Ozone-mediated nitration of naphthalene and some methyl derivatives with nitrogen dioxide. Remarkable enhancement of the 1-nitro/2-nitro isomer ratio and mechanistic implications

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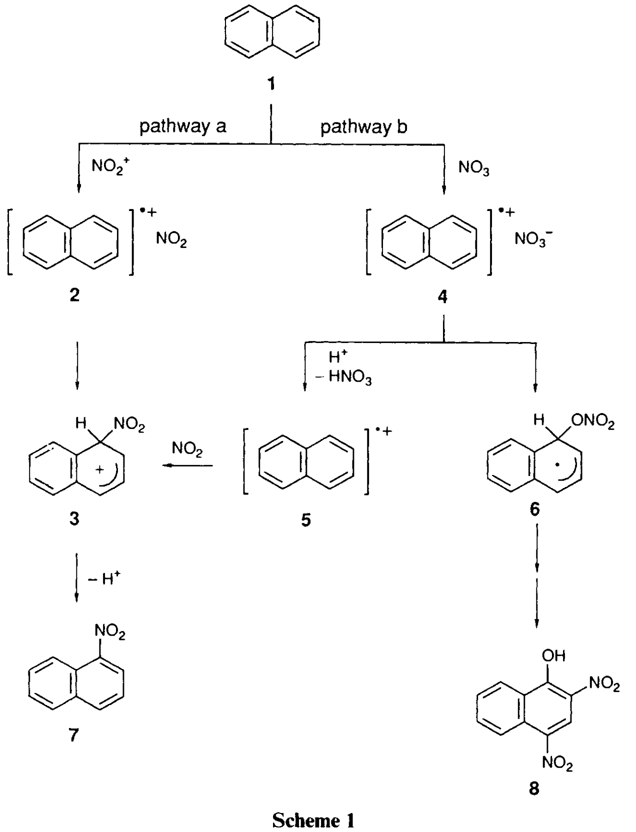
Naphthalene, 1- and 2-methylnaphthalenes were smoothly nitrated with nitrogen dioxide at low temperatures in the presence of ozone to afford the corresponding nitro derivatives in high yields. For naphthalene, the 1-nitro/2-nitro isomer ratios were remarkably high, mostly ranging from 35 to 70. 1,4-Dimethylnaphthalene suffered extensive side-chain substitution under similar conditions. The enhanced regioselectivity as compared with conventional nitrations has been interpreted in terms of the electron transfer mechanism involving the nitrogen trioxide as the initial electrophile.

The nitration of naphthalenes is of great importance from both practical and theoretical points of view. This reaction has long been accepted to occur *via* the ionic pathway involving the nitronium ion (NO_2^+) as the electrophile. However, Perrin in 1977 observed the formation of nitronaphthalenes by controlled potential electrolysis of naphthalene in acetonitrile in the presence of nitrogen dioxide.[1] Based on this observation, he proposed an alternative mechanistic view that a radical cation-radical pair **2** is formed by the electron transfer between naphthalene **1** and nitronium ion and the resulting intermediate **2** collapses to form an arenium ion **3** (Scheme 1; pathway a). His view had received considerable attention and aroused much debate, but later was subject to refutations from theoretical[2,3] and experimental studies.[4–8]

The isomer distribution of the nitration product of naphthalene varies considerably depending on the reaction conditions employed. The 1-nitro/2-nitro isomer ratios are mostly between 10 and 20 under the conventional ionic conditions using nitric acid as the nitrating agent, while the ratios are below 10 under the homolytic conditions using nitrogen dioxide and light or heat. However, when the nitration is carried out under the conditions of electron transfer, the isomer ratio becomes unusually high and often reaches as high as 40–50.[4] Therefore, the enhanced 1-nitro/2-nitro isomer ratio may be regarded as a good criterion to judge whether the reaction proceeds *via* the electron transfer mechanism or not. This attractive criterion advanced by Eberson *et al.*[5] is quite useful to differentiate mechanistic pathways for aromatic nitration. For confirmation, a full collection of the 1-nitro/2-nitro isomer ratio data obtained under a variety of conditions are presented in Table 1.



