

THE KINETICS OF THE OLEFIN-BROMINE REACTION

Part II. The Critical Increment of the Reaction in Acetic Acid

BY S. V. ANANTAKRISHNAN AND R. VENKATARAMAN

(From the Department of Chemistry, Annamalai University, Annamalaiagar)

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It has been shown in Part I that this reaction requires a chain mechanism and that in the presence of a dominant catalyst, an apparently bimolecular constant is obtained. In this part will be presented the influence of temperature on the reaction.

It has already been shown that even in the uncatalysed, autocatalytic reaction, temperature exerts a profound influence, the induction period being completely eliminated at higher temperatures in some cases. The consequences of this thermal activation is felt to an even greater extent in the catalysed reaction. The results are summarised in Tables I, II, III and IV.

TABLE I

Effect of temperature on the hydrogen bromide catalysed reaction between bromine and trans-crotonic acid

Concentration of reactants	Concentration of Hydrogen Bromide (mols. %)	Temperature °C.	Time (mins.) taken for percentage reaction					100 k_2 for 20% reaction	E (calories)
			10%	20%	25%	30%	40%		
M/30	11.01	49.95	36.8	88.0	117.2	148.6	226	8.523	10,140
"	"	42.50	57.2	128.0	170.0	218.4	344	5.860	
"	"	35.40	92.6	198.0	260.6	337	..	3.787	11,840
"	"	25.15	157.2	339	460	2.213	
M/15	"	49.95	10.8	24.8	32.8	42.2	65	15.12	10,400
"	"	42.50	16.3	36.4	48	61.2	94	10.30	
"	"	35.40	24.2	52.3	69.4	90.0	142	7.169	9,840
"	"	25.15	39.2	86	114.8	147.8	238	4.360	

TABLE II

Effect of temperature on the hydrogen bromide catalysed reaction between bromine and tiglic acid

Concentration of reactants	Concentration of Hydrogen Bromide (mols. %)	Temperature °C.	Time (mins.) taken for percentage reaction					100 k_2 for 20% reaction	E (calories)
			10%	20%	25%	30%	40%		
M/30	11.01	50.05	11	23.8	31.4	41	66	31.52	} 6,670 } 5,690 } 6,160
"	"	42.25	13.5	30.8	40.7	52.4	86	24.35	
"	"	35.50	16	37.6	50.3	65.4	105.8	19.95	
"	"	30.10	20.0	45	60.8	78.2	126.4	16.66	
M/15	"	50.05	2.18	4.75	6.37	8.35	12.7	78.94	} 6,210 } 6,180 } 7,520
"	"	42.25	2.64	6.04	8.04	10.62	17.3	62.09	
"	"	35.50	3.25	7.50	10.14	13.12	21.1	49.99	
"	"	30.20	4.25	9.34	12.35	16.06	26.0	40.15	

TABLE III

Effect of temperature on the hydrogen bromide catalysed reaction between bromine and $\beta\beta$ -dimethyl acrylic acid

Concentration of reactants	Concentration of Hydrogen Bromide (mols.%)	Temperature °C.	Time (mins.) taken for percentage reaction					100 k_2 for 20% reaction	E (calories)
			10%	20%	25%	30%	40%		
M/6C	11.01	50.3	13	28	37.3	48	76.2	53.57	} 6,370 } 5,800 } 6,920
"	"	42.6	15.6	35.7	47.8	61.5	97.4	42.02	
"	"	35.5	20.4	44.2	58.3	75.3	119.6	33.94	
"	"	31.6	22.8	50.4	67.6	88.3	150	29.77	
M/30	"	50.3	3.20	6.92	9.18	11.90	19.1	108.4	} 4,400 } 4,460
"	"	42.6	3.72	8.18	10.92	14.4	23.2	91.68	
"	"	35.5	4.24	9.64	12.94	16.88	27.4	77.80	

