118710-84-2; **6g**, 50305-99-2; **6h**, 118597-99-2; **6h**$\cdot SbF_5$, 118598-16-6; **6k**, 118598-01-9; **6l**, 118710-80-8; **6l**$\cdot SbF_5$, 118598-17-7; **7**, 118597-91-4; **7**$\cdot SbF_5$, 118598-12-2; **7** (ethylene ketal), 89408-41-3; **8**, 56000-23-8; **8**$\cdot SbF_5$, 118598-13-3; **9**, 118598-06-4; **9**$\cdot SbF_5$, 118598-18-8; **10**, 89408-39-9; **11**, 118598-08-6; *meso*-4,5-bis((tosyloxy)methyl)cyclohexene, 32970-96-0; *meso*-3,4-bis((tosyloxy)methyl)hexanedioic acid, 118597-88-9; dimethyl *meso*-3,4-bis((tosyloxy)methyl)hexanedioate, 118597-89-0; *cis*-3,4-bis((carbomethoxy)methyl)tetrahydrothiophene, 118597-90-3; biotin methyl ester, 608-16-2.

Supplementary Material Available: Analytical data (^1H NMR, IR, and elemental analyses, melting points, conditions of Kugelrohr distillation) of compounds **5a–f,h,l,n** and **6a–f,h,k,l** (5 pages). Ordering information is given on any current masthead page.

Oxidative Aromatic Nitration with Charge-Transfer Complexes of Arenes and Nitrosonium Salts

E. K. Kim and J. K. Kochi*

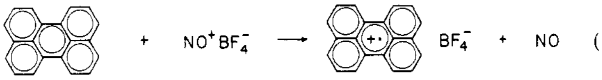
Department of Chemistry, University of Houston, University Park, Houston, Texas 77204-5641

Received October 27, 1988

Brightly colored solutions are obtained immediately upon the exposure of various arenes (ArH) to nitrosonium (NO^+) salts. The colors arise from the charge-transfer transitions of 1:1 complexes $[ArH,NO^+]$ that are reversibly formed as persistent intermediates. However the yellow-red charge-transfer (CT) colors are readily bleached by dioxygen, and the corresponding nitroarenes ($ArNO_2$) can be isolated in excellent yields from acetonitrile solutions. Such an oxidative aromatic nitration of aromatic donors proceeds via the initial autooxidation of the charge-transfer complex. The collapse of the resulting radical ion pair $[ArH^{\bullet+}, NO_2]$ to the σ-adduct, followed by the loss of proton, affords $ArNO_2$. Direct evidence for electron transfer in the initial step when anthracene is treated with $NO^+PF_6^-$ stems for the isolation of (a) the anthracene ion radical salt $[(ArH)_2{}^{\bullet+}PF_6^-]$ along with nitric oxide in dichloromethane solution and (b) the formation of 9-nitroanthracene (admixed with anthraquinone) in the more polar acetonitrile. The aromatic products (and isomer distribution) from oxidative aromatic nitration are highly reminiscent of those from electrophilic aromatic nitration. The possibility of common reactive intermediates in these two distinctive pathways for aromatic nitration is discussed.

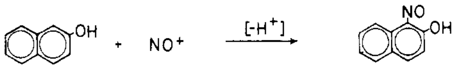
Introduction

Nitrosonium salts can serve effectively either as oxidants or as electrophiles toward different aromatic substrates. Thus the electron-rich polynuclear arenes suffer electron transfer with $NO^+BF_4^-$ to afford stable arene cation radicals, e.g.[1-3]



(1)

Other activated aromatic compounds such as phenols, anilines, and indoles undergo nuclear substitution with nitrosonium species,[4] e.g.



