

Some Applications of MO Methods to the Chemistry of Explosives VII.

—Estimation of Reactivities for Aromatic Nitration from STO-3G Calculations. A Comment on Reactive Species of Nitrobenzene in Concentrated Sulfuric Acid—

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Partial rate factors (p. r. f.'s) at meta and para positions for the nitration of mono-substituted benzenes have been correlated successfully with their proton affinities (ΔE) and the total charge densities of the methyl group substituted on their positions (Δq_{Me}) calculated by the ab initio molecular orbital method at the minimal basis set STO-3G level.

An attempt to elucidate a lower reactivity than predicted from the Hammett relationship for the nitration of nitrobenzene in concentrated sulfuric acid has been done on the basis of a linear relationship between \log (p. r. f.) and ΔE or Δq_{Me} . From the calculations of relative reactivities and positional selectivities for various complexes of nitrobenzene with chemical species existing in concentrated sulfuric acid, it is suggested that the lower reactivity is due to the involvement of its hydrogen-bonded complexes such as $\text{PhNO}_2\text{-H}_2\text{SO}_4$. This is a viable explanation for the lower reactivity of nitrobenzene in the nitration in concentrated sulfuric acid.

Introduction

Relative reactivities for electrophilic aromatic nitration are well known to be satisfactorily correlated with the empirical σ constants originally proposed by Brown and Okamoto¹⁾. However, a deviation from the linear relationship was observed in the nitration of nitrobenzene in concentrated sulfuric acid with nitric acid^{2),3)}. Its lower reactivity was suggested to be due to the involvement of its hydrogen-bonded complex with the solvent molecule²⁾. Our previous finding that the Hammett relationship holds for the nitration of

nitrobenzene in nitromethane with nitronium hexafluorophosphate³⁾, where free nitrobenzene is thought to be involved in the nitration, would also support the above suggestion, but there has been no clear explanation for it. In addition, our previous attempt³⁾ to interpret its lower reactivity in terms of the involvement of its hydrogen-bonded complexes by using the CNDO/2 semi-empirical MO calculations seemed to be insufficient to confirm it in view of the accuracy of the semi-empirical MO method used, although it might support the idea.

On the other hand, some recent attempts to interpret reactivities in quantitative terms for the isodesmic process have been done successfully by ab initio MO calculations of proton affinities⁴⁾ and charge densities⁵⁾ at the minimal basis set STO-3G level⁶⁾.

We found that the relative reactivities for the electrophilic aromatic nitration of mono-substituted benzenes can be correlated with their proton affinities and the total charge densities of the methyl group substituted at their nitration positions. Also, the lower reactivity for the nitration of nitrobenzene in concentrated sulfuric acid may be due to the involve-

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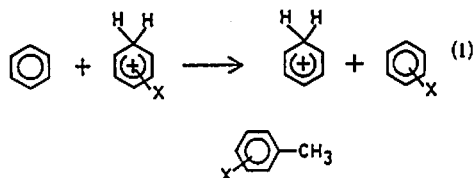
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ment of its hydrogen-bonded complexes with chemical species existing in concentrated sulfuric acid.

Procedure

First, we attempted to correlate the reactivities at meta and para positions for the nitration of mono-substituted benzenes with the difference in proton affinities (ΔE) for an isodesmic proton transfer equilibrium (eq. (1)) and with the difference in the charge densities of the methyl group substituted at their nitration positions (Δq_{Me} , eq. (2)).



$$\Delta q_{Me} = q_{Me}^X - q_{Me}^H \quad (2)$$

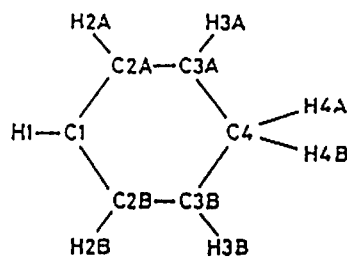
Later we confirmed that the partial rate factors (p. r. f. 's) for the nitration of mono-substituted benzenes can be correlated linearly with the two reactivity indices described previously. We used these indices to estimate the reactivities for the nitration of hydrogen-bonded complexes of nitrobenzene with chemical species existing in concentrated sulfuric acid⁷⁾.

