

Kinetics of Iodination of Benzenes and Their Reactivity

R. JOEL KARUNAKARAN and R. GOPALAN*
Department of Chemistry, Madras Christian College
Tambaram, Chennai-600 059, India

The kinetics of iodination of benzenes have been investigated with the iodinating systems A: I_2 — $NaNO_2$ — HNO_3 and B: I_2 — H_2SO_4 — HNO_3 separately. The data obtained from such studies show the following common features with both the systems: (a) The order of the reaction is 0.5 in $[I_2]$. (b) The reaction shows a dominant substituent effect. (c) The reactivity order is *m*-xylene > *o*-xylene > *p*-xylene > toluene > benzene > iodobenzene > bromobenzene > nitrobenzene > chlorobenzene > fluorobenzene. The activation parameters have been evaluated for each substrate. Analysis of these parameters indicates the involvement of a bulky transition state. A mechanism involving the attack of the benzene by the electrophilic iodine species has been suggested. The iodination involves the initial formation of electrophile HNO_2I^+ in system A and I^+ in system B.

INTRODUCTION

Benzene does not react with molecular iodine. Therefore, traditionally indirect routes are adopted for the preparation of iodobenzenes. A preliminary investigation on the reactivity of benzene with the reagent used for iodinating the naphthalenes indicated a steady consumption of iodine. Therefore, a systematic kinetic study on the iodination of benzenes was conducted. Therefore, the iodinating agents .

System A: I_2 — $NaNO_2$ — HNO_3

System B: I_2 — H_2SO_4 — HNO_3

have been used in this investigation of kinetics and reactivity of iodination of benzenes and substituted benzenes.

EXPERIMENTAL

All the chemicals used in this investigation 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 (T1B85), which maintained the cell compartments at a fixed temperature ($\pm 0.05^\circ C$).

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. Therefore, for all kinetic measurements, the iodine concentration was monitored at 475 nm. The reference solution, *i.e.*, aqueous acetic acid (AcOH 80%, H₂O 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 I₂. 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 slope of the half-order plots by the method of least squares using a computer.

The activation energy is evaluated from the slopes of $\log k_{1/2}$ versus $1/T$ plots using the method of least squares and then the other thermodynamic parameters are evaluated.

RESULTS AND DISCUSSION

Each substituted benzene has been reacted with iodine in presence of NaNO₂ and HNO₃ with system A and of H₂SO₄ and HNO₃ with system B. The study reveals that the reaction is half order in [I₂]. This indicates that the kinetic behaviour of this iodination is parallel to that of naphthalenes.¹

Reactivity of Alkylbenzenes: The kinetics of the reaction with four alkyl substituted benzenes, methylbenzene, *o*-xylene, *m*-xylene and *p*-xylene have been studied. With all the alkyl benzenes, satisfactory linearity has been obtained when [I₂]^{1/2} values are plotted against time values. In Tables 1 and 2 are given the relative $k_{1/2}$ values for these substrates in two different iodinating systems A and B respectively. The data reveal the following:

TABLE-1
SYSTEM A: RELATIVE REACTIVITY

[Sub]: 0.120 M; [NaNO₂]: 0.020 M; Temp.: 40 ± 0.05°C; [I₂]: 0.0008 M;
[HNO₃]: 0.250 M; λ_{\max} : 475 nm; Solvent: 80% HOAc-20% H₂O (v/v)

Substrate	$10^5 \times k_{1/2}/\text{mol}^{1/2} \text{ lit}^{-1/2} \text{ sec}^{-1}$	Relative reactivity
Benzene	7.81	1.00
Toluene	8.35	1.07
<i>o</i> -Xylene	10.60	1.40
<i>m</i> -Xylene	70.70	9.00
<i>p</i> -Xylene	2.52	0.30
Fluorobenzene	0.48	0.06
Chlorobenzene	0.815	0.10
Bromobenzene	1.12	0.14
Iodobenzene	1.85	0.23
Nitrobenzene	0.95	0.12

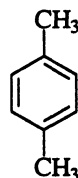
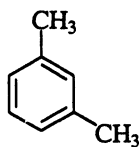
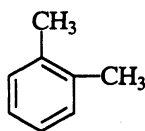
TABLE-2
SYSTEM B: RELATIVE REACTIVITY