(2)

that are usually generated in situ from the treatment of nitrites with acid. It is less well-known, but nonetheless experimentally established,[5,6] that NO^+ forms intensely colored charge-transfer complexes with a wide variety of common arenes (ArH), i.e.

$$ArH + NO^+ \rightleftharpoons [ArH,NO^+] \tag{3}$$

For example, benzene, toluene, xylenes, and mesitylene generate yellow to orange vivid hues when added to colorless solutions of $NO^+PF_6^-$ in acetonitrile. Analogously, the more electron-rich durene, pentamethylbenzene, hexamethylbenzene, and naphthalene afford dark red solutions when exposed to NO^+. According to Mulliken,[7] such colors originate from the charge-transfer transitions ($h\nu_{CT}$) of the reversibly formed 1:1 electron donor–acceptor or EDA complexes, i.e.[8]

$$[ArH,NO^+] \xrightarrow{h\nu_{CT}} [ArH^+,NO] \tag{4}$$

These charge-transfer colors are sufficiently persistent to allow single crystals of various arene CT complexes with NO^+ to be isolated for structural elucidation by X-ray crystallography.[9] We were thus surprised to find that the brightly colored solutions were bleached when exposed to (dry) air—the rate of which showed a tendency for marked acceleration with increasing numbers of methyl substituents on the benzene donor. Such a trend in arene reactivity is diagnostic of oxidation and indeed reminiscent of the oxidative coupling and iodination of arenes with $NO^+BF_4^-$ that was recently reported by Radner.[10] In a

---

(1) Bandlish, B. K.; Shine, H. J. *J. Org. Chem.* **1977**, *42*, 561.

(2) Eberson, L.; Radner, F. *Acta Chem. Scand.* **1984**, *B38*, 861.

(3) See also Musker, W. K.; Wolford, T. L.; Roush, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 6416.

(4) (a) Marvel, C. S.; Porter, P. K. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, p 411. (b) Challis, B. C.; Lawson, A. J. *J. Chem. Soc., Perkin Trans. 2* **1973**, 918. (c) For a summary, see: March, J. *Advanced Organic Chemistry*; McGraw-Hill: New York, 1968; p 397H. Williams, D. L. H. *Nitrosation*; Cambridge University Press: London, 1988.

(5) Hunziker, E.; Penton, J. R.; Zollinger, H. *Helv. Chim. Acta* **1971**, *54*, 2043.

(6) Brownstein, S.; Gabe, E.; Lee, F.; Tan, L. *J. Chem. Soc., Chem. Commun.* **1984**, 1566.

(7) (a) Mulliken, R. S. *J. Am. Chem. Soc.* **1950**, *72*, 600. (b) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley: New York, 1969.

(8) (a) Foster, R. F. *Organic Charge-Transfer Complexes*; Academic: New York, 1969. (b) Andrews, L. J.; Keefer, R. M. *Molecular Complexes in Organic Chemistry*; Holden-Day: San Francisco, 1964.

(9) Brownstein, S.; Gabe, E.; Lee, F.; Piotrowski, A. *Can. J. Chem.* **1986**, *64*, 1661.

(10) (a) Radner, F. *J. Org. Chem.* **1988**, *53*, 702. (b) Radner, F. *J. Org. Chem.* **1988**, *53*, 3548.

