31. *The Kinetics of Iodine Addition to Olefinic Compounds.*

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In a recent investigation on the kinetics of bromine addition it was shown that the reactions in acetic acid were termolecular; in carbon tetrachloride they took place predominantly on a surface film, which was relatively stable within definite concentration–temperature limits characteristic for the adsorbed substance. It is now found that iodine addition follows a similar course, being termolecular with low heats of activation in the dissociating solvents nitrobenzene and acetic acid, heterogeneous in the non-polar media carbon tetrachloride and hexane. Certain constitutive influences are now noted under definitely non-heterogeneous conditions, and found to be in accordance with electronic conceptions.

The surface reactions between iodine and compounds such as allyl alcohol and undecenoic acid are unexpectedly rapid, and it seems necessary to assume a suddenly enhanced activation of the molecules at the moment of impact.

In comparison with the extensive researches on bromine addition, there has been relatively little work on iodine addition in organic solvents. Such investigations are troublesome, being for the most part very slow, and disturbed by the incidence of a reverse reaction, which is catalysed by iodine. Herz and Mylius (*Ber.*, 1907, **40**, 2898) found in the reaction of allyl alcohol with iodine, in carbon tetrachloride, chloroform, and carbon disulphide, that bimolecular constants were obtained in the individual experiments, but they varied considerably with the concentration. The results of Meyer and Pukall (*Z. physikal. Chem.*, 1929, **145**, 360) showed similar discrepancies. Schumacher (*J. Amer. Chem. Soc.*, 1930, **52**, 3132) concluded that the reaction $C_2H_4 + I_2$ in carbon tetrachloride was homogeneous, proceeding by a chain mechanism.

The investigation by Caughley and Robertson (J., 1933, 1323) was designed more especially to examine the equilibria set up between iodine, allyl alcohol, and its addition product. The reactions appeared bimolecular, and it was unexpectedly found, although not explained at the time, that in a series of non-dissociating solvents there were very considerable differences in rate: benzene ($k_2 = 0{\cdot}01$); toluene ($k_2 = 0{\cdot}02$); carbon tetrachloride ($k_2 = 0{\cdot}07$); hexane ($k_2 = 2{\cdot}1$). An investigation of the conditions determining bromine addition (Robertson, Clare, McNaught, and Paul, J., 1937, 335) revealed that the reactions in a solvent like carbon tetrachloride with low internal pressure were heterogeneous, taking place largely on activated surface films. It is significant, therefore, that the k_2 values quoted above are in the inverse order of the internal pressures of the solvents. It was further shown that bromine addition in a dissociating solvent such as acetic acid was a termolecular reaction with a very low heat of activation, two molecules of bromine participating for each molecule of unsaturated compound.

In the light of these results a more detailed examination of iodine addition in a range of solvents has been undertaken. With concentrations of the order M/50, the equilibria for allyl compounds are in the region corresponding with 50% iodine absorption. By having the unsaturated compound in excess ($A = \text{M}/2$, $I_2 = \text{M}/50$), the equilibria are shifted to a region with 95% absorption. The back reactions thus become practically negligible under these conditions over the first 50% of the iodine absorption. There is further the very important advantage that the velocities are greatly increased, thus allowing the necessary data to be much more expeditiously collected.

The Homogeneous Reactions.—Iodine additions in acetic acid and nitrobenzene are termolecular; the compounds examined were allyl alcohol, its acetate, benzoate, and bromide, and undecenoic acid. This is evident from the following considerations :

(1) With the unsaturated compound in excess, constant pseudo-bimolecular values k_2 are obtained, as illustrated by the following typical results :

Iodine consumed, % (x)	10	20	30	40	50
Allyl alcohol in $PhNO_2$ ($I_2 = \text{M}/50$, $A = \text{M}/2$), 25°	2·9	3·0	3·1	3·0	3·1
,, ,, ($I_2 = \text{M}/100$, $A = \text{M}/4$), 25°	1·5	1·5	1·5	1·6	1·6
Undecenoic acid in HOAc ($I_2 = \text{M}/50$, $A = \text{M}/2$), 13°	2·4	2·4	2·4	2·4	2·3
,, ,, ,, ,, 45°	3·7	3·8	3·8	3·9	4·1

(2) By halving the concentrations of both reactants the k_2 values are halved and the times for the same percentage change reduced to a quarter, in accordance with the theoretical expectation, as illustrated above for allyl alcohol.