Calculation

The ab initio MO calculations with the minimal basis set at STO-3G level were conducted on a HITAC M-280H computer in the Computer Centre, at the University of Tokyo, using versions of GAUSSIAN 70⁸⁾ and GSCF 2⁹⁾ computer programs.

The geometries for mono-substituted benzenes were determined by using the bond lengths and angles of the standard models proposed by Pople and Gordon¹⁰⁾. The structure of the Wheland complex (σ -complex) for benzene attacked by an electrophilic proton is shown in Fig. 1. All the structures of hydrogen-bonded complexes of nitrobenzene, shown in Fig. 2, were determined¹¹⁾ by optimizing the length of the O-H bond formed from an oxygen atom of the nitro group in nitrobenzene and a hydrogen atom in the chemical species existing in concentrated sulfuric acid, so as to minimize the CNDO/2 electron energies¹²⁾ of the hydrogen-bonded complexes.

Results and Discussion



BOND LENGTH				BOND ANGLE					
C1	-	C2	1.40 Å	C1	C2	C3	120.0°		
C2	-	C3	1.40	C1	C2	H2	120.0		
C3	-	C4	1.483	C1	C4	H4	125.255		
C1	-	H1	1.08	C2	C3	C4	123.4		
C2	-	H2	1.08	C2	C3	H3	118.3		
C3	-	H3	1.08	C2-C1	H1		119.5		
C4	-	H4	1.09	C2A	C1	C2B	121.0		
				C2A	C4	C3B	112.2		
TORSION ANGLE									
C1	C2	C3	C4	0.0°	C2	C3A	C4	C3B	0.0°
C2A	C4	C3B	C2B	0.0	C1	C2	C3	H3	180.0
C2A	C3A	C4	H4A	120.0	C2A	C3A	C4	H4B	240.0
H1	C1	C2	C3	180.0					

Fig. 1 Bond length, bond angles and torsion angles for the σ -complex of benzene

Reactivity Indices

Figure 3 shows plots of \log (p. r. f.)¹²⁾ against ΔE calculated from eq. (1). From Fig. 3 we can obtain a linear relationship between \log (p. r. f.) and ΔE , as shown in eq. (3).

$$\log(p. r. f.) = (2.88 \pm 0.29) \times 10^{-1} \Delta E - (0.22 \pm 0.17) \quad (3)$$

(coefficient of correlation, $r=0.96$, number of data, $n=10$)

