

KINETICS OF THE OLEFINE-BROMINE REACTION

Part VII. The Reaction between Crotonic and Dimethyl Acrylic Acids and Bromine in Carbon Tetrachloride*

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STUDIES of the reaction in glacial acetic acid have been reported in earlier parts.³ It was then considered desirable to extend the observations to non-hydroxylic solvents and preferably nonpolar solvents. The results of experiments in carbon tetrachloride are reported here.

From the trend of observations in other solvents^{2, 5, 7} that had been reported by different workers and from observations of the reaction in the gas phase,⁶ it was anticipated that the reactions in this solvent will involve a polar surface. Now, all heterogeneous reactions involve the adsorption of one or more reactants in a single or a multimolecular layer and it is necessary also to note the influence of the nature of the surface on such adsorption. In the exploratory work, it is desirable to avoid other complications and in spite of the disadvantages of choosing carboxylic acids, these compounds have been taken up for study. This avoids the complication of the peroxide effect known to be negligible in these and also enables a comparison with the work in other solvents.

EXPERIMENTAL

(i) *Material used*

Carbon tetrachloride.—Pure carbon tetrachloride was kept in contact with an acid solution of potassium dichromate for three days with frequent shaking. The carbon tetrachloride was then separated, washed with distilled water, then with a dilute solution of potassium hydroxide and then again with distilled water. The moist solvent was then dried over anhydrous calcium chloride for several days and fractionated. The middle fraction, b.p. 76.6–76.8/760 mm., was collected and stored over sticks of potassium hydroxide in amber coloured bottles. The use of phosphorous pentoxide for drying this solvent was found to be unsatisfactory and gave erratic results for the course of this reaction. A report of the dielectric constant studies on this aspect of the work is being published separately.

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

Trans-Crotonic acid.—The product supplied by Tennessee Eastman Corporation was used after purification by repeated fractional crystallisation from petroleum ether (60–80°) to constant m.p. and stored in the dark, over anhydrous calcium chloride in a vacuum desiccator. The choice of this procedure was necessitated by the need for minimising the chances of conversion to the *cis* form. Freshly recrystallised samples, m.p. 72° C., was used for each experiment.

2:2 Dimethyl acrylic acid.—The compound was prepared essentially by the method of Barbier and Glaser.⁴ Mesityl oxide (1 mole) was oxidised by an alkaline hypochlorite solution (2 moles hypochlorite and 4 moles sodium

