

318. *The Kinetics of Chlorine, Iodine Chloride, and Bromine Chloride Addition to Olefinic Compounds.*

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The termolecular mechanism of halogen addition, previously demonstrated for bromine and iodine, is now also found to hold for their monochlorides. On the other hand, chlorine is added at a bimolecular rate in dissociating solvents. A theory, involving the formation of addition compounds of the type $\text{>C}^+ - \text{C}^- \text{I} - \text{Cl}$, is proposed to explain the termolecular additions. Certain anomalies occurring on chlorine addi-

tion are discussed, and the mechanism of 1 : 4-addition is proposed for $\alpha\beta$ -unsaturated aldehydes.

PREVIOUS investigations in this series on halogen addition have revealed the marked differences between reactions in dissociating and non-dissociating solvents. In acetic acid solution in the concentration region $m/40$, bromine reacts by a termolecular mechanism (Robertson, Clare, McNaught, and Paul, J., 1937, 335). Subsequent experiments in this laboratory have shown that bromine addition is also termolecular in nitrobenzene solution. In carbon tetrachloride, on the other hand, the bromine additions show abnormal concentration and temperature effects and the reactions are heterogeneous. Iodine addition, when due allowance is made for the reverse reaction, is analogous (Bythell and Robertson, J., 1938, 179), being termolecular in acetic acid and nitrobenzene and bimolecular in carbon tetrachloride and hexane.

There has been little systematic work on the kinetics of the addition of chlorine, iodine chloride, and bromine chloride in solution. The reaction between chlorine and ethylene as gases was examined by Norrish and Jones (J., 1926, 55), Stewart and Fowler (*J. Amer. Chem. Soc.*, 1926, 48, 1187), and Stewart and Smith (*ibid.*, 1929, 51, 3082), and heterogeneous mechanisms established. No investigation is on record of the rate of chlorine addition in solution except an observation for cinnamic acid in carbon tetrachloride at one concentration (Hansen and James, J., 1928, 1955).

The orientation of the products obtained on iodine chloride addition to unsymmetrical ethylene compounds has been established by Ingold and Smith (J., 1931, 2742), and there is an extensive literature on its use as a reagent for the quantitative measurement of unsaturation, but kinetic measurements are lacking. Bromine chloride gives with $\alpha\beta$ -unsaturated acids β -chloro- α -bromo-derivatives, and the rates of such additions were measured in carbon tetrachloride and chloroform by Hansen and James (*loc. cit.*), but only at one concentration. Approximate bimolecular constants were obtained, and constitutive effects noted corresponding to those for bromine addition.

In the present investigation, measurements were made of the rate of addition of the substances mentioned in the title to certain ethylenic substances in acetic acid solution and, in some cases, in nitrobenzene. The reactions in carbon tetrachloride, which, like the corresponding bromine and iodine additions, show abnormal concentration and temperature effects, will be described in a further communication.

EXPERIMENTAL.

The compounds used and the solvents, acetic acid and nitrobenzene, were purified as previously described (J., 1937, 341; 1938, 182). In this investigation a semimicro-procedure was employed, generally two 5-ml. portions of the reacting solutions at the thermostat temperature being mixed in a 10-ml. brown bottle, and portions of 1 ml. being removed at intervals for titration. A standard micro-pipette, delivering 1.000 ± 0.002 ml. of water in 40 secs., and a micro-burette devised by one of us (White, *Ind. Eng. Chem., Anal.*, 1938, 10, 668), reading to 0.005 ml., were used. For constancy in titration it was necessary to run the 1 ml. of halogen solution into a fixed volume, 10 ml., of 5% potassium iodide solution slightly acid with acetic acid, containing 0.5 ml. of preserved starch solution as described by Nicholls (*ibid.*, 1929, 1, 215); the end-point was the disappearance of the final pink tint. With nitrobenzene solutions, titration was difficult owing to complex iodide formation (Dawson, J., 1902, 81, 525), but with the addition of 1.5 ml. of chloroform a sharp end-point was obtainable. The measurements were made rapidly, as there is a tendency for liberation of iodine from the solutions, more especially when iodine chloride is the reactant. Titrations were made with 0.02, 0.01, or 0.005N-sodium thiosulphate, freshly prepared from 0.01N-solution preserved with 1% of amyl alcohol. For the more rapid additions, a stop-clock graduated in 0.01 min. was used.

