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# Kinetics and Mechanism of the Addition of Iodine Monochloride to Alkenes in Acetic Acid

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A kinetic investigation of the addition of iodine monochloride (ICl) to some allyl and vinyl compounds in dry acetic acid medium has been carried out at 20,30,40, and 50 °C. In all the cases, the reaction obeys a total third order kinetics, second order in ICl and first order in the substrate. The product formed has been analysed by $^1$H NMR technique. The reaction stoichiometry was found to be 1:1. The formation of a 1:1 complex between an alkene and ICl has been established for the first time spectrophotometrically and the equilibrium constant evaluated. The effect of the addition of the chloride ion on the reaction rate has been studied. The kinetic and thermodynamic parameters evaluated strongly suggest a mechanism involving dipole-dipole interaction with a bridged iodonium ion intermediate.

This paper deals with the kinetics and mechanism of iodine monochloride addition to some alkenes in acetic acid solvent. Investigations carried out so far on the addition of ICl to unsaturated compounds show that ICl has been mainly used as a reagent to estimate unsaturation. The kinetic aspect of the problem has not received sufficient attention. Only the relative rates of $Cl_2$–, ICl–, and BrCl– addition to alkenes[1] and the kinetics and mechanism of ICl addition to allyl alcohol,[2] stilbene,[3] and α-eleostearic acid[4] have been reported. This paper reports the first systematic study of the kinetics of ICl addition to allyl and vinyl compounds in dry acetic acid. In this article we report and discuss the kinetic and thermodynamic parameters obtained in the present investigation.

## Experimental

*Materials.* Iodine monochloride,[5] 1-hexene,[6] and methyl crotonate[7] were prepared by the procedures given in the literature. Allyl chloride from BDH (LR) and allyl acetate from Fluka AG (Pract.) were purified by distillation. Methyl acrylate and methyl methacrylate both from Koch Light Co., England,[8] acrylamide from American Cyanamide Co., New York,[9] methacrylamide from Rohm and Haas, Philadelphia,[10] allyl bromide from Riedel,[11] and acetic acid from BDH (LR, 99.5% assay)[12] were all purified according to the methods given in the literature. Potassium iodide, sodium thiosulfate and potassium dichromate used were all BDH analytical grade samples.

*Kinetic Measurements.* Required volumes of the ICl and the substrate solutions in dry acetic acid of required concentration were thermostated and then mixed in a 500 cm$^3$ iodine flask with a B-19 standard ground-glass stopper. Known volumes of aliquots were withdrawn after various intervals of time and estimated iodometrically. From the observations made in several experiments, it has been concluded that, unlike in any other halogenation reaction, the loss of ICl from its solution due to volatility is practically nil. It is worth noting that the reproducibility of kinetic runs throughout this study was therefore excellent. Moreover, the reaction was found to be unaffected by light.

*Stoichiometry.* The stoichiometry of the reaction was investigated by employing the well-known method[13] using a mixture of $KBrO_3$ and KBr.

*Product Analysis.* The solutions of the substrate and ICl in dry acetic acid of required concentration were mixed and the reaction was allowed to go to completion at 30 °C (24 h). Then the solvent acetic acid was completely neutralized by the addition of a required quantity of sodium hydrogencarbonate solution. The organic material was then ether extracted, dried with sodium sulfate, the ether was distilled off, and it was subjected to TLC and $^1$H NMR analyses. TLC analysis showed a single spot indicating the formation of one product only. Further analyses of the products of iodochlorination of allylic and vinylic compounds were carried out in Varian T60 NMR spectrometer using carbon tetrachloride as the solvent and TMS as the internal standard.

*UV Absorption Studies.* During the course of this work, the existence of an alkene–ICl complex has been proved for the first time spectrophotometrically.[14] The measurements were made on a Specord UV-VIS recording spectrophotometer. The nature of the complex and its formation constant were also determined experimentally.

## Results and Discussion

The overall order of the reaction and the individual orders in the reactants were determined by the integration and the differential methods, respectively.[15] The total order was found to be three for allyl and vinyl substrates (Fig. 1). The orders in ICl and in substrate were found to be two and one, respectively (Fig. 2).

