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Kinetics and Mechanism of the Addition of Iodine Monochloride to Some Alkenes in Nitrobenzene Solvent. Effect of Polarity of the Solvent

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The kinetics of the addition of iodine monochloride (ICl) to some vinyl compounds in nitrobenzene solvent was investigated. In all cases the reaction follows second order dependence on ICl and first order on the substrate, making the total order three. Rate constants were measured for each substrate at 20°, 30°, 40° and 50 °C. *Arrhenius* plots were made from which activation energies were evaluated. Other kinetic and thermodynamic parameters are reported. A suitable mechanism is proposed for the reaction and based on this, the various parameters are discussed. Solvent effects are discussed and the data with nitrobenzene and acetic acid solvents are compared.

(Keywords: Iodine monochloride; Kinetics; Solvent effects)

Kinetik und Mechanismus der Addition von ICl *zu einigen Alkenen in Nitrobenzol als Lösungsmittel. Effekt der Polarität des Lösungsmittels*

Die Kinetik der Addition von ICl zu einigen Vinylverbindungen in Nitrobenzol als Lösungsmittel wurde untersucht. In allen Fällen ist die Reaktion von zweiter Ordnung hinsichtlich ICl und von erster Ordnung hinsichtlich des Substrats, d. h. mit einer Gesamtordnung von drei. Geschwindigkeitskonstanten wurden für jedes Substrat bei 20°, 30°, 40° und 50 °C gemessen. Aus *Arrhenius*-Diagrammen wurden Aktivierungsenergien ermittelt und auch andere kinetische und thermodynamische Parameter wurden bestimmt. Ein Mechanismus wird vorgeschlagen, wobei die verschiedenen Parameter diskutiert werden. Lösungsmitteleffekte werden ebenfalls diskutiert und die Daten mit Nitrobenzol und Essigsäure als Lösungsmittel miteinander verglichen.

Introduction

This paper deals with the addition of iodine monochloride (ICl) to methyl acrylate, methyl methacrylate, methyl crotonate, acrylamide and methacrylamide in nitrobenzene solvent. The results of the addition of ICl to these compounds in dry acetic acid have been reported[1]. Current literature survey indicates that not much work has been done so far as regards the effect of solvent on the kinetics of ICl addition to alkenes. *Heublein*[2] studied the addition of ICl to stilbene in solvents such as carbon tetrachloride, acetic acid, methyl cyanide and butyl ether. The effect of the solvent on the transition state and the nature of the intermediate was discussed. So it was thought by one of the authors (*NA*) to carry out a thorough and systematic kinetic study of the addition of ICl to some vinylic compounds in dry acetic acid first and then increase the polarity of the medium and compare the results.

Experimental

Nitrobenzene (S. Merck, A.R.) was dried over calcium chloride for two days and distilled. The fraction boiling at 209 °C at ca. 1 atm. pressure was collected. Iodine monochloride and methyl crotonate were prepared as described in literature[3, 4]. Methyl acrylate and methyl methacrylate were purified[5] by distillation under reduced pressure. Acrylamide[6] and methacrylamide[7] were purified by recrystallisation. Potassium iodide, sodium thiosulfate and potassium dichromate used were all A.R. BDH samples.

The progress of the reaction was followed[1] by estimating unconsumed ICl iodometrically. The stoichiometry of the reaction was established by employing the well known method[8] using a mixture of KBr and $KBrO_3$. The product analysis of this reaction was made from ^{1}H-NMR spectra taken in a Varian T 60 NMR spectrometer using carbon tetrachloride as the solvent with 2% tetramethylsilane as the internal standard.

Results and Discussion

Employing the integration and differential methods[9], it was found that the reaction follows third order kinetics in the temperature range investigated and the *Arrhenius* equation is strictly obeyed (Fig. 1) and the order in ICl and in substrate were found to be two and one respectively (Fig. 2).

