

Iodination of Naphthalenes with Iodine and Sodium Iodate in Aqueous Acetic Acid Medium

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In the present investigation, iodination of both activated and deactivated naphthalenes has been studied with the iodinating system: I_2 - $NaIO_3$ - H_2SO_4 in aqueous acetic acid medium. Initially, a systematic kinetic study of iodination of aromatics has been carried out with the same system; from the results, the concentrations of the various reagents for effective iodination were fixed and the formation of an electrophilic iodonium species I^+ which is responsible for the iodination of aromatic nucleus was suggested. The iodination reactions are succeeded by heating the reaction mixture in aqueous acetic acid ($AcOH/H_2O$ 80/20 (v/v)). The identity of the iodinated product of each substrate was established by recording its mass and IR spectral data.

Key Words: Aromatic iodination, Sodium iodate, Sulphuric acid, Kinetic studies, Naphthalenes.

INTRODUCTION

Iodoaromatics and iodoheterocyclics are largely used in antibacterial and antifungal activity. In view of these biomedical applications of iodoaromatics, this iodination process has been attempted. Since iodine is the least reactive one among the halogens towards electrophilic substitution reactions, iodination is achieved by oxidative iodination methods¹. Some of the oxidising agents used for this purpose are: diiodine pentoxide², nitrogen dioxide³, HIO_3 or its salts⁴⁻⁶, HIO_4 or its salts⁶, silver sulphate⁷ and peroxy acetic acid⁸.

In the present study, iodination of naphthalenes is carried out by iodine with acidified $NaIO_3$ in the presence of aqueous acetic acid medium. The major role of $NaIO_3$ is the conversion of molecular iodine to the most reactive electrophilic species, I^+ . The study of chemical kinetics on this iodination has been highly useful in working out the conditions for getting the maximum yield of the product at a cheaper cost with the minimal wastage of chemicals so that the iodination of aromatics was carried out based on the observations from the kinetic studies with the iodinating system $I_2/NaIO_3/H_2SO_4$ in aqueous acetic acid medium. Naphthalene, 1-methylnaphthalene, 2-methyl naphthalene and 1-nitronaphthalene are successfully iodinated by this system with good yield.

EXPERIMENTAL

All the chemicals used in this study were of BDH, AR grade. Purity of the iodo compounds was checked by TLC technique on silica gel-G coated aluminium plate, using hexane as eluent. The chromatogram was developed under a mixture of 1% vaniline and 5% ethanolic H_2SO_4 as reagent. Mass spectral data of all the samples were obtained from GC-MASS SPEC Finnigan MAT 8230MS spectrophotometer and IR spectral data were obtained from FT Bruker IFS66V spectrophotometer.

Initially the kinetics of iodination of naphthalene using the iodinating system $I_2/NaIO_3/H_2SO_4/aq.$ AcOH was standardised, using Shimadzu digital double beam spectrophotometer (150-02) in conjunction with a thermobath (TB 85) which maintained the cell compartments at a fixed temperature ($\pm 0.05^\circ C$)⁹. The usual preliminary adjustments in the spectrophotometer were done carefully before starting each experiment. The maximum absorbance of iodine solutions (0.0001–0.001 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 iodine. Careful analyses (TLC, mass and IR) of the reaction products were done. The results were used on the preparative syntheses of iodo derivatives of naphthalenes.

Iodination of naphthalenes: The reaction mixture was prepared by dissolving aromatic substrate (0.1 M), iodine (0.008 M), sodium iodate (0.2 M) and sulphuric acid (0.04 M) in 40 mL acetic acid and 10 mL water and placed in a round bottom flask fitted with an air condenser and heated (Table-1). In order to remove the unreacted materials, the mother liquor was washed with 10–15% aqueous sodium bicarbonate solution repeatedly and subsequently with water. Finally, the product was extracted using pure ether. After drying the ethereal solution over anhydrous sodium sulphate, the solvent is vapourised off by applying suction to get the iodo product and purified on a short column packed with Al_2O_3 . The reaction products **1a**, **1b**, **1c** and **1d** are successfully isolated by this process with excellent yield.

