

Nitration of toluene with N_2O_5 Kikuo FURUKAWA*, Fujiroku YOSHIKAWA, Yoshiaki AKUTSU,
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In order to clarify the mechanism of aromatic nitration with N_2O_5 , the nitration of toluene with N_2O_5 in CCl_4 was carried out and was investigated the yields of the products and the isomer distributions. As a result, the reaction should be very rapid and should involve a typical electrophilic substitution. Moreover, in order to investigate the effect of the solvent, the nitration of toluene with N_2O_5 powder without CCl_4 was also carried out. The nitration of toluene with N_2O_5/N_2O_4 was also carried out, and the dependence of the isomer distribution and the ratio of produced nitrotoluenes on the ratio of N_2O_5 was showed. As a result, it is suggested that N_2O_5 should be dissociated homolytically in CCl_4 and 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 $25^\circ C$ 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 specific isomer distributions.

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. On the other hand, the industrial method for the synthesis of nitroarenes has used nitric acid or nitric acid catalyzed with acid. However, this method requires acid-resistant facilities and treatment of the waste acid. Therefore, a new nitrating reagent is desired.

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 acid¹⁾. It should be possible to control the reactivity of the nitration by changing the reaction conditions¹⁾. 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 $-25^\circ C$ and $25^\circ C$ 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 work 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 the aromatic nitration with N_2O_5 in CCl_4 between $0^\circ C$ and $70^\circ C$ and suggested a free-radical reaction mechanism by NO_3 . Moodie et al.⁴⁾ reported the kinetics of the aromatic nitration with N_2O_5/HNO_3 and showed the specific high nitration rate with a high concentration of N_2O_5 . Pitts et al.⁵⁾ reported the reaction of polycyclic aromatic hydrocarbons absorbed on a glass fiber filter with gaseous N_2O_5 . However, Ingold's work is the most widely accepted

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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 nitration of toluene as a model arene in CCl_4 was carried out and was investigated the yield of the products and the isomer distribution.

2. Experiment

2.1 Materials

Toluene as an aromatic substrate and carbon tetrachloride as an aprotic nonpolar solvent were used. The aromatic substrate, its nitro derivatives and the solvent 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 ⁹. 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 \times 25m Fused Silica, CBPI).

In order to obtain the rate constant for the nitration of toluene with N_2O_5 , 0.033mol/L of toluene and 0.010mol/L of N_2O_5 in 15ml of CCl_4 solution were used at 25°C. Equimolar reactions of toluene with N_2O_5 were also carried out using 0.5mol/L of substrate / CCl_4 \times 10mL and 1mol/L of N_2O_5 / CCl_4 \times 5mL for 30min between -25°C and 70°C. Reactions of toluene with N_2O_5 / N_2O_4 were carried out using 0.5mol/L of substrate / CCl_4 \times 10mL and 1mol/L of [N_2O_5 + N_2O_4] / CCl_4 \times 5mL for 30min at 25°C and at 50°C.

3. Result and discussion

3.1 Nitration of toluene with N_2O_5 in CCl_4

In order to clarify the mechanism of the aromatic nitration with N_2O_5 , the nitration of toluene with N_2O_5 in CCl_4 was carried out, and the ratios of the amount of reacted toluene and the yields of the produced nitrotoluene were investigated.

In the nitration of toluene with N_2O_5 between -25°C and 25°C, over 70~80% of the toluene was reacted, but at 50°C or above, less toluene was reacted. The results indicated that o-, m- and p-nitrotoluenes were mainly produced and a small amount of dinitrotoluenes was also produced as by-products.