In the measurements with chlorine correction was made, by a series of blank experiments, for the volatility loss which occurred on each opening of the reaction bottle. At time intervals, which within determined limits had little effect on this loss, five separate portions of 1 ml. from 10 ml. of chlorine solution in the pure solvent were removed and titrated. This correction becomes greater with increasing air space in the reaction vessel, but at each concentration is approximately the same fractional amount of total chlorine. The actual loss then can be

calculated for each stage of the reaction. The figures for a typical experimental run are given below, the corrections and the corrected chlorine absorptions being shown. When the zero titration figure, owing to difficulties in manipulating a volatile reagent, is not precisely adjusted, here 2.60 instead of 2.50, a small correction in the k_2 value must be introduced.

cis-Cinnamic acid (M/80) + chlorine (M/80) in acetic acid at 25°.

| | | | | | | | |
|--|------|------|------|------|------|------|------|
| Loss of Cl ₂ , ml. of 0.01N-Na ₂ S ₂ O ₃ | — | — | — | 0.01 | 0.02 | 0.03 | 0.05 |
| Cl ₂ absorption ,, ,, | 2.60 | 2.23 | 1.84 | 1.48 | 1.22 | 0.99 | 0.92 |
| Time (mins.) | 0 | 0.63 | 1.47 | 2.74 | 4.08 | 6.37 | 7.47 |
| k_2 (l. g.-mol. ⁻¹ min. ⁻¹) | — | 21 | 22 | 22 | 22 | 21 | 20 |

Instead of calculating individual k_2 values, we plotted the % of chlorine absorption against the time and calculated k_2 for each 10% of absorption. Several of the earlier runs were carried out in duplicate, and as the observational points fell well on a single curve, the results are clearly reproducible. The following table gives the k_2 values for *cis*-cinnamic acid with the equivalent amount of chlorine in acetic acid at 25°.

| x , %. | M/20. | | M/40. | | M/80. | | M/160. | |
|----------|-------|---------|-------|---------|-------|---------|--------|---------|
| | t . | k_2 . | t . | k_2 . | t . | k_2 . | t . | k_2 . |
| 10 | 0.10 | 22 | 0.22 | 20 | 0.44 | 20 | 0.91 | 20 |
| 20 | 0.23 | 22 | 0.50 | 20 | 0.91 | 22 | 1.93 | 21 |
| 30 | 0.40 | 21 | 0.87 | 20 | 1.55 | 22 | 3.32 | 21 |
| 40 | 0.62 | 21 | 1.34 | 20 | 2.42 | 22 | 5.18 | 21 |
| 50 | 0.97 | 20 | 1.98 | 20 | 3.68 | 22 | 7.75 | 21 |
| 60 | 1.43 | 21 | 2.79 | 21 | 5.68 | 21 | 11.45 | 21 |
| 70 | 2.42 | 19 | 4.63 | 20 | 9.00 | 21 | 20.80 | 18 |

The constancy of the k_2 values over this range indicates the bimolecular character of chlorine addition. Similarly constant k_2 values were found for acrylic acid in acetic acid at 25°, viz., k_2 (mean) = 0.018 for M/40 and 0.017 for M/80.

For *trans*-cinnamic acid, on the other hand, there was a slight upward drift of k_2 with the concentration in acetic acid, and to a smaller extent in nitrobenzene. There follows a summary of the k_2 values for the cinnamic acids :

| Solvent. | Acetic acid. | | | | Nitrobenzene. | | |
|-----------------------------------|--------------|-------|-------|--------|---------------|-------|--------|
| | M/20. | M/40. | M/80. | M/160. | M/40. | M/80. | M/160. |
| <i>cis</i> -; k_2 (25°) | 21 | 20 | 22 | 21 | — | — | 75 |
| <i>trans</i> -; k_2 (25°) | 6.2 | 5.7 | 4.9 | 4.3 | 5.4 | 4.9 | 4.6 |
| ,, (15°) * | — | 3.4 | 2.7 | — | 3.5 | 3.2 | 3.0 |

* Values from slight prolongation log $k-1/T$ curve.

