KINETICS OF THE OLEFINE-BROMINE REACTION

Part XIII. The Influence of Substituents and of Solvent on the Mechanism of the Reaction

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In earlier parts in this series we had reported the results of our studies in a variety of solvents as well as with a variety of compounds which showed clearly the complex nature of the addition mechanism. It is the purpose of the present communication to analyse all aspects of the problem in relation to the mechanism of the process as well as the influence of substituents on the reactivity.

In our earlier reports[4] we observed that the reaction exhibited auto-catalytic behaviour but we found that different olefines needed different concentrations of an added catalyst to lead to a bimolecular rate constant. Robertson, de la Mare and their associates[18] had been reporting consistently termolecular rate constants with a very large number of compounds. Variations had also been reported by some of the American workers.[7] Different methods had been adopted by the different schools in the purification of one of the reactants, bromine, but this could not by itself account for all the difference. The explanation had to be sought elsewhere.

It has been generally observed that any possible mechanistic change is revealed by the $\log k - 1/T$ curve.[11] Our work has been generally above 30° C. while those of Robertson and his associates have been generally at 24° C. Experiments conducted at an intermediate temperature showed that there is a pronounced change in the slope revealing one possible cause of the discrepancies. Unlike gas phase reactions, reactions in solution have been often found to give rate constants of higher orders but this can at best be considered to indicate the complex nature of the mechanism. Chemical reactions involve the making of bonds and the breaking of other bonds and all the reactions can be treated as either three-centre or four-centre processes, the present reaction belonging to the latter category. A higher order means only a mechanism in several stages which are possibly of the same order of magnitude in their rates so that no single stage can be reckoned as the rate

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determining step. The need for such an approach can be readily seen from a study of the drift in " bimolecular " and " termolecular " rate constants.[14] Another feature of the reaction which also needs to be accounted for is the pronounced effect of concentration of the reactants on the apparent value of the " rate constants". It is well known that in reactions of the first order, high dilutions can lead to second order rate constants and this change is attributable to the activation process. In the present reaction one can similarly expect a drift from a higher order to a lower order on account of the lifetime of the activated complex in relation to the possible encounters in solutions of different concentrations. This can be readily noticed from the drift in the rate constants with time as also with different initial concentrations.[14] A few examples of this are presented in Table I.

TABLE I

Influence of concentration of reactants on the " rate constants "

Compound	Solvent	Temperature °C.	Concentration	k_3	k_2
Allyl chloride	1	28	M/40	32·75	0·1932
			M/80	34·77	0·1022
			M/160	38·58	0·0573
2-Methyl allyl chloride	1	28	M/80	987·0	2·867
			M/160	1087	1·615
			M/320	1249	0·9374
Stilbene	2	35	M/100	306·6	0·7311
			M/200	304·8	0·3613
			M/400	306·8	0·1812
Trans-crotonic acid	3	35	M/10	0·617	0·0146
			M/20	0·596	0·0071
			M/40	0·790	0·0047
Dimethyl acrylic acid	4	35	M/20	20·39	0·2415
			M/40	24·16	0·1201

k_2 values refer to the initial stages of the reaction only.

Solvents: (1) 60% acetic acid; (2) 40% acetic acid; (3) 100% acetic acid; (4) 80% acetic acid.

Further evidence of a complex mechanism was provided by an examination of the autocatalytic behaviour exhibited by many of the olefines. A

characteristic feature noticed in some of our earlier work was the existence of an induction period for the reaction whose duration varied with the nature of the compound.[6] While in many of these the reaction showed an acceleration with time after an initial slow period, the absence of homogeneous conditions in solutions in carbon tetrachloride revealed an actual retardation by some product.[3, 4] Where there was acceleration, addition of a reaction mixture half way through an induction period to a fresh mixture reduced the induction period in the reaction.[5] Similarly, using a rate equation of the form

$$\frac{dx}{dt} = k\,(a - x)\,(b - x)\,x$$

led to close values for rate constant and an experimental curve conforming to the theoretically computed curve. It was thus clear that the catalyst is produced during the reaction where there was acceleration. Addition of the dibromide was not found to be of any help but hydrogen bromide had a pronounced influence where the reaction needed a catalyst. As with the induction period there is no uniformity in the behaviour of the different olefines and the clue had necessarily to be sought in the analysis of rate constants and the influence of the structure of the olefine. These show that the minimum concentration of initial addition of hydrogen bromide to eliminate induction period and give a second order rate constant varied with the structure and where third order constants were involved, hydrogen bromide had negligible effect. These could be readily seen from the results presented in Table II.

