

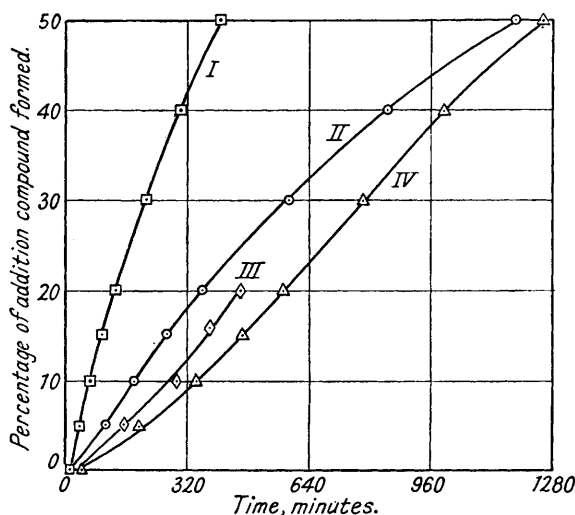
45. *The Influence of Substituents on the Additive Reactivity of Ethylene Derivatives. Part IV. The Mechanism of the Reaction.*

By SEKHARIPURAM V. ANANTAKRISHNAN and R. VENKATARAMAN.

The mechanism of bromine addition to olefins is found to be complex. The influence of positive catalysts like iodine monochloride and hydrogen bromide, combined with that of the negative catalyst antimony tribromide, can best be explained by means of a simple chain mechanism. A tentative scheme for such a mechanism is given. With sufficient concentration of the catalyst, it is found that the reaction apparently becomes bimolecular. Under such conditions, comparison of additive reactivities by a competitive method becomes feasible.

RECENT investigations have shown that the mechanism of bromine addition to ethylene derivatives is still unsolved, as was noticed by Anantakrishnan and Ingold (J., 1935, 984, 1396). It is now generally accepted that, in solution, whether in an ionising or in a non-

FIG. 1.

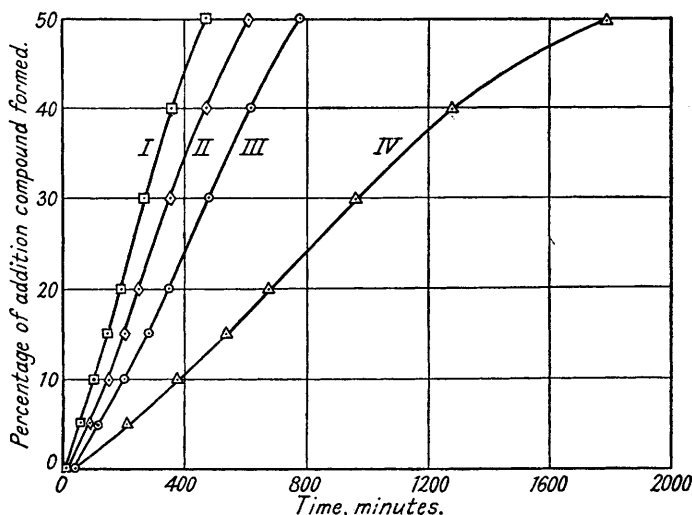


ionising medium, the polarised bromine molecule, rather than the individual ions, takes part in the addition, the reaction being initiated by the positive halogen. The competitive method adopted by Ingold and his co-workers implies the validity of this idea, as well as the conception that under controlled catalytic conditions, in any solvent, the addition reaction may be deemed to be of the first order with respect to the olefin, and that there is only one dominating catalyst. The experiments following Williams's discovery (J., 1932, 2911) that the reaction is autocatalytic in carbon tetrachloride indicated that the same holds good in the case of polar solvents, and that the initial addition of hydrogen bromide or quinoline eliminates this autocatalysis. The recent work of Robertson and his co-workers (J., 1937, 335), which apparently shows that the reaction in acetic acid is termolecular,

however, necessitated a thorough examination of the mechanism before the competitive study was extended.