It is to be noted that, whereas chlorine addition to the *cis*-acid is more rapid in nitrobenzene, yet that to the *trans*-acid proceeds at the same rate in the two solvents. This behaviour, and the upward k_2 drift for the *trans*-acid, are discussed later.

The rates of addition of chlorine to cinnamic and crotonic acids in acetic acid were unaltered by hydrogen chloride or by sodium acetate. With cinnamaldehyde and crotonaldehyde, on the other hand, they are accelerated by hydrochloric and sulphuric acid : M/40-cinnamaldehyde + M/40-chlorine in acetic acid at 25°, $k_2 = 5$ (values rising as reaction proceeds owing to small amount of HCl formation); addition of 200 mols. % of hydrochloric acid gives $k_2 = 21$, and of 400 mols. % of sulphuric acid gives $k_2 = 20$. M/80-Crotonaldehyde + M/80-chlorine in acetic acid at 25°, $k_2 = 42$ (rising values); with 25 mols. % of sulphuric acid, $k_2 = 350$; with 100 mols. % of sodium acetate, $k_2 = 0.6$. The sodium acetate, being a base in acetic acid (Davidson and McAllister, *J. Amer. Chem. Soc.*, 1930, 52, 517), reduces the power of the solvent to act as proton donor and thus lowers the rate of addition.

Iodine monochloride was prepared by mixing equivalents of iodine and chlorine in acetic acid; the titre remained constant for several days, but then decreased, hydrogen chloride being formed. The choice of ethylene compounds is limited; undecenoic acid reacts instantaneously with this reagent, and the more slowly reacting cinnamic and crotonic acids liberate hydrogen chloride, which causes secondary reactions; but the reaction with allyl acetate went to completion at a measurable rate, 1 mol. of the acetate reacting with 1 mol. of the chloride. Owing to the rapidity of this reaction, the early stages were measured by a semimicro-modification of the special rapid technique previously described (J., 1937, 341), and for the later stages the ordinary method was used. The results were reproducible, and furthermore both sets of observations fitted smoothly into the composite curve. From such curves the following results were

obtained, the k_3 values being calculated by the same formula as for bromine addition (J., 1937, 336), as l. g.-mol.⁻¹ min.⁻².

Allyl acetate + iodine monochloride in acetic acid at 25°.

| M/40. | | | M/80. | | | M/40. | | | M/80. | |
|----------|--------------|---------------------|--------------|---------------------|----------|--------------|---------------------|--------------|---------------------|--|
| x , %. | t (mins.). | $k_3 \times 10^3$. | t (mins.). | $k_3 \times 10^3$. | x , %. | t (mins.). | $k_3 \times 10^3$. | t (mins.). | $k_3 \times 10^3$. | |
| 20 | 0.042 | 44 | 0.16 | 45 | 50 | 0.20 | 48 | 0.85 | 45 | |
| 30 | 0.068 | 48 | 0.29 | 46 | 60 | 0.40 | 44 | 1.50 | 47 | |
| 40 | 0.12 | 47 | 0.49 | 46 | 70 | — | — | 2.80 | 46 | |

Acrylic acid differs from cinnamic and crotonic acids in that iodine chloride addition goes to completion in acetic acid at 25°:

| | M/20. | M/40. | M/80. |
|---------------|-------|-------|-------|
| k_3 (mean). | 18 | 18 | 20 |
| t_1 (mins.) | 520 | 2090 | * |

* Reaction not followed to t_1 , as reaction of iodine chloride with the solvent becomes measurable after 5000 mins.

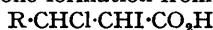
The results for these two compounds reveal that addition of iodine chloride, like that of bromine and iodine, proceeds by a termolecular mechanism.