TABLE IV

Comparison of values of k_2 for the reaction between bromine and *trans*-crotonic tiglic and $\beta\beta$ -dimethyl acrylic acids, catalysed by hydrogen bromide (concentration of reactants, $M/30$) (HBr) = 11.01

Acid	Temperature °C.	100 k_2 for 20% reaction	E (calories)
<i>trans</i> -Crotonic ..	35.4	3.79	10,100
Tiglic	35.5	19.95	6,400
$\beta\beta$ -Dimethyl acrylic	35.5	77.80	4,400

Hinshelwood and co-workers² have shown in other organic reactions the structural influences on energy of activation and it is interesting to examine the relationship in the present instances. At the outset it must be pointed out that quantitative conclusions cannot be drawn at the present stage, but the significant fact will be noticed that substitution of hydrogen by a group belonging to class I of Ingold's classification³ leads to a lower energy of activation for the addition reaction. The experimental values using the Arrhenius equation $k = Ae^{-E/RT}$ are surprisingly low when one compares them with the theoretical deductions of Sherman and co-workers⁴ using the "transition-state" method for the ethylene-bromine reaction. This wide divergence is attributable to several factors: (i) substituted ethylenes may not be expected to require the same energy of activation as the simple unsubstituted ethylene. Before any generalization as to group influences on energy of activation can be made, a better knowledge of mutual group interactions is necessary than is available at present. From *a priori* considerations, however, it can be deduced that the presence of groups activating the ethenoid linkage will tend to lower the energy of activation for the addition reaction as is seen to be the case.

(ii) The "transition-state" method, while it has proved successful in the simpler bimolecular reactions, has still to be applied with success to chain reactions. Treatment of the system as a simple four-electron problem can at best be only a crude approximation.

(iii) The intervention of the solvent cannot be totally excluded, especially, when a polar, hydroxylic solvent is involved as in the present case. It is implicit in the direct calculation of E that there is no great variation in the probability factor. One must admit, however, that the more accurate computation of E will be from the slope of the Log K - 1/T curve (Fig. 1).

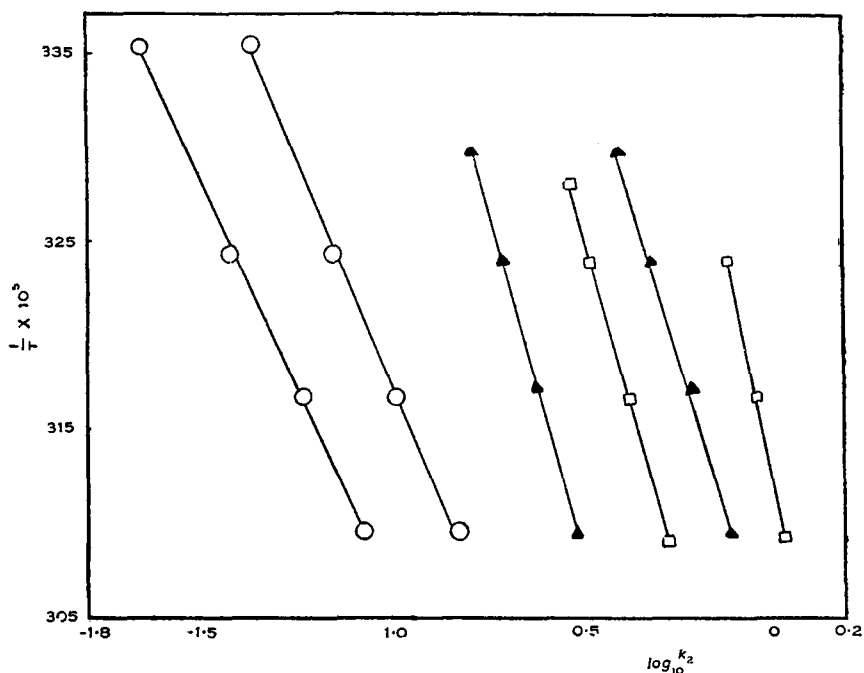


FIG. 1

O-Crotonic acid; ▲-Tiglic acid; □-Dimethyl acrylic acid.