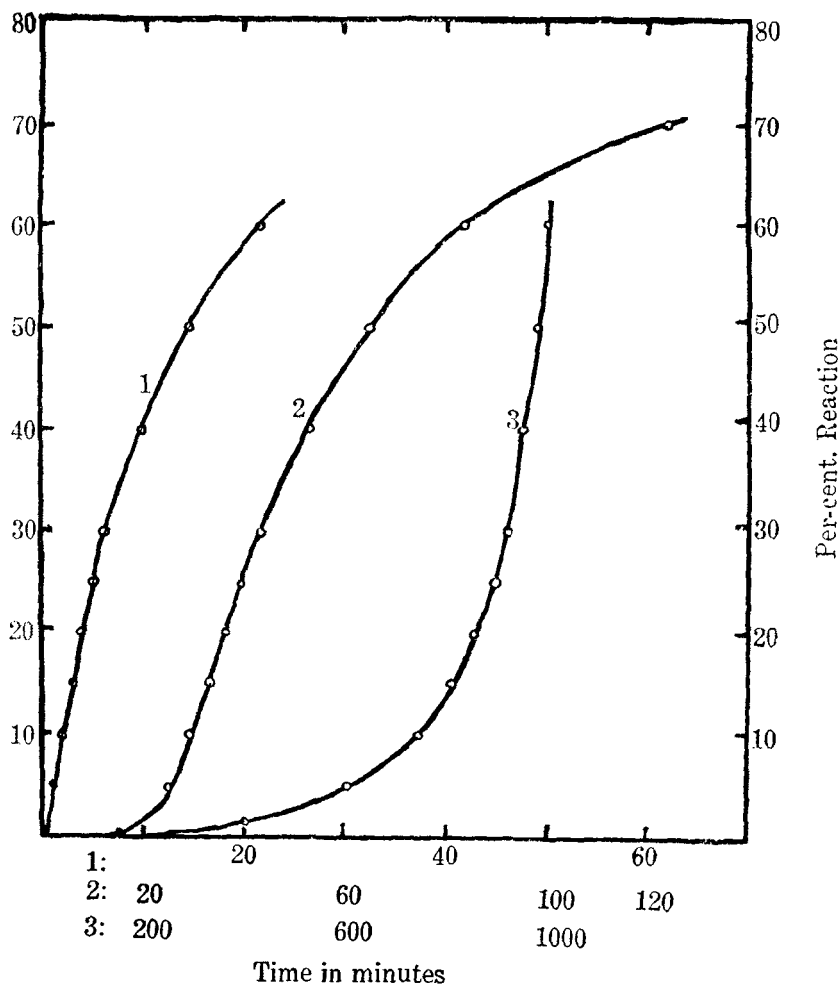


FIG. 1

Reaction between dimethyl acrylic acid and bromine at different concentrations.

hydroxide) keeping temperatures below -5°C . Excess hypochlorite was destroyed by bisulphite and after the removal of the byproduct, chloroform, the solution was acidified with dilute sulphuric acid, keeping temperatures low. Dimethyl acrylic acid separated on standing and a further yield was obtained by ether extraction of solution (yield 70% of theory). The acid was recrystallised from hot water and stored in a desiccator in the dark over phosphorous pentoxide, m.p. 70°C .

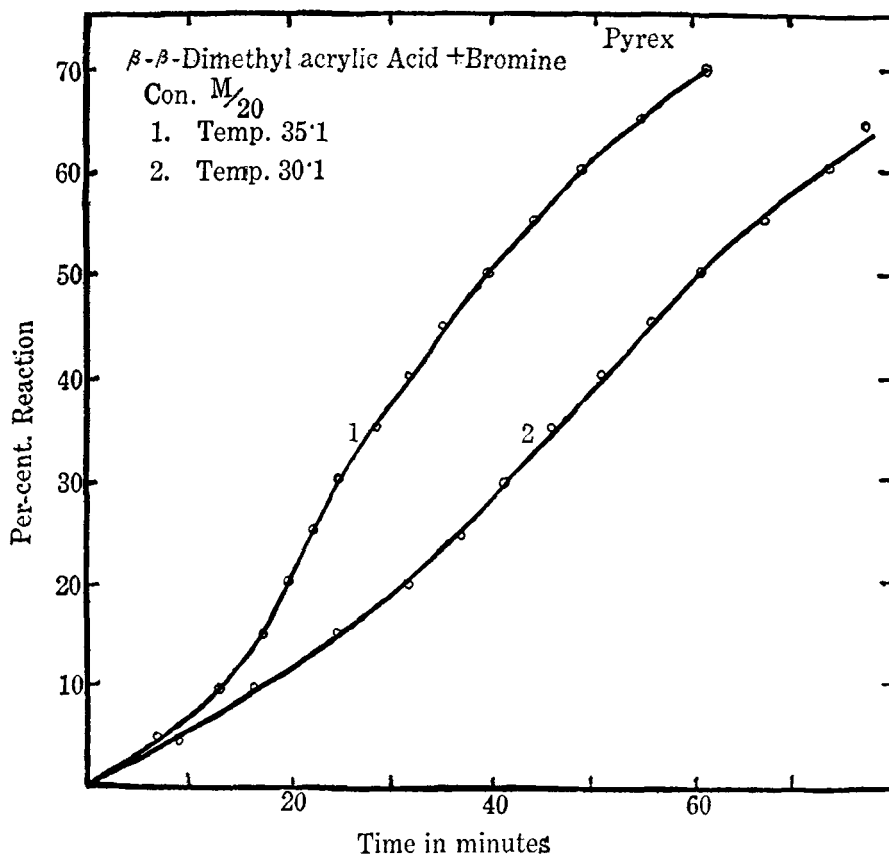


FIG. 2

Bromine was prepared by the method indicated by one of us earlier and the purity checked from time to time.¹

(ii) *Materials added for increasing surface*

Sodium bromide, barium sulphate and lithium bromide, of analytical reagent quality, were dried at 120°C . and stored in a desiccator before use. Alumina, silica and pyrex glass beads were used to provide additional surface.

The beads were treated by the same procedure, with reagents used at the same concentration and in the same order and prepared fresh for each experiment. The beads were soaked in a chromic acid solution for about 12 hours, with frequent shaking, washed thoroughly with distilled water, refluxed thrice with distilled water for 10 minutes at a time and then dried in an air oven at 120° C. for three hours. The beads used were uniform in each case, the pyrex beads being spherical and the others cylindrical. As a first approximation, the surface area was calculated for these shapes from the dimensions and in the different runs, the surfaces were assumed to be proportional to the weights. The relevant data for the purpose are given in Table I.