The yield of nitrotoluenes relative to the reacted toluene was over 87% between -25°C and 25°C. How-

Table 1 Rate constants and isomer diistributions in nitration of toluene with N_2O_5

| Nitrating reagent | Zeroth-order rate constant k_0 / Ms^{-1} | Second-order rate constant $k_2 / M^{-1}s^{-1}$ | Isomer distribution / mol% |
|-------------------|---|--|----------------------------|
| | | | o- : m- : p- |
| $N_2O_5^a$ | 6×10^{-5} | 2×10^2 | 50 : 1 : 43 |
| NO_2 / O_3^b | 4.6×10^{-5} | --- | 57 : 2 : 41 |
| $NO_2 / N_2O_4^c$ | 4.5×10^{-8} | $4.8 \sim 16 \times 10^{-5}$ | 52 : 3 : 45 |
| HNO_3 | 9×10^{-5d} | 1.0^e | 61 : 4 : 31 ^f |

- (a) [toluene] = 0.033M, [N_2O_5] = 0.010M, Solvent; CCl_4 , Reaction temperature; 25°C
Rate = k_2 [toluene] [N_2O_5]
- (b) The reaction rate is dependent on the concentration of induced O_3 gas, Ref. 7
- (c) [toluene] = 0.7M, [N_2O_4] = 6M, Solvent; CH_2Cl_2 , Reaction temperature; 15°C, Ref. 8
Rate = k_2 [toluene] [NO_2]
- (d) [toluene] = 0.09M, [HNO_3] = 7M, Reaction temperature; -10°C, Ref. 9; p17
- (e) 68.3% H_2SO_4 , Ref. 9; p45 Rate = k_2 [toluene] [HNO_3]
 $k_2 = \sim 10^8 M^{-1}s^{-1}$ when describing follows; rate = k_2 [toluene] [NO_2^+], Ref. 9; p46
- (f) 54% H_2SO_4 , Ref. 9; p177

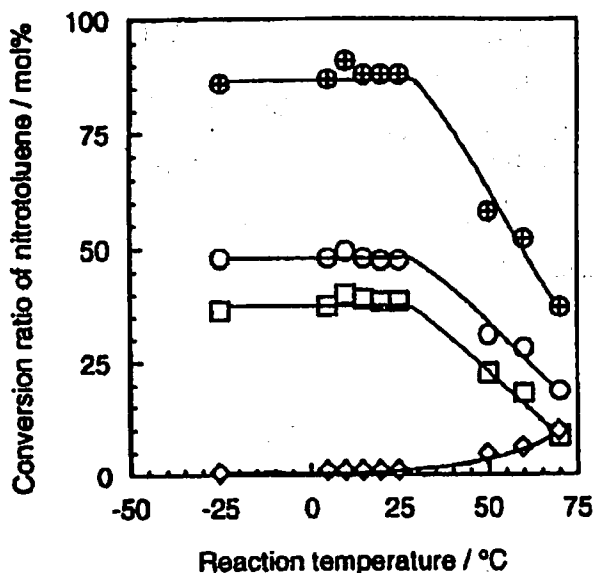


Fig. 1 Conversion ratio of nitrotoluene toward reacted toluene in the nitration of toluene with N_2O_5

Toluene : 0.5mol/L x 10mL
 N_2O_5 : 1mol/L x 5mL
 Reaction time : 30min.

⊕ total of nitrotoluene
 ○ o-nitrotoluene
 ◇ m-nitrotoluene
 □ p-nitrotoluene

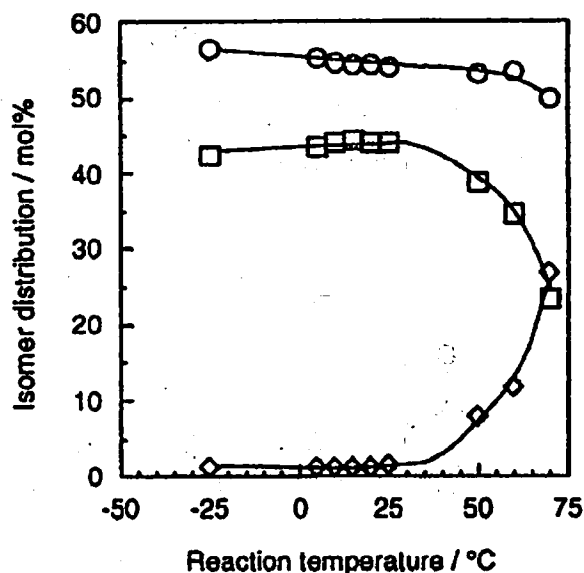


Fig. 2 Isomer distribution of nitroderivatives in the nitration of toluene with N_2O_5

Toluene : 0.5mol/L x 10mL
 N_2O_5 : 1mol/L x 5mL
 Reaction time : 30min.