With equal initial molar concentrations (in the range $1.0\times10^{-3}$—$4.0\times10^{-2}$ mol dm$^{-3}$) of the reactants, the reactions were carried out at 20, 30, 40, and 50 °C. The experimental data fitted well into the integrated third order equation which was used in the form $1/(a-x)^2=2k_3t+1/a^2$. The values of $1/(a-x)^2$ were plotted against the time ($t$) and the rate constant ($k_3$) values were calculated from the slope of the straight line obtained. Figure 3 shows the integration plots for the methyl acrylate–ICl reaction at different temperatures. Plots were made with $\log k_3$ *versus* $1/T$ (Figs. 4 and 5) for the determination of Arrhenius activation energies ($E_a$) for the ICl addition to various alkenes studied. The data were analyzed by a least-squares procedure (computer programmed) to get the $E_a$ values together with their standard deviations. The activation entropies ($\Delta S^{*}$) and the free energies of activation ($\Delta G^{*}$) were evaluated at 30 °C.

The stoichiometry of the reaction was established

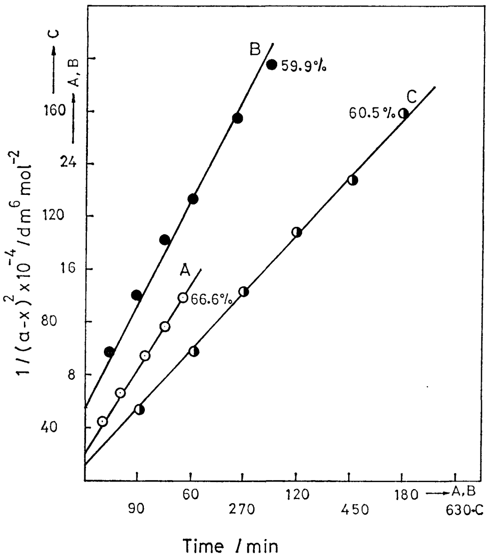


Fig. 1. Plots of $1/(a-x)^2$ against time for allyl chloride-ICl reaction with various equal initial molar concentrations at 50 °C.
A: $8.00\times10^{-3}$ mol dm$^{-3}$, B: $4.45\times10^{-3}$ mol dm$^{-3}$, C: $2.00\times10^{-3}$ mol dm$^{-3}$.

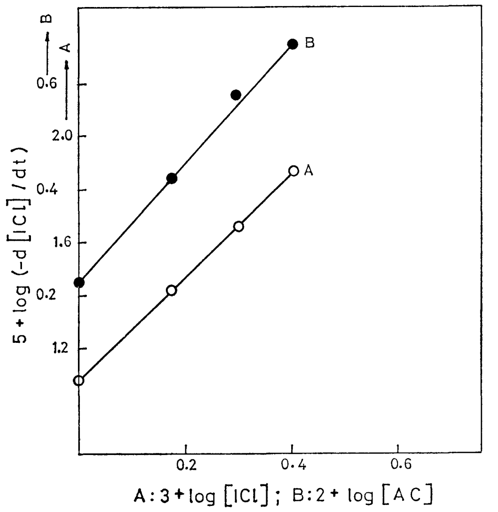


Fig. 2. Plots of log (initial rate) against
A: log [ICl], B: log [AC] for allyl chloride-ICl reaction at 30 °C.

as 1:1. $^1$H NMR analysis showed $CH_2ICHClCH_2X$ (X=Cl, Br, $COOCH_3$, and $CH_2CH_2CH_3$) to be the product of the allyl substrate–ICl reactions. For the methyl acrylate–ICl reaction, the product was found to be $CH_2ClCHICOOCH_3$. The mode of addition of I and Cl is very similar to this in the case of the other vinyl compounds also. The complex between an alkene and ICl had a characteristic absorption in the region 290—310 nm. Applying Benesi-Hildebrand equation[16] to the methyl methacrylate–ICl reaction, as an example, the formation of a 1:1 complex was proved ($\varepsilon_c$=769.3 dm$^3$ mol$^{-1}$ cm$^{-1}$; $K=2.42\times10^{-1}$ dm$^3$ mol$^{-1}$).[14]

Based on the above results, the following mechanism, involving a dipole-dipole interaction, may be proposed:

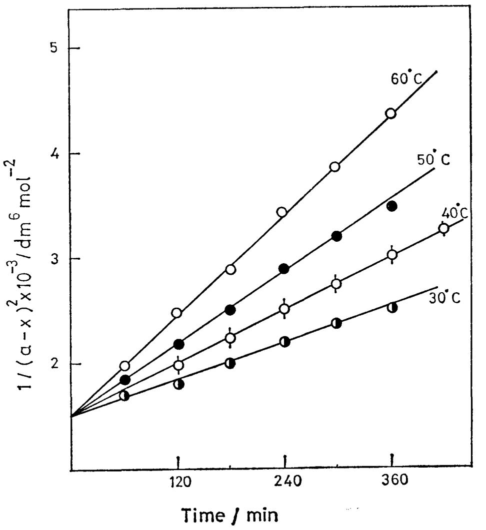


Fig. 3. Plots of $1/(a-x)^2$ against time for methyl acrylate-ICl reaction at different temperatures. [MA]=[ICl]=$2.6\times10^{-2}$ mol dm$^{-3}$.