TABLE I

Material of bead	Average radius		l	Average surface sq. cm.	No. of beads for 100 g.
	External	Internal			
Pyrex	0.287 cm.	..	1.035	377
Silica ..	0.260	0.125	0.675	1.959	456
Alumina ..	0.293	0.157	0.638	2.188	260

(iii) Reaction Vessels and Measuring Vessels

250 ml. and 100 ml. amber coloured Pyrex bottles with well ground stoppers were used as the reaction vessels. The bottles were kept with chromic acid for 24 hours, washed thoroughly with distilled water and then steamed. The vessels were then dried in an air oven at 120° C. for about four hours and kept overnight in a vacuum desiccator.

All measuring vessels were standardised and coated with black enamel and were submitted to the same treatment as the reaction vessels and were used only after 24 hours at room temperature. Under these conditions volume changes were found to be negligible.

The reactions were carried out in an electrically maintained thermostat (temperature controlled to within 0.005° C.). All vessels were tested for evaporation losses, using bromine solutions. The course of the reaction was followed by the iodometric estimation of the unreacted bromine, in aliquot parts, from time to time. Rapid estimations were necessary as some of the dibromides formed slowly liberate iodine.

To economise space, only a few typical runs are presented in the accompanying tables and figures.¹

TABLE III

Influence of Surface on the Reaction between Bromine and Olefine for an Olefine Concentration of 0.0500 M at 30.1° C.

Bromine Concentrations: same order but slightly different.

A: Typical runs with added pyrex beads; B: Typical runs with silica beads.

A Crotonic acid	Time ..	0	106.8	272	683	1060	2494	3983
	Titre ..	9.30	9.00	8.70	7.95	7.40	5.45	4.50
	% reaction ..	0	3.23	6.45	14.32	20.43	41.40	51.60
2-2 Dymethyl acylic acid	Time ..	0	6.70	19.50	31.37	45.78	60.80	82.32
	Titre ..	10.40	10.00	9.10	8.40	6.80	5.20	3.70
	% reaction ..	0	3.85	12.50	19.23	34.61	50.00	64.43
B Crotonic acid	Time ..	0	136	1051	1780	2959	5991	
	Titre ..	9.20	9.00	7.85	7.00	5.80	4.00	
	% reaction ..	0	2.17	14.68	23.91	36.96	53.26	
2-2 Dimethyl acrylic acid	Time ..	0	12.22	23.87	29.97	39.52	46.95	74.77
	Titre ..	10.55	9.85	8.90	8.20	7.25	6.40	4.40
	% reaction ..	0	6.63	15.64	22.47	31.27	39.42	58.29