Kinetic runs were carried out at 20°, 30°, 40° and 50 °C, for ICl addition to the title compounds. With equal initial molar concentrations of the reactants ($2.5 \cdot 10^{-2}\,M$), the experimental data fitted well into the integrated third order equation $1/(a-x)^2 = 2\,k_3 t + 1/a^2$. In all the cases, the reactions were followed to the extent of 60% and above. The values of the rate constant (k_3) were evaluated from the slope of the third order plots of $1/(a-x)^2$ versus time (t). Fig. 3 shows the integration plots for the methyl acrylate-ICl reaction at different temperatures. *Arrhenius* plots are shown in Fig. 4. The actual value of E_a and the "probable error" in E_a were obtained by the method of least squares (computer programmed) for each alkenic substrate using the k_3 values at

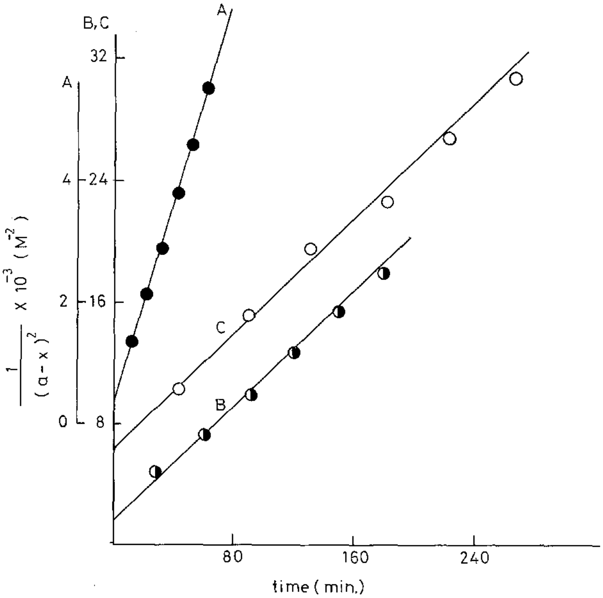


Fig. 1. Plots of $1/(a-x)^2$ versus time for the methyl acrylate—ICl reaction with various equal initial molar concentrations in nitrobenzene at 50 °C; *A* $5.00 \cdot 10^{-2} M$; *B* $2.50 \cdot 10^{-2} M$; *C* $1.25 \cdot 10^{-2} M$

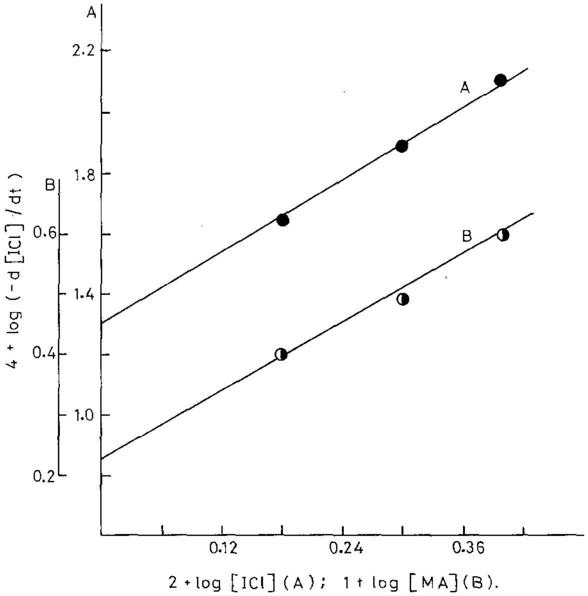


Fig. 2. Plots of log (initial rate) versus *A* log [ICl] and *B* log [*MA*] for the methyl acrylate—ICl reaction in nitrobenzene at 40 °C