0022-3263/89/1954-1692$01.50/0 © 1989 American Chemical Society

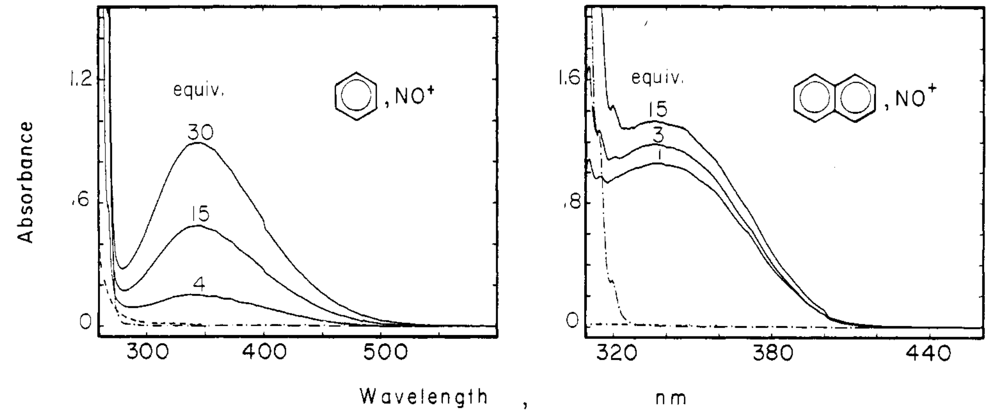


Figure 1. Charge-transfer spectra of ~10^{-3} M $NO^+BF_4^-$ with benzene (left, top to bottom 30, 15, and 4 equiv) and naphthalene (right, 15, 3, and 1 equiv) in acetonitrile at 25 °C. Arene (-•-) and $NO^+PF_6^-$ (---) alone are included for comparison.

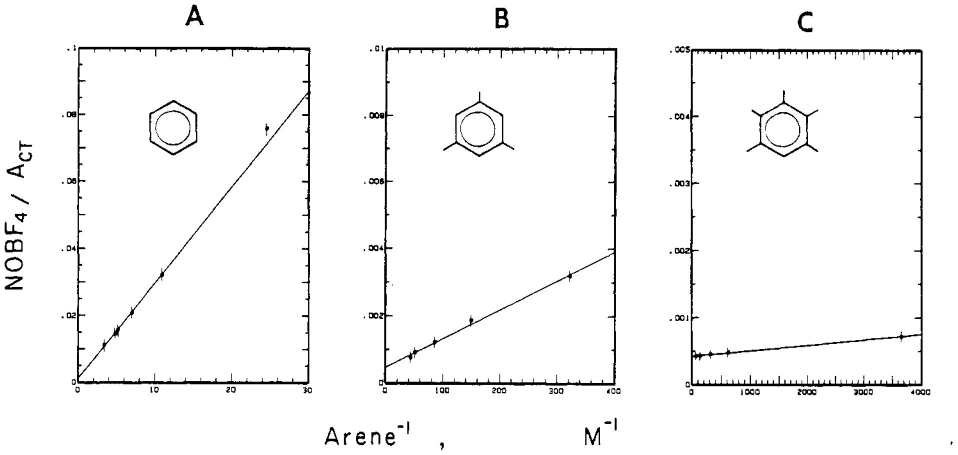


Figure 2. Formation constants of arene CT complexes with $NO^+BF_4^-$ for (A) benzene, (B) mesitylene, and (C) pentamethylbenzene in acetonitrile at 25 °C according to the Benesi–Hildebrand procedure.

Table I. Formation Constants of Arene Charge-Transfer Complexes with NO^+[a]

arene (10^3 M)[b]	IP,[c] eV	$NO^+BF_4^-$, 10^3 M	λ_{CT}, nm	K, M^{-1}	ϵ_{CT}, M^{-1} cm^{-1}
benzene (41–580)	9.23	9.8	346	0.46	780
toluene (45–75)	8.82	6.0	342	5.0	400
mesitylene (3.1–23)	8.42	0.81	345	56	2080
1,3-5-tri-*tert*-butylbenzene (3.3–19)	8.19	0.92	349	34	1730
pentamethylbenzene (2.7–15)	7.92	0.20	337	5100	2400
hexamethylbenzene (0.15–17)	7.71	0.20	337	31000	3000

[a] In acetonitrile at 25 °C. [b] Lower–upper concentration range. [c] From ref 34c and 40.

more general context, the visual observation of charge-transfer complexes also clearly relates to the ability of NO^+ to function as both the oxidant[1-3] and electrophile.[4] As such, CT complexes could also be intermediates, however transitory, in arene oxidation and electrophilic substitution.

In this report we determine the stoichiometry and identify the aromatic products of oxidative nitration that derive from the bleaching of the colored CT complexes $[ArH,NO^+]$ with dioxygen. Before doing so, let us first elaborate on the charge-transfer interactions of various benzenoid donors with the nitrosonium cation in solution.