Any postulated mechanism for the reaction has to take into account the solvation of the reactants, the products and the transition state in any examination of solvent influences. The gas phase reaction has been demonstrated to be a heterogeneous reaction and we had noted that in carbon tetrachloride solution a heterogeneous mechanism is unavoidable.[5] The reaction in polar environments happens to be homogeneous. These lead to the necessary conclusion that the reaction is one between polarised molecules. Now, the halogen molecules are well known to dissociate under the influence of light into atoms before participating in reactions. Does this mechanism have any part in the thermal reaction ? A free radical process will not show any direct correlation with the dielectric constant of the medium. The present reaction is certainly one where this property is essential. Whether in gas phase or in solution a polar environment is a prerequisite. With polarised molecules as the reactants, the only picture for the first stage of the reaction has to be the Roberts and Kimball mechanism.[17] In forming this

TABLE II

Catalysis by hydrogen bromide in relation to structure and reaction order

Compound	Concentration of HBr (moles %) of Br_2	Temp. °C.	"Bimolecular rate constant"	Conc.	Induction period of uncatalysed reaction (minutes)
Crotonic acid	1·05	35	0·0168– 0·0238	M/15	25
	2·10		0·0192– 0·0269		
	6·90		0·0538– 0·0554		
	7·80		0·0521– 0·0545		
Fumaric acid	11·01	35	0·00185– 0·0217	M/30	1062
		43	0·00459– 0·00512		
		50·6	0·0118– 0·0127		
Stilbene	11·01	43	10·80 – 10·89	(M/600 solutions)	
		50·6	15·08 – 0·08		*ca* 3·8

transition state, one has to recognise that initially all the sigma bonds of the ethylene system are in one plane while the pi-electrons are' in the plane perpendicular to this. The formation of the transition state can then be described thus (Fig. 1).
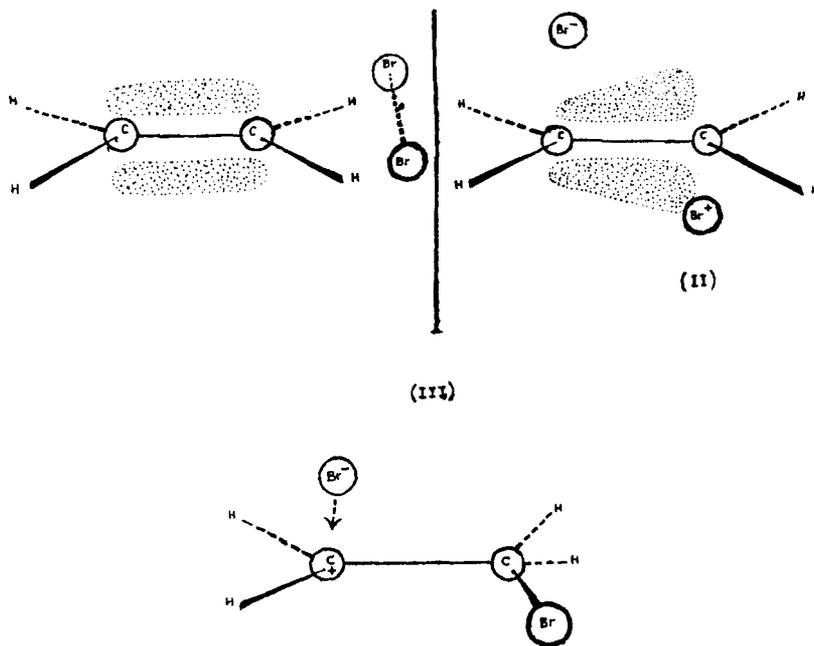

FIG. 1.

A consequence of such a picture is the greater degree of solvation of the transition state compared to the reactants or products. Further, since a polar solvent is more likely to be associated with activated complex than the non-polar one, where solvent mixtures are involved, transient discontinuities in the liquid structure may be present and use of the dielectric constant of the mixture may not indicate a true picture. However, with acetic acid-carbon tetrachloride mixtures, the range of dielectric constants is small and no serious error arises in using this property, while one may expect to notice abnormalities in the region of small additions. A comparison can be made of the rate constants and Arrhenius parameters in mixed solvents. Some of our results are presented in Table III and Fig. 2.