In the competitive method, it was considered desirable to avoid the use of hydroxylic solvents, since there is the possibility of the solvent reacting with bromine and the hydroxyl ion competing with the bromine. At the same time, the nature of the reaction indicated that a polar solvent is desirable to minimise side effects. Since Robertson's experiments were carried out in acetic acid, this solvent was chosen for the present studies so as to decide the question beyond doubt irrespective of the solvent. A later communication will deal with the influence of solvent and of temperature. Also, in the present studies unsaturated aliphatic acids have been preferred to cinnamic acids in order to avoid the complication of the duplex polar character of the phenyl group. In all the cases examined, irrespective of the concentration of the reactants, a distinct period of induction

FIG. 2.



is noticed, the exact period, however, increasing with dilution of the reagents. Further, the induction period appears to arise from some factor depending more on the halogen than on the olefin (see Tables I and II and Figs. 1, 2, and 3).

TABLE I.

Rate of addition of bromine to tiglic acid in acetic acid (Fig. 1).

Curve No.	[Acid].	[Br ₂].	Period of induction, mins.	Time (mins.) taken for percentage reaction.							
				5%.	10%.	15%.	20%.	30%.	40%.	50%.	60%.
I	m/30	m/60	9	33	63	95	133	208	300	410	575
II	m/60	m/60	10	100	178	260	360	590	850	1196	—
III	m/30	m/120	25	153	290	365	420	—	—	—	—
IV	m/60	m/120	24	175	355	475	575	790	1000	1270	1640

Rate of addition of bromine to trans-crotonic acid in acetic acid (Fig. 2).

I	m/15	m/15	4	60	104	152	190	272	360	475	664
II	m/30	m/15	5	86	145	196	244	346	466	612	—
III	m/15	m/30	14	115	204	280	350	480	620	768	945
IV	m/30	m/30	25	218	380	535	675	955	1275	1800	—

The next problem is the elimination of the period of induction and the calculation of the velocity constant. The existence of autocatalysis in the reaction has been observed by a number of workers (Hofmann and Kirmreuther, *Ber.*, 1909, **42**, 4481; Bauer and Moser, *Ber.*, 1907, **40**, 1918; Williams and James, J., 1928, 343; Anantakrishnan and Ingold, *loc. cit.*). It is equally well known that the purity of the bromine used is an essential factor in the observation both of the period of induction and of autocatalysis: the bromine

used in these experiments was purified by the process used by Anantakrishnan and Ingold (*loc. cit.*), for mere distillation over potassium bromide does not afford bromine of sufficient purity. Moreover, it was obvious that hydrogen bromide which might be formed by a

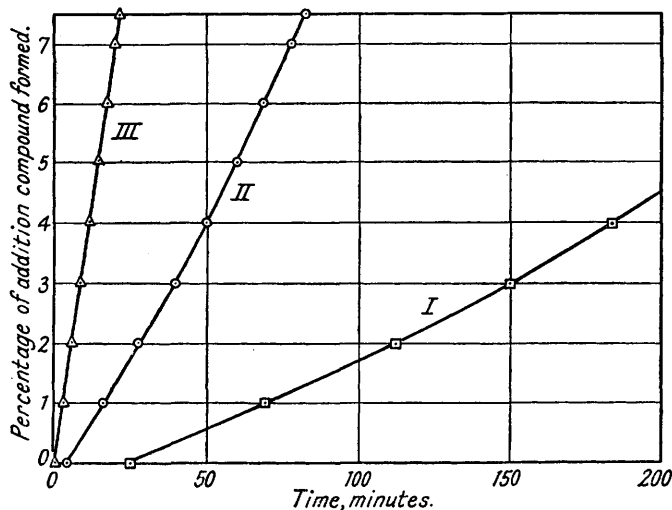
TABLE II.

Effect of concentration and catalysts on the period of induction in the addition of bromine to crotonic acid (Fig. 3).

Curve No.	Solution.			Period of induction, mins.	Time (mins.) taken for percentage reaction.						
	[Acid].	[Br ₂].	[HBr].		1%.	2%.	3%.	4%.	5%.	6%.	7%.
I	M/30	M/30	—	25	70	112	150	183	218	247	282
II	M/15	M/15	—	4	16	28	40	50	60	69	78
III	M/15	M/15	6.90%	0	2	6	9	12	15	18	21

side reaction functions as a catalyst, as found by Williams (J., 1932, 2911) and by Anantakrishnan and Ingold (*loc. cit.*). Contrary to Robertson's observations, hydrogen bromide

FIG. 3.



dissolved in the *dry* solvent functions as a catalyst. Further, Brüner and Fischler (*Z. Elektrochem.*, 1914, 20, 84) noticed that iodine bromide and antimony tribromide also function as catalysts, leading to reactions which give bimolecular constants. It is now found that both hydrogen bromide and iodine monochloride function as very effective catalysts in eliminating the period of induction, and that both give nearly the same bimolecular constant when present in equivalent concentrations. A minimum concentration of catalyst

TABLE III.