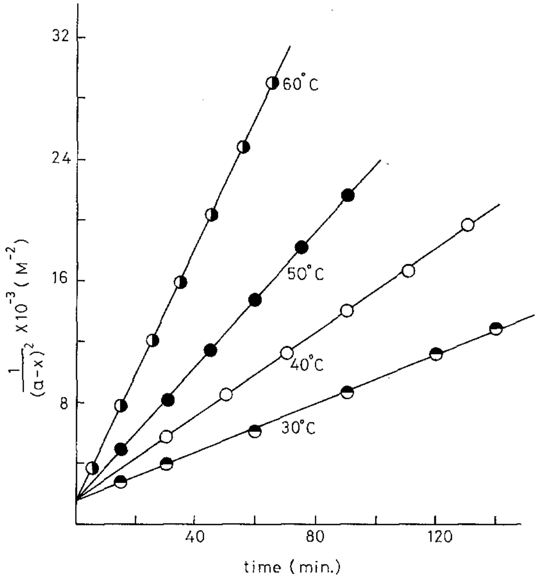


Fig. 3. Plots of $1/(a-x)^2$ versus time for the acrylamide—ICl reaction in nitrobenzene at different temperatures; $[AAm] = [\text{ICl}] = 2.5 \cdot 10^{-2} M$

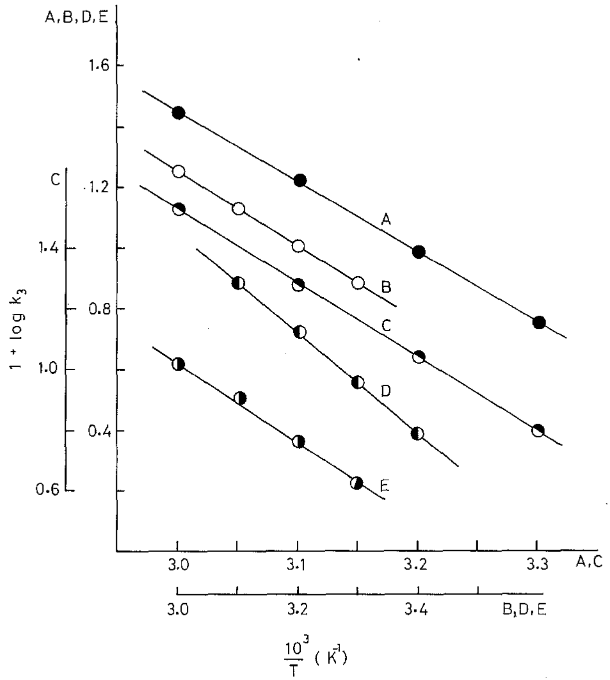


Fig. 4. *Arrhenius* plots of $\log k_3$ versus $1/T$. *A* Methacrylamide; *B* methyl crotonate; *C* acrylamide; *D* methyl acrylate; *E* methyl methacrylate

Table 1. *Specific rate constant (k_3) values, activation energies (E_a), and thermodynamic parameters of activation at 30 °C for the reaction of iodine monochloride with different vinyl compounds in nitrobenzene (NB) and dry acetic acid (AA) media*

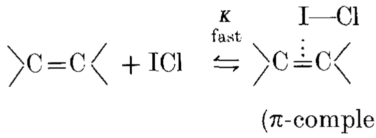
Alkene	Solvent	$10^3 k_3$ $s^{-1} mol^{-2} l^2$	E_a kcal mol^{-1}	$-\Delta S^*$ cal $deg^{-1} mol^{-1}$	ΔH^* kcal mol^{-1}	ΔF^* kcal mol^{-1}
Methyl acrylate	*NB*	360	7.2 ± 0.12	38.8	30.2	18.4
	AA	24	6.7 ± 0.08	45.8	33.9	20.0
Methyl methacrylate	*NB*	1 880	4.9 ± 0.22	43.1	30.5	17.4
	AA	33	5.0 ± 0.29	50.8	55.2	19.8
Methyl crotonate	*NB*	730	5.3 ± 0.17	43.7	31.1	17.9
	AA	20	5.9 ± 0.06	45.6	33.9	20.1
Acrylamide	*NB*	670	11.0 ± 0.39	25.1	25.6	18.0
	AA	25	10.3 ± 0.09	29.3	27.5	18.6
Methacrylamide	*NB*	560	8.9 ± 0.14	32.3	27.9	18.1
	AA	97	5.0 ± 0.33	48.7	34.0	19.2

four temperatures. The thermodynamic parameters of activation for different alkenes were calculated and are recorded in Table 1.

