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Kinetics and Mechanism of Iodination of Naphthalenes

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The kinetics of iodination of naphthalenes have been investigated with the iodinating system A: I_2-$NaNO_2$-HNO_3. The reaction is half order in $[I_2]$. It is first order in the substrate. Though there is a dependence of the reaction kinetics on $[HNO_3]$, no definite order has been observed in $[HNO_3]$. With increasing $[NaNO_2]$, the rate constants for each substrate increase initially and subsequently decrease. It is observed that the reactions are favoured in media of higher acetic acid content. The activation parameters have been evaluated using the Arrhenius relationship. The isokinetic temperature has also been evaluated. A mechanism of iodination has been suggested. It involves the initial formation of electrophilic HNO_2I^+.

INTRODUCTION

Iodine does not react easily with aromatic compounds unlike the other halogens. The literature survey indicates that only a few attempts have been made at synthesising aromatic iodo compounds, that too in the recent past. Since the direct iodination of aromatic compounds with molecular iodine is difficult,[1] a drastic reaction condition involving sodium nitrate/nitric acid, nitric acid/sulfuric acid or sulfuric acid/acetic acid system has been used to effect the reaction[2]. Silver sulphate-iodine[3] combination has also been used. In such a system, the oxidising agent converts the molecular iodine into a more reactive electrophilic species and renders the reaction easier. The other iodinating agents used for this purpose were I_2 with a silver salt, I_2 with $(NH_4)_2S_2O_8$, a catalytic amount of $NO^+BF_4^-$ (or $NaNO_3$) in combination with O_2 and I_2, and I_2 with Ce (IV) salt[4].

Though several attempts of preparing the iodoarenes have been reported, no significant kinetic studies seem to have been undertaken. Butler and Sanderson studied the kinetics of iodination of a number of substituted benzenes by iodine and nitric acid in acetic acid solution[5]. A sufficient amount of nitrite ion was added to the reaction mixture. The formation of an active electrophilic iodine moiety appears to be important in iodination.

No report has been published on complete mechanism of iodination using a mixture of an oxidising agent and iodine. The difficulty in obtaining a homogeneous system and the severe reaction condition required in most of the reactions make kinetic and mechanistic study difficult. Therefore, the iodinating agent $I_2/NaNO_2/HNO_3$ has been used in this investigation of the kinetics and mechanism of iodination of naphthalene and substituted naphthalenes.

EXPERIMENTAL

All the chemicals used in this study were of AR grade. Their purities were ascertained by b.p./m.p. determinations.

The reactions were followed using a Shimadzu Digital Double Beam Spectrophotometer-150-02 in conjunction with a thermobath (TB-85), which maintained the cell compartments at a fixed temperature (± 0.05°C).

The stock solutions of substrates and iodine were prepared by weighing the required amounts of these and made up with 100% pure glacial acetic acid. Similarly, sodium nitrite and nitric acid were also prepared in higher concentrations with doubly distilled water. For each set of experiments, fresh solutions were prepared. The usual preliminary adjustments in the spectrophotometer were done carefully before starting each experiment. The maximum absorbance of iodine solutions (0.0005–0.001 M) under the experimental conditions adopted was determined. It occurs at $\lambda_{max} = 475$ nm. Hence for all kinetic measurements, the iodine concentration was monitored at 475 nm. The reference solution, *i.e.*, aqueous acetic acid (AcOH 80% and H_2O 20% v/v) was kept in the other cell compartment and the absorbance was adjusted to zero. All the reactions were followed using a large excess of the substrate over the concentration of I_2. Excellent linear plots are obtained when $(a - x)^{0.5}$ values are plotted against time values, indicating that the reaction is half-order in iodine. The $k_{1/2}$ values are calculated from the slopes of the half-order plots by the method of least squares using a computer.

Activation energy is evaluated from the slopes of log $k_{1/2}$ *vs.* 1/T plots using method of least squares and then other thermodynamic parameters are calculated.

RESULTS AND DISCUSSION

The kinetics of iodination of naphthalene, 1-methylnaphthalene, 2-methylnaphthalene and 1-fluoro-, 1-chloro- and 1-bromonaphthalene and 1-nitro naphthalene have been studied using the reagent system I_2-$NaNO_2$-HNO_3. The solvent used is aqueous acetic acid.