TABLE III

Influence of solvents on the reaction between olefines and bromine

Compound	% Acetic acid in solvent mixture	$(D-1)/(2D+1)$	k	E_a	$\log_{10} PZ$
Allyl chloride	100	0·3887	508·2	2·82	2·94
	80	0·3598	143·1	1·07	1·14
	60	0·3225	36·15	1·08	0·55
2-Methylallyl chloride	80	0·3598	4642	2·58	3·71
	60	0·3225	1145	1·87	2·6
	40	0·2837	247	0·83	1·2
Stilbene (*trans*)	80	0·3598	3698	5·43	5·63
	60	0·3225	1074	5·52	5·16
	40	0·2837	304·8	5·32	4·49
	20	0·2514	74·53	··	··

k values are in conventional units.

Activation energies are in kilocalories.

In the absence of accurate estimates of the solvation energy of the reactants, products and the transition state and the heat of the reaction, it is difficult to make effective use of the experimental activation energies presented in Table III. Sherman using Eyring's method estimated the activation energy for the reaction treated as a four-centre process and gives a value of the order of 20 K. cals.[8,19] One can then consider that any value of the order of 10 K. cals. is of the right magnitude, but the observed values are very much
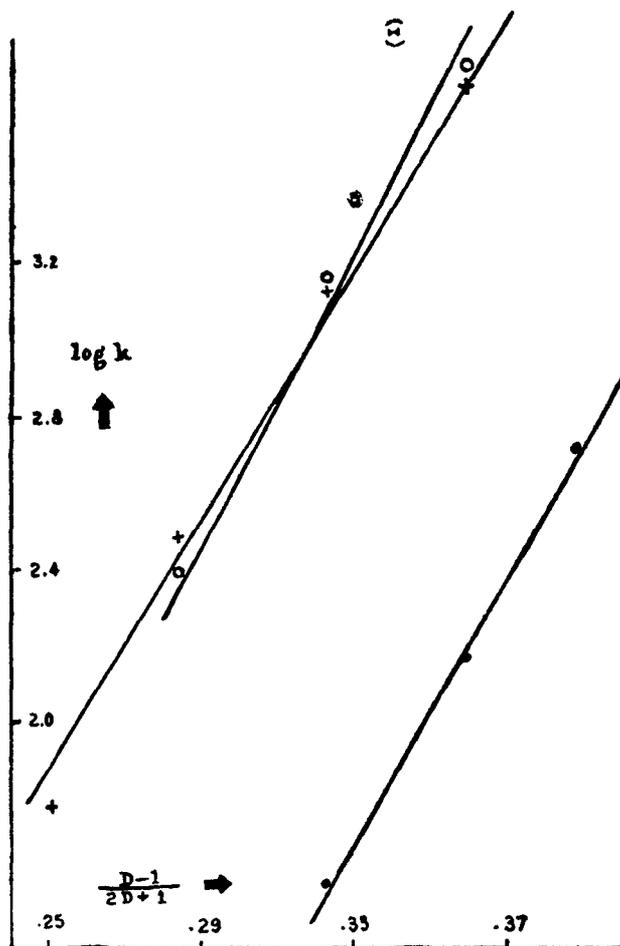
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Fig. 2.

lower and the difference necessarily arises from solvation energies as no large differences can be caused by changes in the free energy of reaction. Changes in the pre-exponential term are, however, interesting in indicating the nature of the reaction. Noyes has shown[16] that in a diffusion controlled reaction, low values of the pre-exponential term are to be expected. The present reactions are clearly of the diffusion controlled type with the solvent taking up part of the energy released in the process. Part of the reduction in the PZ values should be assigned to the requisite entropy of activation as strict geometrical approach in the appropriate position is called for. The nature of the reaction precludes a calculation of the entropy of activation.

For a proper comparison of reactivities of ethylene derivatives, normally it is not correct to use the rate constant alone for comparison on account of the composite nature of this quantity. However, with an apparently complex mechanism, we have no other means of comparison. Even here, the values exhibit such a wide range that one has to further subdivide into groups for estimates of relative values as the reaction environment is not the same in all cases. For a fuller analysis, we can also examine the classification of the substituent groups. Most of the compounds so far studied involve electrophilic attack and the classification of Ingold can be used for the purpose.[11a] Some of the comparative rates are presented in Table IV.