(3) With the reactants, $I_2 = \text{M}/40$, $A = \text{M}/80$ and $I_2 = \text{M}/80$, $A = \text{M}/40$, the initial rate at $x = 10\%$, *i.e.*, before the back reaction is appreciable, is greater when the iodine is in excess.

The iodine additions therefore correspond with the bromine additions, and like them, are also characterised by low heats of activation. The following k_2 values ($I_2 = \text{M}/50$, $A = \text{M}/2$) were obtained at different temperatures.

		14·4°.	25°.	35°.	45°.	55°.	*E*.	$B \times 10^{-3}$.
Allyl acetate in HOAc	k	—	0·085	0·13	0·17	0·22	6,100	19
	(k)	—	0·090	0·12	0·17	0·23		
Allyl alcohol in HOAc*	k	—	0·21	0·29	0·35	0·46	4,800	5·2
	(k)	—	0·21	0·28	0·36	0·45		
Allyl alcohol in $PhNO_2$	k	2·54	3·06	—	4·44	—	3,300	6·2
	(k)	2·50	3·10	—	4·38	—		

* F. p. measurements under similar conditions indicated no esterification.

The values denoted by (k) are obtained from the straight-line log k–$1/T$ curve, and E is calculated graphically. To obtain the B parameters in the Arrhenius equation, $k_3 = Be^{-E/RT}$, the values of k_3 were obtained from the expression $k_2 = bk_3/4$, since rate $= k_3(b - x)[(a - x)/2]^2$, and x is small in comparison with b, the concentration of the component in excess. With increase in the rate of iodine addition there is a reduction of E. The B parameters in the corresponding bromine additions, which proceed 10^4 times as fast, are in the region 10^5 (l. g.-mol.$^{-1}$min.$^{-1}$).

The following table shows the effect of solvent on the rate of iodine addition. For the purposes of comparison pseudo-bimolecular k_2 values are given ($A = \text{M}/2$, $I_2 = \text{M}/50$), although the reactions in the non-polar solvents do not proceed by this mechanism.

Solvent	$PhNO_2$	HOAc	PhCl	CCl_4	C_6H_{14}
Allyl alcohol, k_2 (25°)	3·1	0·22	0·41	0·41	0·65
Allyl acetate, k_2 (25°)	0·94	0·088	0·040	0·006	0·009

The Heterogeneous Reactions.—Whereas iodine additions in nitrobenzene and acetic acid, which form brown solutions, are homogeneous and termolecular, those in chlorobenzene, carbon tetrachloride, and hexane (*i.e.*, the violet solutions) are heterogeneous. This conclusion is reached as a result of the following observations : (1) When the reaction vessel is packed with glass beads, the reaction proceeds more rapidly, and this increase may be very considerable; for instance, in the reaction between M/40-iodine and M/40-allyl alcohol in hexane at 25°, the rate was increased 15-fold. Such " packing " not only enlarges the surface area, but also decreases the average striking distance of the molecules from the surface. (2) On reducing the concentrations of the reactants, a region is reached where there is a rapid diminution in velocity. Similar observations were made with reference to bromine addition, and it was concluded that for a given solvent at each temperature there is a limiting concentration below which the surface film becomes unstable:

Iodine and allyl alcohol, both M/100; k_2 (25°) = 0·058; both M/200, k_2 (25°) = 0·004.
Iodine and undecenoic acid, both M/50; k_2(25°) = 0·070; both M/100, k_2(25°) = 0·011.

(3) Similarly there is a limiting temperature, above which the adsorbed film becomes unstable with a rapid diminution in reaction rate: For M/100-iodine and -allyl alcohol, k_2(25°) = 0·058; k_2(35°) = 0·0009.

With the unsaturated compound in excess the heterogeneous effects are modified owing to its preferential adsorption; and this is reflected in the smaller differences in rate with different solvents. Thus at 25°:

I_2 = M/40, allyl alcohol = M/40; k_2 (CCl_4) = 0·0012; k_2 (C_6H_{14}) = 0·036.
I_2 = M/40, allyl alcohol = M/2; k_2 (CCl_4) = 0·41; k_2 (C_6H_{14}) = 0·65.

