

451. The Kinetics of Halogen Addition to Unsaturated Compounds. Part XVIII. Iodine Addition.

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This is a general revision of the kinetics of iodine addition, with a note on the equilibria in these reactions. The rate of iodine addition over the concentration range that can be measured is given by the expression

$$-d[I_2]/dt = k_4[A][I_2]^3 + k_3[A][I_2]^2$$

the first term being chiefly operative in solvents such as chlorobenzene, carbon tetrachloride, and carbon disulphide, and the second term in *isobutyl* ether, acetic acid, and nitrobenzene solutions. With certain aromatic compounds such as styrene and its derivatives iodine addition is accompanied by polymerisation.

An earlier investigation on the kinetics of iodine addition (Bythell and Robertson, *J.*, 1938, 173) established that these reactions, like the corresponding bromine and iodine chloride additions, showed third-order kinetics, with a small temperature coefficient in acetic acid and nitrobenzene solutions. Erroneous theoretical conclusions, however, were made from the measurements in carbon tetrachloride solution, chiefly as a result of confining the observations to a single compound, allyl alcohol, the behaviour of which is now found to be anomalous. In the meantime several communications on the kinetics of iodine addition have appeared. Bhattacharyya and Rao (*J. Indian Chem. Soc.*, 1941, 18, 253), using 2-pentene and phenylacetylene as reactants, found third-order kinetics for iodine addition in acetic acid and ethyl alcohol solutions. Ghosh *et al.* (*ibid.*, p. 245) state that iodine addition in carbon tetrachloride, carbon disulphide, and benzene solutions proceeds by a fourth-order mechanism. These observers, following Groh and Szelestey (*Z. anorg. Chem.*, 1927, 162, 333), who had previously investigated erucic acid in carbon tetrachloride and carbon disulphide and found fourth-order kinetics, employed an elaborate formula, derived from the integration of the expression, $-d[I_2]/dt = k_4[A][I_2]^3 - k_3[AII][I_2]^2$, and obtaining constant k_4 coefficients for β -amylene and pinene, concluded that the reaction proceeds, $A + I_2 \rightleftharpoons AII + 2I_2$.

We, on the other hand, have followed the simpler procedure of adjusting the concentrations with one reactant A in excess, to reduce the effect of the reverse reaction, and have evaluated the reaction order by measurements at different initial concentrations. To obtain the relative contributions of A and I_2 to the total reaction order, use was made of the formula :

$$t_2/t_1 = (c_1/c_2)^{n-1} (c'/c'')^n$$

where t_1 and t_2 are the times of an equal fractional change of iodine addition, with concentrations c_1 and c_2 for I_2 , and c' and c'' for A, n being the order for I_2 and n' for A. The proposed formula holds only for the initial stages of the reaction, to $\sim 10\%$ iodine addition, over which range, as is found experimentally, the % addition-time curves are approximately straight lines.

Employing this formula, we have established that in polar solvents, *e.g.*, acetic acid, *isobutyl* ether, chloroform, chlorobenzene, and nitrobenzene, the reaction order for the organic compound (A) is unity; in the non-polar solvents carbon tetrachloride and carbon disulphide, on the other hand, the value calculated for A is greater than one. This is not considered to be due to the participation of an addition compound, A, I_2 , in the reaction, because in such a compound the iodine would be unfavourably polarised for electrophilic attack; it is rather a solvent action in which the iodine molecule is polarised by the unsaturated compound, and is not found when the solvent itself is sufficiently polar. Another means by which the iodine molecule may be polarised is by a solid polar catalyst. With glass, such heterogeneous catalysis is slight, being not at all observable in polar solvents, and in carbon tetrachloride and carbon disulphide only at low iodine concentrations, as it is obscured at greater concentrations by the participation of high-order homogeneous reactions. The strongly polar barium sulphate is more effective than glass, and thus iodine addition is analogous to bromine addition, although the catalysis generally is weaker (*cf. J.*, 1945, 509).