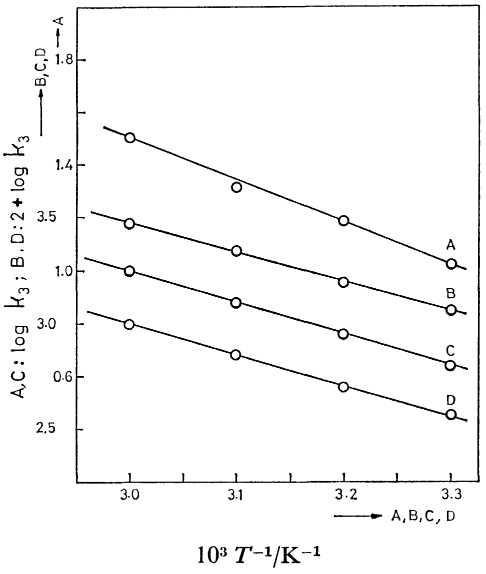
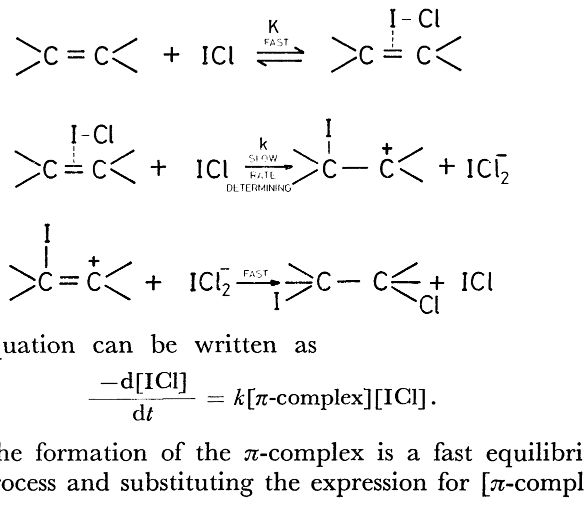


Fig. 4. Plots of log $k_3$ against $1/T$ for allyl compounds.
A: Allyl chloride, B: allyl bromide, C: allyl acetate, D: 1-hexene.



(1)

(2)

(3)

Therefore, based on the above mechanism, the rate equation can be written as

$$\frac{-\mathrm{d}[\mathrm{ICl}]}{\mathrm{d}t} = k[\pi\text{-complex}][\mathrm{ICl}]. \tag{4}$$

The formation of the $\pi$-complex is a fast equilibrium process and substituting the expression for [$\pi$-complex]

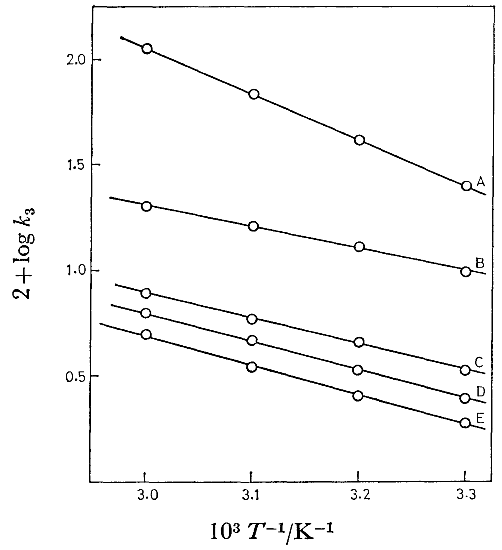


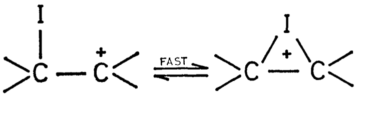
Fig. 5. Plots of log $k_3$ against $1/T$ for vinyl compounds. A: Acrylamide, B: methacrylamide, C: methyl methacrylate, D: methyl acrylate, E: methyl crotonate.

from Eq. 1 in Eq. 4, the rate equation becomes

$$-\frac{d[\mathrm{ICl}]}{dt} = kK[\text{alkene}][\mathrm{ICl}]^2, \qquad (5)$$

where $kK=k_3$, (unit dm$^6$ mol$^{-2}$ s$^{-1}$). This mechanism, in which a dipolar ICl molecule is the attacking species, is thus consistent with the observed overall third order kinetics with first order in alkene and second order in ICl.