TABLE IV

Influence of substituents on additive reactivity of ethylenes

Solvent	Concentration	Compound	Relative rate
Acetic acid	M/40	*Trans*-crotonic acid	1·00
		Tiglic acid	5·00
		$\beta\beta$-Dimethyl acrylic acid	45·0
		Maleic acid	0·10
		Fumaric acid	0·05
		Maleic anhydride	(0·15)*
		Citraconic anhydride	(0·18)*
60% Acetic acid⎱ 40% CCl₄ ⎰	M/80	Allyl chloride	1·40
		Allyl bromide	(1·00)*
		Methylallyl chloride	43·0
		Allyl propionate	29·0
40% Acetic acid⎱ 60% CCl₄ ⎰	M/400	Styrene	154·0
		Trans-stilbene	1·00
		Triphenyl ethylene	17·0
		Tetraphenyl ethylene	0·00
		Cyclohexene	(4500)*

* Estimated values.

It will be observed that electrophilic initiation of attack is facilitated by substituents of the + I group, unsymmetrical substitution being more effective than symmetrical ones. A group in the class —I—T is more deactivating than one of the group — I + T. One of the ± T groups can be activating

but resonance effects may lead to deactivation with symmetrical substitution unlike the 1 group. With several substituents, the final result will be dependent on the overall dipole moment and the resultant polarisability of the double bond. With existing data no quantitative estimate is possible.

While the substitution of hydrogen by alkyl groups modifies the reactivity cumulatively, the results indicate a certain degree of influence by the symmetry properties of the molecules of reactants or even of the transition state. The significance of this can be seen from the observations on allylbromide, *trans*-diphenyl ethylene and the methyl butenoic acids. The absence of reactivity of tetraphenyl ethylene towards bromine is the result not only of energy considerations through pi-electron interactions but also the effective screening of the reaction zone by the bulky groups present.

We have indicated how it is not possible to draw strictly quantitative conclusions from the Arrhenius parameters but some correlation is possible. Fairclough and Hinshelwood[9] had shown that very often the two parameters are related such that the graph $E^{\frac{1}{2}}$—log PZ is linear in many cases though deviations are not unknown. Our results show three different types of behaviour:

(a) Both PZ and E change in the same direction;

(b) E is constant but PZ changes;

(c) PZ is constant and E changes.

Now, the first behaviour is typical of systems when the interval between activation and deactivation is small compared to the attainment of the right phase for the reaction. The second type of behaviour is possible when all the factors indicated by Eyring[10] that modify this pre-exponential term are operative.

We are now in a position to examine the mechanism of the reaction. Unlike the iodine molecule, bromine shows little polarity so that irrespective of any postulated reaction orders, the participation of polymeric molecules can be ruled out. Using the Kirkwood correlation between $\log k$ and $(D - 1)/(2D + 1)$[12] a linear correlation is generally noticed (*cf.* Fig. 2) but, in the region of lowest dielectric constants, there is pronounced deviation from linearity. Deactivation before the attainment of the right configuration and the greater solvation of the transition state by a polar solvent account for this. On the part of the olefine, we have to consider the transmission of electrical effects by substituents to the reaction zone as well as the susceptibility to such changes in electron density. The topology of the

transition state as well as the effect of temperature on mechanistic changes have also to be accounted for. The significant features that have contributed to the mechanism are listed below:

(i) The reaction requires a polar environment;

(ii) The initiation of attack is by a polarised bromine molecule which is mostly electrophilic but structural influences can facilitate nucleophilic attack as well;

(iii) The reaction is a dipole-dipole reaction;

(iv) Both temperature and concentration lead to changes in the reaction order;

(v) Termolecular processes are favoured by low temperatures, non-polar solvents, higher concentrations and deactivating groups;

(vi) Bimolecular processes are facilitated by higher temperatures and dilutions, polar solvents and activating groups.

(vii) Bimolecular processes may be catalysed while termolecular ones are not;

(viii) Changes in configuration are possible only in some cases;

(ix) Autocatalysis as well as retardation by products occur.

Taking all these factors into account with the Roberts and Kimball picture of the initial stage as the basis, we can put forward a mechanism for the reaction:

Stage (i) Formation of a complex between the olefine and the bromine molecule;

Stage (ii) Transformation of this pi-complex into an 'Onium resonance hybrid and bromide ion;

Stage (iii) Formation of the dibromide.

The situation appears to require a concurrent bimolecular and termolecular process as a normal course which can be qualitatively pictured thus (Fig. 3). Where one of the processes becomes dominant, the result is only a change in the mechanism of formation of the 'Onium state.