[Sub]: 0.120 M; [H₂SO₄]: 0.050 M; Temp.: 40 ± 0.05°C; [I₂]: 0.0008 M;
[HNO₃]: 0.250 M; λ_{max}: 475 nm; Solvent: 80% HOAc-20% H₂O (v/v)

Substrate	$10^5 \times k_{1/2}/\text{mol}^{1/2} \text{ lit}^{-1/2} \text{ sec}^{-1}$	Relative reactivity
Benzene	2.82	1.00
Toluene	2.90	1.03
<i>o</i> -Xylene	2.31	0.82
<i>m</i> -Xylene	2.67	0.95
<i>p</i> -Xylene	2.52	0.90
Fluorobenzene	0.62	0.22
Chlorobenzene	1.02	0.36
Bromobenzene	1.15	0.41
Iodobenzene	2.26	0.80
Nitrobenzene	1.25	0.44

Methylbenzene is slightly more reactive than benzene (by about 7%). This enhanced reactivity may be due to the +I_s effect of the methyl group. This is justifiable because the rate-determining step of the reaction involves the attack of an electrophilic iodine species on the substrate molecule. *o*-Xylene is found to be much more reactive than toluene, *i.e.*, by about 40%. By applying the simple principles of statistics, the presence of two electron releasing methyl groups is expected to increase the electron richness at the reaction site and consequently increase the reactivity of the substrate compared to that of the unsubstituted benzene. By extending this argument to its *m*- and *p*-isomers, it would be logical to expect these also to be as reactive as their *o*-isomer. In accordance with this expectation, the *m*-isomer is more reactive than benzene by about 9 times and also more reactive than methyl benzene by about 8 times. However, curiously, its reactivity is much higher than that of *o*-xylene and *p*-xylene by about 6 times and 28 times respectively. The *p*-isomer is not only less reactive, but also much less reactive than benzene itself.

This observed trend in reactivities of xylenes, *viz.*, *m*-xylene > *o*-xylene > *p*-xylene, could be explained based on the relative electron densities of the carbon atoms open for attack.



In *p*-xylene, though there are four carbons available for attack by the electrophile, as each of these carbons is *ortho* to one CH₃ and *meta* to another CH₃, the electronic effect is much similar to that in toluene. A similar situation is encountered with *o*-xylene also. The carbons 3, 4, 5 and 6 are either *ortho* or *para* to one methyl group while *meta* to another methyl group. However, the carbons numbered 2, 4 and 5 are at least devoid of the steric factor encountered with the 3 and 6 centres and with all the carbon atoms in *p*-xylene. However, in *m*-xylene except the carbon 5, the other three carbon atoms are susceptible for attack. Also, at carbons 2, 4 and 6, the electronic +I effects of both the methyl groups reinforce each other, thus accounting for its high reactivity.

But in system B, the reactivities of these alkyl benzenes follow a trend different from that in system A. This may be due to the nature of the attacking electrophilic iodine species. The iodinating species in system B being the relatively small I⁺ ion, the positive charge is localised on that species while the bigger HNO₂I⁺ electrophile (in system A) would have a more dispersed positive charge. Consequently I⁺ ion is expected to be a more active electrophile than HNO₂I⁺ and therefore its discriminating power towards a small difference in electron density due to electron releasing substituents is not appreciable. Hence, in system B all the substrates with electron donating substituents have almost the same reactivity.

Halobenzenes: The kinetics of iodinations have been followed with four halobenzenes, namely fluoro-, chloro-, bromo- and iodo- each at three different temperatures in both the systems A and B. In Tables 1 and 2 are given the relative reactivity, *i.e.*, the relative $k_{1/2}$ values for these substrates at 40°C. These data reveal that

- (i) all the halobenzenes are less reactive than benzene
- (ii) among the halobenzenes, iodobenzene is the most reactive and fluorobenzene is the least reactive.
- (iii) the order of the reactivity is —H > —I > —Br > —Cl > —F

The substitution of a hydrogen by a halogen atom in benzene ring leads to a substantial decrease in the reactivity of the substrate for iodination considering that the iodination is electrophilic; the electron-withdrawing or deactivating *halo* substituents are expected to account for this trend in reactivity. Thus the most electron withdrawing fluoro substituent shows the least reactivity. The iodo substituent makes the iodobenzene the most reactive among the halobenzenes, though by itself is less reactive than unsubstituted benzene. Most of the electrophilic substituents with benzene follow the trend observed in this study². For example, in the electrophilic nitration of halobenzenes, it has been reported that all these substituents lessen the reactivity of benzene.