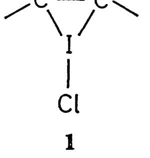
The formation of the $\pi$-complex was identified experimentally as mentioned earlier. The second molecule of ICl which attacks the $\pi$-complex seems to facilitate the heterolysis of the I–Cl bond in the $\pi$-complex by forming $\mathrm{ICl_2}^-$ and the carbonium ion. The open carbonium ion formed in Eq. 2 can rearrange itself, in a very fast step, into a more stable cyclic iodonium ion by the interaction of the unshared electrons of iodine with the carbonium ionic centre, as shown below.



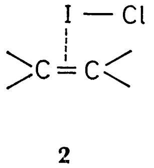
(6)

The existence of the bridged iodonium ion intermediate has been well established by Olah and Bollinger[17] by NMR studies. The activated complex and the measured activation energy correspond to the step (2).

Contrary to the structure **1** proposed in the literature[1] for the $\pi$-complex, structure **2** is proposed by



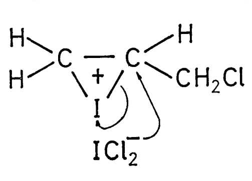
**1**



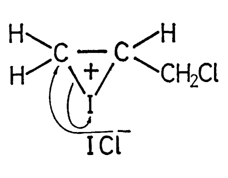
**2**

us. As structure **1** is somewhat rigid, free rotation of the I–Cl bond can be only about the I–Cl axis, thus preventing other types of rotations. Moreover, the structure **1** being rigid, the chances of attack by the second molecule of ICl with it will be very remote. If we assume that the C=C bond be in one plane, the I–Cl bond almost parallel to and above or below this plane and the dotted line to be only a loose molecular binding, then the ICl molecule, as depicted in structure **2**, can freely rotate about the dotted line. The second molecule of ICl can, of course, attack the loosely-bound and freely-rotating ICl molecule from any direction. A carbonium ion intermediate is thus formed from the interaction of neutral but slightly dipolar reactant molecules. The activated complex for such a reaction may therefore be expected to be more polar than the reactants and it should closely resemble the ionic intermediate.

The products formed need some explanation. The allyl chloride–ICl and the methyl acrylate–ICl reactions may be considered as representative examples. In the case of allyl chloride, the iodonium ion formed can be opened in two ways (structures **3** and **4**) by

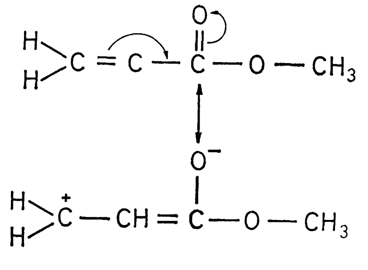


**3**



**4**

the attack of the nucleophile, $\mathrm{ICl_2}^-$. The opening as in III leads to a secondary carbonium ion and that in IV, a primary carbonium ion. Since the former is more stable than the latter, the iodine atom should attach to the primary carbon and the chlorine atom to the secondary carbon and hence the product, $\mathrm{CH_2ICHClCH_2Cl}$. The reverse was, however, found to be the case with methyl acrylate, that is, iodine goes to the secondary carbon and chlorine to the primary carbon. Due to the electron-withdrawing ability of '$\mathrm{COOCH_3}$' group and the extensive conjugation, the primary carbon becomes more positive



than the secondary. Therefore, in the case of methyl acrylate, iodine atom attaches itself to the secondary carbon and chlorine atom to the primary carbon. Ingold and Smith[18] also obtained a similar product for the reaction between $\mathrm{CH_2{=}CH{-}SO_3H}$ and ICl. By analogy with the reactions involving the addition of iodine azide[19] and iodine isocyanate,[20] it may be suggested that the ring opening of the iodonium ion intermediate would be expected to occur in a trans manner leading to trans addition products. The iodonium ion proposed in this investigation is strongly supported by these evidences.