The influence of hydrogen chloride on the addition of iodine chloride was examined. The ion ICl_2^+ is stable in aqueous solution (Philbrick, *J. Amer. Chem. Soc.*, 1934, 56, 1257), but there appears to be no experimental evidence with regard to the existence of HICl_2 in organic solvents. From the very marked change in colour that takes place on addition of hydrogen chloride to iodine chloride in acetic acid, it may be concluded that there is considerable formation of HICl_2 . Hydrogen chloride reduces the rate of addition of iodine chloride considerably, as was found for undecenoic acid and allyl acetate, and with cinnamic acid and *o*-methoxycinnamic acid there is complete inhibition. The following results for allyl acetate show that, together with the slowing down of the reaction, there is a change from the termolecular mechanism to one which is apparently bimolecular. Previous experiments had shown that there was no ester fission under the experimental conditions.

M/40-Allyl acetate + M/40-iodine chloride in acetic acid at 25°, with added hydrogen chloride.

| [HCl]/[ICl] | 0 | 0.25 | 1 | 2 | 8 | 16 |
|----------------------|-----|------|-----|----|----|----|
| k_3 ($x\% = 20$) | 270 | 170 | 130 | 83 | 14 | 12 |
| k_3 ($x\% = 60$) | 150 | 130 | 95 | 84 | 15 | 13 |

The equilibria that $\alpha\beta$ -unsaturated acids form with iodine chloride are influenced by the hydrogen chloride resulting from lactone formation from the addition products,



(cf. Böeseken and Gelber, *Rec. Trav. chim.*, 1927, 46, 1629); the HICl_2 produced inhibits the reaction, whereas if sodium acetate is present to combine with the hydrogen chloride, there is 100% absorption. The following equilibria were measured in acetic acid at 25°, for equimolecular reactants:

| Acid. | <i>trans</i> - <i>o</i> -Methoxycinnamic. | <i>trans</i> -Cinnamic. | Crotonic. |
|----------------------------|---|-------------------------|-----------|
| Absorption of ICl, %, M/20 | 22 | 26 | 80 |
| „ „ M/40 | 13 | 17 | 69 |

Colorimetric measurements (Barratt and Stein, *Proc. Roy. Soc.*, 1929, A, 122, 582) show that in carbon tetrachloride the equilibrium $\text{Br}_2 + \text{Cl}_2 \rightleftharpoons 2\text{BrCl}$ corresponds with 60% BrCl formation. No measurements are available for acetic acid solutions, but a comparison of the tints in the two solvents indicates that the equilibrium is of the same order. Preliminary experiments with cinnamic and crotonic acids in acetic acid had shown approximately constant termolecular values at M/40 and M/80; it was further found that the reaction with two mols. of BrCl and one mol. of acid was considerably more rapid than with the reverse ratio. These additions, however, were accompanied by substitution side reactions, and were not suited for more precise kinetic observation. Dilution of the acetic acid with 80% of carbon tetrachloride made the reaction considerably slower, thus eliminating disturbing side reactions, without apparently introducing heterogeneous disturbances. The value of n (the reaction order) for *cis*-cinnamic acid (M/40—M/80) in this solvent at 25° was 2.9. The rates of addition for different mixtures of bromine and chlorine are given for *cis*-cinnamic acid at 25° (reactants, M/40):

| | Cl_2 . | $4[\text{Cl}_2] + [\text{Br}_2]$. | $[\text{Cl}_2] + [\text{Br}_2]$. | $[\text{Cl}_2] + 2[\text{Br}_2]$. |
|----------------------|-----------------|------------------------------------|-----------------------------------|------------------------------------|
| k_2 ($x\% = 20$) | 0.12 | 0.22 | 0.42 | 0.28 |
| k_2 ($x\% = 50$) | 0.12 | 0.19 | 0.33 | 0.21 |

The maximum rate is given by the equimolecular mixture of the two halogens in accordance with the equilibrium $\text{Br}_2 + \text{Cl}_2 \rightleftharpoons 2\text{BrCl}$. The constancy of the k_2 values as the reaction proceeds indicates its bimolecular character for chlorine, but with the $\text{Br}_2 + \text{Cl}_2$ mixtures k_2 decreases during the reaction as the mechanism tends to become termolecular. Since there is 60% of bromine chloride present in the equimolecular mixture, it can be calculated from the above results that the relative contributions of this and chlorine at the beginning of the reaction are in the ratio 15 : 1. Thus the contamination of the termolecular bromine chloride addition by the bimolecular chlorine addition is slight, and this is in accord with the value, 2.9, obtained for the order of the reaction.