Scheme 1

Recently, we have observed that nitrogen dioxide is activated in the presence of ozone to react with a variety of arenes, giving the corresponding nitro derivatives in high yields (the *kyodai*-nitration).[26] For this novel type of aromatic nitration, we have proposed a mechanism in which the reaction proceeds in a dual mode depending on the oxidation potential of aromatic substrate, *i.e.*, sequences eqns. (1)→(2)→(3) and eqns. (1)→(4)→(5):

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \qquad (1)$$

$$ArH + NO_3 \longrightarrow ArH^{\cdot +} + NO_3^- \qquad (2)$$

$$ArH^{\cdot +} + NO_2 \longrightarrow Ar(H)NO_2^+ \xrightarrow{-H^+} ArNO_2 \qquad (3)$$

$$NO_3 + NO_2 \longrightarrow N_2O_5 \xrightarrow{H^+} NO_2^+ + HNO_3 \qquad (4)$$

$$ArH + NO_2^+ \longrightarrow Ar(H)NO_2^+ \xrightarrow{-H^+} ArNO_2 \qquad (5)$$

In order to obtain further information about the mechanism of this novel nitration, we have investigated the reaction of naphthalene and some methyl derivatives with nitrogen dioxide in the presence of ozone. The high 1-nitro/2-nitro isomer ratios observed therein well substantiate our view that the *kyodai*-nitration of activated and moderately activated arenes proceeds *via* the cation radical generated by the process shown by eqn. (2).

Table 1 1-Nitro/2-nitro isomer ratios observed in the nitration of naphthalene under various conditions

Reagent	Solvent	T/°C	Reaction time/h	Yield (%)[a]	Isomer ratio	Ref.
HNO_3	$MeNO_2$	25	—	—	29	9
	MeCN	84	—	—	11	10
	AcOH	25	—	—	21	9
		50	—	—	16	9, 11
	Ac_2O	0	1	100	16	12
		25	—	—	9	9
		50	—	—	8	11
	H_2SO_4	25	—	—	35	9
HNO_3–NaN_3	Ac_2O	0	1	63	24	12
HNO_2–HNO_3	60% H_2SO_4	25	—	—	25	13
HNO_3–H_2SO_4	AcOH	70	—	—	22	9
	MeCN	25	—	—	16	14
HNO_3–H_2SO_4–Urea	MeCN	—	—	—	9	1
		25	—	—	20	14
$NO_2^+BF_4^-$	$MeNO_2$	25	—	—	12	9, 15
	Sulfolane	25	—	—	10	15
	CH_2Cl_2	20	15	49	12	6
		−30	2	15	15	6
	MeCN	25	—	—	11	14
$AgNO_3$–MeCOCl	MeCN	25	—	—	12	15
$AgNO_3$–PhCOCl	MeCN	25	—	—	12	15
$AgNO_3$–BF_3	MeCN	25	—	—	19	15
$MeONO_2$–$MeOSO_2F$	MeCN	25	—	—	13	15
4-$NO_2pyONO_2^+$[b]	MeCN	25	—	—	10	15
$(NH_4)_2Ce(NO_3)_6$	MeCN	84	—	—	15	19
$Hg(NO_3)_2$–Nafion-H®	HNO_3	Room temp.	1	77	32	16
$C(NO_2)_4$	Gas phase	300	—	—	1	15
$C(NO_2)_4$, $h\nu$	MeCN	23	4	(70)	21	17
		Room temp.	17	56	7	12
	$CHCl_3$	23	16	(99)	9	17
$C(NO_2)_4$–TFA, $h\nu$[b]	MeCN	23	15	(98)	20	17
$pyNO_2^+$[b]	MeCN	Room temp.	—	98	10	12
		23	21	(60)	8	17
2,6-$Me_2pyNO_2^+$[b]	MeCN	−20 ~ 0	0.5	(83)	7	17
$pyNO_2^+$, $h\nu$[b]	MeCN	−40	3	62	6	12
2,6-$Me_2pyNO_2^+$, $h\nu$[b]	MeCN	−40	16	(93)	18	17
4-$MeOpyNO_2^+$, $h\nu$[b]	MeCN	23	7	(46)	14	17
4-$MeOpyNO_2^+$–TFA, $h\nu$[b]	MeCN	23	11	(83)	13	17
N_2O_3	Sulfolane	25	1	2	17	18
N_2O_3–$HClO_4$	Sulfolane	Room temp.	1	32	17	19
N_2O_3–Electrolysis (E = 1.0 V)	Sulfolane	Room temp.	1	38	16	19
$NO_2(N_2O_4)$	Sulfolane	25	1	8	19	20
	CH_2Cl_2	Room temp.	48	59	24	21
	CCl_4	25	—	—	10	22
		50	—	—	5	22
	MeCN	25	—	—	24	15
NO_2–DTBP[b]	CH_2Cl_2	25	—	—	8	22
	CCl_4	25	—	—	4	22
NO_2–$NOClO_4$	Sulfolane	25	1	23	20	18
NO_2–$(NH_4)_2Ce(NO_3)_6$	MeCN	65	—	—	16	15
NO_2–$Zn(NO_3)_2$	Sulfolane	25	1	22	19	18
NO_2–$Cu(NO_3)_2$	Sulfolane	25	1	30	19	18
NO_2–$UO(NO_3)_2$	Sulfolane	25	1	52	19	18
NO_2–Electrolysis	—	—	—	—	11	1
	—	—	—	—	20	14
	CH_2Cl_2	−45	—	100	65	6
(E = 1.0 V)	Sulfolane	25	1	24	19	20
(E = 1.3 V)	—	—	—	—	23	23
(E = 1.7 V)	Sulfolane	25	1	50	20	20
N_2O_5–NO_3–NO_2–Air	Gas phase	25	—	26	2	24
$NaphH^{\bullet +}$ + NO_2	Gas phase	25			300 (calcd.)	2
$(NaphH)_2^{\bullet +}$ + NO_2	CH_2Cl_2	−25	—	49	43	6
$NaphH^{\bullet +}$ + NO_2	CH_2Cl_2	−25	—	119	36	6
$NaphH^{\bullet +}$ + NO_2	$MeNO_2$	—	—	—	50	25