With the organic component in excess, constant pseudo-unimolecular values, k_1, are obtained when the relative adsorption is considerable. Thus for allyl alcohol at 25°:

Iodine consumed, % (x)	10	20	30	40	50	60	70
In C_6H_{14}; I_2 = M/50, A = M/2	0·008	0·010	0·011	0·012	0·012	0·013	0·012
In C_6H_{14}; I_2 = M/100, A = M/2	0·0031	0·0029	0·0029	0·0030	0·0031	0·0032	0·0032
In CCl_4; I_2 = M/50, A = M/2	0·0070	0·0069	0·0067	0·0067	0·0069	0·0069	0·0068

This constancy of k_1 may be, however, in part accidental. The decrease in volume of the solvent under the experimental conditions increases the surface–volume ratio; the resultant increase in k_1 must consequently be offset by a slight decrease in the activity of the surface film.

Whereas the relative rate of iodine addition to allyl alcohol and allyl acetate in dissociating solvents is 3 : 1, yet in carbon tetrachloride and hexane it is 100 : 1. The relative rate of the heterogeneous reactions will depend on (*a*) the density of the surface film, the number of molecules per unit area, (*b*) the effectiveness of the impacts on this film, and such effects may not at present be distinguished. For allyl alcohol this total effect is relatively so great that the temperature coefficient, although irregular, is positive; for allyl acetate, however, under the same conditions, it is negative.

The adsorption effect for allyl alcohol in hexane is so considerable that iodine addition is more rapid in this solvent than in acetic acid. Halogen addition is determined by the polarity of the halogen molecule, bromine chloride, for example, reacting more rapidly than bromine, and this causes the initial attack by the positive halogen atom. In the brown iodine solutions such polarity may be enhanced by the formation of complexes, $XO \rightarrow \overset{\curvearrowright}{I{-}I}$. The high reactivity of iodine in the violet solutions is consequently unexpected, since in such solvents as benzene and carbon tetrachloride iodine is completely non-polar (*Nature*, 1935, **135**, 71). It must therefore be assumed that the iodine molecule becomes polarised immediately prior to addition, by an impact with the surface film. Such an effect might be more considerable with the hydroxyl group than with the less strongly polar acetoxy-group, and the heterogeneous rates thus correspondingly influenced.

Constitution and Iodine Addition.—A general examination, in terms of the electronic theory, of the conditions determining the rate of halogen addition has been made by Ingold and Ingold (J., 1931, 2354). In brief, their theory states that the ease of addition is dependent, not so much upon the induced polarity of the ethylene carbon atoms, as upon the electronic condition of the ethylene system as a whole. This acts in a sense as an electron sink; electron accession to it will favour, and electron regression from it will hinder, halogen addition. Accordingly, the methyl group will have an accelerating, and carboxyl group a retarding, influence, the electromeric effect here acting in the same sense as the inductive effect; with bromine these two influences act reversely, but the inductive effect for this type of reaction is more powerful, so that bromine attached to an ethylene carbon will reduce the rate of halogen addition. To test these theoretical conclusions, we carried out experiments on the relative rates of bromine addition to various compounds in dichloromethane at —35°. Actually, the conditions, *viz.*, low temperature and solvent of small internal pressure, even if hydrogen bromide is present (Ingold and Anantakrishnan, J., 1935, 984), favour heterogeneous reactions, and the rates of addition may be influenced by factors other than those theoretically considered. For instance, whereas allyl acetate and allyl benzoate add bromine at the same rate in acetic acid solution, the heterogeneous rates in carbon tetrachloride are in the ratio 100 : 1. Similarly, allyl alcohol and allyl acetate add iodine in dissociating solvents in the ratio 3 : 1, and in hexane in the ratio 70 : 1.

The iodine additions with certain typical compounds now to be considered have been carried out under conditions where heterogeneous disturbances are absent, and the following relative rates have been obtained from a comparison of the pseudo-bimolecular k_2 values : $CH_2{:}CH_2$ (0·10), $CH_2{:}CH{\cdot}CH_3$ (1), $CH_2{:}CH{\cdot}[CH_2]_8{\cdot}CO_2H$ (3), $CH_2{:}CH{\cdot}CH_2{\cdot}OH$ (0·28), $CH_2{:}CH{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}CH_3$ (0·078), $CH_2{:}CH{\cdot}O{\cdot}COPh$ (0·067), $CH_2{:}CH{\cdot}CH_2Br$ (0·028).

