of a negative catalyst is characteristic of a chain mechanism and for this particular reaction antimony tribromide behaves as an inhibitor. This inhibition can arise from two causes. Either the antimony tribromide forms the pentabromide thereby diminishing the effective initial concentration of bromine or it may remove one of the products formed initially that is a necessary factor in the chain of reactions. The former alternative is not a serious difficulty since the prolongation of the induction period is out of proportion to any that can be expected from the small change in concentration. The second alternative is clearly the one in operation, since it has been found that hydrogen bromide catalyses the reaction (*loc. cit.*), the reaction is autocatalytic, with hydrogen bromide as a possible necessary link in the chain of reactions, and antimony tribromide may remove this catalyst by forming  $\text{HSbBr}_4$  or  $\text{H}_2\text{SbBr}_5$ . While this postulated compound does not appear to have been described, the corresponding alkali salts are well known<sup>10</sup> and as such the hydrogen analogue is not unlikely.

TABLE IV  
*Uncatalysed, HBr Catalysed and SbBr<sub>3</sub> Inhibited Reaction*

Concentration of olefin	Concentration of Br <sub>2</sub>	Catalyst	Concentration of catalyst in mols. %	Induction period	Time for 50% reaction
M/15	M/15	None	..	4 min.	475 min.
"	"	HBr	1.05	0 "	444 "
"	"	"	2.10	0 "	430 "
"	"	"	6.90	0 "	260 "
"	"	ICl	0.95	0 "	393 "
"	"	"	7.80	0 "	267 "
"	"	SbBr <sub>3</sub>	1.00	20 "	494 "
"	"	"	6.40	28 "	600 "



Eichelberger,<sup>16</sup> addition reactions involve the polarized molecule of bromine and not atomic bromine. Also, the relative group influences necessitate initiation of addition by the positive component of this activated bromine molecule, the addition of the negative component being a relatively rapid step.

Among the compounds studied so far, all are capable of forming hydrogen bromide by substitution and in all the cases examined there is pronounced evolution of hydrogen bromide even where there is no induction period. It is clearly necessary to consider hydrogen bromide as an important link in the chain of reactions where activation of double bonds has to take place in addition to activation of the bromine molecule. This view is further confirmed when one considers the observation that with more active olefines, the minimum concentration of catalyst for eliminating the induction period becomes negligible (*cf.*, Crotonic acid and dimethyl acrylic acids). If one were to plot this minimum catalyst concentration as a function of olefin structure taking ethylene as the standard, a curve of the type (Fig. 4) may be obtained.

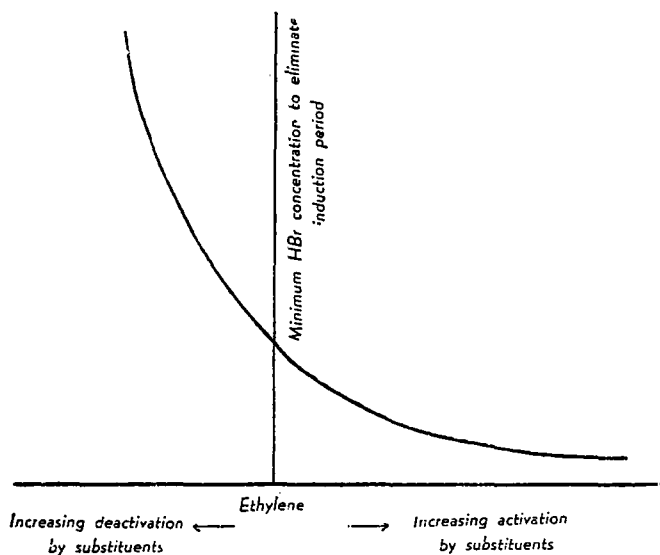


FIG. 4

This curve can also represent the induction period as a function of group characteristic in substituted olefines in the absence of a negative catalyst, if one postulates, as we have tentatively done, that the chain mechanism must involve not only an activation of the bromine molecule but also that of the double bond.

The extreme points on the hyperbolic curve corresponding to "infinite" and "zero" concentrations of catalyst can be taken to represent respectively tetraphenyl or tetrahalogeno ethylenes and tetra alkyl ethylenes.