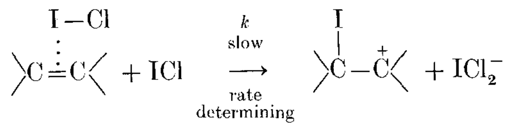
The stoichiometry was established as 1 : 1. The ^{1}H-NMR spectrum of the reaction mixture of methyl acrylate and ICl confirmed that the product is 1-iodo-2-chloromethyl acrylate.

Reaction Mechanism

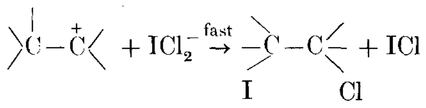
A mechanism is proposed in which the initial step is the formation of a π-complex by fast equilibration of alkene by ICl. The essential reaction sequences thus involved are:



(1)



(2)



(3)

Thus the rate of disappearance of ICl

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

The expression for π-complex from equation (1) is fed into equation (4) to get the equation

$$\frac{-\mathrm{d}[\mathrm{ICl}]}{\mathrm{d}t} = kK\,[\text{alkene}]\ [\mathrm{ICl}]^2 \tag{5}$$

where $kK = k_3$, ($\mathrm{s}^{-1}\,\mathrm{mol}^{-2}\,\mathrm{l}^2$).
This mechanism is the same as that explained for dry acetic acid solvent[1].

The kinetic and thermodynamic parameters reported in Table 1 will now be discussed. The observed rate constant k_3 is the product of the equilibrium constant (K) and the rate constant (k). Likewise the values of ΔS^*, ΔH^* and ΔF^* are the sums of the values of ΔS, ΔH and ΔF for the equilibrium (1) and the ΔS_1^*, ΔH_1^* and ΔF_1^* for step (2). The ΔS^* values are negative showing loss in entropy during the formation of the activated complex. Both the methyl substituted isomeric methyl methacrylate and methyl crotonate have activation energies of 4.9 and 5.3 kcal mol^{-1}, respectively, lower than that in unsubstituted methyl acrylate, 7.2 kcal mol^{-1}. Methyl methacrylate reacts faster and consequently it has a slightly lower E_a value than methyl crotonate. These observations can be attributed to the retention of negative charge on the alkenic carbon atom in methyl methacrylate and the extensive conjugation in methyl crotonate.

Further, the lower E_a value obtained in the case of methacrylamide compared to acrylamide may be due to electron-accession to the double bond due to the extra methyl group present in methacrylamide. However, the rate of addition of ICl to methacrylamide is lower than that to acrylamide because of the more negative ΔS^* value for methacrylamide (-32.3 cal deg^{-1} mol^{-1}) than for acrylamide (-25.1 cal deg^{-1} mol^{-1}). That is, in the case of methacrylamide, the gain in energy is lost in entropy. It is evident from Table 1 that the free energy of activation (ΔF^*) changes slightly with the nature of the substituent. This may indicate that the reaction mechanism is same for all the compounds studied, where the constancy of ΔF^* is essentially due to the linear compensation between ΔH^* and $-T\,\Delta S^*$.

Effect of Solvent Polarity

The kinetics of the addition of ICl to methyl methacrylate was investigated, using various nitrobenzene—acetic acid mixtures as solvents (acetic acid content of the solvents being 0, 20, 40, 60, 80 and 100% *v*/*v*). The mole fraction—rate constant profile (Fig. 5) indicates that, as the acetic acid content of the solvent increases (i.e. with decreasing polarity of the medium), the rate constant decreases. In other words, the rate constant increases with increasing polarity of the medium which is in accordance with the *Hughes-Ingold*[10] theory. It may be inferred that in the alkene—ICl reaction the activated complex is more polar than the reactants[11] and that the nitrobenzene molecules being more polar than acetic acid molecules stabilize the activated complex to a greater extent. This observation also justifies the polar nature suggested for the activated complex.