[a] Numeral in parenthesis refers to conversion. [b] Abbreviations: py = pyridine, DTBP = 2,6-di-*tert*-butylpyridine, TFA = trifluoroacetic acid.

Results and discussion

Nitration of naphthalene

General reviews. Since A. Laurent first obtained 1-nitronaphthalene in 1835 from the reaction of naphthalene with nitric acid,[27] a great number of papers and patents dealing with the nitrations of naphthalene have appeared. Most of these nitrations involve the use of nitric acid or a mixture of nitric acid and sulfuric acid (mixed acid) as the nitrating agent. For many years 1-nitronaphthalene was considered as the sole product from the mononitration of naphthalene. Fierz-David in 1943 reported that the nitration of naphthalene produced

Table 2 *Kyodai* nitration of naphthalene[a]

c/mol dm^{-3}	t/min	T/°C	Conversion (%)	Isomer proportions (%) 1-NO_2:2-NO_2	Isomer ratio
0.002	5	-25	>99	84.7:15.3[c]	—
0.02	5	0	77	95.9:4.1	23
0.02	5	-25	78	97.9:2.1	47
0.2	5	0	19	97.4:2.6	37
0.2	60	0	>99[b]	97.6:2.4	41[d]
0.2	5	-25	20	98.2:1.8	55
0.2[e]	5	-25	18	98.6:1.4	70
1.7	5	0	5	97.2:2.8	35

[a] All reactions were carried out in dichloromethane (50 cm^3) and nitrogen dioxide (0.2 cm^3), unless otherwise indicated. The isomer composition was determined by GLC analysis; 1- and 2-nitronaphthalenes appeared in this order and their correction factors were 1.45 and 1.57, respectively. [b] Nitrogen dioxide (1.0 cm^3) was used. [c] A mixture of dinitronaphthalenes were obtained as the major product. Isomer composition determined by GLC was 1,3- (36.8%), 1,5- (13.4%) and 1,8- (37.0%). [d] Dinitronaphthalenes were obtained as additional product; 1,3- (3.7%), 1,5- (2.3%) and 1,8- (5.1%). [e] Methanesulfonic acid (1 mol%) was added.

