Nitration of benzene with N_2O_5

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In order to clarify the mechanism of aromatic nitration with N_2O_5, the nitrations of benzene and of nitrobenzene with N_2O_5 were carried out and the yield of the products and the isomer distribution of dinitrobenzenes were investigated. As a result, the isomer distribution of the dinitrobenzenes in the nitration of benzene was quite different from that in the nitration of nitrobenzene. Moreover, the ratio of [dinitrobenzenes] / [nitrobenzene] increased with the reaction temperature. The nitration of benzene with N_2O_5/N_2O_4 was also carried out and showed the dependence of the ratio of [dinitrobenzenes] / [nitrobenzene] on the ratio of N_2O_4. As a result, it is suggested that N_2O_5 should be dissociated homolytically in CCl_4, that the aromatic nitration with N_2O_5 in CCl_4 should proceed with NO_3 as the initial attacking species. The thermal decomposition of N_2O_5 over 25℃ should produce a large amount of $N_2O_4 (2NO_2)$ and the attack of NO_2 on the intermediate [Ar(H)(ONO_2)] should form the intermediates [Ar(H)(ONO_2)(H)(NO_2)] following the production of a large amount of dinitrobenzenes.

1. Introduction

Aromatic nitration is well-known to be of the industrial importance as unit processes for syntheses of explosives and intermediates of dyes, medicines and agricultural chemicals. The industrial method for the synthesis of nitroarenes has used nitric acid. However, a new nitrating reagent is desired at present.

Here, N_2O_5 was noted as a nitrating reagent. N_2O_5 is a white crystalline solid, very reactive toward arenes, and the mechanism of the nitration with N_2O_5 should be different from that with nitric acid. It should be possible to control the reactivity of the nitration by changing the reaction conditions[1]. Therefore, it is hoped that further research on aromatic nitration with N_2O_5 should proceed, and that an available method for the synthesis will be developed.

Ingold et al[2] reported the kinetics of the aromatic nitration with N_2O_5 between $-25℃$ and $25℃$ and

showed that the reaction should be a mixture of a noncatalyzed reaction and an autocatalyzed reaction. They also reported the solvent effect on the kinetics and the accelerating effect on the reaction rate produced by the addition of HNO_3, etc. Their works concluded that covalent N_2O_5 should react with arenes under neutral nonionizing conditions, while NO_2^+ should be the nitrating species under ionizing conditions. On the other hand, Titov et al.[3] reported the isolated products for aromatic nitration with N_2O_5 in CCl_4 between 0℃ and 70℃ and suggested a free-radical reaction mechanism by NO_3. However, Ingold's work is the most widely accepted at present, although the detailed mechanism is still not clear.

Here, in order to clarify the mechanism of the aromatic nitration with N_2O_5, the nitrations of benzene and of nitrobenzene with N_2O_5 were carried out and the yield of the products and the isomer distribution of dinitrobenzenes were investigated.

2. Experiment

2.1 Materials

Benzene, nitrobenzene, and chlorobenzene as aromatic substrates and carbon tetrachloride as a non-

polar solvent were used. Aromatic substrates, their nitro derivatives and carbon tetrachloride purchased from Wako Pure Chemical Industries, Ltd. , and Tokyo Chemical Industry Co., Ltd., as the highest commercial grade chemicals were used without further purification. N_2O_4 was purchased from Takachiho Kagaku Kogyo Co., Ltd.

2.2 Experimental method

N_2O_5 was synthesized by ozonolysis of N_2O_4[4]. A certain amount of substrate and solvent was introduced into a three-necked 50mL flask equipped with a condenser. The flask was purged with N_2 gas. The solvated N_2O_5 was added dropwise to the flask while preventing a rise in the temperature of the solution. A certain minutes later, the solution was neutralized with $NaHCO_3$ aq. and analyzed on a gas chromatograph (Shimadzu Co., Ltd., GC-14B) with a flame ionization detector (FID) and a gas chromatograph mass spectrometer (Shimadzu GC-17A, GCMS-QP5000), using a capillary column (Shimadzu Co., Ltd., 0.25mm ϕ × 25m Fused Silica, CBP1).

