KINETICS OF THE OLEFINE-BROMINE REACTION

*Part VIII. The Catalysed Reaction between Bromine and Crotonic and Dimethylacrylic Acids in Carbon Tetrachloride Solutions

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In earlier parts of this series[1] the reaction had been studied in glacial acetic acid solution and a good homogeneous reaction had generally been obtained using hydrogen bromide as the catalyst. Venkatraman[2] had reported that iodine halides catalyse the reaction. The previous part contained a report of our observations in carbon tetrachloride which showed a pronounced heterogeneous reaction and it was considered worth while studying the influence of iodine halides and pyridine.

Experimental

The experimental technique adopted was the same as in the previous parts, solvents and reagents being purified by the same process. Iodine chloride and iodine bromide were B.D.H. products fractionated after drying while A.R. Pyridine was dried over sticks of KOH and distilled before use (b.p. 115° C./760 mm.).

Typical runs are presented in Tables I and II and Figs. 1 and 2.

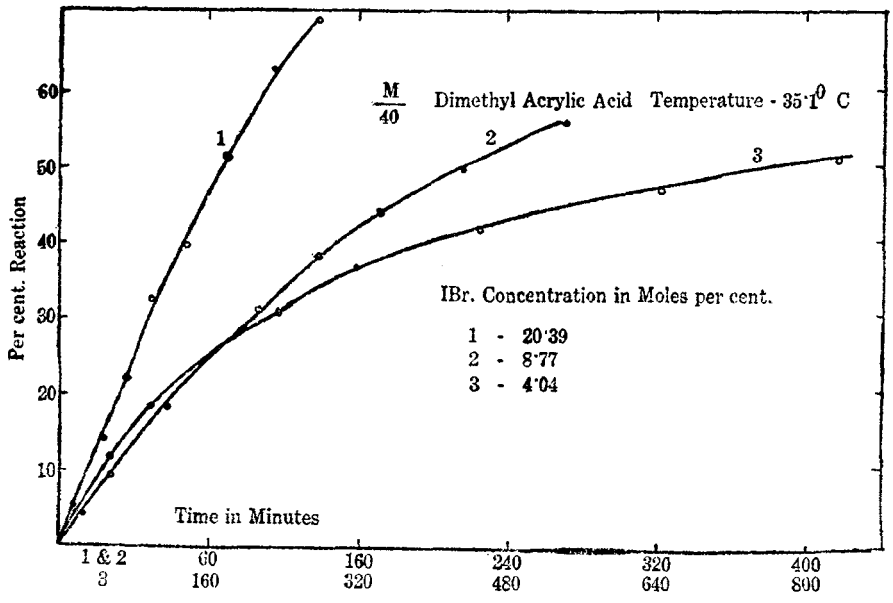

Fig. 1

* Based on thesis of I.M.M. approved for the M.Sc. degree of Madras University.