1-nitronaphthalene (94%), 2-nitronaphthalene (4.5%), 2,4-dinitro-1-naphthol (0.4–3.6%) and small amounts of 1,5- and 1,8-dinitronaphthalenes.[28] The amount of 2-nitro isomer is known to increase as the reaction temperature is raised.[29,30] Further nitration with strong nitric acid gives as the major products 1,5- and 1,8-dinitronaphthalenes in an approximate ratio 1:2,[28,31,32] while a mixture of polynitronaphthalenes mainly composed of 1,3,5- and 1,4,5-trinitronaphthalenes and 1,3,5,7-tetranitronaphthalene was obtained under forcing conditions.[33] The reported partial rate factors for 1- and 2-positions of naphthalene are 470 and 50,[34] or 212 and 11.4.[35]

Previous methods for the nitration of naphthalene include electrolysis in dilute nitric acid;[36] heating with alkali nitrates–bisulfate[37] or nitric acid–pyridine–zinc chloride;[38] reaction with 70% nitric acid in the presence of Nafion-H and mercury(II) nitrate;[16] treatment with nitrosulfonic acid,[39] dinitrogen tri- and tetra-oxides–boron trifluoride complex,[40,41] potassium nitrate–sulfuric acid[42] and ammonium nitrate–trifluoroacetic acid anhydride;[43] reaction with nitrogen dioxide in concentrated sulfuric acid[44] and reaction with nitrosyl chloride.[45]

***Kyodai*-nitration of naphthalene.** Naphthalene reacted with extreme ease with nitrogen dioxide in the presence of ozone even at -25 °C, giving a mixture of isomeric nitronaphthalenes in nearly quantitative yield (Table 2). The results indicate that the α-selectivity is quite high, the 1-nitro/2-nitro ratios being in the range 23–70. These values are comparable to those (36–65) reported for the reaction of naphthalene cation radical salts with nitrogen dioxide,[4,5] but contrast to the values (10–20) reported for the conventional nitration based on the use of nitric acid. The high positional selectivity was kept almost unchanged throughout the mono-nitration stage, which strongly suggests that the reaction proceeds *via* a single mechanistic pathway.

At high conversion, dinitronaphthalenes were formed as additional products. Interestingly, the isomer composition of dinitronaphthalenes was quite unusual in that 1,3-dinitronaphthalene was an important component. The dinitration of naphthalene by conventional methods affords a mixture of 1,5- and 1,8-dinitronaphthalenes in an approximate ratio 1:2,[31] where the 1,3-isomer was formed only in a slight amount.

Nitration of methylnaphthalenes

1-Methylnaphthalene. 1-Methylnaphthalene was previously nitrated by nitric acid,[46] acetyl nitrate,[5] methyl nitrate–aluminum chloride,[47] *N*-nitropyridinium tetrafluoroborate[12] or nitrogen dioxide.[5] At the mono-nitration stage, 1-methyl-4-nitronaphthalene was the major product, accompanied by 2-, 5- and 8-nitro isomers as the second important products.[5,9,12] The 3-nitro isomer was also formed as the minor product. The isomeric ratios varied considerably depending on the nitrating agent employed. Further nitration with strong acid led to 1-methyl-4,5-dinitronaphthalene as the major product, the 2,4- and 4,8-dinitro isomers being the second major products. Under forcing conditions, 1-methyl-2,4,5-trinitronaphthalene was obtained as the main product.

As shown in Table 3, the *kyodai*-nitration of this hydrocarbon gave 84–93% of the 4-nitro derivatives. The high positional selectivity compared with that of the usual electrophilic nitration suggests the involvement of a radical cationic species as the intermediate for ring substitution. Addition of methanesulfonic acid facilitated the reaction appreciably. 4-Methyl-2-nitronaphth-1-ol was also formed in a trace amount.