TABLE-I
IODINATION OF NAPHTHALENES IN AQUEOUS ACIDIC ACID
(AcOH/ H_2O -80/20 (v/v))

Substrate	T ($^\circ C$)	Time (h)	Product	Yield (%)
Naphthalene	80	7	1-Iodonaphthalene (1a)	82
1-Methylnaphthalene	70	5	1-Methyl 4-iodonaphthalene (1b)	94
2-Methylnaphthalene	70	6	2-Methyl 1-iodonaphthalene (1c)	86
1-Nitronaphthalene	95	9	1-Nitro 2-iodonaphthalene (1d)	68

RESULTS AND DISCUSSION

This present study mainly focuses on the iodination of aromatics and the characterization of the iodo product, initially, a systematic kinetic study of the same has been carried out using the system I_2 - $NaIO_3$ - H_2SO_4 in aqueous acetic acid medium in order to fix the concentrations of various reagents for the effective iodination and also to check the possibility of formation of electrophilic iodonium ion which is responsible for aromatic iodination. Thus a set of experiments was conducted by varying the concentration of iodine by maintaining all the other experimental conditions identical. Each of the reactions has been followed with a large excess of [Substrate] with respect to [Iodine]. Excellent linear plots were obtained when $(a - x)^{0.5}$ values are plotted against time value, indicating that the reaction is half-order in iodine which is the evidence for the formation of iodonium ion I^+ . Fig. 1 shows a representative plot. After performing several preliminary investigations on systematic kinetic studies of iodination of naphthalenes, the reaction condition, that is favourable for smooth and effective iodination, was identified and given below:

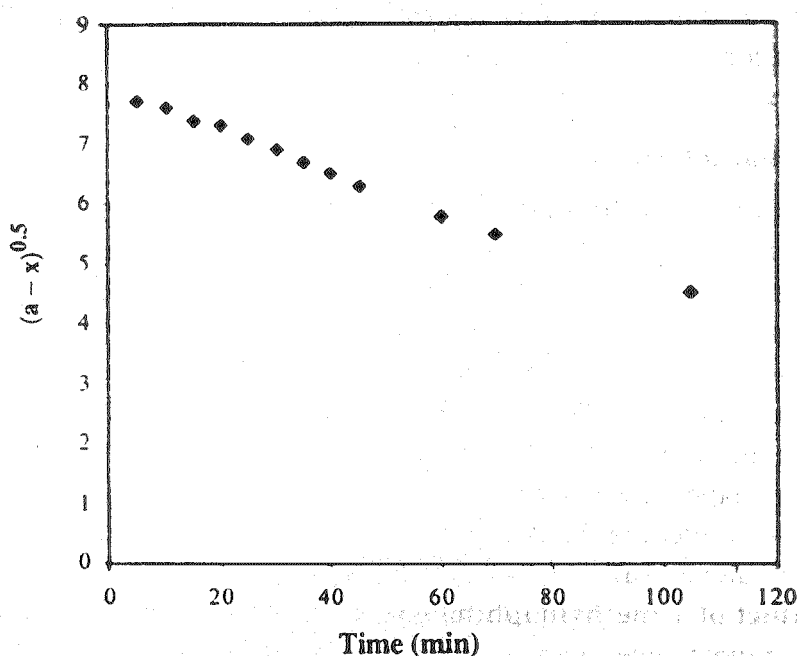


Fig. 1. Time vs. $(a - x)^{0.5}$ plot

$[I_2]$	0.0008M	$[H_2SO_4]$	0.004M
$[NaIO_3]$	0.02M	Solvent AcOH/ H_2O	80/20 (v/v)

The product obtained under kinetic conditions was subjected to mass and IR spectral analysis and mono-iodination on aromatic nucleus was confirmed. Based on the kinetic results, the amount of various reagents used for the iodination of naphthalenes were calculated and used in preparative synthesis. A mixture of iodine (0.008 M), sodium iodate (0.02 M) and sulphuric acid (0.004 M) in aqueous acetic acid (AcOH/ H_2O 80/20 (v/v)) was used for the iodination of 0.1 M of the substrates and excellent yields of iodo products were obtained. From our experiments it was observed that water content of the medium to some extent favours

the iodination reaction. Naphthalene, 1-methylnaphthalene, 2-methylnaphthalene and 1-nitronaphthalene are successfully iodinated by this method with good yield. It is noticed that all the iodo products are stable at room temperature. By comparing the R_f values of iodo derivatives with their substrates, it is concluded that iodination is likely to take place with a single product formation and not a mixture of iodo products. The identity of the iodo product was established by recording its mass and IR spectra. The product analysis supports the formation of mono-iodinated product directly. The crucial role of IO_3^- is in oxidizing iodine to an electrophilic species, I^+ . Therefore, in this system, the iodination takes place most probably by the attack of I^+ on aromatic nucleus.