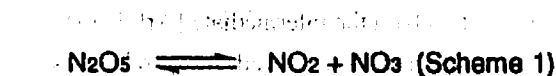
○ o-nitrotoluene
 ◇ m-nitrotoluene
 □ p-nitrotoluene

ever, at 50°C or above, a lower yield of nitrotoluenes and more of the side-chain oxidized products were obtained (Fig. 1). The reaction rate of the nitration of toluene with N_2O_5 was very rapid and much larger than that with NO_2/N_2O_4 (Table 1). Under these reaction conditions, the reaction of toluene with NO_2 (as the initial attacking species) could be neglected. The second-order rate constant for the nitration with N_2O_5 was also larger than that with HNO_3/H_2SO_4 .

The isomer distributions were almost constant between -25°C and 25°C (Fig. 2). They were quite similar to those with NO_2/N_2O_4 and with NO_2/O_3 , and similar to that with HNO_3/H_2SO_4 (Table 1). The results indicated that the reaction involves a typical electrophilic substitution. However, at 50°C or above, the ratio of the meta-isomer increased while that of the para-isomer decreased (Fig. 2).

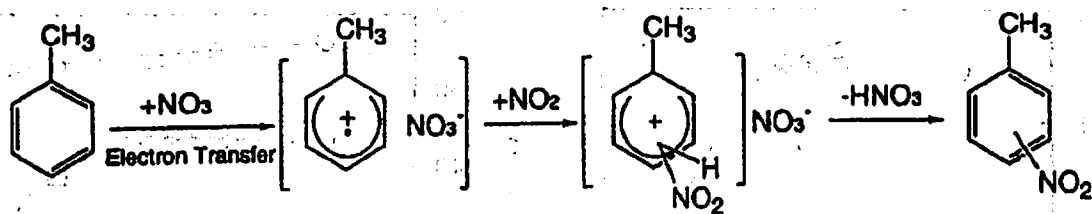
3.2 Nitration of toluene with N_2O_5 without solvent

In order to investigate the effect of the solvent, the nitration of toluene by direct contact with N_2O_5 powder without the solvent was carried out. As a re-