2-Methylnaphthalene. Since 2-methyl-1-nitronaphthalene is important as the starting material for some pharmaceuticals, the nitration of 2-methylnaphthalene was examined by many workers.[5,9,12,48] However, most early works were qualitative in nature. 2-Methylnaphthalene was easily nitrated with nitric acid to form 2-methyl-1-nitronaphthalene as the major product. Important isomers included the 4-, 8- and 5-nitro derivatives, in decreasing order of amount. The 6- and 3-nitro isomers were not important.[5,9]

The *kyodai*-nitration of 2-methylnaphthalene, carried out at 0 and -25 °C under similar reaction conditions, gave a mixture of six isomeric mononitro derivatives with the respective percentage ratios 72.8:13.9:6.2:5.2:1.5:0.4 and 80.1:11.2:4.3:3.2:0.9:0.4. The major product was the 1-nitro isomer and the second major product was the 4-nitro isomer. The other four isomers were 8-, 5-, 3- and 6-nitro derivatives in decreasing order of amount. The positional selectivity at 1-position was again higher as compared with the values of conventional nitrations, except for the case where the 2-methylnaphthalene cation radical was reacted with nitrogen dioxide.[5]

1,4-Dimethylnaphthalene. The nitration of 1,4-dimethylnaphthalene is confusing in the literature. The major product reported was either 1-methyl-4-nitromethylnaphthalene,[12,49] 1,4-dimethyl-5-nitronaphthalene,[5,50] 1-methyl-4-methylene-1-nitro-1,4-dihydronaphthalene,[51] 1,4-dimethyl-1-nitro-4-nitrooxy-1,4-dihydronaphthalene[52] or 1,4-dimethyl-2-nitronaphthalene.[5,12]

The *kyodai*-nitration of 1,4-dimethylnaphthalene proceeded somewhat sluggishly and the side-chain nitration was the major reaction that took place. This tendency became especially prominent as the reaction temperature was raised and the concentration of the nitrating agent was increased (Table 4). The relative increase in side-chain nitration may in part be attributed to the direct attack by nitrogen dioxide.[5] Interestingly enough, the 2-nitro isomer was favoured over the 5-nitro isomer in the *kyodai*-nitration, while the opposite trend was observed in the conventional nitration based on the use of nitric acid. This is in accordance with an observation that the radical cation of 1,4-dimethylnaphthalene reacts with nitrogen

Table 3 Nitration of 1-methylnapthalene

Reagents	c/mol dm^{-3}	t/min	T/°C	Conversion (%)	Isomer proportions (%) 2-:3-:4-:5-:8-NO_2
NO_2–O_3 [a]	0.02	10	0	98	5.3:5.2:88.3:0.8:0.3
	0.02	10	−25	95	8.6:4.2:85.1:1.8:0.3
	0.2	60	0	> 99	12.2:0.7:85.0:1.6:0.5
	0.2	10	−25	81	8.6:0.8:84.4:6.1:0.1
	0.2	60	−25	95	3.5:2.1:92.6:1.0:0.8
	0.2 [b]	10	−25	88	7.8:1.31:85.0:5.8:0.1
	1.7	60	−25	15	4.8:2.1:85.7:7.3:0.1
HNO_3–Ac_2O [c]			0	94	29.8:2.4:49.2:6.8:11.8
HNO_3–Ac_2O [d]			0		29:2:51:8:10
NO_2, CH_2Cl_2 [e]			20		18:—:66:10:6
$ArH^{\bullet +}$ + NO_2 [e]			< −20		8:—:88:1:3

[a] All reactions were carried out in dichloromethane (50 cm^3) containing nitrogen dioxide (1.0 cm^3), unless otherwise indicated. [b] Methanesulfonic acid (1 mol%) was added. [c] This work; HNO_3 (2 equiv.)–Ac_2O, 1 h. [d] From ref. 12. [e] From ref. 5.