Effect of catalysts on the rate of addition of bromine to trans-crotonic acid in acetic acid (concentration of reactants, M/15) (Fig. 4).

Curve No.	Catalyst.	Mols. % of catalyst.	Period of induction, mins.	Time (mins.) taken for percentage reaction.						
				5%.	10%.	15%.	20%.	30%.	40%.	50%.
I	—	—	4	60	104	152	190	272	360	475
	HBr	1.05	0	56	99	136	170	232	316	444
	"	2.10	0	54	87	116	150	223	313	430
II	"	6.90	0	15	31	48	68	115	176	260
	ICl	0.95	0	45	84	116	149	217	295	393
III	"	7.80	0	20	32	49	68	118	184	267
	SbBr ₃	1.00	20	70	121	160	199	283	371	494
IV	"	6.40	28	90	161	225	280	388	511	—

is, however, necessary to give a bimolecular constant, and in these two cases, it seems to be about 7.5 mols. of catalyst per 100 mols. of olefin (Tables III and IV).

TABLE IV.

Value of k_2 and k_3^* for the reaction between trans-crotonic acid and bromine (concentration, $M/15$) in acetic acid, with and without catalysts (unit of time = 1 min.).

Catalyst.	Mols. of catalyst per mol. of each reactant.	Period of induction, mins.		Values of k_2 and k_3 for percentage reaction.						
				5%.	10%.	15%.	20%.	30%.	40%.	50%.
None	—	4	$100k_2$	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
			$100k_2$	1.41	1.68	1.95	2.21	2.77	3.16	3.37
HBr	1.05	0	k_3	0.868	1.07	1.27	1.49	2.02	2.53	4.05
			$100k_2$	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
,,	2.10	0	$100k_2$	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
			$100k_2$	1.75	1.09	2.28	2.52	2.96	3.39	3.82
ICl	0.95	0	k_3	1.08	1.26	1.49	1.70	2.16	2.71	4.58
			$100k_2$	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
,,	7.80	0	$100k_2$	1.13	1.38	1.67	1.89	2.27	2.70	3.0
			k_3	0.695	0.872	1.08	1.27	1.66	2.16	3.6
			$100k_2$	0.88	1.04	1.18	1.34	1.17	1.96	—
SbBr ₃	1.00	20	k_3	0.540	0.656	0.768	0.904	1.21	1.57	—
			$100k_2$	0.88	1.04	1.18	1.34	1.17	1.96	—
			k_3	0.540	0.656	0.768	0.904	1.21	1.57	—

* Values of k_3 were calculated by Robertson's equation (*loc. cit.*); k_2 and k_3 are respectively the bimolecular and termolecular constants.

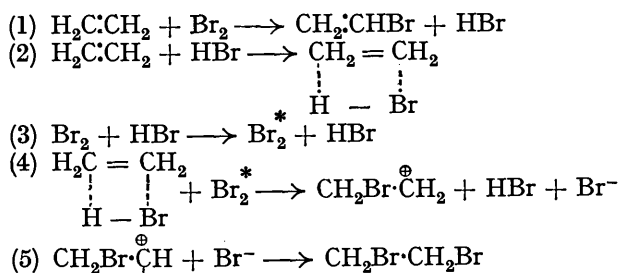
It is significant that the efficient catalysts are both compounds which can form higher complexes with bromine. Also, it has been established that there is some association, possibly electrostatic, between ethylene and hydrogen bromide (Maass and Wright, *J. Amer. Chem. Soc.*, 1924, **46**, 2664).

Combined with the work on ethylene, the present experiments clearly show that the induction period and autocatalysis are quite general and not peculiar to certain compounds. This view is supported by the observation of most workers in this field that, even in the cases where apparently no induction period exists, there is evolution of hydrogen bromide during the reaction.