Effect of Varying $[I_2]$ on the Reaction Rates

Butler and Sanderson[5], in their study on iodination of mesitylene, suggested that the iodination species contained only one atom of iodine, *i.e.*, HNO_2I^+. To check this possibility in the present study, a set of experiments was conducted by varying the initial concentration of iodine maintaining all the other experimental conditions identical. Each of the reactions has been followed with a large excess of substrate concentration with respect to iodine concentration. $[I_2]^{0.5}$ values have been plotted against time; a satisfactory linear plot is obtained. The absorption data are checked for their first order conformity; no satisfactory linearity has been obtained with any case. Therefore the order of the reaction is undoubtedly 0.5 in $[I_2]$. The data for each reaction fitted into a satisfactory $(a - x)^{0.5}$ versus time plot. The half-order rate constant, $k_{0.5}$ was obtained from the slope of each plot.

The iodination of all the aromatic hydrocarbons obeyed half-order kinetics with respect to the $[I_2]$. However, beyond about 80% of the reaction, a slight deviation from the half-order pattern was observed in each case (*i.e.*, the decrease in absorbance beyond about 80% reaction is less than what is expected for strict half-order kinetics). This deviation may be due to the reversibility of the reaction. It is well-known that iodination of some organic compounds is reversible. This reversibility has been well-substantiated by several investigators, as reported in the literature[6]. Therefore, the iodination of naphthalene also appears to be reversible. However, this reversibility seems to be feeble. Excess of HNO_3 used is expected to retard backward reaction. Therefore, very slight deviation observed in each of the half order relationships, that too only beyond 80% of the reaction, may be ignored.

Though each reaction has been found to be half order in iodine, curiously, the $k_{0.5}$ values obtained for a substrate are not independent of the initial concentration of iodine, *i.e.*, beyond 0.001 M of iodine, contrary to expectaton, the $k_{0.5}$ values decrease as the $[I_2]$ increases. This trend may be explained in two ways:

(a) π-bonds of the substrate molecule may form a π-complex with the molecular iodine. The formation of such a complex is expected to stabilise the hydrocarbon molecule and consequently decrease the reactivity of the hydrocarbon for iodination. Iodination being electrophilic, immobilisation of the π-cloud by complexation may not favour the attack by the active iodine species on the aromatic moiety of the π-complex. The formation of this complex would amount to decrease in the availability of unencumbered, free hydrocarbon molecules. The formation of such a π-complex between aromatic systems and I_2 has been well substantiated by the literature reports[7].

(b) Another mechanistic possibility is the conversion of the active iodinating species to a less active iodinating species with increase in iodine concentration.

With naphthalene, on increasing $[I_2]$ from 4×10^{-4} M to 20×10^{-4} M, the $k_{0.5}$ decreases by about 3-fold. However, with 1-methylnaphthalene, for similar increase in $[I_2]$ the decrease in $k_{0.5}$ is only 1.5-fold. For 2-methylnaphthalene the decrease is very slight. Methylnaphthalenes are more reactive than naphthalene in electrophilic substitution reactions. This enhanced reactivity of the methylnaphthalenes may be assumed to compensate for the decreased reactivity of iodine species with increase in $[I_2]$.

Effect of [Substrate] on the Reaction Rates

To ascertain the order of the reaction in [substrate], the kinetics have been monitored at different initial concentrations of each substrate. In so doing, all the other experimental parameters have been maintained identical. These data reveal that the $k_{0.5}$ values increase with increasing [substrate] for each substrate. A plot of log $k_{0.5}$ values versus log [substrate] is linear. The slope of each plot is one. In addition, $k_{0.5}$[substrate] values for each substrate are constant. These reveal that the order of the reaction in each substrate used is one. At this stage, therefore, the rate expression for the iodination can be denoted as

$$\text{Rate} = -\frac{dx}{dt} = k[I_2]^{0.5}\,[\text{sub}]$$

Effect of $[HNO_3]$ on the Reaction Rates

The iodination kinetics for each substrate have been followed at different $[HNO_3]$ values keeping all other experimental parameters constant. The $k_{0.5}$ values increase with increase in $[HNO_3]$ for all the substrates.

The dependence of the rate on $[HNO_3]$ is an indication that the nitric acid molecule is involved in the reaction. Though the $k_{0.5}$ values for each substrate increase with increasing $[HNO_3]$, this increase does not conform to any definite order with respect to $[HNO_3]$.