Concentration of reactants: I. M/30. II. M/15 for crotonic and tiglic acids. Dimethyl-acrylic acid: I. M/60. II. M/30.

While the introduction of a second methyl group definitely lowers the energy of activation, the value of E appears to be independent of the relative position of the activating groups with reference to the ethenoid link. The observed difference in reaction velocity between tiglic acid and $\beta\beta$ -dimethyl acrylic acid is obviously due to a difference in the probability factor. No doubt, the greater reactivity of the compound with asymmetric methyl groups can be anticipated from considerations of electromeric displacements as well as of dipole moment. There are, however, limitations to the conclusions that can be drawn from these. While there is a certain amount of correspondence between increased dipole moment and activity of the double bond, it has been noticed that an increase in the number of activating groups results in increased activity even where the moments oppose each other (*cf.*, asym. dimethyl ethylene and tetramethyl ethylene). With the same substituents the compound with a higher dipole moment may be expected to be more reactive, *i.e.*, asymmetric substitution may have a dominant influence. In comparing a series of alkyl ethylenes, this phenomenon was encountered and it was then anticipated¹ that symmetrical dimethylethylene

should react at a slower rate with bromine than the asymmetrical analogue. In the present instance we have the analogous position except for the complication of a carboxyl group that will affect the quantitative aspect of the addition (Table V).

TABLE V

Substance	Substituted product		Relative increase in speed of addition
CH ₃ CH = CH ₂	Symmetrical	Butene-2	2.2*
	Asymmetric	2 methyl propene-1	3.5**
CH ₃ CH = CH COOH	Substituent in 2 position	Tiglic acid	5**
	Substituent in 3 position	Dimethyl acrylic acid	19**

* Calculated value ** Experimental values

It is necessary, here, to consider the relative values of E and of PZ in this case in greater detail. Using molecular models of the type designed by H. A. Stuart⁵ the mean molecular diameters are as given in Table VI.

TABLE VI

Substance	Mean mol. diameter in Å × 10 ⁸
<i>trans</i> -Crotonic acid ..	6.8
Tiglic acid ..	7.5
$\beta\beta$ -Dimethyl acrylic acid ..	7.5

It will be noticed that the molecular dimensions of the two dimethyl acrylic acids ($\alpha\beta$ and $\beta\beta$) are approximately the same and as such no great difference in the collision number may be expected. This naturally means that the greater reactivity of the $\beta\beta$ acid is attributable to an orientation effect. This cannot, however, explain the variation in E with concentration. The tendency to rise with increasing dilution suggests that in the limiting case of the unsubstituted olefin, the value calculated by Sherman may be obtained, especially if a nonpolar solvent is used. This investigation is now in progress.

It is thus clear that much more information than is available now is needed before any theoretical treatment with rigorous methods can be developed to explain all the vagaries of this apparently simple reaction. We are, however, justified in concluding that the ethylene-bromine reaction involves the activation of the bromine molecule as well as the activation of the double bond. Where structural influences are insufficient for such activation the role of the catalyst becomes an important factor, such catalytic activation presumably diminishing with increase of temperature. The change in the energy of activation with concentration and the necessity for the introduction of an orientation factor require an approach from the "transition-state" method for any calculation of reaction constants.

Experimental

The procedure adopted is the same as in Part I, a more steady temperature being obtained with a surface-layer of liquid paraffin for higher temperatures. The nature of the solvent precluded measurements beyond the ranges investigated.

Summary

The dark reaction, catalysed and uncatalysed, between methyl substituted acrylic acids and bromine has been investigated at 25° C., 35° C., 42° C., and 50° C. in glacial acetic acid solution. An analysis of the critical increment shows not only group influence but also an orientation effect.

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