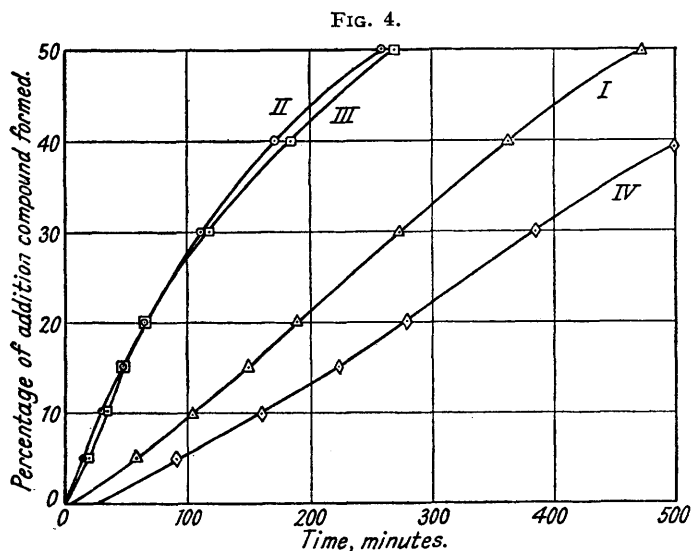
As shown by the values of the constants k_3 and k_2 in Table IV, both for the reaction in which there is no initial addition of catalyst and for the one with catalyst, a simple termolecular reaction cannot account for the course followed. Obviously, the reaction can only be interpreted by a chain mechanism. The work of Pease and Walz (*J. Amer. Chem. Soc.*, 1931, **53**, 3728) indicated a chain mechanism for the thermal chlorination of methane analogous to the photochemical reaction. It is well known that the photochemical reaction between bromine and ethylene in solution or in the gaseous phase is definitely a chain reaction, and it is not unlikely that the thermal reaction also depends upon reaction chains.

Semenoff ("Chemical Kinetics and Chain Reactions," Oxford, 1935, p. 463) considers that "the kinetics of any chemical reaction is that of a chain mechanism and that the particular cases involving reactions with short chains or those reactions requiring but little energy of activation, which can be interpreted without recourse to chains are rare." Later, he states "that the existence of an induction period and the further progress of the reaction according to curves of the type $1 - e^{-kt}$ or e^{-kt} can be attributed to the development of chains." Now an examination of the curves (Nos. IV of Figs. 1, 2, and 4) clearly shows that we are dealing with a reaction of this type. It will be noticed that in the latter half of the reaction, the curve deviates from the theoretical exponential type as may be expected from the gradual decrease of the effective concentration of the initial substances owing to reaction (see Semenoff, *op. cit.*, p. 67). Since the initial addition of hydrogen bromide in sufficient quantity eliminates the period of induction and also, apparently, reduces the reaction to one of a simple bimolecular mechanism, it is obvious that the hydrogen bromide

plays an important part in the mechanism of addition, which may be considered to take place as follows :



Stage (1) accounts for the formation of small amounts of hydrogen bromide in the initial stage; stage (2) indicates the possible electrostatic attraction between the olefin and hydrogen bromide. Stage (3) explains the rôle of hydrogen bromide as an activator. It is unnecessary to postulate the formation of hydrogen perbromide since it is known that



the formation of this requires the presence of an ionising solvent, and hydrogen bromide is known to catalyse the reaction even in carbon tetrachloride (Williams, *loc. cit.*). Also, it follows that hydrogen perbromide is not necessarily an activator for the bromine molecules, and hydrogen bromide itself serves as the activator. The rate-determining step is stage (4) when there is a dominant catalyst, all the others being comparatively rapid. Reactions (4) and (5) conform to our present ideas that the positive component of the polarised bromine molecule initiates the addition to the double bond (Ingold and Ingold, J., 1931, 2354; Orton and King, J., 1911, 109, 1369; Soper and Smith, J., 1926, 1582; Read and Read, J., 1928, 745; Jackson, *J. Amer. Chem. Soc.*, 1926, 48, 2166). The hydrogen bromide released in stages (1) and (4) takes part in the reaction again, the chain of reactions being repeated.

A similar mechanism can be suggested for the reaction in which iodine monochloride functions as a catalyst.

