研究論文

Nitration mechanism of alkylbenzenes with NO_2

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In order to clarify the mechanism for the aromatic nitration with NO_2, we have carried out the nitration of alkylbenzenes with NO_2 and have investigated the relationship between the partial rate factors and the electron densities at the substitution positions, the relationship between the relative rates in the competitive nitrations of alkylbenzenes and the ionization potentials of the substrates, and the substrate selectivity in the competitive nitration of mesitylene / naphthalene by Galli's method. As a result, the reaction should be an electrophilic substitution involving a radical cation formed from the one-electron transfer process, which should be the rate-determining step.

1. Introduction

Since diesel exhaust gas is known to contain nitrogen oxides (NO_X) and polyaromatic hydrocarbons (PAHs), the production of nitro-polyaromatic hydrocarbons (nitro-PAHs) in the exhaust gas and / or in the atmosphere may occur[1~3]. The nitro-PAHs can possibly be harmful to living organism due to their mutagenic and carcinogenic properties[4]. Therefore, in order to retard the formation of nitro-PAHs, it is necessary to clarify the mechanism for the aromatic nitration of PAH with NO_X.

On the other hand, aromatic nitration with nitric acid is well-known to be of industrial importance as a unit process for the syntheses of explosives, intermediates of dyes, medicines and agricultural chemicals. Many studies on this reaction have been carried out not only in the fields of industrial chemistry but also in the field of physical organic chemistry. As a result, the reaction mechanism involving NO_2^+ as an important attacking species has been suggested.

Nitro-PAHs are considered to be formed from the reaction involving several nitrogen oxides (NO_2[4], N_2O_5[5,6], HNO_3[7], etc.) in the atmosphere. Although NO_2 is considered as one of the most important attacking species toward PAH in the atmosphere, only a few studies have been done concerning the mechanism for aromatic nitration using NO_2.

Radner[8] has reported that the nitration of PAHs with NO_2 in a nonpolar solvent quantitatively yields mononitro-PAHs and the reaction showed high positional selectivity. Pryor et al.[9] and Sasaki et al.[10,11] have attempted to clarify the mechanism for the aromatic nitration with NO_2 in the liquid phase, suggesting that a one-electron transfer process should play an important role in the aromatic nitration. However, the detailed mechanism is still not clear.

Therefore, we have studied the nitration of alkylbenzenes with NO_2 in a nonpolar solvent to clarify the mechanism for the aromatic nitration with NO_2 and to further obtain some ideas for retarding the formation of nitro-PAHs in the atmosphere.

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2. Experimental

2.1 Materials

Benzene, toluene, o-, m- and p-xylenes, mesitylene, ethylbenzene, cumene and naphthalene were used as the aromatic substrates and dichloromethane as the solvent.

The aromatic substrates, their nitro derivatives and dichloromethane were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., Ltd., Kanto Kagaku Co., Inc. and Fluka as the highest commercial grade chemicals available and were used without further purification. 2-Nitromesitylene was synthesized by Blatt's method[12]. N_2O_4 was purchased from Takachiho Kagaku Kogyo Co., Ltd..

2.2 Experimental Method

A certain amount of substrate and N_2O_4 and 15ml of dichloromethane were introduced into a three-necked 100ml flask equipped with a condenser. The mixture was stirred for about 5 hours. The reaction temperature was maintained at 15℃.

The alkylbenzene ($1.0\times10^{-2} \sim 2.3\times10^{-2}$ mol) and 1.6×10^{-1} mol of N_2O_4 (3.2×10^{-2} mol of N_2O_4 for mesitylene) were used for the nitration of each substrate. For the competitive nitration of alkylbenzenes, $7.2\times10^{-3} \sim 1.1\times10^{-2}$ mol of alkylbenzene (except for mesitylene), 9.4×10^{-3} mol of toluene and 1.6×10^{-1} mol of N_2O_4 were used. For the competitive nitration of mesitylene / p-xylene, 1.0×10^{-2} mol of mesitylene, 1.1×10^{-2} mol of p-xylene and 3.2×10^{-2} mol of N_2O_4 were used. For the competitive nitration of mesitylene / naphthalene, 1.4×10^{-2} mol of each substrate and 1.6×10^{-2} mol of N_2O_4 were used.

Substrates and their reaction products were directly extracted from the reaction mixture at different times and analyzed using a gas chromatograph (Shimadzu Co., Ltd., GC-6A) with a flame ionization detector (FID) and by gas chromatography - mass spectrometry (Shimadzu GC-14A, GCMS-QP1100EX) using a stainless steel column (3mmϕ×3m Silicone OV-101 5% Uniport HP 60 / 80, GL Sciences Inc.).