The question then arises about the role of nitric acid in iodination. A possibility is its interaction with $NaNO_2$ to form N_2O_4. N_2O_4 may then form NO_2, the latter interacting with H^+ provided by HNO_3 to form NO_2H^+. The NO_2H^+ may then react with molecular iodine forming an active iodinating species HNO_2I^+.

$$N_2O_4 \rightleftharpoons 2NO_2$$

$$NO_2 + H^+ \rightleftharpoons NO_2H^+$$

$$NO_2H^+ + \tfrac{1}{2}I_2 \rightleftharpoons HNO_2I^+$$

Effect of [NaNO2] on the Reaction Rate

The $k_{0.5}$ values for the iodination of three substrates are evaluated with different initial concentrations of $NaNO_2$, keeping the other experimental parameters invariant.

The $k_{0.5}$ values reveal that a very low or a very high concentration of $NaNO_2$ does not favour the reaction. Moderate reaction rates are noticeable when [$NaNO_2$] is in the range 0.005 M to 0.050 M.

For each substrate, on plotting $k_{0.5}$ values against [$NaNO_2$], a dome-shaped curve has been obtained (Fig. 1). The peak points, however, occur at different [$NaNO_2$] for the three substrates.

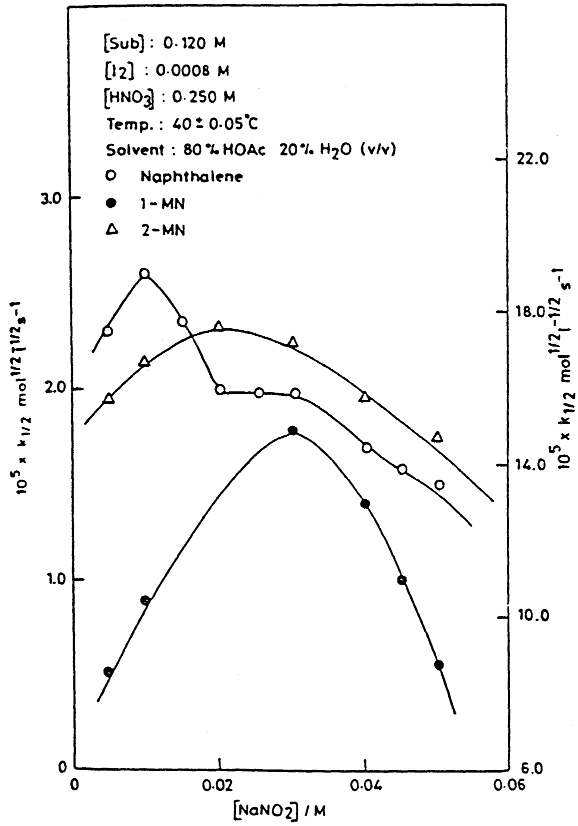


Fig. 1. System A: Effect of nitrite ion

Beyond 0.01 M [$NaNO_2$] in the case of naphthalene and beyond 0.02 M [$NaNO_2$] in the case of the methylnaphthalenes, the rate of iodination shows a decreasing trend. This may be due to complexation between the aromatic hydrocarbon and N_2O_4 generated. Such a complexation has actually been reported by Addison and Sheldon[8]. Therefore, the availability of the active substrate molecule for iodination may be decreased by the influence of N_2O_4 and hence the rate decreases. This complexation is expected to be predominant especially at higher [$NaNO_2$]. The existence of such complexes in the less polar solvents is expected to be more probable.

In this study, 80% HOAc-20% H_2O is used as the medium, which is less polar when compared with the solvent used in Butler and Sanderson's work; they used 10% HOAc as the medium for their study. The complexation is more likely in 80% HOAc and this accounts for the decreases in $k_{0.5}$ values at very large concentrations of $NaNO_2$.

Role of $NaNO_2$: The iodination does not occur in the absence of $NaNO_2$. However, $NaNO_2$ is unlikely to be involved in any direct reaction with the substrate. Presumably, it is involved in the formation of some active iodine species. A possibility is the formation of N_2O_4 by the interaction between $NaNO_2$ and HNO_3. In the sequence of reactions leading to the iodination, all the three steps must be fast equilibria. The vital aspect of the iodination reaction in this study seems to be the formation of the electrophilic iodine species aided by N_2O_4. This may account for the increase in $k_{0.5}$ values with increase in [$NaNO_2$]. Though it is actually so initially, further increase in [$NaNO_3$] depresses the reaction. This anomalous observation may be justified on the assumption that the solubility of N_2O_4 in the reaction medium is limited and consequently this limits the role of N_2O_4 in promoting the reaction.