Results

I. Formation of Arene Charge-Transfer Complexes with Nitrosonium Salts. Colorless solutions of 10^{-3} M nitrosonium tetrafluoroborate in acetonitrile immediately took on characteristic color when either benzene or naphthalene was added in millimolar amounts. The accompanying changes in the electronic absorption spectra of the solutions are shown in Figure 1 in comparison with the spectra of benzene and naphthalene alone (dashed lines). The growth of the absorption bands at $\lambda_{CT} \sim 350$ nm with increasing amounts of arene was quantitatively evaluated by the Benesi–Hildebrand relationship,

$$\frac{[NO^+BF_4^-]}{A_{CT}} = \frac{1}{\epsilon_{CT}} + \frac{1}{K\epsilon_{CT}[ArH]} \tag{5}$$

where A_{CT} and ϵ_{CT} are the absorbance and extinction coefficient, respectively, at the spectral maxima.[11] Typical Benesi–Hildebrand plots for the formation of the charge-transfer complexes under conditions in which the arene concentration [ArH] in acetonitrile was in excess of $[NO^+BF_4^-]$ are illustrated in Figure 2. The linear fit of the absorbance data was obtained by the method of least squares, typically with correlation coefficients $r > 0.99$. The resulting values of the formation constant K for complex formation, i.e.

$$ArH + NO^+BF_4^- \overset{K}{\rightleftharpoons} [ArH,NO^+BF_4^-] \tag{6}$$

and the extinction coefficient ϵ_{CT} obtained from the slope

---

(11) (a) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703. (b) Person, W. B. *J. Am. Chem. Soc.* **1965**, *87*, 167.

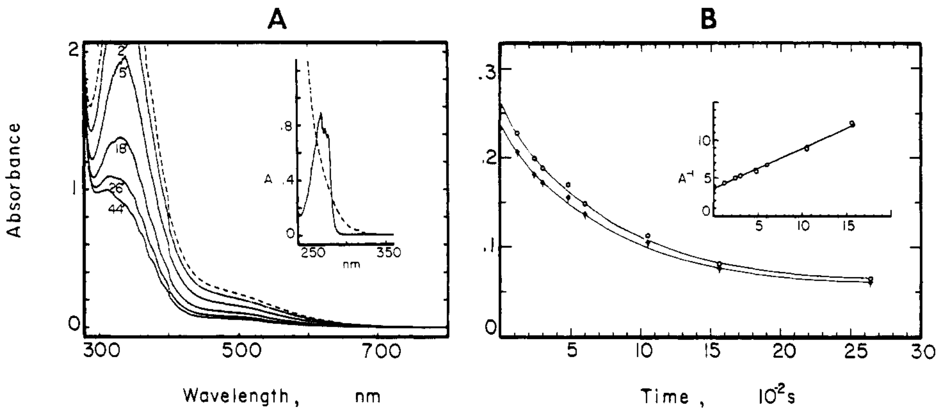


Figure 3. (A) Progressive bleaching of the charge-transfer absorption band of the $[C_6(CH_3)_5H,NO^+]$ complex in acetonitrile at 25 °C under an atmosphere of dioxygen. [The inset shows the uncomplexed arene donor (—) and $NO^+BF_4^-$ (- - -) at the same concentration of 3 and 1 mM, respectively.] (B) Absorbance decay at $\lambda = 486$ (○) and 504 (◆) nm with the second-order plot in the inset.

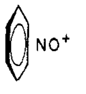
Table II. Oxidative Aromatic Nitration with NO^+ Charge-Transfer Complexes[a]

arene (10 mmol)	$NO^+BF_4^-$ (10 mmol)	solvent,[b] mL	time, h	$ArNO_2$,[c] 10 mmol	mat. bal,[d] %
toluene (0.85)	(1.9)	NM (4)	21	2-, 3-, 4-nitro (0.53/0.03/0.1)[e]	98
p-xylene (4.7)	(5.7)	AN (20)	75	2-nitro (3.2)	75
mesitylene (12.2)	(10.2)	AN (15)	48	2-nitro (1.3)	67
durene (3.2)	(4.2)	AN (20)	7	3-nitro (3.2)[e]	100
durene (4.1)	(4.8)	NM (20)	6	3-nitro (3.7)[e]	92
pentamethylbenzene (4.7)	(3.6)	AN (25)	4	1-nitro (3.6)[e]	100[f]
1,4-dimethylnaphthalene (2.8)	(4.3)	AN (20)	3.5	2-nitro (1.9)	68
4-methoxytoluene (7.5)	(7.9)	AN (30)	8	3-nitro (7.0)[e]	93