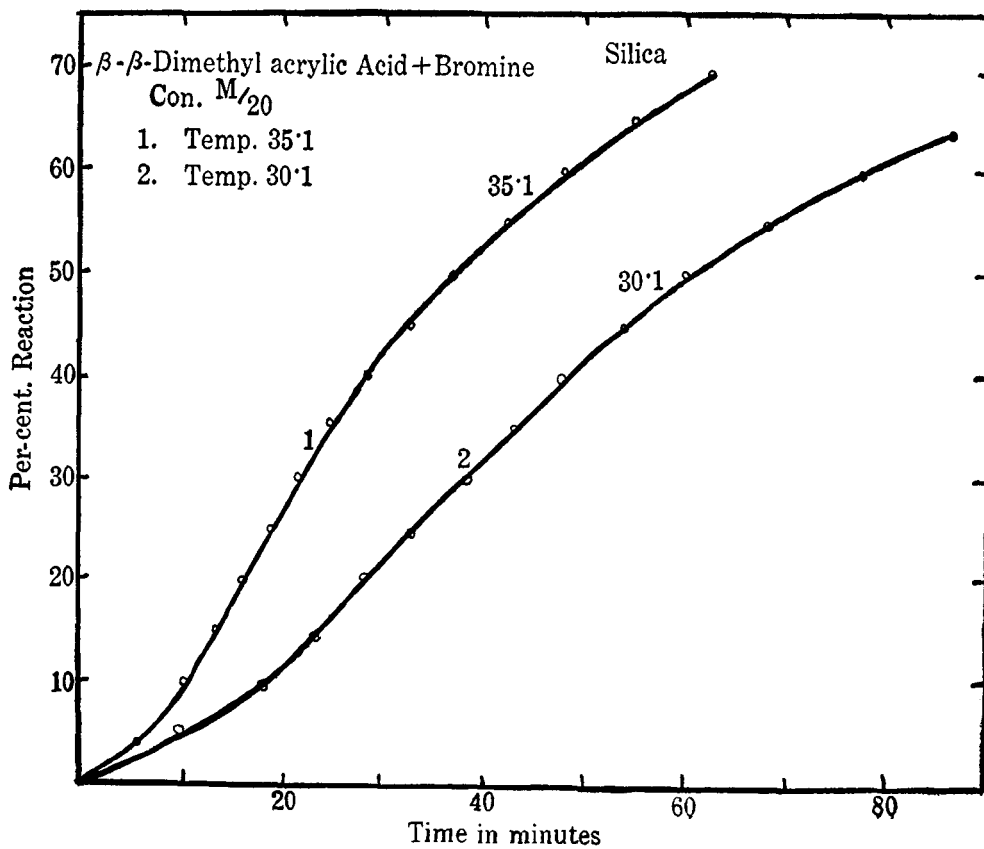


FIG. 3

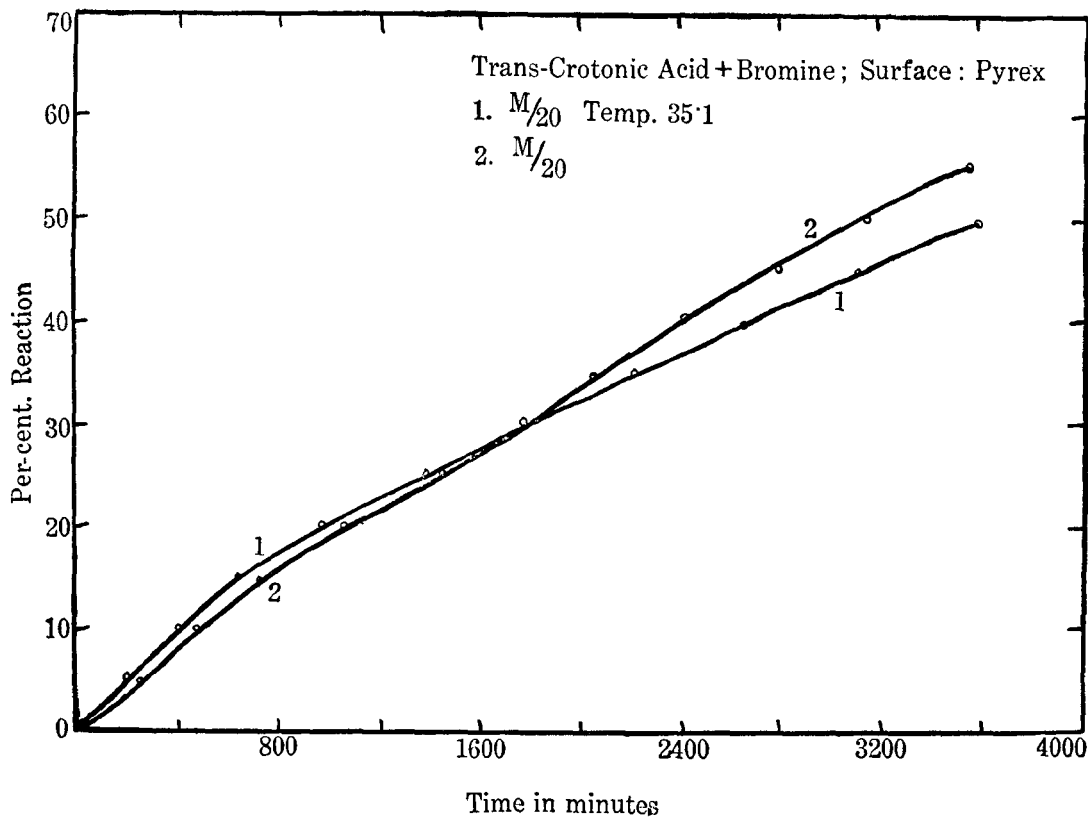


FIG. 4

DISCUSSION OF RESULTS

Schwab⁹ has remarked that where there is a surface reaction between ethylene and the halogens, both reactants are slightly adsorbed and the experiments of Gwyn Williams⁶ have borne out these. The typical runs are reported below and the illustrative curves (Figs. 2, 3 and 4) show the trend.