Effect of Acetic acid on the Reaction: The iodination of naphthalene is studies in various water-acetic acid mixtures, maintaining the other experimental conditions identical. With all the naphthalenes, the solvent influence is uniform; the reactions were favoured by decreasing water content or increasing acetic acid content of the medium.

In the present study, the solvent effects are investigated at 40°C. Then, for each hydrocarbon, the log $k_{0.5}$ values are plotted against ($\varepsilon - \frac{1}{2}\varepsilon + 1$). No linear relationship has been obtained for any of the naphthalenes. Therefore, the reaction may not be of dipole-dipole type. Then a plot of log $k_{0.5}$ *vs.* $1/\varepsilon$ was drawn for each naphthalene. Such plots are linear with positive slopes for all the hydrocarbons studied. This substantiates that the iodination of the hydrocarbons used involves an ion and a dipole in the rate determining step. The results on solvent effects may therefore be considered to indicate that the iodination involves a cationic or electrophilic iodinating species and a dipolar hydrocarbon molecule.

Effect of Added NO_3^-: The formation of HNO_2I^+ in this study has been assumed to involve NO_3^- ion.

$$2HNO_3 + NO_2^- \longrightarrow NO_3^- + N_2O_4 + H_2O$$

Therefore, it is logical to anticipate a change in $k_{0.5}$ values when NO_3^- ions are introduced into the reaction medium. This has been checked by the addition of varying concentrations of KNO_3 (0.01 M to 0.40 M). This addition does not influence the magnitudes of $k_{0.5}$ value. This may be accounted for considering the relative concentrations of I_2 and HNO_3 (0.0008 M : 0.25 M); there is already available a large excess of HNO_3 over I_2 in the reaction medium. Hence, whatever may be the role of NO_3^- on the formation of the electrophilic iodine species, this role must have reached a saturating point with the available NO_3^- ion generated from HNO_3 itself. Any addition of NO_3^- ions in the form of KNO_3 therefore is not expected to influence $k_{0.5}$ values. However, the use of a low $[HNO_3]$ (comparable with that of I_2) in conjunction with added KNO_3 might reveal the effect of NO_3^- on $k_{0.5}$ values. But efforts to perform the reaction at such a low $[HNO_3]$ indicated no observable reaction rate.

Effect of Temperature: To study the effect of temperature on the iodination of the hydrocarbons, the reactions were carried out at different temperatures under identical concentrations of reagents. For each hydrocarbon, the log $k_{0.5}$ values were plotted against the reciprocal of absolute temperatures. These plots are linear, indicating that the iodination obeys the Arrhenius equation. From the slope of these plots, the energy of activation and the other thermodynamic parameters were calculated (Table-1).

TABLE-1
SYSTEM-A: ACTIVATION PARAMETERS AT 40 ± 0.05°C

Compound	$10^5 \times k_{0.5}$/mol$^{1/2}$ lit$^{-1/2}$ sec^{-1}	E_a	$-\Delta S^{\neq}$ J K^{-1} mol^{-1}	$\Delta G^{\neq}$ kJ mol^{-1}	$\Delta H^{\neq}$ kJ mole^{-1}
Naphthalene (1)	17.7	33	219	99	31
1-Methylnaphthalene (2)	124.000	67	96	94	64
2-Methylnaphthalene (3)	23.200	65	116	99	62
1-Fluoronaphthalene (4)	0.980	61	153	107	59
1-Chloronaphthalene (5)	0.652	36	238	108	33
1-Bromonaphthalene (6)	0.596	43	217	108	40
1-Nitronaphthalene (7)	0.406	60	165	109	57

A plot of $\Delta H^{\neq}$ versus $\Delta S^{\neq}$ is expected to be linear, according to the isokinetic relationship suggested by Leffler[9]. For iodination of all hydrocarbons, such linear plots (Fig. 2) have actually been obtained. The activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are given in Table-1. The numbers in the graph indicate the serial numbers of the hydrocarbons listed in Table-1. The linearity of $\Delta S^{\neq}$ versue $\Delta H^{\neq}$ plot indicates that all the hydrocarbons studied are iodinated with essentially the same mechanism. The slope of this plot 'β' is the isokinetic temperature. It represents the temperature at which all the hydrocarbons are likely to undergo the reaction at the same rate. The value of the slope is 247 K.