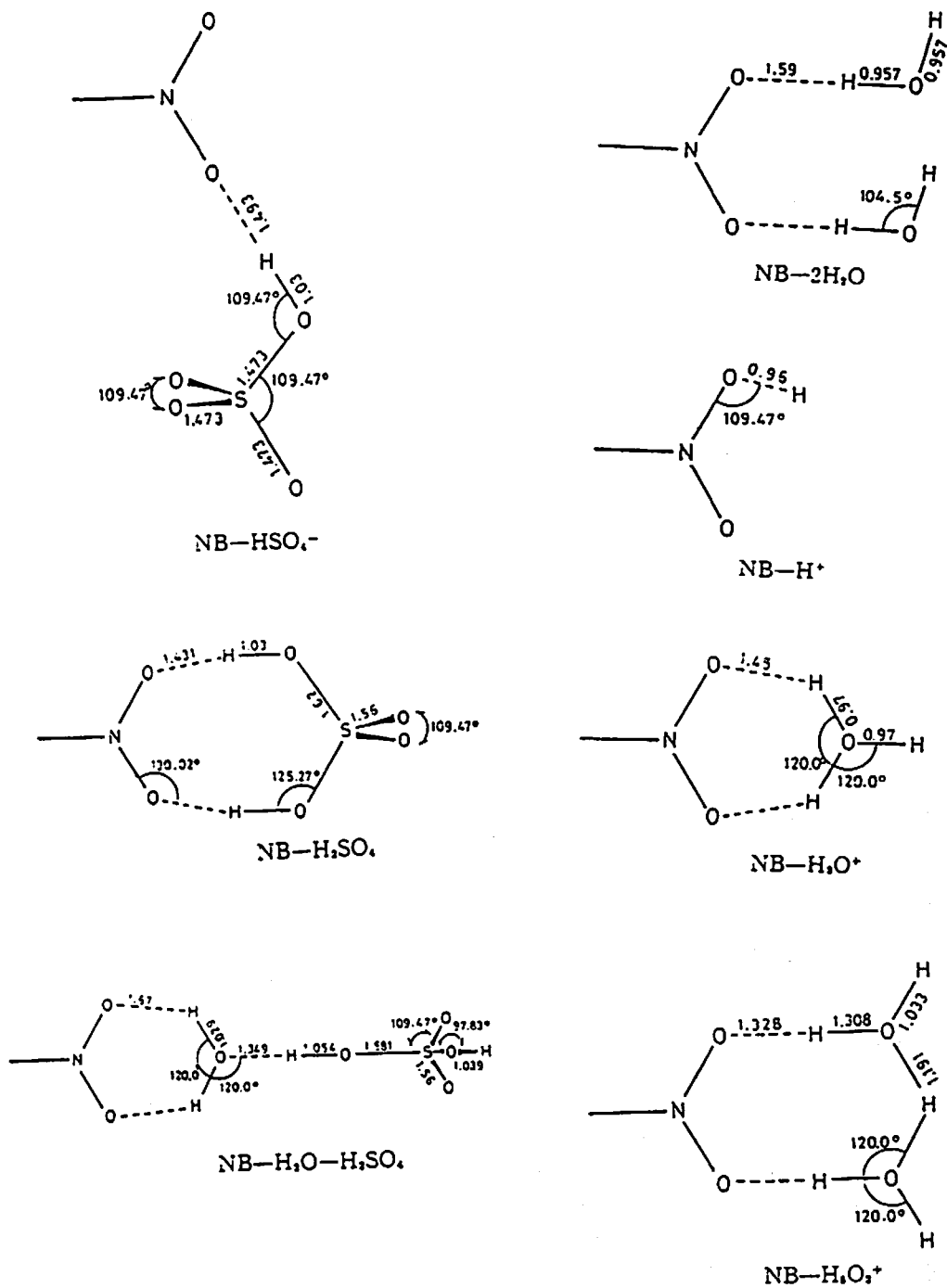
Our previous experience¹²⁾ showed that the relative reactivities for electrophilic aromatic nitration can be correlated better with the charge densities of the methyl group attached to the attacked carbon atom rather than with the charge densities of the attacked carbon atom itself. Then we attempted to evaluate Δq_{Me} as a reactivity index.

Figure 4 shows plots of \log (p. r. f.) against Δq_{Me} . We obtained a good relationship between \log (p. r. f.) and Δq_{Me} for the nitration of mono-substituted benzenes at their meta and para positions, except for chlorobenzene at its para-position.

$$\log(p. r. f.) = (3.22 \pm 0.25) \times 10^2 \Delta q_{Me} + (0.21 \pm 0.17) \quad (4)$$

$$(r = 0.98, n=8)$$

The result may come from the characteristic properties of the ab initio MO calculation at STO-3G level, although it cannot be explained clearly at the present



(length in angstroms, angle in degrees)

Fig. 2 Structures of hydrogen-bonded complexes of nitrobenzene determined, optimizing the CNDO/2 electron energies of the length of the O-H bond formed from an oxygen atom of the nitro group in nitrobenzene and a hydrogen atom in the chemical species existing in concentrated sulfuric acid

time.

Figures 3 and 4 show that both ΔE and Δq_M can be

useful reactivity indices to estimate log (p. r. f.) for the nitration of mono-substituted benzenes. In addi