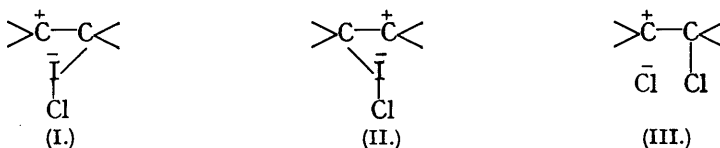
DISCUSSION.

The results so far obtained in this series of investigations on halogen addition show that whereas addition of chlorine is bimolecular, that of Br_2 , I_2 , ICl , and BrCl to olefinic compounds is termolecular. As the relative rates are approximately the same for different compounds in acetic acid, it is possible to make a general comparison :

| | | | | |
|----------------|-----------------|----------------|-----------------|-----------------|
| I_2 . | IBr . | ICl . | Br_2 . | BrCl . |
| 1 | 3×10^3 | 10^6 | 10^4 | 4×10^6 |

An absolute comparison with the rate of chlorine addition cannot be made, as this proceeds by a mechanism of a different order, but in $\text{M}/40$ -solutions in acetic acid, this addition proceeds at 10^6 the rate of iodine addition.

Termolecular halogen addition, in which two molecules of X_2 participate for each molecule of unsaturated compound, might be expected to involve the formation of a complex A, X_2 , which reacts with a second molecule of X_2 . Olefins are known to form co-ordination compounds with certain metallic salts and thus act as donor molecules. As both bromine and iodine can expand their outer ring of electrons, such addition compounds would be theoretically possible (I).



The further possibility that (I) might be stabilised by resonance, (II) being the alternate form of the resonance hybrid, is not excluded. This condition has been proposed by Winstein and Lucas (*J. Amer. Chem. Soc.*, 1938, **60**, 836) to explain the addition of ethylenes to silver salts. Such resonance, however, involves the formation of what is virtually a three-membered ring, with consequent molecular strain. On the other hand, the opposite charges on the carbon and the halogen might confer stability on the pyramidal structure. Whether there is resonance or not, the momentary influx of electrons occasioned by collision of I with a second molecule of ICl might be expected to promote anionisation and cause a rupture of the $\text{I}-\text{Cl}$ link, thus causing an all-over termolecular reaction.

From a consideration of the relative stability of HICl_2 and HBr_3 , in comparison with the extreme instability of HCl_3 , it can be concluded that the chlorine atom, compared with bromine and iodine, expands its outer ring of electrons only with difficulty. In addition of chlorine there is less likelihood of intermediate complex formation and the reaction is consequently bimolecular, as the formation of the $\text{C}-\text{Cl}$ link immediately breaks the bond between the two chlorine atoms (III).

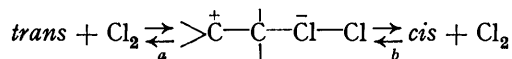
This theory also explains the behaviour of HICl_2 on addition. In this compound the increase in the outer ring of iodine electrons must decrease the tendency to form the addition complex. The rate-determining change then becomes the slow bimolecular reaction between HICl_2 and the ethylene compound.

The theory may further be applied to the reverse reaction to halogen addition. This occurs readily with iodine, but with bromine only when there is considerable electronic regression from the ethylenic system, e.g., with $\text{CHPh}:\text{CPh}:\text{CN}$ (Bauer and Moser, *Ber.*, 1907, **40**, 918), or with $\text{CHPh}:\text{CHPh}$ in the presence of a catalyst such as pyridine (Pfeiffer, *Ber.*, 1912, **45**, 1810); with chlorine, it does not occur at all. Iodine acts as a catalyst in

decomposing compounds of the type $>CI\cdot CI<$ (cf. J., 1938, 182). The possibility of interaction between iodine and I joined to carbon is indicated by the high solubility of iodine in methylene iodide. With a second iodine atom on an adjoining carbon atom from which there is electronic regression, the conditions are suitable for the formation of the intermediate complex, $>\overset{+}{C}-\overset{|}{\underset{|}{C}}-\bar{I}-I$, and the consequent setting up of equilibrium. The action of pyridine in causing the reaction, $CHBrPh\cdot CHBrPh \longrightarrow CHPh\cdot CHPh + Br_2$, is due to the electron-donating capacity of the nitrogen atom of the pyridine. The corresponding dichloro-compound may be heated to 200° with pyridine without change, and this is attributed to the relative reluctance of chlorine to extend its outer ring of electrons. For the same reason, addition of iodine chloride, like that of chlorine, is not reversible, as was found for undecenoic acid, allyl acetate, and acrylic acid. When the reaction is apparently reversible, e.g., with cinnamic acid, this is due to secondary changes, viz., lactone formation with the production of unreactive $HICl_2$ from the liberated hydrogen chloride.