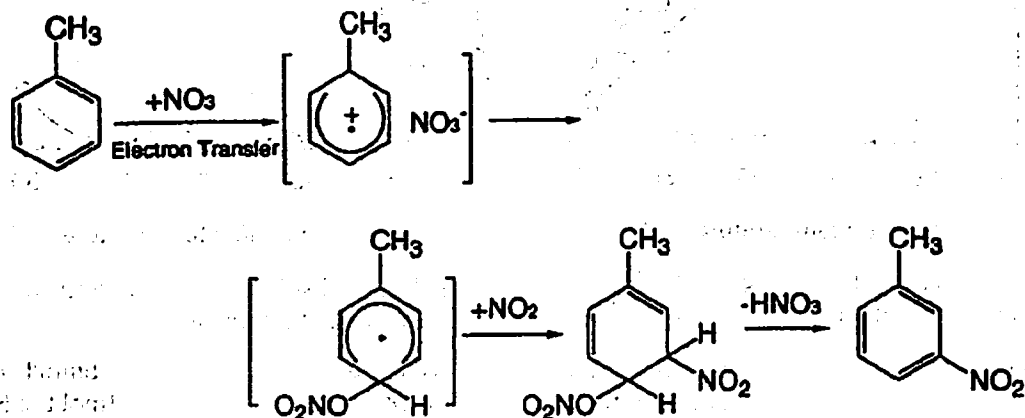


sult, the isomer distributions in the nitration of toluene without the solvent were almost constant and were not dependent on the reaction temperature (Fig. 3). The solvent should play an important role in the reaction, suggesting that N_2O_5 should be dissociated homolytically in CCl_4 (Scheme 1) and that the nitration of toluene with N_2O_5 in CCl_4 should proceed involving the initial attack of NO_3 on toluene, although it is suggested that the behavior of N_2O_5 powder should differ from that of N_2O_5 in CCl_4 because of its ionic structure of $[NO_2^+ \cdot NO_3^-]$ in the solid state. However, the further investigation of the solvent effect of N_2O_5 should be required. Under those reaction conditions with a solvent, the possibility is suggested that the mechanism of aromatic nitration with N_2O_5 should proceed involving a radical cation via a one-electron transfer from the arene to NO_3 (Scheme 2)^{7, 10, 11}.

Moreover, the ratio of m-nitrotoluene increased with the reaction temperature in the nitration of toluene with N_2O_5 . The result is thought to be attributed to the postulation that the thermal decomposition of



Scheme 2 Nitration of toluene with N_2O_5 in CCl_4



Scheme 3 Nitration of toluene with N_2O_5 in CCl_4 at high temperature

N_2O_5 ¹²⁾ over $25^\circ C$ should lower the nitrating ability and should produce a large amount of N_2O_4 ($2NO_2$); the attack of NO_2 on the intermediate $[Ar(H)(ONO_2)]$ should then form the intermediate $[Ar(H)(ONO_2)(H)(NO_2)]$ following the production of a large amount of *m*-nitrotoluene (Scheme 3), resulting in the specific isomer distributions.

3.3 Nitration of toluene with N_2O_5/N_2O_4

Here, it is suggested that the thermal decomposition¹²⁾ of N_2O_5 over $25^\circ C$ should produce a large amount of N_2O_4 ($2NO_2$) and that the attack of NO_2 on the intermediate $[Ar(H)(ONO_2)]$ should result in the production of a large ratio of *m*-nitrotoluene. Therefore, in order to prove the postulation for the nitration of toluene at high temperature, the nitration of toluene with N_2O_5 / N_2O_4 at $25^\circ C$ and $50^\circ C$ was carried out and was investigated the isomer distributions and the yields of the produced nitrotoluenes.

As a result, the ratio of *m*-nitrotoluene increased with the ratio of $[N_2O_4] / [N_2O_5 + N_2O_4]$ (Fig. 4), while that of *p*-nitrotoluene decreased; almost the same results were obtained at both reaction temperatures. In addition, the ratio of the produced nitrotoluenes was nearly proportional to the ratio of N_2O_5 (Fig. 4). Furthermore, in the equimolar reaction of toluene with NO_2 / N_2O_4 ¹³⁾ between $-25^\circ C$ and $70^\circ C$, no reaction

product was detected. This result suggested again that the nitrating ability of NO_2 could be neglected under these reaction conditions and that the reaction should proceed involving the initial attack of NO_3 . Therefore, the results should support the postulation of the nitration of toluene at high temperature.

4. Conclusions

In order to clarify the mechanism of the aromatic nitration with N_2O_5 , the nitration of toluene with N_2O_5 in CCl_4 was carried out and was investigated the yields of the products and the isomer distributions. As a result, the reaction should be a typical electrophilic substitution and was very rapid compared with that using NO_2 / N_2O_4 . Moreover, in order to investigate the effect of the solvent, the nitration of toluene with N_2O_5 powder without CCl_4 was also carried out. As a result, the isomer distributions were different, and N_2O_5 is suggested to be dissociated homolytically in CCl_4 ; the aromatic nitration with N_2O_5 in CCl_4 should thus proceed with NO_3 via a one-electron transfer mechanism.