While it is thus seen that a chain mechanism involving hydrogen bromide is necessary, a more detailed study is needed before any correct scheme can be postulated. Further, in a study of additive reactivity of ethylene derivatives, the premises have to be examined before a comparison can be made.

Using the common equations in reaction kinetics

$$\frac{dx}{dt} = k_x [a - x]^1 [\text{Br}]^m [k_{x_1} (\text{cat}_1)^{n_1} + k_{x_2} (\text{cat}_2)^{n_2} + \dots]$$

$$\frac{dy}{dt} = k_y [a' - x']^{1'} [\text{Br}]^{m'} [k_{y_1} (\text{cat}_1)^{n_1'} + k_{y_2} (\text{cat}_2)^{n_2'} + \dots]$$

If one is to compare the relative velocities, it is necessary and sufficient that the following conditions are fulfilled:

(1) The reaction is of the first order with respect to the olefin, irrespective of the substituent groups.

(2) The reaction is of the same order with respect to the halogen, not necessarily the first.

(3) There is only one dominant catalyst and its influence is also of the same degree in all olefins taken up for comparison.

(4) The comparison is made under nearly identical conditions, there being no heterogeneous disturbances.

(5) In competitive methods, association between olefins should also be absent.\*

This leads to the result

$$\frac{dy}{dx} = \frac{k_y}{k_x} \cdot \left[ \frac{(a-x)^1}{(a'-x')^{1'}} \cdot \frac{[\text{Br}]^m}{[\text{Br}]^{m'}} \cdot \frac{[k_{x_1} (\text{cat}_1)^{n_1}]}{[k_{y_1} (\text{cat}_1)^{n_1'}]} \right]$$

in which the factors in square brackets cancel out except for a constant on division leaving finally a ratio  $\frac{k_x}{k_y}$  representing the ratio of the velocity constants.

As has been established<sup>2</sup> the polar solvent by itself is not a sufficient catalyst and the addition of hydrogen bromide in sufficient amount is necessary to reduce the system to an apparently simple type. The kinetics of addition of bromine to crotonic acid, tiglic acid and  $\beta\beta$ -dimethyl acrylic acids have been studied under these conditions (Tables V and VI).

\*C. K. Ingold (Private Communication).



TABLE V

Values of  $k_2$  and  $k_3$  for the reaction between *trans*-crotonic acid and bromine (concentration, M/15) with and without catalysts

Catalyst	(Catalyst)*		Values of $k_2$ and $k_3$ for percentage reaction						
			5%	10%	15%	20%	30%	40%	50%
..	..	100 $k_2$	1.32	1.60	1.74	1.97	2.36	2.78	3.16
		$k_3$	0.81	1.02	1.14	1.33	1.72	2.22	3.79
HBr	1.05	100 $k_2$	1.41	1.68	1.95	2.21	2.77	3.16	3.37
		$k_3$	0.87	1.07	1.27	1.49	2.02	2.53	4.05
..	2.10	100 $k_2$	1.46	1.92	2.28	2.50	2.88	3.21	3.49
		$k_3$	0.90	1.21	1.49	1.69	2.10	2.56	4.19
..	6.90	100 $k_2$	5.25	5.38	5.52	5.52	5.59	5.68	5.76
		$k_3$	3.24	3.41	3.60	3.72	4.07	4.55	6.92
ICl	0.95	100 $k_2$	1.75	1.09	2.28	2.52	2.96	3.39	3.82
		$k_3$	1.08	1.26	1.49	1.70	2.16	2.71	4.58
..	7.80	100 $k_2$	3.95	5.21	5.41	5.52	5.45	5.44	5.62
		$k_3$	2.43	3.30	3.53	3.72	3.97	4.35	6.70
SbBr <sub>3</sub>	1.00	100 $k_2$	1.13	1.38	1.67	1.89	2.27	2.70	3.0
		$k_3$	0.70	0.87	1.08	1.27	1.66	2.16	3.6
..	6.40	100 $k_2$	0.88	1.04	1.18	1.34	1.17	1.96	..
		$k_3$	0.54	0.66	0.77	0.90	1.21	1.57	..

\* Molar percentage of catalyst per mol. of each reactant.