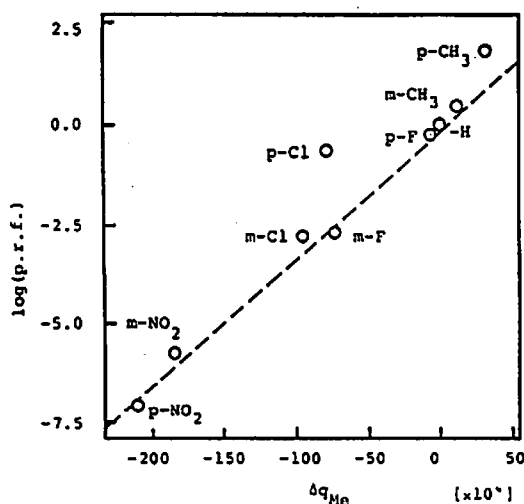


Fig. 3 Relationship between $\log(p. r. f.)$ for the nitration and ΔE

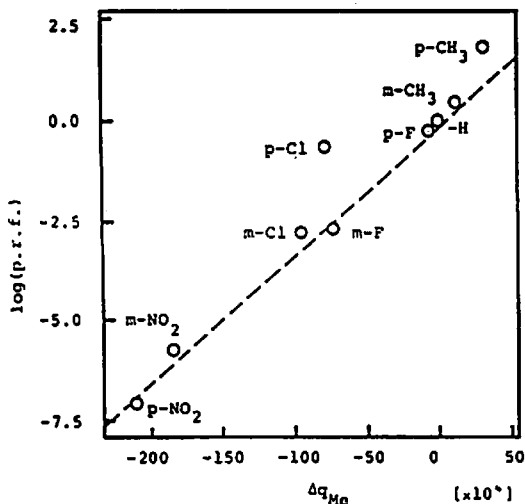


Fig. 4 Relationship between $\log(p. r. f.)$ for the nitration and Δq_{Me}

tion, we have attempted to estimate the isomer proportions for the nitration of mono-substituted benzenes from ΔE or Δq_{Me} , using Brown's "selectivity factor" (S_f):

$$S_f = \log((p. r. f.)_p / (p. r. f.)_m) = \log(p. r. f.)_p - \log(p. r. f.)_m \quad (5)$$

Thus, the S_f values for the nitration of mono-substituted benzenes can be obtained from eqs. (6) and (7).

$$S_f = (2.39 \pm 0.22) \times 10^{-1} (\Delta E^p - \Delta E^m) - (0.29 \pm 0.11) \quad (6)$$

$$(\tau = 0.99, n=4) = (4.15 \pm 0.79) \times 10^2 (\Delta q_{Me}^p - \Delta q_{Me}^m) - (0.05 \pm 0.20) \quad (7)$$

$$(\tau = 0.97, n=4)$$

Reactivities and Selectivities for Hydrogen-bonded Complexes of Nitrobenzene during Nitration in Sulfuric Acid

As SCF-MO calculation did not converge for most σ -complexes for hydrogen-bonded nitrobenzene, we could not obtain their ΔE values. Thus, we used the Δq_{Me} value as a reactivity index to estimate the nitration of hydrogen-bonded complexes of nitrobenzene in sulfuric acid.

Table 1 shows $\log(p. r. f.)$ for the nitration of hydrogen-bonded complexes obtained from Δq_{Me} calculated at the STO-3G level. We obtained a few significant findings from the results. Namely, the hydrogen-bonded complexes with such protonated species as H^+ , H_3O^+ , $H_3O^+ - H_2O$ do not contribu-

Table 1 $\log(p. r. f.)$ at meta and para positions for the hydrogen-bonded complexes of nitrobenzene (NB) calculated from eq. (4)

Complex	m-position		p-position	
	Δq_{Me}	$\log(p. r. f.)$	Δq_{Me}	$\log(p. r. f.)$
NB	-0.0185	-5.11 ~ -6.34	-0.0208	-5.80 ~ -7.18
NB-HSO ₄	-0.0275	-7.79 ~ -9.50	-0.0056	-1.28 ~ -1.90
NB-H ₂ O	-0.0179	-4.94 ~ -6.17	-0.0242	-6.81 ~ -8.36
NB-2H ₂ O	-0.0270	-7.64 ~ -9.33	-0.0280	-7.94 ~ -9.68
NB-H ₂ SO ₄	-0.0331	-9.45 ~ -11.44	-0.0364	-10.43 ~ -12.59
NB-H ₂ O-H ₂ SO ₄	-0.0234	-6.57 ~ -8.08	-0.0334	-9.54 ~ -11.55
NB-H ⁺	-0.0680	-19.82 ~ -23.56	-0.0782	-22.85 ~ -27.10
NB-H ₃ O ⁺	-0.0589	-17.11 ~ -20.40	-0.0689	-20.08 ~ -23.87
NB-H ₃ O ₂ ⁺	-0.0602	-17.50 ~ -20.85	-0.0705	-20.56 ~ -24.42

