

# THE KINETICS OF THE OLEFINE-BROMINE REACTION

## Part V. Influence of Substituents on the Applicability of the Kinetic Equation of the Catalysed Reaction

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IN Part I of this series it was observed that the induction period and the minimum concentration of catalyst needed to eliminate this varied with the olefine and a hypothetical curve was drawn correlating these.<sup>3</sup> The kinetic equation derived in Part IV (preceding paper) must be consistent with this observation if it is to be a general one. Two similarly substituted trans ethylene derivatives were chosen for this study, fumaric acid and stilbene. The choice of these was determined by the following considerations: In dealing with a reaction involving the polarisability of the double bond, the complication of dipole moment influence has to be minimised and symmetrically substituted trans compounds present the obvious choice. An increase in the number of activating groups attached to the doubly bound carbon leads to a very fast reaction which renders accurate experimental work difficult with available equipment. Alpha-beta unsaturated acids have been shown by Kharasch<sup>5</sup> to be free from the complication of a peroxide effect. Phenyl ethylene reacts faster than ethylene but one may expect the symmetrical diphenyl ethylene to be less reactive through the opposing influences of the phenyl groups. The deactivation, however, cannot be as great as with the two carboxyl groups. Combining with the earlier observations, it was expected that a more exact correlation between activation and catalytic influence could be obtained. The results of the kinetic investigations are given below (Figs. 1 and 2) (Tables I, II, III, IV, V and VI).

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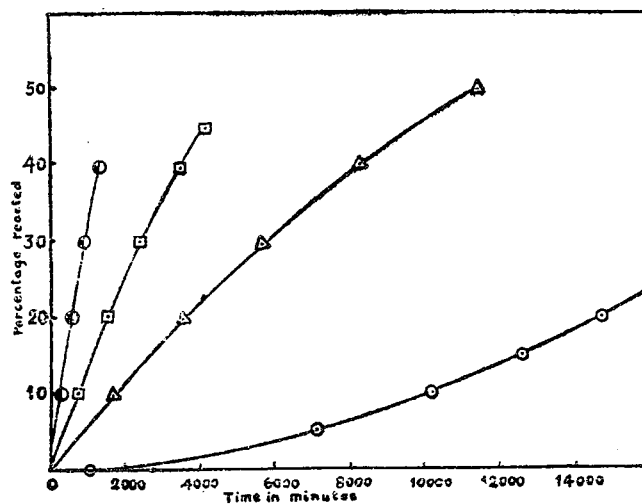


FIG. 1.

I. Uncatalyzed Reaction.

II, III, IV. Catalyzed reactions at 35°·5 C., 43°·5 C. and 50°·6 C.

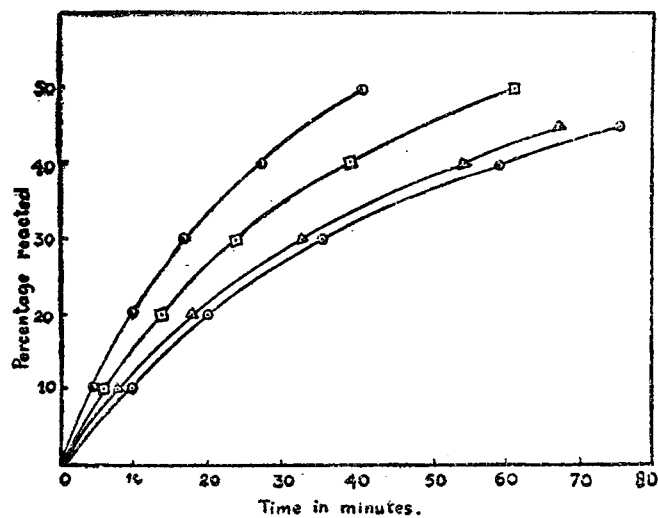


FIG. 2

I. Uncatalyzed Reaction.

II, III, IV. Catalyzed reactions at 35°·5 C., 43° C. and 50°·55 C.

TABLE I

Concentration of Fumaric acid\* ; Concentration of Bromine M/30 ; Concentration of Hydrogen Bromide 11.01 moles % of Bromine ; Temperature of reaction : 35°.5 C.

Reaction %	Time in minutes	Rate Constant Eqn. 5 (Part IV)	Rate Constant " Bimolecular "
5	852	0.0189	0.00185
10	1698	0.0194	0.00196
15	2604	0.0193	0.00203
20	3576	0.0194	0.00210
25	4596	0.0191	0.00217

\* Note.—After writing up this paper, the authors came across the work of P. W. Robertson *et al.* in which fumaric acid happens to be one of the compounds studied. The bearing of that on the present work will be considered in a later communication.