Reactions of benzene and of nitrobenzene with N_2O_5 were carried out using 0.5mol/L of substrate × 10mL and 1mol/L of N_2O_5 × 5mL for 30min between −25℃ and 70℃. Reactions of benzene with N_2O_5/N_2O_4 were also carried out using 0.5mol/L of substrate × 10mL and 1mol/L of [N_2O_5 + N_2O_4] × 5mL for 30min at 25℃. Competitive nitrations were also carried out using 1mol/L of each substrate × 25mL and 0.7mol/L of N_2O_5 × 2mL for 15min between

−25℃ and 70℃. The competitive nitrations of benzene/chlorobenzene and of chlorobenzene/nitrobenzene were carried out three times. The relative rates were obtained by the calculation of the ratio of each of the nitroderivatives produced.

3. Result and discussion
3.1 Nitrations of benzene and of nitrobenzene with N_2O_5

In order to investigate the mechanism of the aromatic nitration with N_2O_5, the nitration of benzene with N_2O_5 was carried out, and the ratios of the amount of reacted benene and the yields of the produced nitrobenzene and dinitrobenzenes were obtained.

More than 90% of the benzene was reacted between −25℃ and 25℃, but at 50℃ or above, only about 40% of the benzene was reacted. It is suggested that the ability for nitration should be lowered by the thermal decomposition of N_2O_5. In the nitration of benzene with N_2O_5, nitrobenzene was mainly produced. o-Nitrophenol and o, m, and p-dinitrobenzenes were also produced.

Titov et al.[3] reported the isolation of phenolic products from the nitration of benzene with N_2O_5 in CCl_4. Suzuki et al.[5] also reported that the mechanism of aromatic nitration with NO_2/O_3 and showed that o-nitrophenol was produced as a by-product in the nitration of benzene with NO_3. It is suggested that N_2O_5 should be dissociated homolytically in CCl_4 and that the nitration of benzene with N_2O_5 in CCl_4 should pro-
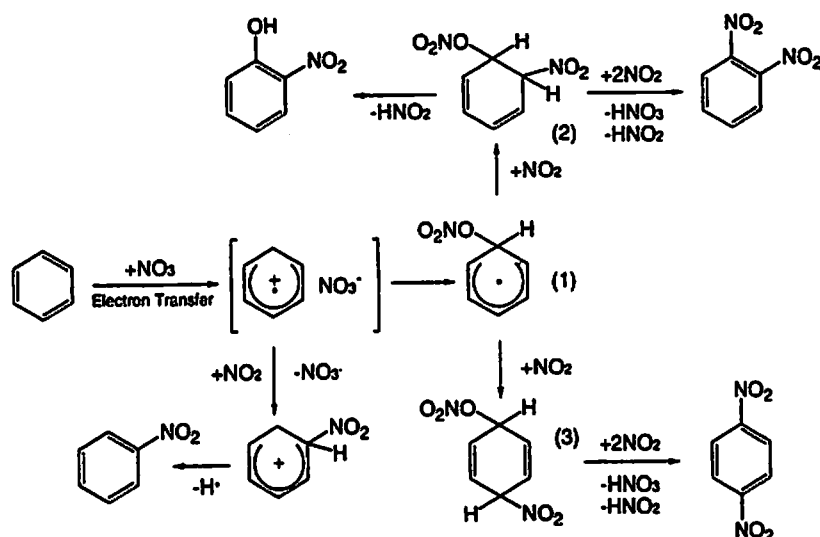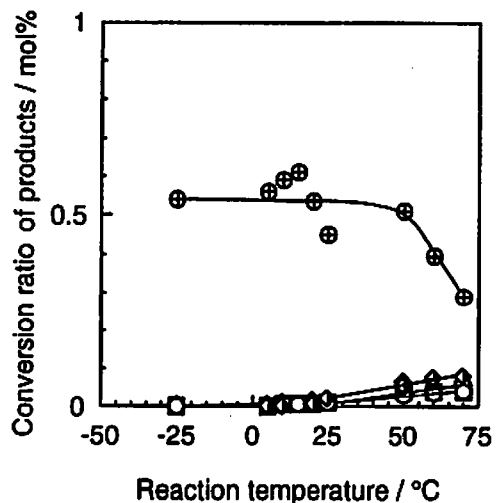

Scheme 1 Nitration mechanism of benzene with N_2O_5 in CCl_4

ceed involving a radical cation formed by a one-electron transfer from benzene to NO_3 (Scheme 1).