An inspection of these shows clearly the presence of an induction period which is sensitive to changes in the concentration of reactants as well as changes in the structure of the olefine and in the case of crotonic acid the reaction even appears to have a negative temperature coefficient. It is generally considered that reactions in carbon tetrachloride simulate a gas reaction. Preliminary experiments have shown that both reactants are adsorbed in varying amounts. A fuller study of this is in progress. The heterogeneous reaction is unmistakably shown by the elimination of the induction period and a quickening of the reaction by packing the vessel with beads of different materials.

A qualitative comparison shows that the effectiveness of the surface in catalysing the reaction is in the order

Pyrex glass > Silica (fused) > Alumina (fused)

A rough comparison can be made by transforming the results obtained so that they refer to the same surface area. As a first approximation, one may assume that the time required for a given fraction of the reaction is inversely proportional to the surface. The results obtained by such computation are given in Tables IV and V below.

TABLE IV

Reaction between Dimethyl Acrylic Acid and Bromine: at Constant Surface Area

Concentration	Surface	Time for 25% reaction min.		Time for 50% reaction min.	
		30° C.	35° C.	30° C.	35° C.
0.066 M	Pyrex ..	16.1		40.0	
	Silica ..	30.8		80.9	
	Alumina ..	39.4		86.7	
0.05 M	Pyrex ..	42.6	17.3	70.8	30.4
	Silica ..	53.9	25.3	111.2	48.5
0.025 M	Pyrex ..		139.0		216.0
	Silica ..		197.0		283.0

Note: There have been small variations in the bromine concentrations.

TABLE V

Reaction between Trans-Crotonic Acid and Bromine at Constant Surface Area at 35° C.

Concentration	Surface	Time for 10% reaction min.	Time for 25% reaction min.	Time for 50% reaction min.
0.1 M	Pyrex ..	450	1103	4622
	Silica ..	665	3036	
0.05 M	Pyrex ..	535	1172	4207
	Silica ..	945	1984	6823

An inspection of the tables clearly shows pronounced differences between the two acids. While consideration of structural factors may be deferred, the first stage in any mechanistic study is an analysis of the reaction order and the trend of rate constants. In spite of the choice of a nonpolar solvent, a heterogeneous reaction in solution may not show the simplicity of a gas reaction. The present observations are also inadequate for assessing the influence of the products of the reaction. It is also likely that there is a simultaneous homogeneous reaction.

Taking the time required for a given fraction of a reaction, the figures obtained lead to an approximate relationship

$$(c_1/c_2)^3 = t_2/t_1$$

in the initial stages, but, the right-hand side tends to smaller values as the reaction proceeds, the equality being nearly reached when the square of the concentration terms are used. With silica surfaces, the third power relationship does not hold even at the start and falls off later to the first power.

In acetic acid solutions, Robertson and co-workers⁸ find that the reaction is of the third order at the low temperatures at which they worked while Anantakrishnan and Venkatarman working at or above 30° C. find that the reaction is of the second order. The gas reaction according to Gwyn Williams⁶ is apparently of the third order. The difficulty in accepting a third or higher order for the reaction is the definite positive temperature coefficient, though the position is rather complex with crotonic acid which has a small negative temperature coefficient.

It is quite clear, however, that the reaction requires a polar environment for initiation of the reaction, though, it is just possible, that the polarised molecule after leaving the surface may initiate the homogeneous phase of the reaction in the nonpolar solvent also. The data so far obtained is not adequate for the purpose of separating the two phases of the reaction. Preliminary experiments have shown that the addition of dry crystals of sodium bromide or barium sulphate accelerate the reaction while the relative influences of the three different surfaces studied indicate that the presence of both cations and anions at the surface facilitate the reaction. Using only glassy surfaces, it is not practicable to study the geometrical factor but complex silicates appear to afford a better environment than either silica or alumina.

We have to thank the Tennessee Eastman Corporation for a gift of the crotonic acid used.

SUMMARY

The reaction between trans-crotonic acid as well as 2: 2-dimethyl acrylic acid and bromine has been studied in carbon tetrachloride solution in the dark. The reaction is found to be quite a complex one involving both homogeneous and heterogeneous phases. The course of the reaction is governed by the nature of the olefine and the nature of the catalysing surface.

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