These results are in accordance with the theory of Ingold and Ingold. The methyl group has an accelerating influence, and the effect is greater with $[CH_2]_8{\cdot}CO_2H$, which acts as an alkyl, the distant carboxyl group being negligible. The hydroxyl group and the bromine atom reduce the rate when substituted in propylene, and the electron-absorbing groups acetyl and benzoyl cause the allyl esters to be less reactive than allyl alcohol. One exception, however, has been noted; allyl iodide, which might be expected to have a reaction rate of the same order as allyl bromide, does not add iodine in acetic acid solution. This may be due to the instability of the ion formed at the first stage of the addition; $CH_2I—\overset{\oplus}{C}H—CH_2I$, owing to the presence of two iodine atoms with their relatively loosely held electrons, breaks up immediately into allyl iodide and the positive iodine ion. Allyl iodide with bromine, it may be noted, reacts rapidly at first, but the reaction then slows down very considerably, reaching an equilibrium : this is possibly due to a similar change,

$$CH_2Br—\overset{\oplus}{C}H—CH_2I \longrightarrow CH_2Br–CH{=}CH_2 + \overset{\oplus}{I}.$$

The tentative suggestion is made that the rapid surface reactions discussed above are possibly simple prototypes of the reactions taking place on the surface of the living cell. These similarly indicate a high effectiveness of impact; they show also a falling off in rate at higher temperatures; and they increase suddenly in rate above a certain limiting concentration of reactant, as appears for example in the action of certain hormones.

EXPERIMENTAL.

The reacting compounds and solvents were as described in previous communications (J., 1933, 1323; 1937, 335). The nitrobenzene (Merck), m. p. 5·35°, was unaffected in solvent activity after fractionation. The hexane, after being left for 24 hours with 96% sulphuric acid, had b. p. 67·5—68·5°/750 mm. The ethylene and propylene, prepared by the phosphoric acid method (Newth, J., 1901, **79**, 915) and purified by ice-cooling and passage over potassium hydroxide and calcium chloride, were absorbed in acetic acid–carbon tetrachloride (1 : 1), the ethylene not being sufficiently soluble in pure acetic acid. Independent experiments had shown that the reactions in this mixed solvent were not heterogeneous. The strengths of these solutions were determined with Wijs's reagent and diluted accordingly. The velocity ratio of ethylene to propylene was thus determined; the latter was compared with allyl alcohol in this same solvent, and the relative velocities of the various compounds obtained.

The titrations were carried out as previously described; the values of k obtained from the smoothed curves are in l./g.-mol.-min. In the nitrobenzene experiments it was necessary to add some substance such as ether before titration. Most of the significant results have already been quoted in the text. When k_2 values are quoted for the heterogeneous reactions to show comparative rates, the $x = 20\%$ values are given.

For certain of the reactions in acetic acid and nitrobenzene the equilibria were examined, and found not to conform with the simple equation, $I_2 + A \rightleftarrows AI_2$. This is due in part to the termolecular nature of the forward reaction, and in part to the catalytic influence of iodine on the reverse reaction. The dissociation of ethylene di-iodide in carbon tetrachloride has been examined by Polissar (*J. Amer. Chem. Soc.*, 1930, **52**, 956) and found to be autocatalytic. Similarly, measurements of the dissociation of the addition compounds of allyl alcohol and iodine, and allyl acetate and iodine, were found (experiments of F. G. Caughley and J. L. Mandeno) to give rising k_1 values in alcoholic solution, whereas k_1 would be expected normally to fall owing to the incidence of the reverse reaction.

The effect of water on the rate of iodine addition in acetic acid has also been examined. The following values, for A = M/2, I_2 = M/40, were obtained at 25° :

H_2O, %	0	5	10	15
k_2	0·21	0·49	0·84	1·4

For the corresponding bromine additions the influence of water is very much greater, 10% of water increasing the rate 100-fold. In the bromine additions it was shown that there was a change from a termolecular to a bimolecular rate. With iodine, no such effect is observable.

This investigation is being extended to the corresponding reactions of chlorine, bromine chloride, and iodine chloride.

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