3. Calculation method

We calculated the electron densities at the substitution-positions, the ionization potentials of the substrates and the heats of formation for their σ-complexes with NO_2 and NO_2^+ by the PM3 method, semi-empirical molecular orbital method MOPAC ver.6[13], and compared them with the relative rates.

4. Results and discussion

4.1 Nitration of alkylbenzene

4.1.1 Products

During the nitration of substrates with NO_2, the ring-nitrated products were mainly produced. Aldehydes and ketones produced from the oxidation of the side-chains of the substrates were also detected, i.e., benzaldehyde from toluene, tolualdehyde from xylene, and acetophenone from ethylbenzene and cumene. As we are interested in only the ring-nitration with NO_2, no further identification of the oxidation products was done. Each isomer distribution of the ring-nitrated products was similar to that for the nitration with HNO_3 / H_2SO_4[14].

We obtained the pseudo-first-order rate constants for the formation of ring-nitrated products in the competitive nitration of substrates according to Eq. 1 in order to calculate their relative rate constants (K) and the partial rate factors (f/f_0).

$$\ln\frac{a}{a-x}=kt \qquad (1)$$

a: initial concentration of substrate
x: concentration of ring-nitrated products
k: rate constant
t: time

The relative rate constants, the partial rate factors and the isomer distributions are shown in Table 1.

The nitration rates of the alkylbenzenes with NO_2 are much smaller than those with HNO_3 / H_2SO_4[14], e.g., the pseudo-first-order rate constant for that of benzene is 2.9×10^{-6} s^{-1}. Since the concentration of NO_2 is approximately estimated to be 0.02[15] to 0.06 M[16], the second-order rate constant for benzene would be $4.8 \sim 15\times10^{-5}$ $M^{-1}s^{-1}$.

4.1.2 Effects of alkyl substituents on aromatic nitration rates

The relative rate constants for the nitration of

Table 1 Relative rate constants, partial rate factors and isomer distributions in the nitration of alkylbenzens with NO_2

Substrate	Relative rate constant K	Product	Partial rate factor f/f_0	Isomer distribution / mol%	
				this work	ref.*
benzene	1	1-nitro	1	—	—
toluene	2.5×10	o-nitro	3.9×10	52	64
		m-nitro	1.8	3	4
		p-nitro	6.8×10	45	32
o-xylene	1.7×10^2	3-nitro	1.8×10^2	35	34
		4-nitro	3.3×10^2	65	66
m-xylene	9.2×10^2	2-nitro	1.3×10^2	5	18
		4-nitro	2.6×10^3	95	80
		5-nitro	0	0	2
p-xylene	2.6×10^2	2-nitro	3.9×10^2	—	—
mesitylene	3.6×10^3	2-nitro	7.2×10^3	—	—
ethylbenzene	3.2×10	o-nitro	5.5×10	57	50
		m-nitro	2.3	2	4
		p-nitro	7.9×10	41	46
cumene	2.4×10	o-nitro	2.1×10	29	43
		m-nitro	3.0	4	5
		p-nitro	9.6×10	67	52

*Nitraion with HNO_3/H_2SO_4[14a]

benzene, toluene, xylenes and mesitylene decrease in the following order : mesitylene > m-xylene > p-xylene > o-xylene > toluene > benzene. It is postulated that the electron density on the aromatic ring should become higher with an increase in the number of methyl groups substituted on the aromatic ring, resulting in an increased electrophilic nitration. The relative rate constants for the nitration of benzene, toluene, ethylbenzene and cumene are in the following decreasing order : ethylbenzene ≧ cumene, toluene > benzene. It is also postulated that the larger alkyl group should increase the electron density on the aromatic ring, resulting in promoting electrophilic nitration. However, the degree of the increase was not as high as that for the introduction of multiple methyl substituents.

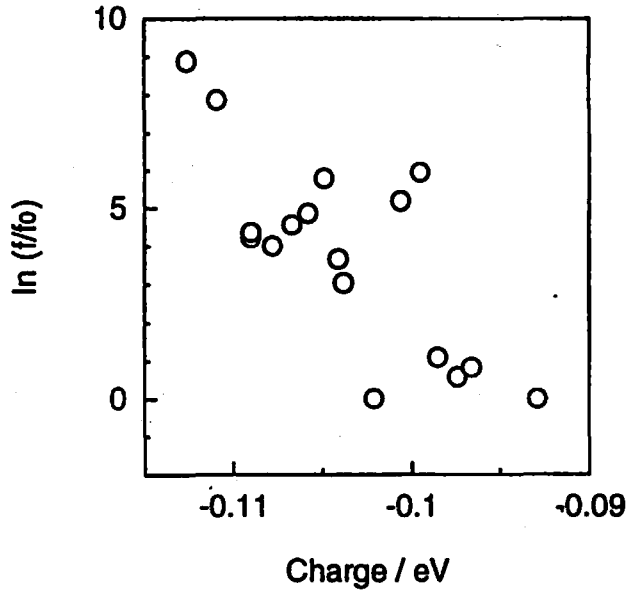


Fig. 1 Relationship between logarithm of partical rate factors and net atomic charges