In spite of the deactivating nature of the halo substituents, the fact that the halobenzenes are iodinated by the reagents employed in this study is worth noting especially because iodobenzenes are difficult to prepare by simple synthetic procedures.³

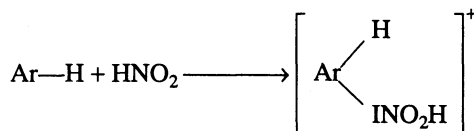
Nitrobenzene: The kinetic study of iodinations of nitrobenzene shows that the reactivity of this substrate, compared to that of benzene, plummets from 1 to 0.12 with system A and from 1 to 0.44 with system B. The nitro group is a powerful deactivating one for electrophilic substituents on the benzene ring. This effect may justify the significantly decreased reactivity of the nitrobenzene for iodination. However, that such a decrease in reactivity is much more in system A (0.12) than in system B (0.44) needs an explanation. This may be found in the fact that N_2O_4 formation is possible in system A but not in system B which may promote the formation of reactive iodinating species¹.

Thus, the generation of a more powerful iodinating electrophile under the conditions employed in system A compensates at least partially for the reduced reactivity of nitrobenzene. This view is further corroborated by the observation that a similar trend has been noted with the other electron withdrawing substituents also in this study.

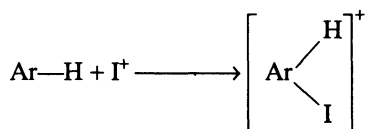
Arrhenius Parameters

The iodination kinetics were studied with all the benzenes in both the iodinating systems A and B at different temperatures. For each case, satisfactory Arrhenius correlations have been obtained. From such figures the activation parameters have been evaluated. These are given in Tables 3 and 4. Comparison of these data indicates the following:

- (i) For all substituents the ΔG^\ddagger values do not vary appreciably and centre around 100 kJ/mole.
- (ii) The ΔS^\ddagger values are also negative ranging from -86 to -342 entropy units for system A and -34 and -273 entropy units for system B. These values may be taken to indicate the high ordering of the molecular skeleton of the reacting species in the transition state. Such an ordered transition state may be visualized as depicted in Schemes 1 and 2.



Scheme 1: Transition state in system A



Scheme 2: Transition state in system A

TABLE-3
SYSTEM A: ACTIVATION PARAMETERS AT 40°C

Substrate	$10^5 \times k_{1/2}/\text{mol}^{1/2} \text{ lit}^{-1/2} \text{ sec}^{-1}$	E_a	$-\Delta S^\ddagger$	ΔG^\ddagger	ΔH^\ddagger
Benzene	7.810	45	188	101	47
Toluene	8.350	33	225	101	31
<i>o</i> -Xylene	10.600	36	212	100	34
<i>m</i> -Xylene	70.700	39	190	96	36
<i>p</i> -Xylene	2.520	81	86	106	79
Fluorobenzene	0.480	53	186	108	50
Chlorobenzene	0.815	22	281	107	19
Bromobenzene	1.120	20	342	106	1
Iodobenzene	1.850	50	183	105	48
Nitrobenzene	0.951	50	188	107	48

E_a : kJ mol⁻¹; ΔS^\ddagger : JK⁻¹ mol⁻¹; ΔG^\ddagger : kJ mol⁻¹; ΔH^\ddagger : kJ mol⁻¹

TABLE-4
SYSTEM B: ACTIVATION PARAMETERS AT 40°C

Substrate	$10^5 \times k_{1/2}/\text{mol}^{1/2} \text{ lit}^{-1/2} \text{ sec}^{-1}$	E_a	$-\Delta S^\ddagger$	ΔG^\ddagger	ΔH^\ddagger
Benzene	2.820	96	34	104	93
Toluene	2.900	101	36	110	99
<i>o</i> -Xylene	2.310	95	40	104	92
<i>m</i> -Xylene	2.670	91	53	104	87
<i>p</i> -Xylene	2.520	57	159	104	54
Fluorobenzene	0.621	62	154	108	60
Chlorobenzene	1.020	36	235	107	33
Bromobenzene	1.150	23	273	106	21
Iodobenzene	2.260	66	130	104	64
Nitrobenzene	1.250	48	195	106	45

E_a : kJ mol⁻¹; ΔS^\ddagger : JK⁻¹ mol⁻¹; ΔG^\ddagger : kJ mol⁻¹; ΔH^\ddagger : kJ mol⁻¹