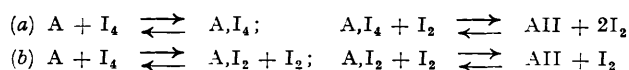
As the result of a number of measurements, examples of which are given in the Experimental part, the rate of iodine addition may be shown by the general expression :

$$-d[I_2]/dt = k_4[A][I_2]^3 + k_3[A][I_2]^2$$

In chlorobenzene, and in carbon tetrachloride and carbon disulphide (violet solutions) when the concentration of the organic compound is not too great, with iodine concentration *ca.* M/50,

the first term chiefly is operative at 25°, whereas the second term is dominant in the solvents acetic acid, *isobutyl* ether, and nitrobenzene (brown solutions). The fourth-order reactions have a very small temperature coefficient, often not much greater than unity, whilst third-order addition is rather more sensitive to temperature. The reversible nature of iodine addition precludes the search for a second-order reaction at low concentrations. It is believed, however, that this mode of addition may not proceed, since on the addition of water to the solvent acetic acid (which for bromine addition causes a considerable increase in rate and a progressive change from third- to second-order kinetics) iodine addition is only slightly accelerated, and the reaction order remains unchanged.

It is apparent that, before it becomes reactive, the iodine molecule requires to be polarised, if not by a solid polar catalyst or a polar solvent, at least by another molecule of iodine, but it is not necessary to assume, as was done by Groh and Szelestey (*loc. cit.*), that in the fourth-order reactions iodine reacts as I_4 molecules. Groh and Tacaes (*Z. physikal. Chem.*, 1930, **149**, 195) have shown that iodine does not obey Beer's law in carbon tetrachloride and carbon disulphide solutions, but this could also be explained as due to association to I_4 molecules. On this assumption two alternative schemes are available for fourth-order kinetics :



According to each of these the final reaction is the relatively slow rate-determining stage, but whereas (*i.e.*, during the initial part of the reaction) in (*a*) stationary concentrations are maintained, in (*b*) the intermediate, A, I_2 , accumulates as the reaction proceeds. Iodine addition in showing mixed third- and fourth-order kinetics is thus similar to bromine addition and substitution, which reactions have been discussed in previous communications (*J.*, 1947, **633**; 1948, 101).

The reason why the reaction order is less in the brown solutions, in which there is compound formation, is due to the fact that the equilibrium, $I_4 \rightleftharpoons 2I_2$, is shifted to the right by the action of the solvent, which establishes a new equilibrium, $I_2 + S \rightleftharpoons S, I_2$. Two main factors appear to determine the relative rates of iodine addition in the brown solutions, compared with the reactions in a solvent such as carbon tetrachloride : (*a*) the polarity of the solvent which tends to increase the rate, and (*b*) compound formation ($S \rightarrow I-I$) which would be expected to decrease the rate. In a solvent such as *isobutyl* ether the second effect appears to be dominant, and rates are considerably less than in carbon tetrachloride, but in the more strongly polar nitrobenzene iodine addition is more rapid than in carbon tetrachloride.

The compounds on which the above conclusions are based included hex-1-ene, pent-2-ene, cyclopentene, dec-1-ene, undecenoic acid, and oleic acid. With the concentrations examined, the iodine absorption at equilibrium was in the region of 90%, so that the influence of the back reaction is inconsiderable at the initial stages of the forward reaction. Other compounds, *e.g.*, *tert.*-butylethylene, 2-methylbut-1-ene, trimethylethylene, tetramethylethylene, gave on the attainment of equilibrium at similar concentrations a lower iodine absorption, so that such measurements could not conveniently be used for fixing the reaction order, or for investigating the influence of constitution on the rate of iodine addition.

The reactions of the above-mentioned compounds appeared to give equilibria which changed in accordance with the law of mass action, and varied in a regular way with the temperature. It was concluded, therefore, that the iodine addition, the kinetics of which were being investigated, was free from any accompanying polymerisation. But such disturbing effect in certain instances was found to be very considerable; reactions were observed to proceed with a rapid initial absorption, to show a temperature coefficient less than unity, and to give equilibria which varied in an irregular manner both with concentration and temperature. The substances that show such abnormalities are chiefly aromatic compounds, with a phenyl or substituted-phenyl group attached to the ethylene system, styrene, α -methylstyrene, $\alpha\beta$ -dimethylstyrene, indene, 1 : 2-dihydronaphthalene, and anethole.