The yield of nitrobenzene relative to the reacted benzene was about 50% between $-25\,^\circ\text{C}$ and $25\,^\circ\text{C}$. However, at $50\,^\circ\text{C}$ or above, a lower yield of nitrobenzene was obtained (Fig. 1).

The isomer distribution of the dinitrobenzenes in the nitration of benzene was quite different from that in the nitration of nitrobenzene (Fig. 2, 3). m-Dinitrobenzene was obtained in the nitration of nitrobenzene with N_2O_5, which should be similar to that with HNO_3/H_2SO_4 and should be a typical electrophilic substitution[6,7]. The result indicated that the mechanism of the formation of dinitrobenzenes in the nitration of benzene should be different from that of nitrobenzene.
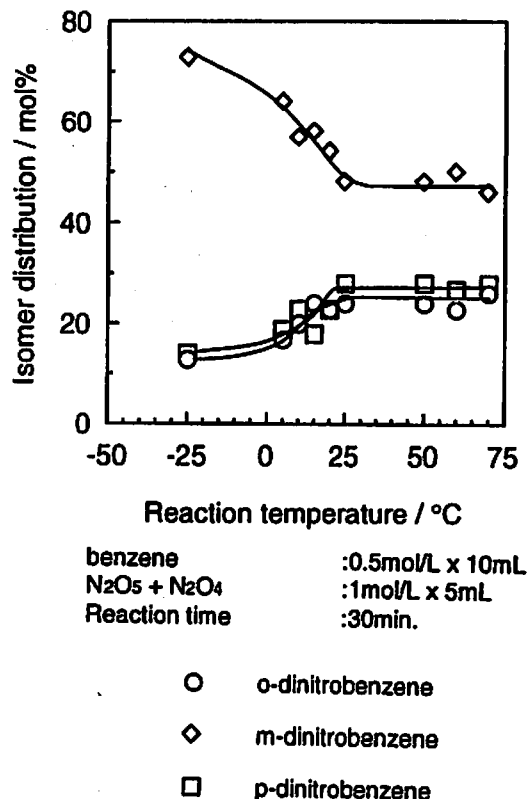
Moreover, the ratio of [dinitrobenzenes]/[nitrobenzene] increased with the reaction temperature in the nitration of benzene with N_2O_5 (Fig. 4). Since the relative rates of nitrobenzene/benzene were about $0.01 \sim 0.05$ between $-25\,^\circ\text{C}$ and $70\,^\circ\text{C}$ in the competi-

benzene	:0.5mol/L x 10mL
N2O5 + N2O4	:1mol/L x 5mL
Reaction time	:30min.

O   o-dinitrobenzene

◇   m-dinitrobenzene

□   p-dinitrobenzene

Fig. 2 Isomer distribution of dinitrobenzenes in the nitration of benzene with N_2O_5

benzene	:0.5mol/L x 10mL
N2O5 + N2O4	:1mol/L x 5mL
Reaction time	:30min.