Table 1 shows that as the concentration of added chloride ion increases, the rate of the reaction between

TABLE 1. EFFECT OF ADDED CHLORIDE ION ON ALLYL CHLORIDE-ICl REACTION AT 30 °C
[Allyl chloride] = [ICl] = $4.0\times10^{-3}$ mol dm$^{-3}$.

| [Chloride ion] $\times10^4$/mol dm$^{-3}$ | $(-d[ICl]/dt)$ $\times10^3$/mol dm$^{-3}$ s$^{-1}$ |
|---|---|
| 5.6 | 22.05 |
| 6.7 | 19.45 |
| 8.7 | 15.09 |
| 10.5 | 13.03 |
| 12.3 | 9.56 |

allyl chloride and ICl decreases. This may be due to the equilibrium process

$$ICl + Cl^- \rightleftharpoons ICl_2^-, \qquad (7)$$

which results in a decrease of [ICl] available for the reaction. Since ICl is the attacking species, the reaction rate decreases as more and more chloride ion is added to the system. The formation of $ICl_2^-$ is well established and its existence has been reported.[21)]

Another possible mechanism to explain the third order kinetics is to postulate the existence of the dimeric species $(ICl)_2$, which can simply react with the alkene to give the products. No evidence could be obtained for the existence of such a dimer, however. From spectrophotometric measurements, it was found that the solutions of ICl in acetic acid obeyed Beer's law over a range in which the concentration of ICl was increased twenty times.

From Table 2, it is seen that the $\Delta S^*$ values are negative showing loss in entropy during the formation of the activated complex. The large negative values for $\Delta S^*$ are consistent with the fact that the overall reaction is of the third order. The $E_a$ values for the compounds allyl chloride, allyl bromide and allyl acetate are more or less constant. It may be said that the substituents, which are far away from the double bond, do not have any significant effect on the electron density at the reaction site. This is true because the unsubstituted simple alkene, 1-hexene, also has the same $E_a$ value. The subtle changes in the rate constants are due to variations in $\Delta S^*$. In the case of methyl acrylate, methyl methacrylate, methyl crotonate, acrylamide and methacrylamide, the $E_a$ value for a methyl substituted alkene is always lower than that of the corresponding unsubstituted one. It is evident that the electron density at the double bond of the former is greater due to both inductive (+I) and hyperconjugative effects of a methyl group. The same reason can be attributed to the difference in the $E_a$ and $k_3$ values observed between methyl methacrylate and methyl crotonate.

The rate constants are reversed in the case of the pair, acrylamide and methacrylamide because of the very high and negative $\Delta S^*$ value for methacrylamide compared to that for acrylamide. That is, the gain in energy is lost in entropy, in the case of methacrylamide.

The $\Delta G^*$ values remain more or less the same for the allyl substrates studied, showing that $E_a$ and $\Delta S^*$ compensate each other. The same is found to be the case with the vinyl substrates too.

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TABLE 2. KINETIC AND THERMODYNAMIC PARAMETERS FOR ALLYLIC AND VINYLIC COMPOUNDS

| Compound | $k_3$ (at 30 °C) / dm$^6$ mol$^{-2}$ s$^{-1}$ | $E_a$ / kJ mol$^{-1}$ | $\Delta S^*$ (at 30 °C) / J K$^{-1}$ mol$^{-1}$ | $\Delta G^*$ (at 30 °C) / kJ mol$^{-1}$ |
|---|---|---|---|---|
| Allyl chloride | 10.49 | 30.6±1.1 | −133.1 | 68.3 |
| Allyl bromide | 11.11 | 27.2±0.4 | −143.6 | 68.3 |
| Allyl acetate | $6.25\times10^{2}$ | 30.1±0.4 | −100.5 | 58.2 |
| 1-Hexene | 3.67 | 28.1±0.7 | −150.3 | 71.2 |
| Methyl acrylate | $2.43\times10^{-2}$ | 28.1±0.3 | −191.8 | 83.7 |
| Methyl methacrylate | $3.33\times10^{-2}$ | 20.9±1.2 | −212.7 | 82.9 |
| Methyl crotonate | $1.95\times10^{-2}$ | 24.7±0.3 | −190.9 | 84.2 |
| Acrylamide | $25.00\times10^{-2}$ | 43.1±0.4 | −122.7 | 77.9 |
| Methacrylamide | $9.72\times10^{-2}$ | 20.9±1.4 | −203.9 | 80.4 |