Reference is now made to the catalysis of iodine addition. Nozaki and Ogg (*J. Amer. Chem. Soc.*, 1942, **64**, 713) claim that hydrogen iodide is a powerful catalyst in acetic acid solution, although this is not evident from their quoted results. On taking precautions to remove traces of oxides from the unsaturated compounds, and making measurements in nitrogen atmosphere to prevent oxidation of the hydrogen iodide, we have found that hydrogen iodide reduces the rate of iodine addition to oleic acid and styrene and, if in sufficient concentration, completely inhibits the reaction. This corresponds with the effect of hydrogen bromide, which reduces the

rate of bromine addition to compounds containing electron-contributing groups, although it has the reverse effect if electron-attracting groups are present (*J.*, 1947, 630). Such a compound is propylpropionic acid, and here there was found catalysis by hydrogen iodide, as hydrogen tri-iodide has become the nucleophilic reagent.

Nozaki and Ogg (*loc. cit.*) found that lithium chloride causes marked catalysis of iodine addition in acetic acid solution. We have confirmed this, and examined several other catalysts that are electrolytes in acetic acid (cf. table, *J.*, 1949, 295). It was indicated that the special reactivity of lithium chloride, which was much greater for iodine than for bromine under similar conditions, might be due to the formation of iodine chloride.

A preliminary examination has been made of the significance of the equilibria in reversible iodine addition. For the actual determination of the equilibrium constant of the reaction, the concentrations of the reactants were chosen to give approximately 50% iodine absorption, under which condition the experimental error is at a minimum. For the purpose of considering the relationship between such equilibria and the nature of different ethylene compounds, it is more realistic to present the results as relative iodine absorption for the same initial concentrations of reactants:

Percentage iodine absorption for $M/4\text{-A} + M/50\text{-I}_2$, in acetic acid at 25°.

$\text{Me}\cdot[\text{CH}_2]_3\text{CH}\cdot\text{CH}_2$	$\text{CH}_2\cdot\text{CH}\cdot[\text{CH}_2]_5\text{CO}_2\text{H}$	$\text{CMe}_2\cdot\text{CHMe}$	$\text{CMeEt}\cdot\text{CH}_2$	$\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2$
98	96	64	39	14
<i>cyclo</i> Hexene			<i>cyclo</i> Pentene	
85			51	

The difference between trimethylethylene and 2-methylbut-1-ene and compounds of the type $\text{CHR}\cdot\text{CH}_2$, and also the difference between the two cyclic compounds, suggest that a steric factor may operate to hinder the forward and favour the back reaction. With *tert.*-butylethylene there is the possibility of rearrangement of the positive carbon ion formed in the first phase of the addition:



so that the significance of the equilibrium becomes ambiguous. Likewise bicyclic terpenes, such as norbornylene and camphene, in which the hindrance to *trans*-addition with inversion would be virtually complete, cannot be used as a diagnostic to test steric effects. With these two compounds the reactions proceed with complete absorption of iodine. This is consistent with the fact that such compounds undergo rearrangement on halogen addition with the production of 1 : 3-di-iodohydrocarbons, which do not dissociate, like the 1 : 2-derivatives, and iodine addition to norbornylene takes place at about the same rate as to *cyclopentene* and *cyclohexene*. As camphene adds iodine in chlorobenzene solution at a slower rate than *cyclohexene* by a factor of about 25, and on the other hand adds bromine more rapidly by a factor of about 2 (unpublished work), for this compound there is a possibility of steric hindrance in the iodine reaction. α -Pinene, on the other hand, shows irregular kinetics and incomplete iodine absorption, corresponding with the fact that the reaction is more complex, *cymene* being known to be one of the products.

EXPERIMENTAL.

In the rate and equilibrium measurements sometimes the method of stopping the reaction with sodium thiosulphate and back-titrating with iodine was used, at other times it was found that the direct method of adding the reaction mixture to potassium iodide solution and titrating with sodium thiosulphate gave more consistent results. Herewith a typical measurement:

10 ml. of 1.08M-oleic acid + 0.208M-I₂ in CCl₄; 24°; 1 ml. added to 5 ml. of 0.01M-Na₂S₂O₃, and titrated with 0.103N-I₂.

Time (mins.)	0	1.7	3.2	5.2	6.6	8.6
Titre (ml. of I ₂)	0.83	1.20	1.47	1.71	1.88	2.11

From the curve, $x = 20$, $t = 4.5$; 2nd expt., $x = 20$, $t = 4.6$.