The isomer distribution in the nitration of toluene in CCl_4 was affected by the reaction temperature. The ratio of *m*-nitrotoluene increased with the reaction temperature. Therefore, it is suggested that the thermal decomposition of N_2O_5 over $25^\circ C$ should produce a large amount of N_2O_4 ($2NO_2$) and that the attack of

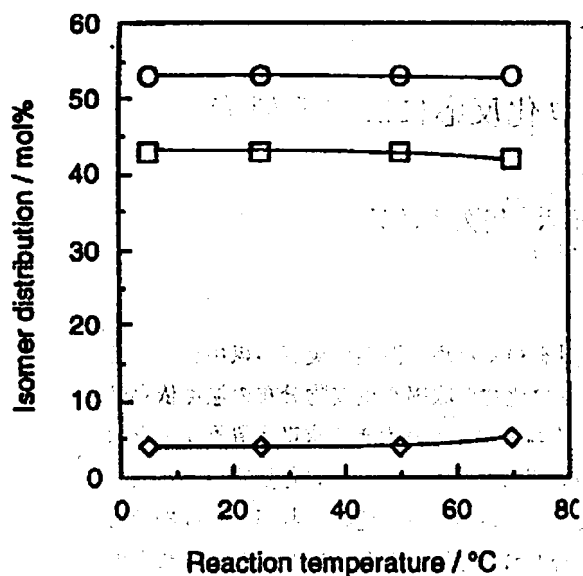


Fig. 3 Isomer distribution in the nitration of toluene by direct injection of N_2O_5 powder (without solvent)

- o-nitrotoluene
- ◇ m-nitrotoluene
- p-nitrotoluene

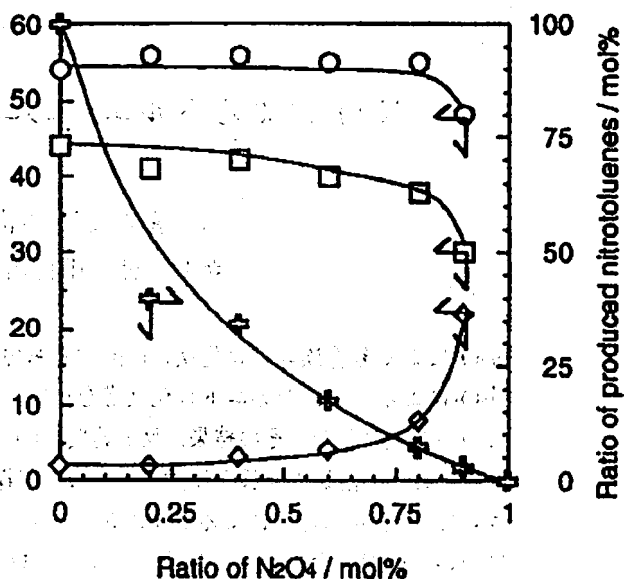


Fig. 4 Isomer distribution and ratio of produced nitrotoluenes in the nitration of toluene with N_2O_5 / N_2O_4

Toluene : 0.5mol/L x 10mL
 $N_2O_5+N_2O_4$: 1mol/L x 5mL
 Reaction temperature : 25°C
 Reaction time : 30min.

- o-nitrotoluene
- ◇ m-nitrotoluene
- p-nitrotoluene
- ✦ Ratio of produced nitrotoluenes

NO_2 on the intermediate $[Ar(H)(ONO_2)]$ should form the intermediates $[Ar(H)(ONO_2)(H)(NO_2)]$ following the specific isomer distributions.

The nitration of toluene with N_2O_5 / N_2O_4 was also carried out, and the isomer distribution was investigated. As a result, the ratio of m-nitrotoluene increased with the ratio of $[N_2O_4]$. Furthermore, the ratio of produced nitrotoluenes was nearly proportional to the ratio of N_2O_5 . Therefore, this result should support the postulation above.

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N₂O₅によるトルエンのニトロ化反応に関する研究

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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によるトルエ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、反応速度はNO₂によるニトロ化より大きく求電子置換反応を示した。また、溶媒の影響を検討するため、溶媒を用いずにトルエンのニトロ化反応も行った。さらに、N₂O₅/N₂O₄によるトルエ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について検討したところ、生成した環ニトロ化物の割合はN₂O₅の割合に比例した。これらの結果から、四塩化炭素溶媒中ではN₂O₅はホモリテックに解離し、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℃以上では特異的な生成物分布を示すことについて、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)]を生成する機構を示した。

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