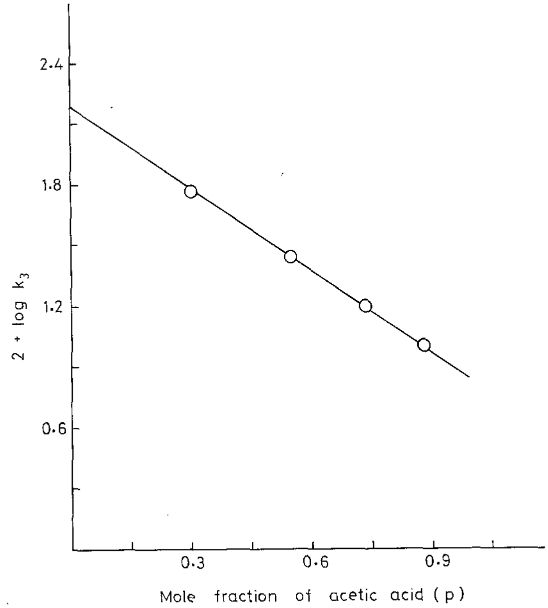


Fig. 5. Plot of $\log k_3$ versus mole fraction of acetic acid (p) for the methyl methacrylate—ICl reaction at 30 °C; $[MMA] = [ICl] = 2.5 \cdot 10^{-2} M$

It is worthy to mention here that in the bromination of aromatics (a dipole—dipole reaction) in acetic acid—water mixtures of varying proportions, *Seshadri* and *Ganesan*[12] found that the results fitted well into the emprical equation $k_{(aq)} = k_{(dry)}\, e^{\alpha p}$, where $k_{(aq)}$ and $k_{(dry)}$ are the rate constants in aqueous and dry acetic acids respectively, "p" is the molefraction of water and "α" is a constant; that is, a plot of log k versus "p" was quite linear. In the present case also, this equation is valid over a wide range of molefractions in nitrobenzene—acetic acid mixtures as solvents (Fig. 5).

Considering the different theories of solvent effects put forward by various workers[13–16], the data in Table 1 are analysed. The rate constants for the alkene—ICl reactions studied are higher in nitrobenzene than in acetic acid. A substrate with an electron-releasing methyl substituent on the alkenic carbon atom has a lower activation energy than the corresponding substrate without the methyl group (e.g. E_a for methyl methacrylate, 4.9 kcal mol^{-1}; methyl acrylate, 7.2 kcal mol^{-1}). This is true in both the solvents, nitrobenzene and acetic acid. Further, the E_a value for a given substrate remains more or less constant in both the solvents except in the case of methacrylamide where the value of E_a is higher in nitrobenzene. In this context, it is very relevant to quote *Frost* and *Pearson*[17]. According to them, most of the factors that determine the energy barrier are properties of the reactants such as strength of the bonds and the forces resulting from interaction of the filled electron levels in different molecules. The dielectric properties of the solvent play only a secondary role. Since the solvent lowers the energy of both the reactants and the activated state by solvation, even this effect tends to cancel.

It can therefore be concluded that the variations in rate constant for a given substrate in nitrobenzene and acetic acid are mainly controlled by the ΔS^* values. This is so because the solution entropy is made up of terms due to magnitude of volume, charge, shape, structure and solvation of the species. The fact that the ΔF^* values for vinyl compounds are almost constant in both the solvents amply confirms the proposal that the same reaction mechanism is operating in both nitrobenzene and acetic acid solvents. The relationship between ΔH^* and ΔS^* is linear indicating that the same mechanism operates for all the substrates in both the solvents.

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