Activation Parameters

The $\Delta S^{\neq}$ values for all the substrates are highly negative. It ranges from –238 to –96 J K^{-1}/mole. These negative values indicate the formation of crowded transition states. Each substrate is a big molecule which reacts with a species containing a big iodine atom from the transition state. Such a transition state is expected to be bulky and hence the negative $\Delta S^{\neq}$ values may be justified.

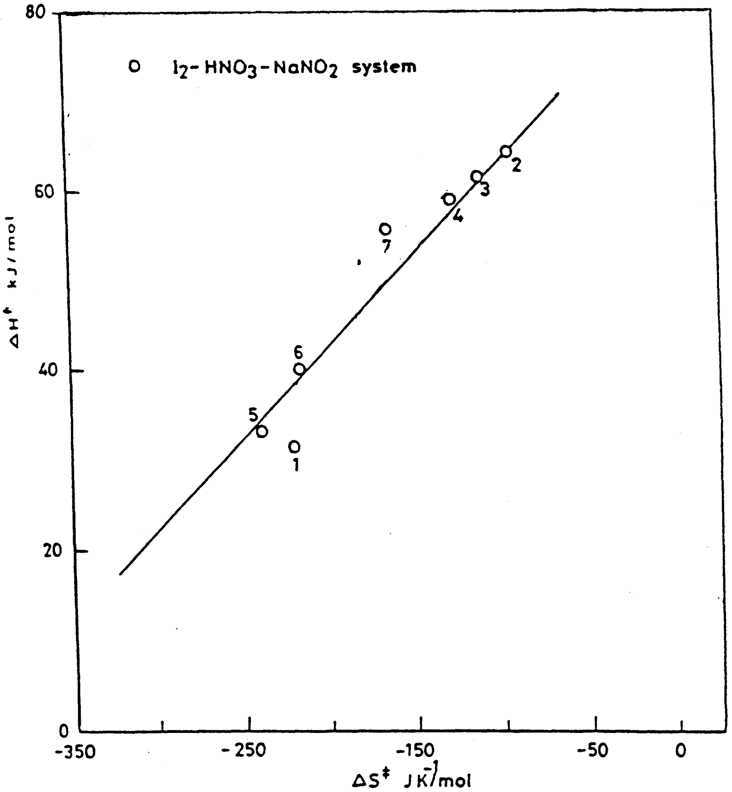


Fig. 2. Enthalpy-entropy plot

The $\Delta G^{\neq}$ values are appreciable for all the substrates; they are in the range from 31 to 64 kJ mol^{-1}. The iodination reactions are neither isoentropic nor isoenthalpic as revealed by the data in Table-1. These facts reveal that the reactions are affected by both electronic effects and kinetic steric effects.

Fig. 3 represents the Exner[10] plot for iodination of naphthalenes. The log $k_{0.5}$ values at 40°C are plotted against log $k_{0.5}$ values at 50°C for various substrates. A satisfactory linearity has been obtained according to the equation

$$\log k_2 = a + b \log k_1$$

The slope b is related to the isokinetic temperature (β) by the expression

$$\beta = T_1T_2[(1 - b)/(T_1 - bT_2)]$$

For iodination reactions, β is equal to 177 K. This may be compared with the isokinetic temperature value 245 K obtained by plotting $\Delta H^{\neq}$ values against $\Delta S^{\neq}$ values.

Mechanism

The salient features of this iodination reaction for all the hydrocarbons are

(i) The reaction is half order in iodine.

(ii) It is first order in substrate.