The substituent effects on the iodination of naphthalenes reveal that iodination takes place due to the attack of an electrophilic iodonium species on the substrate molecule at an electron rich carbon.

As the iodination of aromatics is not well established as the other halogenations, this investigation discusses the iodination of naphthalenes in aqueous acetic acid medium using acidified sodium iodate as oxidant. The results may help in adopting a simple and an efficient procedure for the iodination of naphthalenes with easily available chemicals.

Compound characterization

Iodo product of naphthalene: Mass spectrum of iodo product of naphthalene shows a molecular ion peak with m/e value 254 indicating mono-iodonaphthalene. IR spectrum shows aryl =C-H stretching at 3051 cm^{-1} , skeletal ring stretching vibration C=C bands at 1592, 1560, 1499, 1451 cm^{-1} , out-of-plane -CH bands at 780 cm^{-1} for substituted naphthalenes which contains three adjacent hydrogen atoms on the ring and 764 cm^{-1} arising from the four free hydrogen atoms on the other ring. These data most likely suggest the mono substitution in naphthalene which occurs at position 1. This is confirmed by observing C-I stretching band at 576 cm^{-1} . Therefore, the most likely product is 1-iodonaphthalene (1a)

Iodo product of 1-methylnaphthalene: Mass spectrum of the iodo product of 1-methyl naphthalene with a peak at m/e value 268 indicates the mono iodination on the substrate. IR spectrum shows aryl =C-H stretching at 3067 cm^{-1} , C-CH_3 stretching bands at 2945, 2859 cm^{-1} , skeletal ring stretching vibrations for C=C at 1591, 1559, 1504, 1450 cm^{-1} , out-of-plane -CH bands at 819 cm^{-1} corresponding to two adjacent free hydrogens on one ring and at 752 cm^{-1} responsible for the four adjacent free hydrogens on the other ring. Two free hydrogens in the adjacent position could be explained only if the iodination occurs at position '4'. Iodination is further confirmed by C-I stretching band obtained at 575 cm^{-1} . This confirms that the final product is 1-methyl 4-iodonaphthalene (1b).

Iodo product of 2-methylnaphthalene: In the mass spectrum of the iodo product of 2-methyl naphthalene, it is observed that there is a molecular ion peak with m/e value at 268, which could indicate the iodo product. IR spectrum of the

same shows aryl C—H stretching at 3049 cm^{-1} , C—CH₃ methyl group stretching bands at $2915, 2852\text{ cm}^{-1}$, skeletal ring stretching vibrations C=C bands at $1595, 1550, 1500, 1435\text{ cm}^{-1}$, out-of-plane —CH bands at 806 cm^{-1} corresponding to two free adjacent hydrogens and at 765 cm^{-1} for the four free hydrogen atoms on the other ring. In this case the two free hydrogen atoms which are adjacent in their positions could be explained only if the iodination occurs at position '1' in the substrate, 2-methyl naphthalene. The iodination on substrate is confirmed by C—I stretching obtained at 576 cm^{-1} . Therefore, the final product is 2-methyl 1-iodonaphthalene (1c).

Iodo product of 1-nitronaphthalene: The prominent molecular ion peak at 299 in the mass spectrum of the iodo product of 1-nitro naphthalene indicates the mono-iodination on the substrate. IR spectrum of the same shows aryl C—H stretching at 3059 cm^{-1} , very strong bands at $1520, 1337\text{ cm}^{-1}$ responsible for aromatic nitro group, out-of-plane —CH band at 871 cm^{-1} for the ring containing one isolated hydrogen atom and 764 cm^{-1} corresponds to the four free adjacent hydrogen atoms on the other ring. From the IR data it could be possible to conclude that iodination occurs likely at position 3 on the substrate. This could be authenticated by C—I stretching band at 582 cm^{-1} . Therefore the product is 1-nitro 3-iodonaphthalene (1d).

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