[a] Under 1 atom of O_2 at 3 °C in the dark. [b] NM = nitromethane, AN = acetonitrile. [c] Isolated yield, unless indicated otherwise. [d] Based on recovered arene. [e] GC analysis. [f] Based on $NO^+BF_4^-$.

and intercept, respectively, at the monitoring wavelength are listed in Table I for some representative arenes with $NO^+BF_4^-$. Since the values of K and ϵ_{CT} at 25 °C were found to be invariant with the anion (e.g., PF_6^- and BF_4^-), it will be omitted in the subsequent presentation.

Although $NO^+PF_6^-$ was insoluble in dichloromethane, it dissolved readily when an arene donor was present. These highly colored solutions (Table I) upon standing at -20 °C, deposited crystals of the CT complexes. In this manner, the 1:1 arene complexes $[ArH,NO^+PF_6^-]$ were isolated with ArH = mesitylene, durene, pentamethylbenzene, and hexamethylbenzene (see Experimental Section). We judged from the similarity of these crystalline complexes with those previously isolated by Brownstein and co-workers from liquid sulfur dioxide,[9] that the relevant charge-transfer interaction derives from the centrosymmetric structure of the electron donor–acceptor pair, i.e.



Such CT structures were stable in acetonitrile solutions since the vivid colors of the complexes from all the alkylbenzenes and naphthalenes listed in Table I persisted for prolonged periods when the solutions were protected from light and air. Likewise the ^1H NMR and IR spectra[5,12] of these solutions remained unchanged for days under these conditions. However the CT complexes were less persistent in dichloromethane solutions—the apparent degree of stability being dependent on the ionization potential of the arene. For example, the NO^+ complexes of benzene, toluene, and xylene showed no apparent change for weeks at room temperature. In contrast, solutions of the corresponding complexes of durene, pentamethylbenzene, and hexamethylbenzene in dichloromethane began to redden perceptibly after several days. The concomitant growth of new absorption bands centered at $\lambda \sim 550$ nm was reminiscent of the formation of binuclear cations.[13] The CT absorption bands of the naphthalene complexes with $NO^+PF_6^-$ were noticeably diminished after a day, and the red-brown dichloromethane solutions turned progressively greener. Finally when anthracene dissolved in dichloromethane was added to $NO^+PF_6^-$ at room temperature, the green solution evolved a gas and deposited shiny black crystals. The IR spectrum of the gas showed a sharp band at 1875 cm^{-1} and a pair of broad bands centered at 1845 and 1906 cm^{-1} characteristic of the P, Q, and R branches of nitric oxide.[14,15] The identity of the latter was further confirmed by its rapid conversion to nitrogen dioxide by the introduction of dioxygen, i.e.[16,17]

$$2NO + O_2 \rightarrow 2NO_2 \qquad (7)$$

The paramagnetic black crystals [ESR, $g = 2.0023$] were analyzed iodometrically and identified as the salt of anthracene π-dimer cation $[(C_{14}H_{10})_2^{\bullet+}, PF_6^-]$,[18,19] as pres-

---

[12] Brownstein, S.; Morrison, A.; Tan, L. K. *Can. J. Chem.* **1986**, *64*, 265.

[13] See (a) Sankararaman, S.; Haney, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5235. (b) Lau, W.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7100.

[14] Fately, W. G.; Bent, H. A.; Crawford, B., Jr. *J. Chem. Phys.* **1959**, *31*, 204.