A plot of ΔH^\ddagger vs. ΔS^\ddagger in each system (Fig. 1), produces a linear plot. The iso-kinetic temperatures obtained from these plots are respectively 303 and 309 K in system A and system B. The linearity of these plots indicates that all the chosen substrates undergo iodination through similar mechanisms in each iodinating system. Besides this, the validity of the Exner relationship has been checked: $\log k_{1/2}$ at 40°C values are plotted against $\log k_{1/2}$ at 45°C for all the substrates studied with the systems A and B. A satisfactory linearity has been obtained (Fig. 2). A slope value b is used in the expression (Exner) for evaluating the iso-kinetic temperature β .

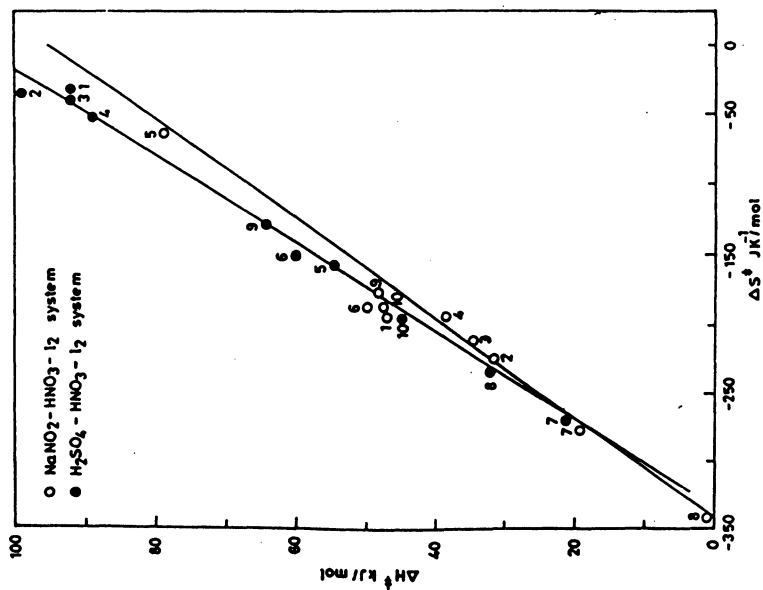


Fig. 1. Enthalpy-Entropy plot: Benzene

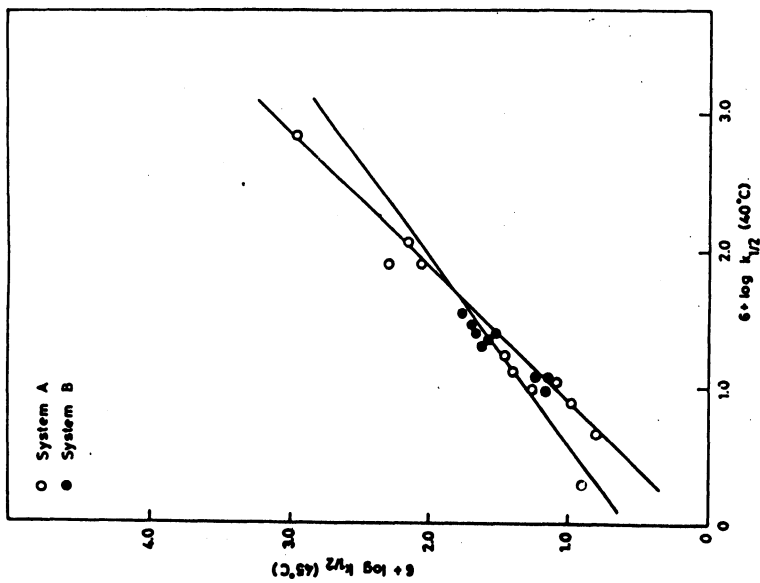


Fig. 2. Exner plot: Benzenes

$$\beta = T_1 T_2 \left[\frac{1 - b}{T_1 - b T_2} \right]$$

The β values obtained by this method for iodinating systems A and B are 272 and 292 K respectively. These values are comparable to the iso-kinetic temperatures (303 K and 309 K) obtained previously by plotting the ΔH^\ddagger value against the ΔS^\ddagger values⁴.

As iodination of aromatics is not well-established as the other halogenations, this investigation indicates to some extent the mechanistic nuances of iodination. The results may help in adopting simple and easy laboratory practice hitherto uncommon for preparing aryl iodides.

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