TABLE II

Concentration of Fumaric acid ; Concentration of Bromine M/30 ; Concentration of Hydrogen Bromide 11.01 moles % of Bromine ; Temperature of reaction : 43° C.

Reaction %	Time in minutes	Rate Constant Eqn. 5 (Part IV)	Rate Constant " Bimolecular "
5	344	0.0450	0.00459
10	712	0.0450	0.00468
15	1100	0.0453	0.00481
20	1512	0.0453	0.00495
25	1956	0.0452	0.00512

TABLE III

Concentration of Fumaric acid ; Concentration of Bromine M/30 ; Concentration of Hydrogen Bromide 11.01 moles % of Bromine ; Temperature : 50°.6 C.

Reaction %	Time in minutes	Rate Constant Eqn. 5 (Part IV)	Rate Constant " Bimolecular "
5	134	0.117	0.0118
10	274	0.116	0.0122
15	427	0.112	0.0124
20	598	0.107	0.0125
25	790	0.109	0.0127

The thermal reaction between Stilbene and Bromine is a fast one and it was found that a concentration of M/30 the reaction was completed in less than half an hour. To bring the speed of the reaction within measurable control, it was found necessary to work with concentrations of M/600.

TABLE IV

Concentration of Trans-Stilbene; Concentration of Bromine M/600; Concentration of Hydrogen Bromide 11.01 moles % Bromine; Temperature 35° 5 C.

Reaction %	Time in minutes	Rate Constant Eqn. 5 (Part IV)	Rate Constant " Bimolecular "
5	3.8	8.12	8.21
10	7.9	7.74	8.44
15	12.6	6.91	8.40
20	18.4	6.36	8.15
25	24.8	5.84	8.06
30	32.7	..	7.87

TABLE V

Concentration of Stilbene; Concentration of Bromine M/600; Concentration of Hydrogen Bromide 11.01 % of Bromine

Temperature	43° 0 C.		50° 55 C.	
	Reaction %	Time in minutes	Rate Constant " Bimolecular "	Time in minutes
5	2.9	10.89	2.1	15.04
10	6.1	10.93	4.35	15.33
15	9.7	10.89	6.95	15.24
20	13.9	10.79	9.95	15.08
25	18.5	10.81	13.10	15.26
30	23.8	10.80	16.95	15.17

TABLE VI

(All values refer to 35° 5 C.)

Reacting Olefine	Concentration Moles/litre	Induction Period in minutes	" Velocity Constant " mol./litre, min. <sup>-1</sup>
Crotonic acid	.. M/30	25	0.038
Tiglic acid	.. ,	4	0.20
Dimethylacrylic acid	.. ,	1.2	0.78
Fumaric acid	.. ,,	1062.0	0.0020
Allyl Chloride	.. M/300	Less than 2	1.22
.. Bromide	.. ,,	2.5	0.72
Stilbene	.. ,,	Ca 3.8	0.40 (estimated) by extrapolation

It will be noticed that fumaric acid gives a reasonable " bimolecular " constant only at about 50° C. even though the proportion of catalyst is the same as that used in earlier experiments. On the other hand, stilbene at 35.5 can be considered to behave equally well by the use of Equation 5 or

the bimolecular rate equation and at higher temperatures gives a good bimolecular constant. Qualitatively, therefore, one may conclude that the minimum concentration of the catalyst required for giving a "bimolecular" constant is greater in the case of an olefine with deactivating groups than that of one with activating groups, the limiting value being reached earlier in the latter case.

To get a better picture of the role of activating groups, one can compare the limiting value of the constants where possible with the induction periods observed or what probably amounts to the same thing, with the minimum concentration of catalyst required to give a bimolecular constant.

If one were to plot the values of the "velocity constant" at comparable concentrations against the induction periods, a curve asymptotic towards both axes can be obtained but the experimental values for the purpose has still to be obtained. The figures in the table (Table VI), however, clearly show the trend expected.

One may then justifiably consider that the rate equation derived in the previous part (IV) fits in with the behaviour of both structural influences and catalytic influences.