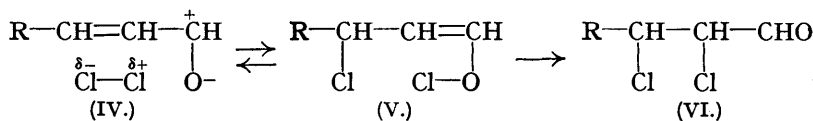
Although it seems that addition of chlorine does not proceed *via* a complex of the type A,Cl_2 , certain considerations indicate that such complexes may nevertheless be formed to a limited extent. Whereas *cis*-cinnamic acid gives constant k_2 values over a considerable concentration range, for the *trans*-acid there is a definite upward drift. Further, the *trans*-acid adds chlorine at approximately the same rate in acetic acid and nitrobenzene, whereas for the *cis*-stereoisomer the addition proceeds 3—4 times faster in the latter. Also, addition of bromine and of iodine is more rapid in this than in acetic acid. This upward drift of the reaction coefficients and the abnormally high k_2 value in acetic acid for the *trans*-acid may be explained by the formation of a certain amount of the *cis*-acid during addition of chlorine, for this was shown to take place during that of bromine (J., 1937, 337).

Such a stereo-inversion would involve the momentary formation of a single link between the ethylene carbons. Once the bond between the two chlorine atoms is broken and a positive charge appears on the carbon atom (III), the process goes immediately to completion, the operation involving the rupture of the Cl-Cl link being the rate-determining change. If, however, a small amount of the addition complex A,Cl_2 of the type (I) is formed by a reversible change, and the positive carbon atom assumes a planar configuration, the dissociation of the complex could yield both *cis*- and *trans*-acids:



The equilibria *a* and *b* are regarded as being largely away from the direction of the complex, a very small concentration of which would give the effect observed. Equilibrium *a* would shift in the direction of the complex with rising concentration of reactants, and this is in accord with the found increase of k_2 with the concentration.

Cinnamaldehyde and crotonaldehyde differ from the corresponding acids in that addition of chlorine in acetic acid is accelerated by proton donors, and reduced in rate by proton acceptors. According to the theory of Ingold and Ingold (J., 1931, 2354), compounds with the powerfully electron-attracting aldehydo-group should add halogen less rapidly than compounds with carboxyl attached to the ethylene carbon, but this has not been found. Further, on comparison of the rates of chlorine addition, the following relative values are obtained: cinnamic acid $10 >$ crotonic acid; crotonaldehyde $70 >$ cinnamaldehyde. Again, bromine addition to crotonaldehyde is more rapid than that of chlorine, whereas the reverse is normally found. There are thus reasons to believe that addition of chlorine to $\alpha\beta$ -unsaturated aldehydes proceeds by a special mechanism. As during addition hydrogen chloride is liberated only to a small extent, the process involving successively enolisation, chlorine addition, and hydrogen chloride elimination is excluded as the rate-determining reaction. The theory is proposed that the initial stage is 1:4-addition, giving a



rapidly attained equilibrium between (IV) and (V); the attachment of a proton of the catalyst to the oxygen of (V) accelerates the rate-determining change of (V) into (VI).

A similar interpretation could be given for the unexpectedly rapid addition of bromine to acraldehyde and crotonaldehyde in methylene chloride, in the presence of excess of hydrogen bromide, observed by Anantakrishnan and Ingold (J., 1935, 1396), who suggested that for these compounds the addition might proceed by an initial attack of the negative atom of the bromine molecule. The theory of 1 : 4-addition for this type of compound permits the halogen to maintain its normal rôle as an electrophilic reagent.

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