KINETICS OF THE ADDITION OF IODINE MONOCHLORIDE TO OLEFINS

ADDITION of iodine monochloride (ICl) to carbon-carbon double bonds is a well-known reaction used as a test for unsaturation, especially in oils and fats. Although the relative rates of ICl-addition to some olefins have been measured[1,2] detailed kinetic investigations on this reaction have not been carried out so far; especially the Arrhenius parameters have not been evaluated. This reaction can be classified as a dipole-dipole reaction similar to other electrophilic reactions such as aromatic bromination by molecular bromine, aromatic chlorination by molecular chlorine, bromine-addition and chlorine-addition to olefins. For all these reactions, it has been theoretically shown and experimentally proved that the Arrhenius activation energy is related to the electron-density at the reaction cent e[3-7]. In this communication some significant results obtained in a kinetic study of ICl-addition to methyl acrylate and methylmethacrylate are reported. Anhydrous acetic acid and nitrobenzene were used as solvents.

With equimolar initial concentrations of methyl-acrylate and ICl, the overall reaction obeyed the integrated third order rate equation $1/(a - x)^2 = 2k_3 t + 1/a^2$, where a is the initial concentration of ICl and x is the amount of ICl reacted in time t; that is plots of $1/(a - x)^2$ against time (t) were linear and gave an intercept of $1/a^2$ on the zero-time ordinate. Figure 1 shows typical plots for initial concentrations
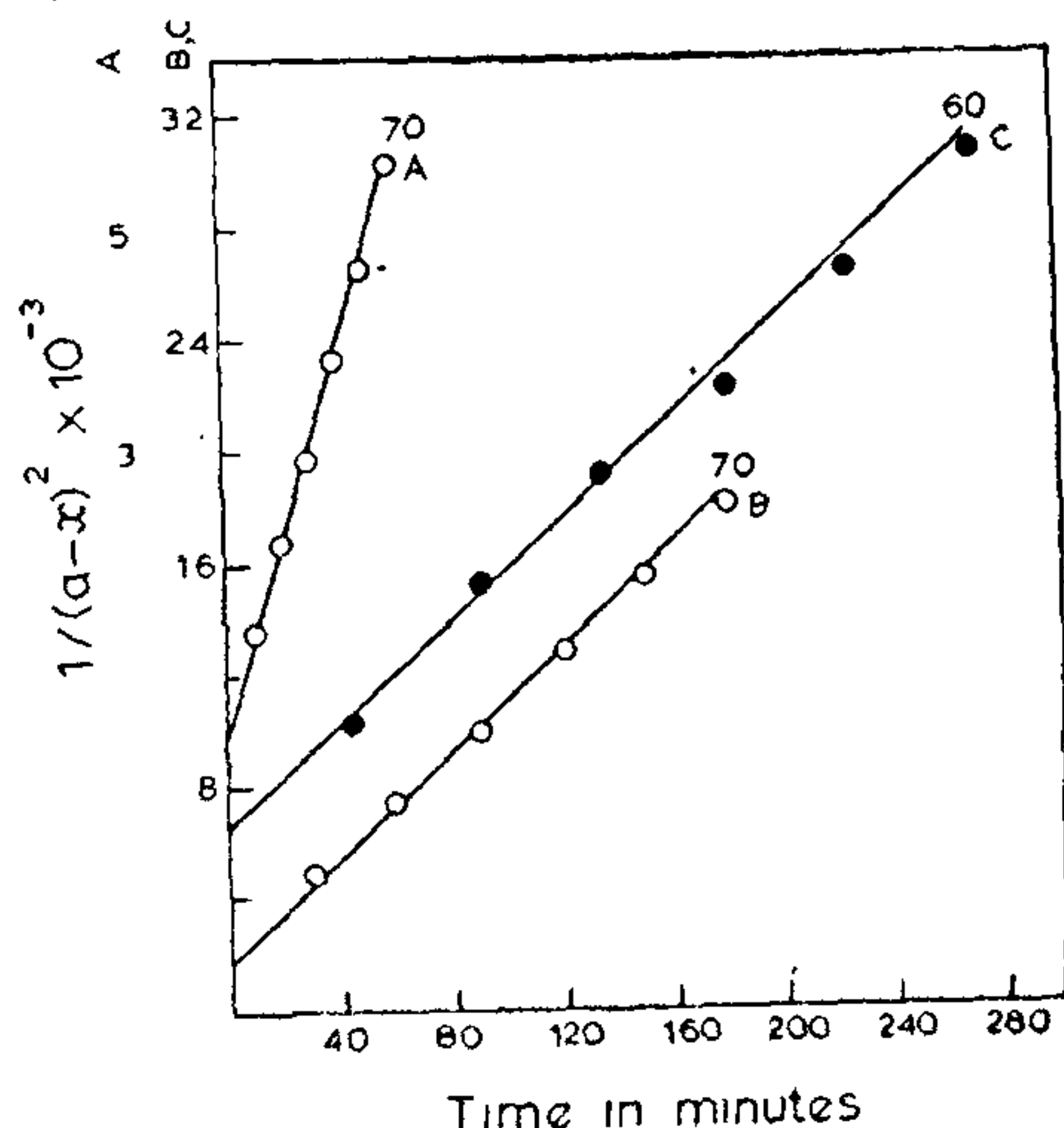