Reactions in Acetic Acid Solution.—Undecenoic acid, previously examined at one concentration only, constant pseudo-bimolecular coefficients being obtained to $x = 50\%$ absorption, is now measured at the following concentrations:

% Reaction, x	10	20	30	40	50
Time (mins.) : 0.47M-A + 0.02M-I ₂	2.2	5.0	7.5	12.5	18
„ „ : 0.25M-A + 0.01M-I ₂	9.5	22	34	49	72
Overall reaction order, n	3.1	3.1	3.1	3.0	3.0

Hydrogen iodide catalysis was examined with freshly distilled compounds, and in an inert atmosphere. A negative effect was obtained for compounds reacting by the electrophilic mechanism, and positive catalysis for propylpropionic acid, which can react by a nucleophilic mechanism, as shown by the following reactions in acetic acid at 24° :

0.33M-Styrene + 0.0133M-I ₂ + catalyst	None	0.0033M-HI	0.033M-HI
I ₂ absorption (% , 50 mins.).....	17	7	0
0.33M-Oleic acid + 0.0133M-I ₂ + catalyst	None	0.005M-HI	0.05M-HI
I ₂ absorption (% , 10 mins.).....	59	32	0
0.33M-Propylpropionic acid + 0.0133M-I ₂ + catalyst ...	None	0.05M-HI	
I ₂ absorption (% , 1400 mins.).....	6.6	31	

Reactions in Carbon Tetrachloride Solution.—Iodine addition in this solvent was found to be less sensitive to catalysis than bromine addition, and a change from air conditions to a sulphuric acid-dry nitrogen atmosphere did not appreciably alter the rates for pent-2-ene and oleic acid. On packing the vessel with glass-beads a slight acceleration was observed when the iodine concentration was small, but this effect disappeared at higher concentrations. It is concluded, therefore, that the high reaction orders to be recorded are for homogeneous iodine addition. The following results were obtained for oleic acid in carbon tetrachloride at 24° :

% Reaction, x	10	20	30	40
Time : 1.08M-A + 0.208M-I ₂	1.8	4.5 *	8.0	13.2
,, 0.54M-A + 0.104M-I ₂	10.3	30	54	85
Overall reaction order, n	3.5	3.6	3.6	3.7

* 14.5°, $t = 5.4$; 40°, $t = 3.1$; 25°, + BaSO₄, $t = 0.9$.

Experiments with 1.00M-oleic acid + 0.04M-I₂ and half these concentrations gave $n(x = 20) = 3.7$. The relative contributions of the reactants to the total order, calculated from the four runs are A, $n = 1.3$; I₂, $n = 2.4$. Pent-2-ene shows similar kinetics, giving at 16° reaction orders : A, $n = 1.3$; I₂, $n = 2.5$. For these two reactions in carbon tetrachloride the pseudo-bimolecular coefficients fall as the reaction proceeds, in accordance with the finding that the reaction order for iodine is greater than 2. The previously found constant pseudo-unimolecular values for allyl alcohol in this solvent are abnormal and possibly related to its association.

Reactions in Chlorobenzene.—Herewith are the results for cyclopentene at 25°, as times for $x = 20\%$ iodine absorption : 0.25M-A + 0.02M-I₂, $t = 3.5$; 0.0125M-A + 0.01M-I₂, $t = 29$; 0.0125M-A + 0.02M-I₂, $t = 7.8$; hence A, $n = 1.1$; and I₂, $n = 2.9$. 0.25M-Camphene + 0.02M-I₂; 25°, $x = 20$, $t = 246$; norbornylene, same concns., 25°, $x = 20$, $t = 4.2$. The pseudo-bimolecular coefficients for this reaction, at $x = 10$, $k_2 = 3.7$, at $x = 60$, $k_2 = 2.2$, as there is no back reaction, indicate a reaction order, for A + I₂, >3.

The materials used were in part as described in earlier communications, and included also : pent-2-ene, b. p. 36—37°/760 mm.; trimethylethylene, b. p. 37—38°/741 mm.; tetramethylethylene, b. p. 72—73°/756 mm.; cyclopentene, b. p. 44°/755 mm.; cyclohexene, b. p. 82°/750 mm.; norbornylene, subliming at 52°; camphene, m. p. 43—44°.

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