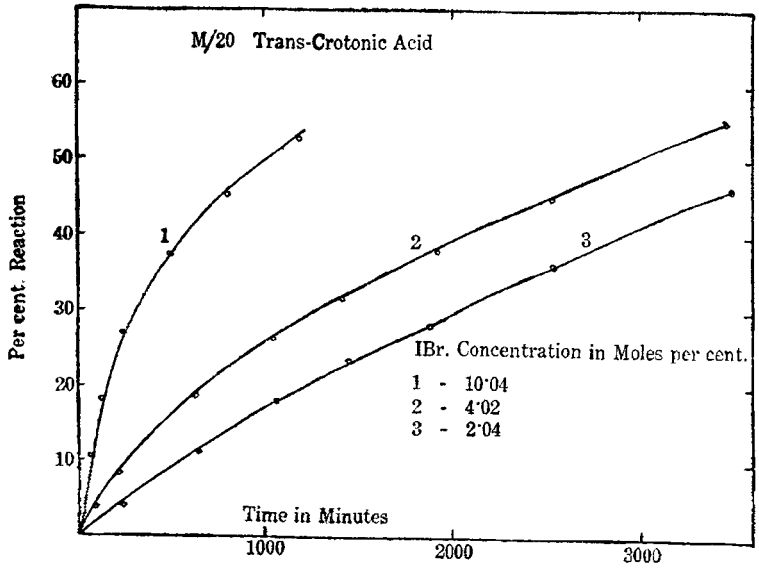

FIG. 2

TABLE I. *Catalysed Reaction between Bromine and Dimethyl Acrylic Acid*

Concentration of Reactants and temp.	Catalyst	Catalyst / Bromine moles %							
M/15 at 30° C.	IBr	5·712	Time	0	4·38	8·28	10·78	14·00	21·22	37·6
			Titre	11·15	9·80	8·60	8·00	7·00	5·90	4·55
			% Reaction	0	12·85	24·29	30·00	39·72	50·00	62·85
		3·087	Time	0	1·97	3·82	7·45	11·42	18·07	28·20
			Titre	10·5	9·50	9·00	7·90	7·00	5·80	5·10
			% Reaction	0	6·12	11·23	21·43	31·63	43·88	51·02
		1·528	Time	0	2·58	4·45	9·98	13·92	22·00	37·98
			Titre	10·5	9·70	9·10	7·70	6·80	6·05	4·70
			% Reaction	0	3·54	9·60	23·74	32·83	40·41	54·63
	ICl	3·068	Time	0	1·97	72·25	79·50	88·67	95·97	126·9
			Titre	10·00	9·90	9·10	8·15	6·85	6·10	4·72
			% Reaction	0	1·03	9·27	20·10	32·44	40·21	53·60
		1·511	Time	0	22·55	47·10	59·35	74·58	104·5	
			Titre	10·00	9·70	8·90	7·40	6·15	4·80	
			% Reaction	0	3·06	11·17	26·40	39·09	52·79	
M/20 at 35° C.	IBr	3·992	Time	0	2·07	5·33	9·52	11·50	16·25	25·92
			Titre	9·60	9·20	8·50	7·40	6·60	5·80	4·50
			% Reaction	0	4·26	11·70	23·42	31·92	40·42	54·26
		0·9982	Time	0	2·20	4·87	8·88	11·88	14·50	21·35
			Titre	9·50	9·50	8·30	8·35	7·40	6·70	5·60
			% Reaction	0	2·13	5·31	12·21	22·35	29·80	41·50
	Pyridine	2·002	Time	0	1·72	6·43	13·52	17·13		
			Titre	9·60	9·40	8·60	7·20	6·60		
			% Reaction	0	2·08	10·42	25·00	31·25		

TABLE II. *Catalysed Reaction between Trans Crotonic Acid and Bromine*

Catalyst and Temp. °C.	Catalyst / Bromine moles %		Concentration of reactants : M/10						
IBr at 30°	9·874	Time	0	14·08	22·42	46·83	92·55	170	371
		Titre	10·10	9·40	9·10	8·00	6·90	5·70	4·40
		% Reaction	0	7·64	10·91	22·95	34·97	48·80	62·30
	5·014	Time	0	25·27	54·35	130	202	313	438
		Titre	9·50	9·10	8·60	7·45	6·60	5·60	5·00
		% Reaction	0	4·44	10·00	22·78	33·01	43·34	50·00
ICl at 30°	10·84	Time	0	209	1000	1580	1670	1769	1853
		Titre	9·50	9·20	8·90	8·20	7·50	6·81	6·10
		% Reaction	0	3·60	7·23	14·45	24·09	31·93	40·97
	5·142	Time	0	80·83	483	583	693	1000	1236
		Titre	9·25	9·10	7·65	6·90	6·25	5·35	4·55
		% Reaction	0	1·71	18·28	26·86	34·29	44·28	53·71
IBr at 35°	4·827	Time	0	1·07	12·77	151·5	1214	2594	
		Titre	10·15	10·10	9·90	9·05	8·00	7·05	
		% Reaction	0	0·52	2·58	11·34	22·16	32·47	
	1·922	Time	0	9·28	50·60	553	1223	4085	
		Titre	9·95	9·90	9·55	9·10	8·15	7·05	
		% Reaction	0	0·51	4·10	8·72	18·46	29·75	
	0·9506	Time	0	10·45	52·0	626	2760	40·94	
		Titre	9·95	9·90	9·60	8·80	7·45	7·00	
		% Reaction	0	0·51	3·05	11·68	25·39	29·95	

DISCUSSION OF RESULTS

In any catalysed reaction, the function of the catalyst is essentially to alter the activation energy of the reaction. This may be brought about by changes in the activation of either or both reactants. The first observable effect is the elimination of the induction period which is noticed in the present observations with all the catalysts studied (see Figs. 1 and 2). The behaviour of iodine chloride appears to be quite complex and after a fuller investigation will be communicated later. The insolubility of pyridine perbromide precluded a study of higher concentrations than the one reported. The trend, however, seems to be analogous to that of iodine bromide.