FIG. 1. ICl addition to methylacrylate in nitrobenzene at 50° C. Plots showing overall third order kinetics for equimolar initial concentrations of methylacrylate and ICl; A, 5·00 10⁻² M; B, 2·50 10⁻², M; C, 1·25 10⁻² M.

of $5·00 \times 10^{-2}$, $2·50 \times 10^{-2}$ and $1·25 \times 10^{-2}$ M. The numerical figure near the last point on each graph shows the percentage conversion for that particular kinetic run. The values of k_3, the third order rate constant, evaluated from the slopes ($2k_3$) of the straight lines are $0·75$, $0·78$ and $0·74$ M^{-2} sec^{-1}, which are nearly constant. By adopting isolation and differential methods, the order in methyl acrylate was found to be one and the order in ICl to be two, which are in good agreement with the overall order being three. The same results regarding the order of the reaction were obtained for the reaction between methyl-methacrylate and ICl in nitrobenzene and acetic acid solvents.

The rate constants (k_3) for the methylacrylate-ICl reaction were evaluated accurately, by carrying out the runs in duplicate in nitrobenzene medium, at 20°, 30°, 40°, and 50° C. Using these k_3 values, the value of the Arrhenius activation energy (E_a) was evaluated to be $7·2 \pm 0·12$ kcal.mole^{-1} by the method of least squares. Similarly the value of E_a for methylmethacrylate-ICl reaction was $4·9 \pm 0·22$ kcal. mole^{-1}. The complete Arrhenius equations for the reactions of ICl with methyl acrylate and methylmethacrylate in acetic acid and nitrobenzene solvents were

Methylacrylate (acetic acid medium),
$k_3 = 1·6 \times 10^3 \exp(-6700 \pm 80/RT)$

Methyl methacrylate (acetic acid medium),
$k_3 = 1·3 \times 10^2 \exp(-5000 \pm 290/RT)$

Methylacrylate (nitrobenzene medium),
$k_3 = 6·3 \times 10^4 \exp(-7200 \pm 120/RT)$

Methyl methacrylate (nitrobenzene medium),
$k_3 = 6·3 \times 10^3 \exp(-4900 \pm 220/RT)$.

The error factor ($\pm$) for each E_a is given as obtained from the least squares calculation. They only show the order of magnitude of the accuracy of each E_a. It is seen that the introduction of a methyl group increases the electron-density at the reaction centre (carbon-carbon double bond) and reduces the value of E_a. This is quite consistent with earlier experimental observations on similar dipole-dipole reactions[1,4,6,7] and is in accordance with the theoretical approach developed by Ganesan[5], based on the activated-complex theory treatment of such reactions.

Experimental

25 ml of the ICl solution and 25 ml of the olefin solution in a given solvent were thermostated and mixed in a 50 ml ground glass stoppered iodine flask. 5 ml aliquots were pipetted out at various time intervals and added to 10% potassium iodide solution (containing 6% sodium bicarbonate when acetic acid was used as the solvent) in a conical flask, to quench

the reaction, and the liberated iodine was titrated against standard sodium thiosulphate.