[15] Picard, R. H.; Winick, J. R.; Sharma, R. D.; Zachor, A. S.; Espy, P. J.; Harris, C. R. *Adv. Space Res.* **1987**, *7(10)*, 23.

[16] Smith, J. H. *J. Am. Chem. Soc.* **1943**, *65*, 74.

[17] The autoxidation probably proceeds stepwise via $NO_3^{\bullet}$.

[18] (a) Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1969**, *65*, 2558. (b) Shida, T.; Iwata, S. *J. Am. Chem. Soc.* **1973**, *95*, 3473. (c) Masnovi, J. M.; Kochi, J. K. *J. Phys. Chem.* **1987**, *91*, 1878 and refs. therein.

[19] For the isolation of related arene π-dimer salts, see: (a) Fritz, H. P.; Gebauer, H.; Friedrich, P.; Ecker, P.; Artes, R.; Schubert, U. *Z. Naturforsch.* **1978**, *33b*, 498. (b) Keller, H. J.; Nöthe, D.; Pritzkow, H.; Wehe, D.; Werner, M.; Koch, P.; Schweizer, D. *Mol. Cryst. Liq.* **1980**, *62*, 181. (c) Fritz, H. P.; Gebauer, H. *Z. Naturforsch.* **1978**, *33b*, 702.

Table III. Oxidative Aromatic Nitration in Dichloromethane[a]

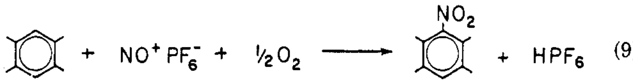
arene (10 mmol)	$NO^+PF_6^-$ (10 mmol)	solv, mL	time, h	$ArNO_2$[b] (10 mmol)	byprod[c] (10 mmol)	mat. bal[d]
durene (1.1)	0.8	9	4.5	3-nitro (0.38)	B (0.16)[e]	83
pentamethylbenzene (7.0)	7.7	28	24	1-nitro (6.3)	–	90[f]
naphthalene (8.2)	3.0	25	39	1-nitro (1.9) 2-nitro (0.11)	–	90
anthracene (7.3)	7.1	20	4	9-nitro (4.6)	AQ (0.6)[g]	76

[a] Under 1 atom of O_2 at 3 °C in the dark. [b] Isolated yield, unless indicated otherwise. [c] Byproduct isolated. [d] Based (%) on $NO^+PF_6^-$ unless indicated otherwise. [e] B = 2,4,5-trimethylbenzaldehyde, ND = nitro dimer (vide supra). [f] GC analysis based on arene. [g] AQ = 9,10-anthraquinone.

ented in the Experimental Section. Accordingly, the oxidation of anthracene could be described by the one-electron process,[20]

$$2C_{14}H_{10} + NO^+PF_6^- \rightarrow (C_{14}H_{10})_2^{\bullet +}PF_6^- + NO \quad (8)$$

II. Autoxidation of Arene Charge-Transfer Complexes with NO^+. The colored solutions of the arene–NO^+ complexes in acetonitrile were bleached when dry air was admitted. In order to examine this phenomenon more carefully, all the subsequent thermal studies were carried out in an ice bath (3 °C) under 1 atm of pure dioxygen in the dark. Under these conditions, the color change was directly related to the disappearance of the charge-transfer band, as illustrated in Figure 3 for a typical CT complex such as $[C_6(CH_3)_5H,NO^+BF_4^-]$. Such a bleaching of the charge-transfer band was generally accompanied by the uptake of 0.5 equiv of dioxygen. Qualitatively the rate of bleaching paralleled the variations in the ionization potential of the arenes as qualitatively indicated in Table II (column 5).[21] Workup of the reaction mixture revealed the formation of predominant amounts of aromatic nitration products, such as the quantitative conversion of durene to 3-nitrodurene according to the stoichiometry



(9)

Similar results were obtained when nitromethane was used as the solvent. Furthermore, toluene was converted in high yields to a mixture of *o*- and *p*-nitrotoluene when the autoxidation was carried out in nitromethane. As such, the conversion of nitrosonium ion to the nitrated products in Table II will be hereafter referred to as *oxidative aromatic nitration*.