In order to quantitatively estimate the substituent effects of alkyl groups, we have attempted to compare the partial rate factors with the electron densities at the position of nitro-substitution (Fig.1). A linear correlation between the partial rate factors and the electron densities could be obtained. The more negative the electron density, the larger the rate of nitration at

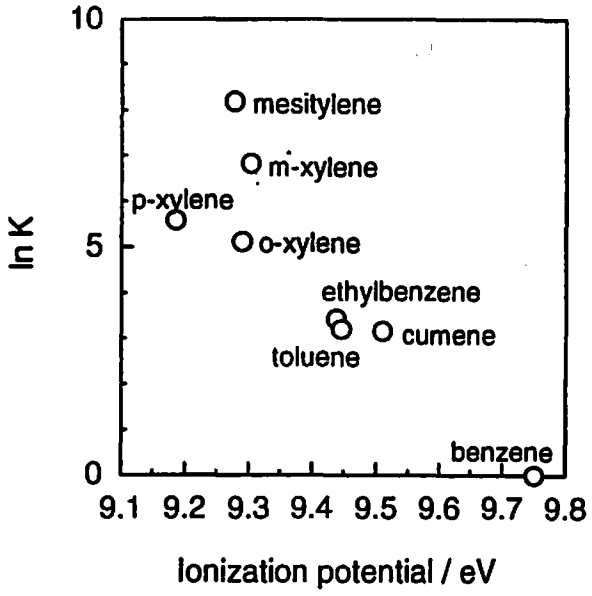


Fig. 2 Relationship between logarithm of rate constants in the competitive nitrations and ionization potentials of substrates

that position, indicating that the partial rate factor should be almost dependent on the electron density at the site of nitro-substitution. Previously, Sasaki et al. showed from a study of the substituent effects on the aromatic nitration with NO_2 that the aromatic nitration with NO_2 in CCl_4 should be electrophilic based on a negative Hammett's ρ value (-1.7)[11], and here, we can again suggest that the reaction should be approximately electrophilic. Although it is generally suggested that the classical σ-complex mechanism should favor the attack at the most electron rich positions of the system[17], Keumi et al.[18] suggested that the high electron density at the substituent position should be responsible for the electron transfer mechanism during the nitration of dibenzofuran with $C(NO_2)_4$ / trifluoroacetic acid / light exclusively occurring at the 3-position indicating that the aromatic nitration with NO_2 may be elucidated by the electron transfer mechanism.

4. 1. 3 Substrate selectivity in competitive nitration

In order to obtain additional information on the mechanism for the aromatic nitration with NO_2, we compared the relative rate constants during competitive nitration with their ionization potentials because the relative rates of the one-electron transfer should be dependent on the energy level of the HOMO (of the substrates) - LUMO (of NO_2) gap. As a result, the relative rates were found to be dependent on the ionization potentials (Fig. 2). As the ionization potential is smaller, namely, one electron is easily released from the substrate, the nitration rate becomes larger. Kowert et al.[19] studied the homogeneous electron transfer reaction between aromatic molecules and their radical cations and indicated that the energy required to remove one electron from the parent molecule should play a key role in determining the electron transfer rate. Kochi et al.[20] studied the aromatic nitration with N-nitropyridinium cations and showed that the nitration rate should be correlated with the HOMO-LUMO gap in the $[ArH,XPyNO_2^+]$ complex, suggesting that the mechanism should include a stepwise process in which the substrate is selectively controlled by the charge transfer process. Therefore, the result should suggest the reaction involving a one-electron release from the substrate.

Furthermore, it is reported that NO_2 should react with the reducing agents via the electron transfer[21], and it is also suggested that the SOMO energey level[22] of NO_2 (-9.75eV) should be low enough to allow a one-electron transfer from the substrate to NO_2. Therefore, we suggest the possibility of a one-electron transfer mechanism for the aromatic nitration with NO_2.