⊕   nitrobenzene

◆   o-nitrophenol

O   o-dinitrobenzene

◇   m-dinitrobenzene

□   p-dinitrobenzene
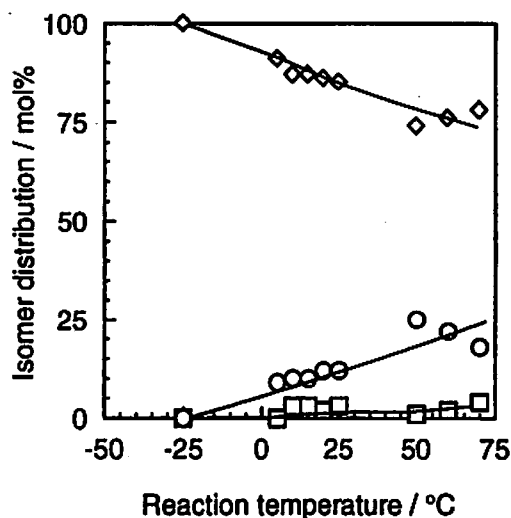
Fig. 1 Conversion ratios of products in the nitration of benzene with N_2O_5

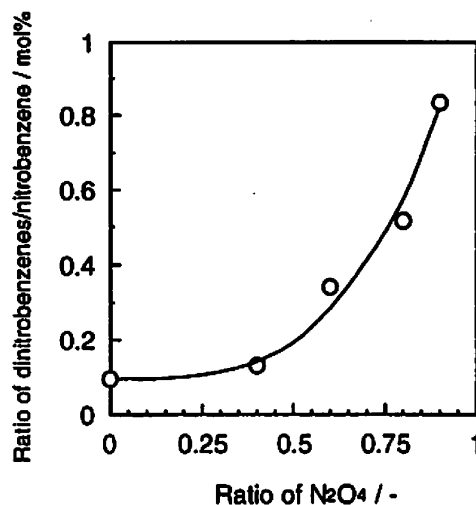| benzene	:0.5mol/L x 10mL
N2O5	:1mol/L x 5mL
Reaction time	:30min.

O   o-dinitrobenzene

◇   m-dinitrobenzene

□   p-dinitrobenzene

Fig. 3 Isomer distribution in the nitration of nitrobenzene with N_2O_5
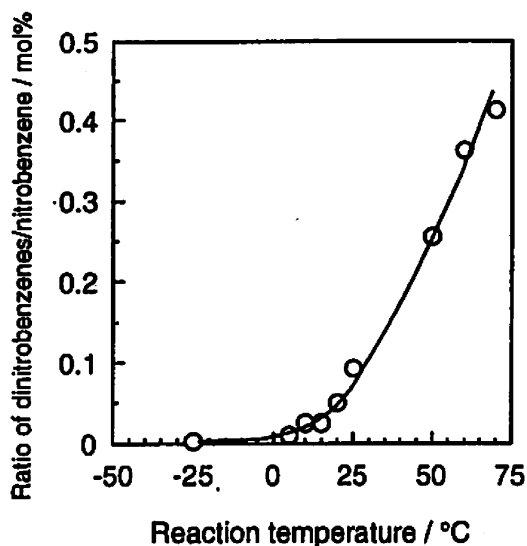
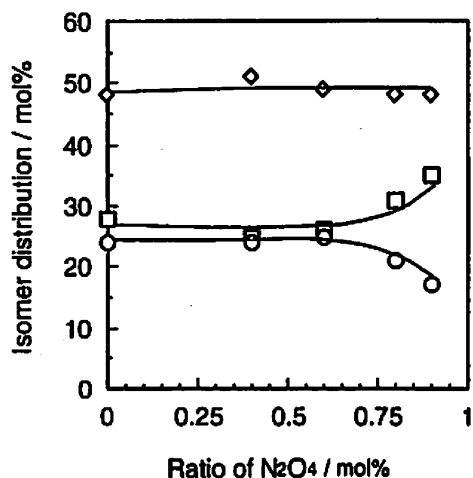Fig. 4 Ratio of dinitrobenzenes/nitrobenzene in the nitration with N_2O_5

Fig. 5 Ratio of dinitrobenzenes/nitrobenzene in the nitration with N_2O_5/N_2O_4

tive nitration, a large part of the dinitrobenzenes should be not formed by the reaction of nitration of the formed nitrobenzene but directly formed by the reaction of benzene with N_2O_5. Therefore, the result is suggested to be attributed to the postulation that the thermal decomposition of N_2O_5 over 25°C should produce a large amount of N_2O_4 (2NO_2) and that the attack of NO_2 on the intermediate [Ar(H)(ONO_2)] 1 should form the intermediate [Ar(H)(ONO_2)(H) (NO_2)] 2, 3 following the production of a large amount of dinitrobenzenes (Scheme 1), resulting in the specific dinitroisomers.