TABLE VI

Comparison of values of  $k_2$  for the addition of bromine to *trans*-crotonic, tiglic and  $\beta\beta$ -dimethyl acrylic acids (concentration of reactants, M/30)

Acid	Temperature °C.	Values of 100 $k_2$ for percentage reaction						
		5%	10%	15%	20%	25%	30%	40%
<i>trans</i> -Crotonic	35.5	0.72	0.88	0.99	1.11	1.22	1.35	1.57
Tiglic	35.45	5.85	6.95	7.67	8.28	8.85	9.47	10.61
$\beta\beta$ -Dimethylacrylic	35.5	39.9	49.4	54.0	57.5	59.9	61.2	61.0

An examination of the tables shows that under controlled catalytic conditions, the reaction gives a "bimolecular" constant which varies with the nature of the olefin. In our hands, this addition reaction fails to give the termolecular constants reported by Robertson for cinnamic acid.

Confining our attention just now to the bimolecular constants, a systematic variation of the different reactants resulted in the conclusion that the reaction is of the first order with respect to the olefin.

TABLE VII

*Effect of concentration of crotonic acid on the rate of addition of bromine to crotonic acid, catalysed by hydrogen bromide (t = 35.5° C.)*

Solution			Time (mins.) taken for percentage reaction						
(Acid)	(Br <sub>2</sub> )	(HBr)	5%	10%	15%	20%	25%	30%	40%
M/10	M/30	11.01%	16	33	51	70	91	113	163
M/15	"	"	25	51	80	110	142	176	256
M/20	"	"	30	65	102	141	185	233	345
M/30	"	"	45	101	160	224	294	374	..

TABLE VIII

*Effect of concentration of tiglic acid on the rate of addition of bromine to tiglic acid, catalysed by hydrogen bromide (t = 35.5° C.)*

Solution			Time (mins.) taken for percentage reaction							
(Acid)	(Br <sub>2</sub> )	(HBr)	5%	10%	15%	20%	25%	30%	40%	50%
M/10	M/30	11.01%	3	6.1	9.4	12.7	16.8	21.0	32.2	46.2
M/15	"	"	4	8.9	14.0	19.2	25.5	32.2	49.4	72.8
M/20	"	"	5.2	11.4	18.2	25.6	34	44.6	69.3	100.8
M/30	"	"	8.6	18.2	29.0	42.2	55.8	71.5	112.5	..

As an approximation, it is well known that in reactions of the first order, the time required for the same extent of the reaction (expressed in mols. per cent.), is inversely proportional to the concentration. Bearing in mind that all the reactants are present in comparable amounts, it will be noticed that this relationship holds good as regards the unsaturated compound, when

the concentration of bromine and of hydrogen bromide is kept constant, while olefin concentration was varied (*vide* Tables VII and VIII above).

A similar process of "isolation" applied to bromine and to hydrogen bromide, however, leads to different results. Whatever the "order" of the reaction may be, it is clearly not of the "first order" in either case.

TABLE IX

*Effect of concentration of bromine on the rate of its addition to trans-crotonic acid, catalysed by hydrogen bromide ( $t = 35.5^\circ \text{C.}$ )*

Solution			Time (mins.) taken for percentage reaction							
(Acid)	(Br <sub>2</sub> )	(HBr)*	5%	10%	15%	20%	25%	30%	40%	50%
M/15	M/30	11.01	26	55	85	120	157	195	282	384
"	2M/75	"	22	45	72	102	133	166	232	312
"	M/50	"	19	41	65	90	115	141	193	245
"	M/75	"	23	45	66	87	109	131	178	230
"	M/150	"	22	43	66	94	122	153	232	347

\*Concentration is expressed as molar percent. per mol. of olefin.

TABLE X

*Effect of concentration of bromine on the rate of its addition to tiglic acid, catalysed by hydrogen bromide ( $t = 35.45^\circ \text{C.}$ )*

Solution			Time (mins.) taken for percentage reaction							
(Acid)	(Br <sub>2</sub> )	(HBr)*	5%	10%	15%	20%	25%	30%	40%	50%
M/15	M/30	5.51	4.4	8.8	13.5	19.0	25.0	31.9	48.9	71.2
"	2M/75	"	4.8	10.0	15.7	21.8	28.9	36.9	56.8	84.5
"	M/50	"	5.8	12.0	18.8	26.3	35.1	44.8	67.7	98.0
"	M/75	"	7.6	15.5	24.4	34.0	45.0	57.4	88.5	..
"	M/150	"	10	20.8	32.0	45.6	63.3	86.4	..	..