In Part I of this series<sup>2</sup> it was observed that the experimental observations of Williams<sup>7</sup> on the addition of bromine to ethylene in carbon tetrachloride solution showed the characteristics of a chain reaction and that the per cent. reaction-time curve could be represented by the relation of the type:

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

It was anticipated then that in the non-polar solvent there is a likelihood of a heterogeneous reaction complicating the interpretation. The recent observations of Robertson and co-workers appears to indicate the presence of a definite heterogeneous reaction in this solvent. All observations in acetic acid, however, indicate that the reaction in this polar solvent is definitely homogeneous. While the polar solvent can function as an activating medium for the reaction, in the case of olefines where deactivating groups are present and where the concentration of the added external catalyst is not adequate, the competition between the acetanion and the bromide ion in the latter steps in the reaction may slow down the rate and the reaction-time curve stimulates one of a degenerate branching chain. This anticipation is borne out by the uncatalysed addition to fumaric acid at 35° C. (Fig. 3).

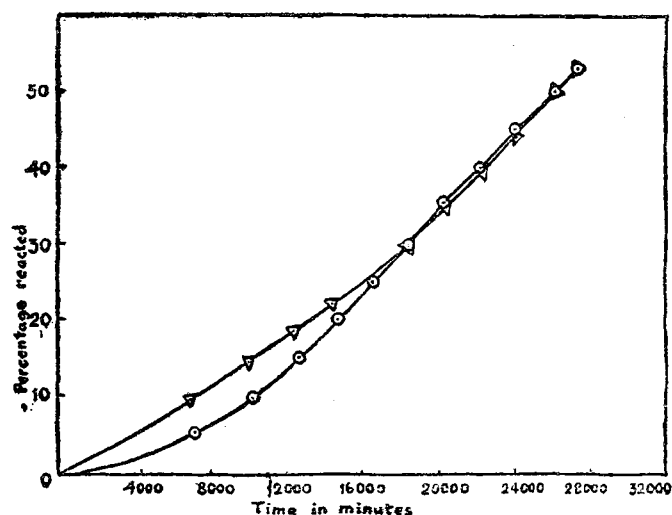


FIG. 3

I. Theoretical, II. Experimental.

Strict conformity between the theoretical and experimental values may not be expected in the initial stages of chain development but the coincidence is nonetheless striking. The maximum value of the reaction rate is reached when about 50% of the reaction is over, again, conforming to Semenov's generalisations on degenerate branching chains.<sup>6</sup> It is expected that further work in progress will reveal other similar instances.

A word of explanation is necessary for the choice of an aryl ethylene in the investigation. Competition experiments had shown<sup>2</sup> that the introduction of the phenyl nucleus activates the double bond. From the genesis of the T-effect, that the location of two groups of this class of substituents may be expected to neutralise each other's influence, especially if the trans form were chosen. Unpublished observations of one of us in the competition experiments (S. V. A.) indicated that this does not take place. The present investigations also show that the double bond is definitely activated even with two phenyl groups symmetrically located.

#### EXPERIMENTAL

The reaction velocities were measured by the usual methods as described in Part I, the same accuracy in thermostat control being maintained. Bromine was prepared by the method described by Anantkrishnan and Ingold<sup>2</sup> and its purity tested by the criterion indicated by one of us.<sup>1</sup> Pure Fumaric acid (Kahlbaum's) was repeatedly recrystallised from alcohol to

constant melting point 290° C. in a sealed tube. The substance was stored in a vacuum desiccator till used.

Stilbene was prepared from benzoin by the method of Ballard and Dehn<sup>4</sup> and the pure trans form used in the investigation.

#### SUMMARY

A study of the reaction between bromine and fumaric acid and bromine and stilbene brought out clearly the validity of the rate equation derived in the previous part. The uncatalysed addition reaction of fumaric acid exhibits the characteristics of a degenerate branching chain.

#### REFERENCES

1. Anantkrishnan, S. V. .. *Annamalai University Journal*, 1942, 11, 170.
2. ——— and Ingold, C. K. .. *J.C.S.*, 1935, 984.
3. ——— and Venkatraman, R. .. *Proc. Ind. Acad. Sci.*, 1940, 12 A, 290.
4. Ballard and Dehn .. *J.A.C.S.*, 1932, 54, 3969.
5. Robertson and co-workers .. *J.C.S.*, 1937, 335 ; 1938, 182 ; 1945, 129, &c.
6. Semenoff .. *Chemical Kinetics and Chain Reactions (O.U.P.)*  
p. 463.
7. Williams .. *J.C.S.*, 1932, 979.
8. Kharasch and Mayo .. *J.A.C.S.*, 1933, 55, 2368.