An examination of curves IV of Figs. 1, 2, and 4 shows that the rate of reaction increases up to a certain limit and then begins to diminish. In the initial stages, the supply of hydrogen bromide also increases with time. Hence, the concentration of the complex increases with time, thus accounting for the increased rate or autocatalysis up to a limit when the diminution of the concentration of the reactants asserts itself and the reaction rate begins to fall. The induction period is the period taken to set up the chains representing the first four

stages. By the initial addition of hydrogen bromide, the period required by stage (1) is eliminated, and the stationary stage is reached earlier, or the induction period is absent. The initial addition of a sufficient quantity of hydrogen bromide apparently makes any change in its concentration by the reactions (1) to (4) negligible, and the addition reaction becomes for all practical purposes a bimolecular one.

The effect of the addition of antimony tribromide to the reactants is apparently anomalous, as revealed by a closer study of Table III, for it appears to function as a negative catalyst. This further confirms the idea that the catalyst-bromine complex is not necessarily a source of activated bromine molecules. It is just possible that antimony tribromide combines with bromine to form the pentabromide, thereby diminishing the initial concentration of bromine; but it cannot fully account for the extended period of induction or the observed slowness of the reaction, since the concentration of bromine would be diminished by only about 6.5%. The increase in the period of induction with increase in concentration of antimony tribromide is a clear indication that it helps to remove one of the important factors constituting the chain of reactions in stages (1)–(4). It is quite possible that it removes the hydrogen bromide as HSbBr_4 , the corresponding alkali salts of which are well known, thereby prolonging the period of induction. This diminution of hydrogen bromide concentration is an important factor in the chain of reactions, leading to the retardation. The existence of a negative catalyst constitutes further evidence in favour of a chain mechanism (Christiansen, *J. Physical Chem.*, 1924, **28**, 145).

It is clear, therefore, that the bromine-olefin addition is not a simple bimolecular or termolecular reaction, but a chain reaction, involving the stages indicated. The reaction may, however, be simplified into an apparently bimolecular reaction by the initial addition of a sufficient concentration of the catalyst, thus enabling us to compare the additive reactivities of olefins, the competitive method still remaining a valuable tool for comparing fast addition reactions, if this precaution is adopted.

EXPERIMENTAL.

The reactions were all studied at 35.5°.

Solvent. The acetic acid was Kahlbaum's (99–100%) acid; when purified by the method of Orton and Bradfield (J., 1927, 983), it was 99.85% pure.

Bromine. Bromine was purified as indicated on p. 226.

trans-Crotonic acid. The acid was prepared by the condensation of malonic acid with acetaldehyde in presence of pyridine in absolute alcohol (Scheibler and Magasanik, *Ber.*, 1915, **48**, 1814). It was recrystallised to constant m. p. (72°) from light petroleum, and kept in a vacuum desiccator until required.

Tiglic acid. The B.D.H. acid was similarly recrystallised to constant m. p. (64°).

Hydrogen bromide. Kahlbaum's 48% acid was allowed to drop on phosphoric oxide, and the resulting gas was passed through a drying train of phosphoric oxide and then through a trap of glass-wool before it was absorbed in acetic acid. The hydrogen bromide content of the solution was determined as silver bromide, and the required concentration obtained by dilution, the content being similarly checked just before the experiment. 1 or 2 C.c. of this solution were added to the reactants.

Iodine monochloride. Kahlbaum's sample was used. The amount of iodine chloride added was estimated separately by reaction with potassium iodide.

Antimony tribromide. The required amount of Kahlbaum's sample was dissolved in acetic acid, and this solution was added to the reactants.

100 C.c. of a solution of bromine in acetic acid of the required concentration were kept in a brown bottle in a closed thermostat; in another brown bottle the solution of the appropriate acid was kept. 100 C.c. of the latter solution were added to the bromine solution by means of a darkened pipette, the mean time of addition being taken as the starting point. Any initial catalyst was added to the bromine solution before the addition of acid. A known volume of the reacting solution was run into a cold saturated solution of potassium iodide at the requisite intervals.

The authors thank Prof. C. K. Ingold, F.R.S., for his kind interest in the work. One of them (R. V.) expresses his indebtedness to the Annamalai University for the award of a Studentship.