\*Concentration is expressed as molar percentage per mol. of olefin.

TABLE XI

Effect of concentration of bromine on the rate of its addition to  $\beta\beta$ -dimethylacrylic acid, catalysed by hydrogen bromide ( $t = 35.5^\circ \text{C.}$ )

Solution			Time (mins.) taken for percentage reaction							
(Acid)	(Br <sub>2</sub> )	(HBr)*	5%	10%	15%	20%	25%	30%	40%	50%
M/30	M/60	11.01	3.8	8.1	12.5	17.6	23.1	29.4	45.7	68.2
„	M/75	„	4.7	9.4	14.4	20.2	26.6	34.0	52.1	75.5
„	M/100	„	5.7	11.6	17.6	24.6	32.3	41.0	62.2	90.4
„	M/150	„	7.0	14.2	22.4	31.6	42.0	53.0	79.2	114.0
„	M/300	„	11.8	23.6	36.4	50.8	67.5	85.0	125.8	..

\*Concentration is expressed as molar percentage per mol. of olefin.

TABLE XII

Effect of concentration of hydrogen bromide on the rate of addition of bromine to *trans*-crotonic acid, (concentration of reactants, M/30) ( $t = 35.5^\circ \text{C.}$ )

Mols. % of HBr	Time (mins.) taken for percentage reaction						
	5%	10%	15%	20%	25%	30%	40%
44.04	17	35	57	80	107	138	219
22.02	26	53	87	120	162	210	331
11.01	45	101	160	224	294	374	..
5.51	69	145	228	315	412	522	782
2.76	105	213	322	438	567	702	1015
1.38	134	270	402	532	670	805	1132
0.00	218	380	535	675	822	955	1275

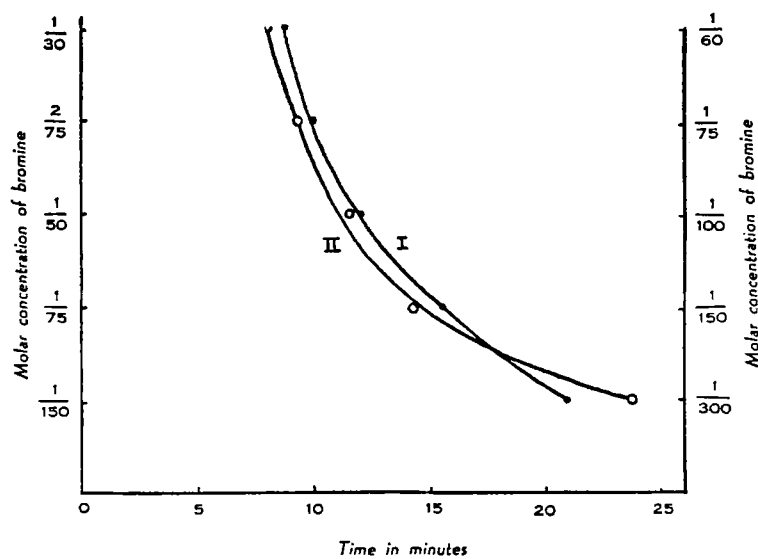
TABLE XIII

Effect of concentration of hydrogen bromide on the rate of addition of bromine to tiglic acid (concentration of reactants,  $M/30$ ) ( $t = 35.5^\circ \text{C.}$ )

Mols. % of HBr	Time (mins.) taken for percentage reaction							
	5%	10%	15%	20%	25%	30%	40%	50%
44.04	4.2	9.0	14.5	20.5	28.0	36.4	61.3	99.5
22.02	5.8	12.0	19.2	28.0	37.7	49.5	81.8	131.0
11.01	8.6	18.2	29.0	42.2	55.8	71.5	112.5	..
5.51	12.0	25.6	40.0	55.0	72.7	93.5	145.0	221.5
2.75	16.3	33.2	50.0	68.5	88.5	110.8	167.5	249
1.38	19.5	38.2	57.0	76.5	97.5	120.5	177.5	263.0
0.00*	27.0	48.0	69.0	90.6	113.0	135.7	188.4	..