Table 2 Selectivity factors for hydrogen-bonded complexes of nitrobenzene (NB) calculated from eq. (7)

Complex	$\Delta q_{Me}^p - \Delta q_{Me}^m$	Sf
NB	-0.0023	-1.39~ -0.62
NB-HSO ₄ ⁻	0.0219	7.51~ 10.57
NB-H ₂ O	-0.0063	-3.36~ -1.79
NB-2H ₂ O	-0.0010	-0.74~ -0.18
NB-H ₂ SO ₄	-0.0033	-1.88~ -0.96
NB-H ₂ O-H ₂ SO ₄	-0.0100	-5.19~ -3.21
NB-H ⁺	-0.0102	-5.29~ -3.28
NB-H ₃ O ⁺	-0.0100	-5.19~ -3.21
NB-H ₃ O ₂ ⁺	-0.0103	-5.34~ -3.31

te greatly to the nitration under the conditions used because of their very low reactivities. The complex with HSO₄⁻ also may not contribute significantly, notably because it has too high a reactivity at its para-position, but also because, as previously observed¹²⁾, the UV spectrum of the hydrogen-bonded complex of nitrobenzene in concentrated sulfuric acid showed a red shift, although the UV spectrum of the complex with HSO₄⁻ should show a blue shift.

From the standpoint of reactivities, we may say that the complexes with H₂O, 2H₂O, H₂SO₄ and H₂O-H₂SO₄, which have somewhat lower reactivities than nonhydrogen-bonded ones, are primarily involved in the nitration of nitrobenzene in concentrated sulfuric acid. The CNDO/2 semi-empirical method could also give us a similar conclusion as the ab initio method, in spite of its limitations.

On the other hand, as shown in Table 2, each hydrogen-bonded complex can have a different isomer proportion, namely, a different selectivity factor for the nitration. Our previous observation³⁾ showed that the selectivity factor for the nitration of nitrobenzene in 85-98.5wt. % sulfuric acid does not vary with the concentration of sulfuric acid.

Moreover, as shown in Table 2, nitrobenzene and its hydrogen-bonded complex with a sulfuric acid molecule can show similar selectivity factors, -0.62~-1.39 and -0.96~-1.88, respectively, to the observed factor, -1.49, for the nitration of nitrobenzene in concentrated sulfuric acid. This suggests that only one hydrogen-bonded complex may be involved in the nitration under the above conditions.

Thus, the hydrogen-bonded complex of nitro

benzene with a sulfuric acid molecule is thought to be primarily involved in the nitration of nitrobenzene in 85-98.5wt. % sulfuric acid.

Conclusion

The present results provide important evidence that we can obtain p. r. f.'s for the nitration of mono-substituted benzenes from the ab initio MO calculations at the minimal basis set STO-3G level, and also that the lower reactivity for the nitration of nitrobenzene in concentrated sulfuric acid is primarily due to the involvement of its hydrogen-bonded complex with a sulfuric acid molecule.

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分子軌道法の火薬化学への応用 (第7報)

STO-3G計算による芳香族ニトロ化反応の反応性評価-濃硫酸中での
 ニトロベンゼンの反応種に関するコメント

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モノ置換ベンゼンのニトロ化反応におけるメタおよびパラ位の部分速度因子(p. r. f.)が、STO-3Gを用いた ab initio 分子軌道法計算によるその位置のプロトン親和力(ΔE)および置換メチル基の全電荷密度(Δq_{Me})とよく関係つけられた。

\log (p. r. f.)と ΔE および Δq_{Me} とが直線関係にあることを用いて、濃硫酸中でのベンゼンのニトロ化の反応性が Hammett 式から予測される値より小さい理由を説明することを試みた。濃硫酸中に存在する種々の化学種とニトロベンゼンとのコンプレックスについて相対反応性および選択性の計算を行った結果、その低反応性は $\text{PhNO}_2\text{-H}_2\text{SO}_4$ のような水素結合錯体が反応に関与しているためと思われる。これは濃硫酸中でのニトロベンゼンのニトロ化の低反応性の可能な説明と言える。

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