Table 4 Nitration of 1,4-dimethylnaphthalene

Reagents	c/mol dm^{-3}	t/min	T/°C	Conversion (%)	Product distribution (%) 2-NO_2:5-NO_2:SC [b]
NO_2–O_3 [a]	0.02	10	0	> 99	52.7:10.0:37.3
	0.02	10	−25	98	19.9:5.2:74.9
	0.2	10	0	97	18.1:0.3:81.6
	0.2	45	0	> 99	30.8:6.4:62.8
	0.2	10	−25	97	9.0:0.1:90.9
	0.2 [c]	10	−25	98	9.1: < 0.1:90.9
HNO_3–Ac_2O [d]			−10		6:18:76
$NO_2{}^+BF_4{}^-$, CH_2Cl_2 [e]			0		100:0:0
Py–$NO_2{}^+$, MeCN [e]			50		8:0:92
Py–$NO_2{}^+$, MeCN, *hν* [e]			0		8:0:29 [f]
$C(NO_2)_4$, MeCN, *hν* [g]			0		8:0:24 [h]
$C(NO_2)_4$, MeCN, collidine, *hν* [g]			0		81:0:19
HNO_3–H_2SO_4–NaN_3, AcOH [i]			20		14:82:4
NO_2, CH_2Cl_2 [i]			20		3:5:92
$ArH^{\bullet +}$ + NO_2 [i]			−20		95:5: < 0.1

[a] See footnote *a* in Table 3. [b] 1-Nitromethyl-4-methylnaphthalene. [c] Methanesulfonic acid (1 mol%) was added. [d] From ref. 5. [e] From ref. 12. [f] Adduct (71%) was reported. [g] From ref. 53. [h] Adduct (68%) was reported. [i] From ref. 4.

Table 5 Comparison of the ratios of the most abundant isomer to the sum of all other isomers formed in the nitration of naphthalene, 1-methyl- and 2-methylnaphthalenes

	Nitrating condition			
Substrate	$NO_2{}^+$ [a]	NO_2 [a]	$ArH^{\bullet +}$ + NO_2 [a]	NO_2–O_3 [b]
Naphthalene	11	25	36–65	23–70 [c]
1-Methylnaphthalene	1.3	1.9	7.3	5.4–13
2-Methylnaphthalene	1.3	1.9	5.3	2.7–4.0

[a] From ref. 4. [b] Data from Tables 2–4. [c] Some values are ignored, if dinitro products were formed.

dioxide to give the 2-nitro derivative.[5] ^1H NMR inspection of the crude product mixture ruled out the presence of any adducts which may lead to side-chain substitution products.

Mechanistic consideration

Eberson *et al.* have demonstrated that the ArH–$NO_2{}^+$ type and $ArH^{\bullet +}$–NO_2 type reactions differ significantly from each other with regard to the product distributions. For naphthalene, the high 1-nitro/2-nitro ratios of 36–65 have been found for the former type of reactions,[4] while the low values of 10–20 have been reported for the latter. The ratios of the most abundant isomer to the sum of all other isomers observed in the *kyodai*-nitration of naphthalene and two mono-methyl derivatives are compared with those calculated from the literature data (Table 5). Our values compare favourably with those from the $ArH^{\bullet +}$–NO_2 type reactions, but show significant difference from the values of the ArH–$NO_2{}^+$ type reactions. Thus we may safely consider that the *kyodai*-nitration of naphthalene proceeds *via* the electron transfer mechanism depicted in Scheme 1.

Nitrogen dioxide and ozone react rapidly to form nitrogen trioxide, which oxidizes naphthalene **1** to yield a radical cation–nitrate anion pair **4** (Scheme 1; pathway b). Physicochemical parameters obtained from AM1 calculations[54] show the energetic preference of the process $NO_3 \longrightarrow NO_3{}^-$ over the process $NO_2{}^+ \longrightarrow NO_2$ (Table 6). The vertical ionization potential as well as the bond reorganization energy[57] of the former process are considerably lower as compared with those of the latter process. The nitrate anion in the pair **4** would be rapidly removed by an adventitious acid source to give a cation radical **5**, which is trapped by nitrogen dioxide to lead to the expected nitro compound **7** *via* a common arenium ion intermediate **3**. A noticeable facilitating effect of the added protonic acid observed under certain conditions (Table 3) may in part be attributed to its role as the scavenger of the $NO_3{}^-$ moiety from the cation radical-anion pair **4**. The enhanced 1-nitro/2-nitro ratio (up to 70) observed in the presence of methanesulfonic acid at a low conversion stage may well be understood on this basis. The ion-radical pair **4** might in part