\* This reaction alone was carried out at  $35.45^\circ \text{C.}$

Comparing the time taken for the same extent of reaction (10% has been chosen for the curves) the general nature of the curve (Fig. 5) indicates that



I. Tiglic acid.

Time in minutes

II.  $\beta\beta$ -Dimethylacrylic acid.

FIG. 5

the order of the reaction is the same with respect to bromine in this addition process. When both olefin and hydrobromic acid are present in excess,

crotonic acid, however, presents an anomalous case in concentrations of the order of  $M/75$  as the reaction then appears to be independent of bromine concentration.

With hydrogen bromide as the variant (Fig. 6) there is no direct proportionality between concentration of catalyst and time taken for the same

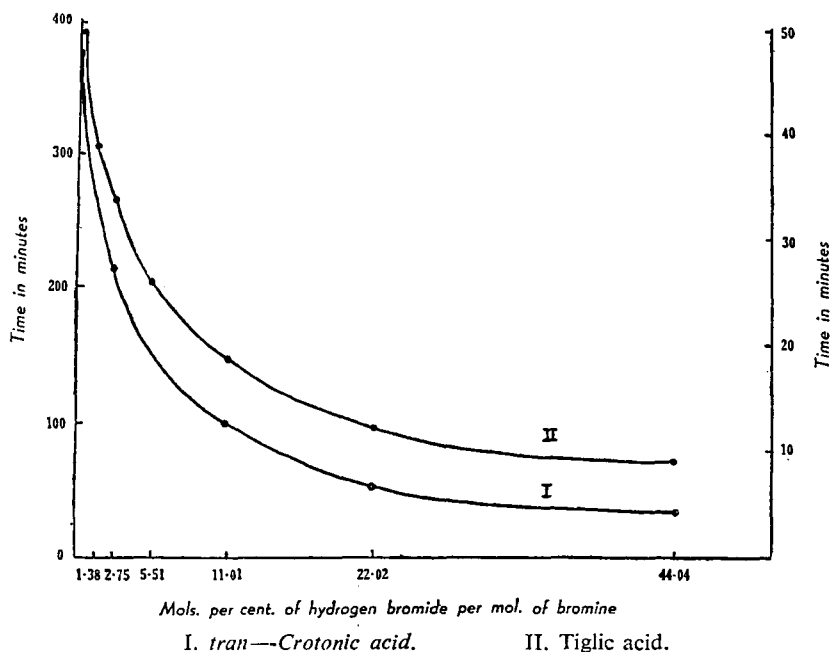


FIG. 6

extent of the reaction. Hydrogen bromide in this reaction falls in the category of catalysts showing considerable and specific variations when present in small quantities but tending to a maximum of activity at higher concentrations. In a reaction in which molecules can acquire slowly the energy of activation in the absence of a catalyst while the catalyst speeds up the process, it can be shown that the reaction should be of the first order with respect to the reactant and for various catalysts the maximum should be the same.<sup>7</sup> Again, if, while molecules are activated independently, the co-operation of the catalyst is needed for final transformation, the reaction should be of the second order and the limiting rate independent of the nature of the catalyst. On the other hand, if reactant molecules are activated by the catalyst and the two remain temporarily associated in the form of a complex that undergoes the completed reaction, at the same time exposed to deactivation by further collisions, the reaction should be of the first order with respect to the reactant and the limiting value will vary with catalyst.

An examination of tables given before suggest that such a complex is likely in the present case.

### *Experimental*

The reactions were carried out in an electrically heated thermostat of the usual type, care being taken to shut out all access of light inside the vessel. The temperatures were maintained within the range  $\pm 0.015^\circ\text{C}$ . Pure benzene, crystallisable, for molecular weight determinations, was shaken with mercury for several days before use in the thermoregulator. The choice of benzene rather than toluene the usual liquid used in thermoregulators was determined by its greater expansion and ease of purification. The reactants were kept in dark amber-coloured, glass-stoppered bottles and the course of the reaction followed by iodimetric estimation of the halogen. Amber coloured pipettes, further darkened in the bulb portion, were used in transferring solutions. The number of readings and the volume taken for each reading were determined by statistical considerations for accuracy.

