

Kinetics of Reaction between Iodine & *o*-Chloromercuriphenol in Methanol, Ethanol, *n*-Propanol, Isopropanol, *n*-Butanol & *n*-Pentanol

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The substitution reaction of *o*-chloromercuriphenol with iodine in methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol and *n*-pentanol has been found to have a total order of two; one each with respect to iodine and *o*-chloromercuriphenol. The values of ΔH^\ddagger , ΔE^\ddagger and ΔS^\ddagger have been found to vary from 5.19 to 14.33 kcal mole⁻¹, 5.82 to 14.96 kcal mole⁻¹, and -39.6 to -15.2 e.u. at 40°, respectively. A reaction mechanism based on electrophilic substitution has been proposed in which I₂.solv or I⁺.solv acts as the attacking agent.

It appears that amongst the aromatic mercury compounds relatively a larger number of reactions of halogens with benzylmercuric halides and their derivatives have been investigated¹, but the number of corresponding reactions with phenylmercuric halides and their derivatives investigated so far is rather small. The kinetics of reaction of *o*-chloromercuriphenol with iodine in methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol and *n*-pentanol have been studied and the results are reported in this paper.

Materials and Methods

o-Chloromercuriphenol was prepared by a modification² of the method reported in literature³. Iodine (BDH) was purified by repeated sublimation. All the solvents (BDH) used were purified by standard techniques⁴. Millimolar solutions of *o*-chloromercuriphenol and iodine were used for kinetic studies.

Kinetic measurements—The reactions at 20°, 30° and 40° ± 0.05° in each solvent were followed by measuring the rate of disappearance of iodine spectrophotometrically at different time intervals. A Bausch and Lomb spectronic 20 spectrophotometer was used for measuring the transmittance at 450-460 nm which is the λ_{max} of solvated iodine molecules. Concentrations of iodine in the reaction mixtures were determined using calibration curves.

Results and Discussion

The total order of the reaction of iodine with *o*-chloromercuriphenol was found to be two by the graphical method (linear plot of $1/a-x$ versus t at equimolecular concentrations of the reactants). The pseudo-first order reaction with respect to each reactant, while keeping the concentration of the other in excess could not be tried in the present study because (a) the solubility of *o*-chloromercuriphenol in the alcohols was not very high, and (b) when the [iodine] was increased in excess over [*o*-chloromercuriphenol], the reaction proceeded

to completion at a very fast rate. The specific rate constants at different temperatures in each solvent were obtained from the slopes of $1/a-x$ versus time plots, and the values so obtained are given in Table 1. The energy of activation (ΔE^\ddagger) in each solvent was calculated from the plot of $\log k$ versus $1/T$. The entropy of activation (ΔS^\ddagger) was obtained from the equation:

$$\ln k = \ln \left(\frac{RT}{Nh} \right) + \frac{\Delta S^\ddagger}{2} - \frac{\Delta H^\ddagger}{RT}$$

where $\Delta H^\ddagger = \Delta E^\ddagger - RT$, and other symbols have their usual significance. The values of ΔE^\ddagger and ΔS^\ddagger are given in Table 1.

The substitution reactions of alkyl- or arylmercuric halides with halogens have been reported to follow either a free radical pathway or an electrophilic mechanism¹ depending on the reaction conditions. The reactions involving free radicals are of first or second order in halogen but usually of zero order in organomercurial⁵, and the reactions involving an electrophilic substitution pathway have total order of two, one each in halogen and organomercurial⁶. The reactions of benzylmercuric halides with iodine in non-polar solvents, like CCl₄, involves free radical mechanism⁷ whereas the same reactions change over to the electrophilic substitution path when carried out in polar solvents in the presence

TABLE 1—SPECIFIC RATE CONSTANTS (k) AT DIFFERENT TEMPERATURES AND THE ACTIVATION PARAMETERS FOR THE REACTION OF IODINE WITH *o*-CHLOROMERCURIPHENOL IN DIFFERENT SOLVENTS

Solvent	k (litre mole ⁻¹ min ⁻¹)			ΔE^\ddagger (kcal mole ⁻¹)	ΔS^\ddagger (e.u.)
	20°	30°	40°		
Methanol	0.50	0.72	1.24	5.82	-39.6
Ethanol	0.74	1.10	1.51	6.47	-37.6
<i>n</i> -Propanol	0.10	0.18	0.30	10.21	-26.8
Isopropanol	0.10	0.18	0.34	11.18	-23.6
<i>n</i> -Butanol	0.27	0.50	1.11	13.02	-16.8
<i>n</i> -Pentanol	0.05	0.11	0.26	14.96	-15.2

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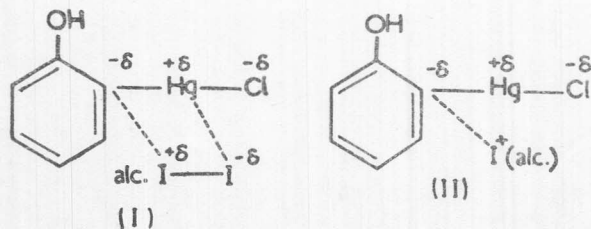
of CdI_2 or other source of iodide ions^{7b,8}. Though comparatively a fewer number of reactions of phenylmercuric halides with halogens have been investigated, their results are similar to those found in the case of benzylmercuric halides⁹.