4. 2 Substrate selectivity by the Galli's method

In a previous study on the aromatic nitration with NO_2^+, many arguments have been made about the mechanism of the aromatic nitration via a one-electron transfer process[23]. Nagakura et al.[24] theoretically developed on the idea of the one-electron transfer mechanism. Furthermore, Perrin[25] reported the one-electron transfer mechanism for the reaction between the naphthalene radical cation and NO_2 in a thought-provoking article. However, it is not easy to distinguish between the one-electron transfer mechanism and the classical σ-complex mechanism.

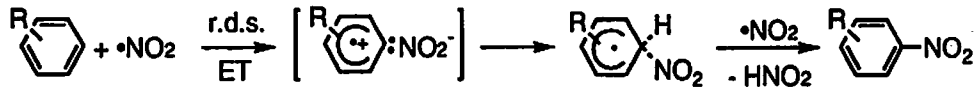
Here, in order to clarify the mechanism for

Table 2 Calculated ionization potentials of substrates and stabilization energies of σ-complexes

Substrate	IP / eV	ΔE_{stab}[a] / kJ mol^{-1}	
		σ-complex with NO_2	σ-complex with NO_2^+
mesitylene	9.28	-70.5	64.4
naphthalene	8.83	-56.6[b]	69.4[b]

a: ΔE_{stab} = H value(σ-complex) − H value(substrate) − H value (NO_2 or NO_2^+)

b: Calculated for σ-complex at 1-position (which is predominantly produced[21])



(σ-complex)

Scheme 1 Mechanism for the nitration of alkylbenzenes with NO_2

the aromatic nitration with NO_2, we have carried out competitive nitration using Galli's method[26].

Galli et al. suggest that substrate selectivity in the competitive reaction of mesitylene / naphthalene (substrates in excess) should be useful as a probe to distinguish between the one-electron transfer mechanism and the classical σ-complex mechanism during electrophilic aromatic substitution. Since mesitylene has a higher σ-basicity than naphthalene, mesitylene should have a higher reactivity than naphthalene for the classical σ-complex substitution mechanism. Since naphthalene can be more easily oxidized to a radical cation than mesitylene, naphthalene should have higher reactivity than mesitylene for the one-electron transfer substitution mechanism. The ionization potentials and the stabilization energies of the σ-complexes with NO_2 and with NO_2^+ for each substrate are shown in Table 2.

In the competitive nitration of mesitylene / naphthalene, 2-nitromesitylene and 1- and 2-nitronaphthalenes were mainly produced, and the relative formation rate of K_{MES} / K_{NAPH} was $(1.4 \pm 0.1) \times 10^{-2}$. It is significantly different from the relative formation rate of $K_{MES} / K_{NAPH} = 20 \pm 1$[26] during the nitration with NO_2^+. This fact indicates that the one electron-transfer mechanism should play an important role. Although the stabilization energy for the σ-complex of naphthalene with NO_2 is somewhat more stable than that of mesitylene with NO_2, the difference in the relative rate between the competitive nitration with NO_2 and that with NO_2^+ is remarkable and should be important. Therefore, the result suggests that the aromatic nitration with NO_2 should be elucidated by an electrophilic process involving a radical cation formed by a one-electron transfer, which should be the rate-determining step (Scheme 1).

5. Conclusion

In order to clarify the mechanism for the aromatic nitration with NO_2, we have studied the nitration of alkylbenzenes with NO_2 in a nonpolar solvent. As a result, the reaction was an electrophilic substitution and the rate of nitration was chiefly dependent on the electron density at the substitution position. During the competitive nitration of alkylbenzenes, the substrate selectivity was shown to be dependent on the ionization potentials of the substrates.

The competitive nitration of mesitylene / naphthalene has also be done using Galli's method. During the competitive nitration of mesitylene / naphthalene, NO_2 predominantly reacted with naphthalene resulting in the production of 1- and 2-nitronaphthalene. The selectivity was much different from that of the nitration with NO_2^+. Based on these results, It can be suggested that

the nitration of alkylbenzenes with NO_2 should be elucidated by the mechanism involving a radical cation formed from the one-electron transfer process, which should be the rate-determining step.

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NO_2によるアルキルベンゼンのニトロ化反応に関する研究

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NO_2による芳香族ニトロ化反応に関する基礎的知見を得るため，NO_2によるアルキルベンゼンのニトロ化反応を行い，反応機構について検討した。その結果，基質の置換位置の電子密度と部分速度因子との比較から，反応は求電子的傾向を示し，また基質間相対反応速度とイオン化ポテンシャルとの相関や，Galliの方法によるメシチレン/ナフタレン競争反応の検討から，反応は一電子移動過程を含むラジカルカチオンが関与する機構で進行する可能性が示された。

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