Table 6 Physicochemical parameters for the relevant nitrogen oxide species calculated by the AM1 method

Relevant redox pairs	Vertical ionization potential/eV	Bond reorganization energy/kJ mol^{-1}	Standard electrode potential/V (*vs.* NHE)
NO_3/NO_3^-	5.43	106	2.3–2.6 (H_2O)[55]
NO^+/NO	9.04 (9.25)[a]	82 (88, 293)[b]	1.55 (MeCN),[56] 1.60 ($MeNO_2$)[56]
NO_2^+/NO_2	10.24 (9.79)[a]	536 (435, 585)[b]	1.59 (MeCN)[56]

[a] Values in parentheses are taken from ref. 25. [b] Bond and total reorganization energies taken from ref. 7.

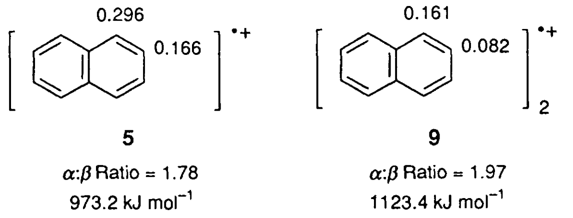


Fig. 1 Frontier electron densities for the radical reaction calculated by the PM3 method for the monomeric and dimeric cation radicals derived from naphthalene

collapse into the radical intermediate **6**, which then would lead to a dinitronaphthol **8**, a compound reported by early workers.[28]

Although the nitro-trinitromethyl adduct formation is important in the charge-transfer nitration of naphthalenes with tetranitromethane,[58–61] the nucleophilic attack of the nitrate anion onto the cation radical would be less important in our case because of the weak nucleophilic nature of nitrate anion.[62] Nitrate anion has a lower *n*(MeI) value (1.5) compared to those of trinitromethanide ion or pyridine (2.9 and 5.2, respectively).[58,63]

Gas phase nitration of naphthalene with dinitrogen pentaoxide has been known to show the low 1-nitro/2-nitro isomer ratios of 2.1–2.5.[24] Furthermore, the free radical nitration of naphthalene with dinitrogen tetraoxide in carbon tetrachloride in the dark has been reported to yield a significant amount of dinitronaphthalenes even at low conversion.[22] The absence of dinitronaphthalenes at an early stage of the *kyodai*-nitration rules out a possible intervention of the free radical mechanism.

The 1-nitro/2-nitro isomer ratios in the *kyodai*-nitration are often subject to variation depending on the substrate–reagent ratios employed. This may partly be rationalized by the known equilibrium between the monomer and dimer radical cations of naphthalene [eqn. (6)].[64] Difference in reactivity of these cation radicals toward nitrogen dioxide necessarily results in the different isomer distribution of the nitration product. The frontier electron densities for the radical reaction[65] calculated by the PM3 method[54] for the monomeric and dimeric cation radicals derived from naphthalene are shown in Fig. 1. Obviously, substitution at the 1-position is favoured for the dimeric cation radical **9**, which is in accord with the high 1-nitro/2-nitro ratios observed at an initial stage of the reaction, where the dimeric cation radical exists in high concentration. Moreover, the dimeric radical cation **9** is energetically more favoured ($\Delta G = -20$ kJ mol^{-1}) over the monomeric one **5** (see Experimental). This aspect of aromatic nitration remains to be elucidated.

$$ArH^{\cdot+} + ArH \rightleftharpoons (ArH)_2^{\cdot+} \tag{6}$$

In summary, naphthalene reacts easily with nitrogen dioxide in the presence of ozone at low temperatures to give a mixture of 1- and 2-nitronaphthalenes in almost quantitative combined yield. Formation of the further nitration products is less prominent as compared with the conventional nitration based on the use of nitric acid. The observed 1-nitro/2-nitro ratios are in the range 23–70, which is incompatible with the classical electrophilic mechanism based on the nitronium ion as electrophile, but compatible with the non-classical mechanism in which the nitrogen trioxide is involved as the initial electrophile.