These electrophilic substitution reactions of organomercurials with iodine in the presence of iodide ions are of second order and it has been proposed that in these reactions the attacking species is the triiodide, I_3^- , ion⁸. In the present study in the absence of CdI_2 the reaction follows a second order kinetics in lower aliphatic alcohols. That this reaction does not follow a free radical pathway under these conditions was established by the observation that the reaction was not inhibited by the presence of a small amount of hydroquinone, a well-known inhibitor for free radical reactions.

That the reaction follows an ionic mechanism is also supported by the dependence of specific rate constant and the energy of activation on dielectric constant of the solvent (Table 1). The plot of ΔE^\ddagger versus the dielectric constant of the solvents was linear.

The electrophilic mechanism proposed for the present reaction does not involve triiodide ions as the attacking species since no CdI_2 or other iodides were added to the system. The possibility of the presence of I_3^- ions in alcoholic system in the absence of iodides has been indicated by the UV and visible spectroscopic results¹⁰. However, the formation of I_3^- in alcohols requires the presence of I^+ ions in solution to maintain a proper equilibrium. It is evident that out of the two species, I^+ and I_3^- , it is I^+ which would be a better electrophile. It is thus reasonable to assume that in the present reaction I^+ or $\text{I}^+(\text{alc.})$ may be the attacking species. In fact, the attacking species may even be the complex $\text{I}_2(\text{alc.})$ itself. The iodine molecule will be polarized in $\text{I}_2(\text{alc.})$ such that one iodine atom would be slightly positive and other slightly negative and the structure (I) may be proposed for the transition state complex.

In the case of pyridine- ICl complex the $\text{I}-\text{Cl}$ bond is lengthened (2.41 Å) as compared to the $\text{I}-\text{Cl}$ bond in ICl molecule¹¹ (2.32 Å), indicating a high polarization of ICl molecule in pyridine- ICl complex. Similar polarization, of course to a smaller extent, would be expected in the case $\text{I}_2(\text{alc.})$. Rutov *et al.*¹² have shown that though the reaction of benzylmercuric halides with bromine in non-polar solvents is of free radical type, the mechanism is changed to an electrophilic substitution pathway in the presence of small amount of oxygenated solvents like water, alcohols and esters. They suggested that the attacking species under these conditions may be a complex of bromine with oxygen containing molecule.



It is obvious from Table 1 that the specific rate constant does not vary regularly with the dielectric constant of the solvent according to Amis' $\log k$ versus $1/D$ relation¹⁴, the main deviation being at *n*-butanol. It is, therefore, difficult to conclude without supporting evidence that the activated complex could be formed by ionic species attaching itself to the reactant. However, some insight can be obtained by studying the activation energy and entropy of activation, which, however, are only derived data and do not hold primary significance.

The assumption that $\text{I}_2(\text{alc.})$ or $\text{I}^+(\text{alc.})$ (or I^+) may be the attacking species is supported by the nature of variation of activation energy in different alcohols. The energy of activation increases in passing from methanol to *n*-pentanol whereas the dielectric constant decreases from methanol to *n*-pentanol. As the dielectric constant decreases from methanol to pentanol, it is expected that the degree of polarization of iodine molecule in $\text{I}_2(\text{alc.})$ will decrease in that order. The decreasing polarization of iodine molecule will obviously make the formation of transition state complex less favourable; thus the highest activation energy would be expected in the case of *n*-pentanol and it is found to be so (Table 1). Similar situation would exist even if $\text{I}^+(\text{alc.})$ or I^+ is the attacking species because after all the formation of $\text{I}^+(\text{alc.})$ or I^+ may be assumed to be a case of complete polarization of iodine molecule in $\text{I}_2(\text{alc.})$. The transition state complex in the case of $\text{I}^+(\text{alc.})$ or I^+ functioning as the attacking species may be represented by structure (II).

It may be noted that methanol does not fall on the linear plot of ΔE^\ddagger versus dielectric constant. No attempt has been made to explain this abnormal behaviour of methanol as it is characteristic of the first homologue of any series to behave rather abnormally as compared to other members of the same series.

The formation of transition state complex $\text{I}_2(\text{alc.})$ would require a larger change in ΔS^\ddagger as compared to that required for the formation of I_3^- transition complex. The literature⁹ value of ΔS^\ddagger for the reaction of phenylmercuric bromide with iodine in methanol in the presence of CdI_2 is -13 e.u. which is quite different from that of the reaction of *o*-chloromercuriphenol with iodine in methanol in the absence of CdI_2 ($\Delta S^\ddagger = -39.2$ e.u. at 20°). The energy of activation increases by a factor of $2\frac{1}{2}$ while going from methanol to *n*-pentanol, so does the entropy. The plot of ΔH^\ddagger versus ΔS^\ddagger was found to be linear with a slope of ~ 1 . The variation in the free energy of activation (ΔG^\ddagger) in various solvent is small; ΔG^\ddagger varies from 17.58 to 18.02 kcal mole⁻¹. This indicates that although the enthalpy effects are large, they are somewhat compensated by the entropy of activation. Such compensating effects have been observed for other systems¹³ also. It is assumed that in the lower alcohols, the solubility of the reactants and their polarization would be more pronounced thereby resulting in higher enthalpy values for activation complex, while at the same time the activated complex is configurationally more stable, thus resulting in higher negative entropies. For the

higher alcohols, these effects may not be expected to be so pronounced.

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