A. R. acetic acid was used after purification by the method of Orton and Bradfield.<sup>11</sup>

Bromine was purified by the method of Anantkrishnan and Ingold.<sup>1</sup>

Hydrogen bromide was prepared by the action of bromine on decalin the resulting gas being purified by passing through a train consisting of U-tube cooled to  $-78^\circ$  with solid carbon dioxide and methanol, a tower of naphthalene, two tubes of phosphorous pentoxide and a tower of glass wool, before absorption in purified acetic acid. The hydrogen bromide content of this solution was estimated before each experiment. Kahlbaum's pure iodine monochloride and antimony tribromide were used after distillation, rejecting head and tail fractions.

Crotonic acid was prepared by the method of Scheibler and Magasanik.<sup>14</sup>

*Tiglic Acid.*—The B. D. H. product was used after recrystallisation to constant melting point.

*$\beta\beta$ -Dimethyl Acrylic Acid.*—The method described by Sikhibhushan Dutt<sup>3</sup> failed to give any yield of the acid in our hands. A modified method of Massot<sup>9</sup> was therefore adopted. A mixture of malonic acid (1 mol.), acetic anhydride (1.2 mols.) and dry acetone (4 mols.) was refluxed on the water-bath for three days. The brownish green fluorescent solution was distilled under ordinary pressure, fractions upto  $130^\circ\text{C}$ . being collected to remove excess acetone and acetic acid. The residue was then distilled under reduced pressure. The remaining acetic acid distilled at  $56^\circ/40\text{ mm.}$ , the  $\beta\beta$ -dimethyl acrylic acid distilling at  $112^\circ/20\text{ mm.}$  (yield 25% theoretical). The reduced

yield is probably due to formation of dimethyl glutaric acid as by-product. Distillation under ordinary pressure was not satisfactory, since the boiling point 195°–200° was very near the decomposition point (204°).

### Summary

The kinetics of the olefin-bromine reaction has been studied in acetic acid solution using three related aliphatic monobasic acids. The course of the reaction clearly indicates a chain mechanism. It is found that the reaction is of the first order with respect to the olefin and the influence of the catalyst hydrogen bromide is pronounced, the experimental evidence favouring a complex formation between olefin and catalyst.

### REFERENCES

1. S. V. Anantkrishnan and C. K. Ingold *J.C.S.*, 1935, 1396.
2. ——— and R. Venkataraman *Ibid.*, 1939, 224.
3. S. Dutt .. *J. Ind. Chem. Soc.*, 1924–25, 297.
4. A. Fowler and E. A. Guggenheim *Statistical Thermodynamics*, 1939 (C.U.P.).
5. Francis .. *J. Amer. Chem. Soc.*, 1925, 47, 2340.
6. Hennion, Vogt and Weber *Ibid.*, 1939, 61, 1457.
7. C. N. Hinshelwood .. *Kinetics of Chemical Change in Gaseous Systems*, 3rd edition, 1933, O.U.P.
8. C. K. Ingold and E. H. Ingold *J.C.S.*, 1931, 2354.
9. Massot .. *Ber.*, 1894, 27, 1225.
10. J. W. Mellor .. *Comprehensive Treatise on Inorganic Chemistry*, Vol. IX.
11. K. J. P. Orton and A. C. Bradfield *J.C.S.*, 1927, 983.
12. Pease and Walz .. *J. Amer. Chem. Soc.*, 1931, 53, 3728.
13. P. W. Robertson, *et al* .. *J.C.S.*, 1937, 335; 1938, 182; 1939, 1509.
14. Scheibler and Magasanik .. *Ber.*, 1915, 48, 1814.
15. N. Semenov .. *Chemical Kinetics and Chain Reactions*, 1933 (O.U.P.), p. 463, *et seq.*
16. Terry and Eichelberger .. *J. Amer. Chem. Soc.*, 1925, 47, 1067.
17. Thiele .. *Annalen*, 1899, 306, 87.
18. Williams and James .. *J.C.S.*, 1932, 2911.