The catalytic effect of hydrogen ions is not abnormal. Winstein and Lucas,[21] R. W. Taft[20] as well as McCauley and Lien[15] have provided evidence for the association of the proton with the pi-electrons of an olefinic system and this polarisation can facilitate the formation of the bromonium
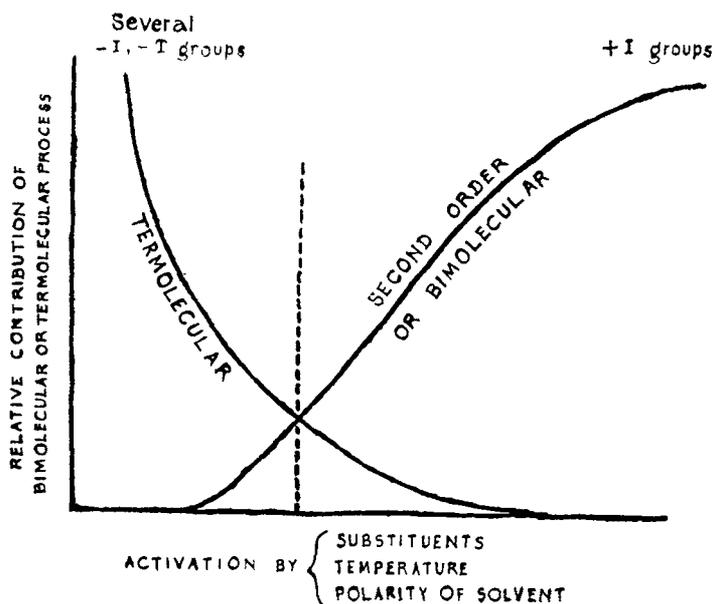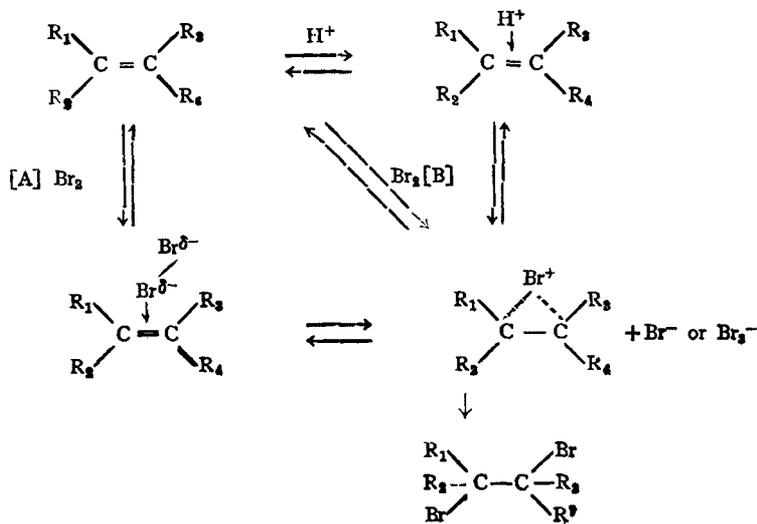
Fig. 3.

complex. The ionisation potentials of carbon and of bromine are sufficiently close to stabilise the resonance hybrid of the 'Onium type and not the least function of glacial acetic acid in facilitating the reaction is its effect on the carbonium ion stabilisation. We may then put forward the mechanism below for the addition process:

We have thus to conclude that the olefine-bromine reaction is a complex concurrent second order and third order reaction in which one or other is dominant in a few cases depending on structure and environmental conditions. There is as yet inadequate experimental work under conditions in which the reaction is initiated by the anionic part of the polarised bromine molecule. Further elucidation needs data with compounds with a carbonyl or nitro group adjacent to the double bond and also a solvent environment stabilising a carbon ion. Similarly the generalisation usually found in text-books that the *cis*-form is more reactive than the *trans*-isomer is also one which requires modification. Some of our own observations as well as the work of Buckles and Yuk[7] have shown that there are instances where the *trans*-form is more reactive and only further work can reveal whether there are not other examples of this type. Even in these variants, the essential feature is still one involving the pi-complex indicated in the mechanism so that the reaction is essentially bimolecular. A comparison of additive reactivity and substituent influence is, however, one that can be made only among the group following the same mechanism and the results of the competition experiments[2] gives an approximate degree of comparison, assuming that the presence of a fast reacting olefine does not modify the rate of a slower one. This aspect, too, needs elucidation.

SUMMARY

A complete analysis of the work on the addition of bromine ethylene derivatives under varying conditions of structure, solvent and temperature brings out the composite nature of the reaction. With the Roberts-Kimball postulate as the starting-point, it is found that the variations in reaction order can be readily understood from the variations in the importance of the rate determining step. A mechanism incorporating all the details is presented.

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