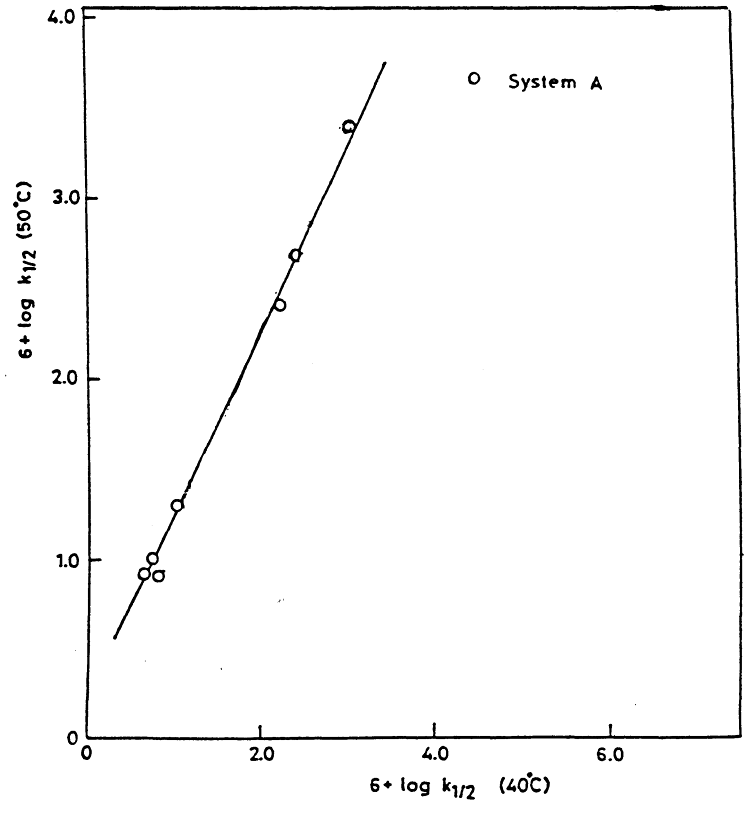


Fig. 3. Exner plot

(iii) No definite order in HNO_3 has been observed.

(iv) No definite order is obtained with respect to $NaNO_2$ also.

(v) The reaction shows a significant substituent effect; electron withdrawing groups retard the iodination and electron releasing groups accelerate it.

(vi) The reaction is favoured by media of higher acetic acid content, *i.e.*, lower dielectric constant.

(vii) The energy of activation is high and the entropy of activation is highly negative.

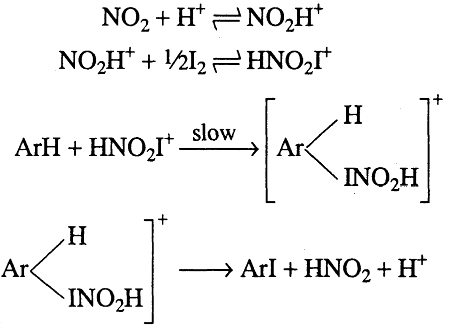
(viii) The reaction is not influenced by the addition of KNO_3.

Based on these observations the following mechanism may be considered:

The molecular iodine is inactive towards the substrate used. Therefore, the formation of an active iodine species is invoked. It may be initially N_2O_4 from HNO_2I^+. This is expected to be a powerful electrophile. It is visualised to attack this substrate molecule to form a σ-complex

This step is assumed to be the slow step. The σ-complex thus formed is then assumed to break down in a fast step forming mainly the iodo substitued product. This mechanism is depicted in Scheme-1.

$$N_2O_4 \rightleftharpoons 2NO_2$$



$$NO_2 + H^+ \rightleftharpoons NO_2H^+$$

$$NO_2H^+ + \tfrac{1}{2}I_2 \rightleftharpoons HNO_2I^+$$

$$ArH + HNO_2I^+ \xrightarrow{slow} \left[Ar\begin{matrix} H \\ INO_2H \end{matrix} \right]^+$$

$$\left[Ar\begin{matrix} H \\ INO_2H \end{matrix} \right]^+ \longrightarrow ArI + HNO_2 + H^+$$

Scheme-1

The substituent effect substantiates this mechanism. An electron releasing group like $—CH_3$ enhances the reaction rate. Such a group is expected to help the formation of the transition state involving the attack at an electron rich carbon in the substrate molecule by the electrophile.

This assumption is substantiated by the enhanced reactivities of methylnaphthalenes compared to those of naphthalene. An NO_2 group on the ring would decrease the electron density at the carbon and this in turn would decrease to ease of attack by the electrophilic iodine moiety. Accordingly, nitronaphthalene is less reactive than naphthalene.

In the transition state, a dispersal of charges is likely due to the formation of σ-complex by the interaction between the dipolar substrate molecule and the cationic iodinating species. Hence, relative to the reactants, the transition state would be solvated more in media of low dielectric constants than in media of high dielectric constants. Accordingly, increasing acetic acid content increases the ease of reaction, which lends additional support to this mechanism.

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