Experimental

Materials

General experimental details were given in previous papers.[66] All reagents and solvents used were reagent-grade commercial products. Dichloromethane was dried by distillation from calcium hydride. Nitrogen dioxide (99% pure) was obtained in a cylinder from Sumitomo Seika Co. Ltd. and used after transfer distillation. An apparatus (Nippon Ozone Co. Ltd., type ON-1-2) was used for the generation of ozone. The machine produced ozone at a rate of 0.6 mmol min^{-1} with an oxygen flow of 10 dm^3 h^{-1} under an applied voltage of 80 V. Its efficiency was calibrated by iodometric titration. Naphthalene was recrystallized from ethanol before use. 1- And 2-methylnaphthalenes and 1,4-dimethylnaphthalene were used as obtained. All products were known and identified by ^{1}H NMR and IR spectroscopies, GC-MS or by direct comparison with the authentic samples.

Kyodai-nitration of naphthalenes: typical procedure

1-Methylnaphthalene and nitrogen dioxide were dissolved in an appropriate molar ratio in a freshly distilled dichloromethane (50 cm^3) and the solution was placed in a 50 cm^3 flask fitted with a gas inlet tube and a vent which permits waste gas to escape. The mixture was cooled to −25 °C or 0 °C externally with a cooling bath (EYELA COOL ECS-1 with two thermo controllers THS-40 and THD-50), while a stream of ozonized oxygen was introduced under vigorous stirring through the gas inlet tube, which should dip just below the surface of the liquid in the flask. Throughout the reaction, ozonized oxygen was fed continuously at a low flow rate. Under these reaction conditions, the loss of nitrogen dioxide was not so significant. The progress of the reaction and the product composition were intermittently monitored by GLC using cyclododecane as an internal standard on a Shimadzu gas chromatograph instrument GC-14A, fitted with a fused silica capillary column (J&W Scientific, DB-5-30N-STD, 30 m × 0.25 mm i.d., 5% phenyl-methylsilicone, df = 0.25 mm) and a flame ionization detector. Peak areas were determined using a Shimadzu C-R5A Chromatopac computing integrator. After the lapse of an appropriate time, the reaction was quenched with ice-cooled water and excess nitrogen dioxide was expelled by blowing argon into the solution. The reaction mixture was diluted with saturated aq. sodium hydrogen carbonate (50 cm^3) and the organic phase was separated, washed with brine (50 cm^3) followed by water (30 cm^3), and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure left a mixture of unreacted substrate and isomeric nitro-1-methylnaphthalenes as an oily residue. ^{1}H NMR inspection of this crude product mixture ruled out the presence of any addition products. The isomer compositions were estimated by GLC analysis at the injection-port temperature of 200 °C. The isomers appeared in the order 8-, 2-, 5-, 4- and 3-nitro as had been reported previously.[9,12]

Molecular orbital calculations

All semi-empirical calculations were carried out with the MOPAC[62] (version 6.10) program using the PM3 or AM1 Hamiltonian implemented on a Sony Tektronix CAChe system (version 3.5). Unrestricted Hartree-Fock wave functions were employed and the calculations were carried out by full optimization using an extra keyword PRECISE. The frontier electron densities for radical reactions were defined by Fukui *et al.* as a sum of the HOMO and SOMO coefficients.[65] The reorganization energy of the inner sphere (λ_i) for the process $NO_3 \longrightarrow NO_3^-$ was calculated as the difference between the heat of formation ($\Delta_f H$) of the assumed nitrate ion which has the same structure as nitrogen trioxide, and $\Delta_f H$ with the UHF-optimized structure of nitrate ion. Standard heat of formations of relevant species were NO_3, 152.0; NO_3^-, -371.7; NO^+, 954.7; NO, 5.0; NO_2^+ 925.2; NO_2, -62.6 kJ mol^{-1}, respectively. The standard heat of formation for a neutral naphthalene molecule was calculated by PM3 Hamiltonian to be 170.2 kJ mol^{-1}, so the energy difference of the equilibrium between the dimeric cation radical on one side and monomeric cation radical and naphthalene on the other [eqn. (6)] was estimated as $\Delta G = 1123.4 - (973.2 + 170.2) = -20.0$ kJ mol^{-1}.

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