For a homogeneous reaction in which both reactants are activated by the catalyst, it has been shown earlier, that the rate equation can be represented by

$$\frac{dx}{d\epsilon} = k_2' [A] [Br_2] \frac{f}{f+1}$$

It has also been noticed that at higher temperatures, the rate equation reduces to a simple bimolecular one in acetic acid solutions. In the nonpolar solvent used in the present work, no constancy in the rate constant could be found as may be seen from the Figs. 3 and 4 showing the drift of the " bimolecular

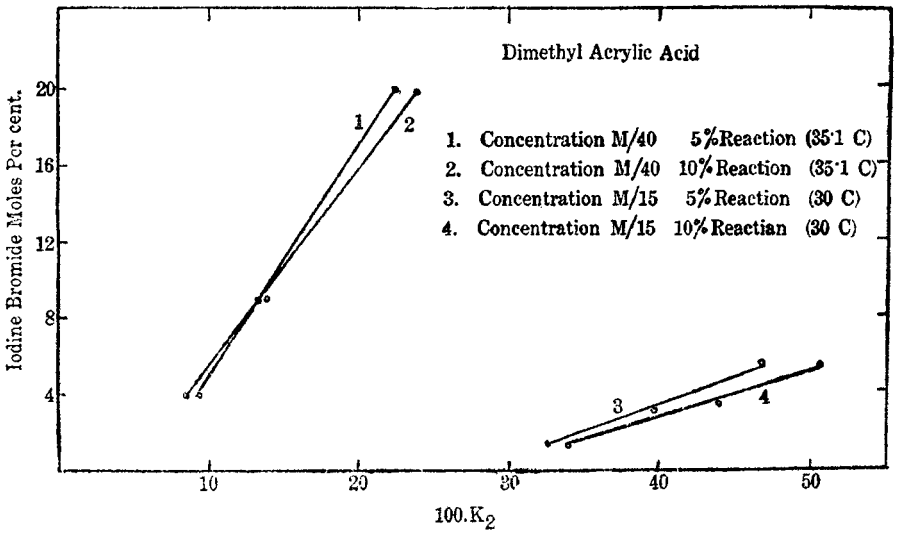

FIG. 3

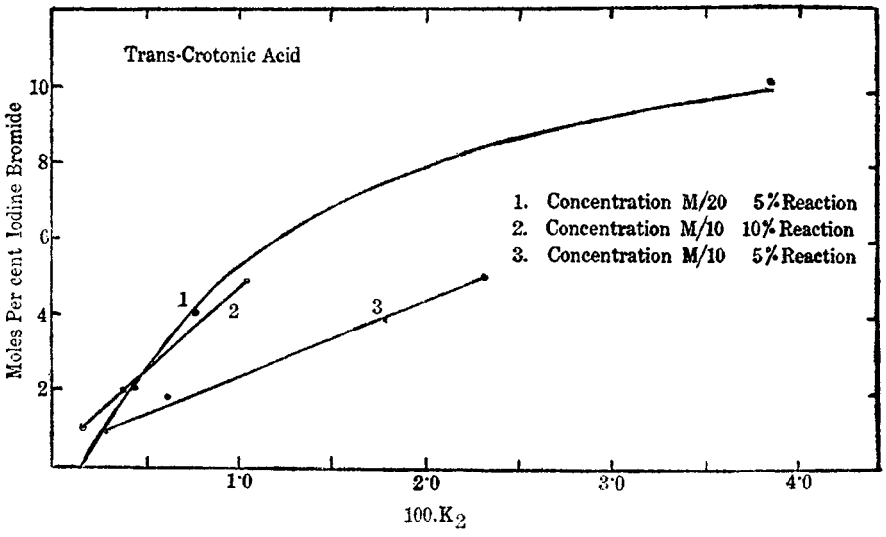

FIG. 4

rate constants " with the extent of reaction. The addition of the catalyst is not adequate for changing over to homogeneous conditions. This is well

rought out by a comparison of the time required for a given fraction of the reaction with reference to the catalyst concentration.

The catalysed reaction also brings out the pronounced influence of structure. Temperature does not seem to have any appreciable effect with dimethyl acrylic acid while it is quite noticeable with crotonic acid. This is in keeping with the observations in acetic acid solutions that the influence of catalysts on the dimethyl acrylic acid is small on account of the prior activation of the double bond by the two methyl groups on the same carbon atom.

One aspect of the catalysed reaction which has to be explained and which requires further study is the fact that initially the catalysed reaction is faster than the one with increased surface for the same initial concentration but the later stages are definitely slower. This is noticeable primarily with trans crotonic acid. Two possible causes of such slowing down are changes in frequency factor which is related to the shape of the olefine molecule and retardation by products of the reaction in a non-polar solvent. This is still under investigation.

SUMMARY

Iodine bromide and chloride as well as pyridine have been used as catalysts for the reaction between bromine and crotonic and dimethyl acrylic acids. The reaction is quite complex and does not seem to conform to any simple rate equation. Even with the addition of the catalyst, the heterogeneous part of the reaction does not seem to be eliminated.

REFERENCES

1. Anantakrishnan, S. V. and Venkatraman .. *Proc. Ind. Acad. Sci.*, 1946, **23A**, 306, etc.
2. Venkatraman, R. .. *Ibid.*, 1941, **13A**, 259.