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EFFECT OF ANIONS IN THE PAPER CHROMATOGRAPHIC SEPARATION OF Co(II), Ni(II), Cu(II) AND Zn(II), WITH DIFFERENT NEUTRAL MONODENTATE LIGANDS

COMPLEXING agents are often used in paper chromatographic separation of transition metal ions[1-5]. The mobility of these ions on the paper depends very much on the composition of the complexes formed with the ligands. In the presence of non-coordinating anions, divalent 3d transition metal ions normally form six coordinate complex species of the general formula $[ML_6]^{2+}$ where L is a neutral monodentate ligand. It has been proved already that these transition metal ions form complexes of varied composition with the ligands in presence of different halide anions[6-10]. It is proposed to study the effect of varying composition of complexes brought about by different anions on the R_f values of metal ions.

Experimental

For the present investigation, the ligands Diphenyl-sulphoxide (DPSO), Pyridine–N–Oxide (PNO) and Quinoline–N–Oxide (QNO) and the anions ClO_4^-, Cl^- and Br^- with the divalent transition metal ions Co, Ni, Cu and Zn were chosen.

Chromatography was performed on Whatmann No. 1. paper strips (18 × 2·5 cm) in glass jars (20 × 4·5 cm). Metal perchlorates were prepared by treating 70% perchloric acid with metal carbonates and crystallising them in water. 0·06 Molar solution of metal ions were prepared by dissolving the metal perchlorates in 95% ethanol and were used for spotting. The ligands DPSO, PNO and QNO were prepared by methods

reported previously[11, 12]. The R_f values of the cations were calculated for the following solvent systems :

1. 6M $HClO_4$ + iso-Propanol + Acetone
   (1 : 1 : 1, V/V)
2. 6M $HClO_4$ + iso-Propanol + Acetone
   (1 : 1 : 1, V/V) + 2% ligand
3. 6M HCl + iso-Propanol + Acetone
   (1 : 1 : 1, V/V)
4. 6M HCl + iso-Propanol + Acetone
   (1 : 1 : 1, V/V) + 2% ligand
5. 6M HBr + iso-Propanol + Acetone
   (1 : 1 : 1, V/V)
6. 6M HBr + iso-Propanol + Acetone
   (1 : 1 : 1, V/V) + 2% ligand.

Cu(II), Co(II) and Ni(II) were identified by spraying with 0·1% alcoholic solution of rubeanic acid and exposing to vapours of ammonia[13]. Cu(II), Co(II) and Ni(II) gave olive green, yellow and bright blue spots respectively. Zn(II) was detected by spraying with a mixture of 0·02% cobalt sulphate solution and ammonium mercury thiocyanate reagent[21]. It gave a blue spot.

Results and Discussion

The R_f values of the transition metal ions Co(II), Ni(II), Cu(II) and Zn(II) in different solvent systems with and without the neutral monodentate ligands DPSO, PNO and QNO are listed in Table I.

TABLE I

R_f values of metal ions in different solvent systems

Solvent system	Cobalt	Nickel	Copper	Zinc
1	0·76	0·71	0·78	0·77
2 with DPSO	0·25	0·28	0·22	0·30
2 with PNO	0·47	0·41	0·52	0·40
2 with QNO	0·33	0·39	0·31	0·35
3	0·68	0·58	0·72	0·68
4 with DPSO	0·56	0·46	0·59	0·55
4 with PNO	0·61	0·53	0·72	0·59
4 with QNO	0·60	0·49	0·67	0·57
5	0·54	0·49	0·62	0·61
6 with DPSO	0·37	0·34	0y55	0·59
6 with PNO	0·52	0·49	0·69	0·64
6 with QNO	0·42	0·39	0·60	0·61

In solvent system 1 the cations are considered to be in hydrated form, since perchlorate anion is essentially non-coordinating. But in systems 3 and 5 where coordinating anions alone are present they may form the species $[MX_4]^{2-}$ or $[MX]^{4-}_6$ where X is Cl^- or Br^-. It has been reported in literature[14-18], that divalent metal perchlorates form solid complexes of the type $[ML_6]$ $(ClO_4)_2$, with neutral monodentate ligands.