3.2 Nitration of benzene with N_2O_5/N_2O_4

Here, it is suggested that the thermal decomposition[8] of N_2O_5 over 25°C should produce a large amount of N_2O_4 (2NO_2)and that the attack of NO_2 on the intermediate [Ar(H)(ONO_2)] 1 should form the intermediate [Ar(H)(ONO_2)(H)(NO_2)] 2, 3 following the production of a large amount of dinitrobenzenes. Therefore, in order to prove the postulation regarding the nitration of benzene at high temperature, the nitration of benzene with N_2O_5/N_2O_4 was carried out and the ratio of [dinitrobenzenes]/ [nitrobenzene] was investigated.

As a result, the ratio of [dinitrobenzenes]/ [nitrobenzene] increased with the ratio of [N_2O_4]/ [N_2O_5+N_2O_4] (Fig. 5). The isomer distribution in the

Fig. 6 Isomer distribution in the nitration of benzene with N_2O_5/N_2O_4

nitration of benzene with N_2O_5/N_2O_4 (Fig. 6) was similar to that with N_2O_5 at 25°C or above. Therefore, the results should support the postulation regarding the nitration of benzene at high temperature.

4. Conclusions

In order to clarify the mechanism of aromatic nitration with N₂O₅, the nitrations of benzene and of nitrobenzene with N₂O₅ were carried out and the yield of the products and the isomer distribution of dinitrobenzenes were investigated.

As a result, it is suggested that N₂O₅ should be dissociated homolytically in CCl₄ and that the aromatic nitration with N₂O₅ in CCl₄ should proceed with NO₃ via a one-electron transfer mechanism.

The isomer distribution of the dinitrobenzenes in the nitration of benzene was quite different from that in the nitration of nitrobenzene. Moreover, the ratio of [dinitrobenzenes]/[nitrobenzene] increased with the reaction temperature. Therefore, it is suggested that the thermal decomposition of N₂O₅ over 25℃ should produce a large amount of N₂O₄(2NO₂)and that the attack of NO₂ on the intermediate [Ar(H)(ONO₂)] should form the intermediates [Ar(H)(ONO₂)(H)(NO₂)] following the production of a large amount of dinitrobenzenes.

The nitration of benzene with N₂O₅/N₂O₄ was also carried out, and the ratio of [dinitrobenzenes]/[nitrobenzene] was investigated. As a result, the ratio of [dinitrobenzenes]/[nitrobenzene] increased with the ratio of [N₂O₄]. Therefore, this result should support the postulation regarding the nitration of benzene at high temperature.

5. Reference

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N₂O₅によるベンゼンのニトロ化反応

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N₂O₅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，四塩化炭素溶媒中においてN₂O₅によるベンゼンおよびニトロベンゼンのニトロ化反応を行い，環ニトロ化物の収率や生成物分布の温度依存性について検討した。その結果，ベンゼンのニトロ化反応により生成したジニトロベンゼンの生成物分布は，ニトロベンゼンのニトロ化反応によるそれとは大きく異なった。また，反応温度の上昇とともに，ベンゼンのニトロ化反応におけるジニトロベンゼン/ニトロベンゼンの生成比が上昇した。その結果を検討するために，N₂O₅/N₂O₄によるベンゼンのニトロ化反応を行ったところ，ジニトロベンゼン/ニトロベンゼンの生成比はN₂O₄の割合に依存した。以上の結果から，四塩化炭素溶媒中ではN₂O₅はホモリティックに解離しNO₃を攻撃活性種とする機構が提案された。また，反応温度25℃以上では，N₂O₅の熱分解により生成した多量のNO₂が反応中間体 [Ar(H)(ONO₂)] を攻撃して [Ar(H)(ONO₂)(H)(NO₂)] を生成し，多量のジニトロベンゼンを生成する機構を示した。

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