III. Oxidative Aromatic Nitration in Dichloromethane. The color change accompanying the exposure of arene–NO^+ complexes to dioxygen in a dichloromethane solution was more complex than that in the more polar acetonitrile—the reddish solutions of durene and pentamethylbenzene finally turning brown and then purple. Moreover, the dichloromethane solutions of naphthalene and anthracene with $NO^+PF_6^-$ were green during and after reaction with dioxygen in this medium. Figure 4 typically illustrates the rapid rates at which dichloromethane solutions containing 10^{-2} M $NO^+PF_6^-$ and mesitylene consumed 0.5 equiv of dioxygen. By comparison, the CT solution of the less effective donor *p*-xylene in acetonitrile took up less dioxygen, and the consumption occurred at slower rates.

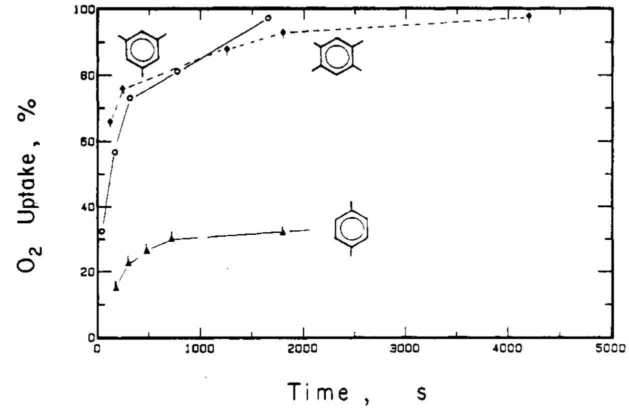
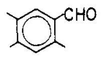
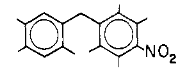


Figure 4. Consumption of dioxygen by the NO^+ charge-transfer complexes of durene in $MeNO_2$ (◆), mesitylene in CH_2Cl_2 (○), and *p*-xylene in MeCN (▲) at 3 °C, based on the 2:1 stoichiometry in eq 9.

Analysis of these solutions after autoxidation also revealed a more complex mixture of products. Although oxidative aromatic nitration was still the predominant reaction (as shown in Table III, column 5), significant amounts of byproducts such as aldehyde, alcohol, nitro dimer, and quinone were detected, as described in the Experimental Section. Inspection of the results in Table III shows that the principal difference between oxidative aromatic nitrations carried out in acetonitrile with dielectric constant $\epsilon = 37.5$[22] and in the less polar dichloromethane ($\epsilon = 9.1$) was the significantly increased appearance of aromatic products derived from side-chain attack, such as the partial conversion of durene to[23]



and


Since these byproducts clearly arose by loss of hydrogen on a methyl substituent, we examined the effect of added base on the course of oxidative aromatic nitration.

IV. Oxidative Aromatic Nitration with Added Base. Although pyridine is an organic base with many desirable properties, it is also an effective nucleophile capable of neutralizing the nitrosonium ion.[24] Accordingly, we chose the sterically most hindered pyridine base 2,6-di-*tert*-butyl-4-methylpyridine or DBMP[25] for the study of oxidative nitration. In order to minimize the competition from neutralization, the oxidative nitration was carried out at 3 °C in dichloromethane as the medium in which the suspension of the insoluble $NO^+PF_6^-$ was essentially unaffected by the presence of DBMP. This system was then charged with 1 atm of dioxygen, and the

---

[20] (a) Arene π-dimer cations are best considered as charge-transfer complexes of arene cation radical as the acceptor and the neutral arene as the donor. [Sankararaman, S.; Takahashi, Y.; Kochi, J. K. *J. Am. Chem. Soc.*, in press.] (b) Thus the overall oxidation in eq 8 represents a stepwise process involving the prior electron-transfer step to afford $AnH^{\bullet +}$, followed by the formation of the CT complex.

[21] The reaction times were used only as highly qualitative measured of reactivity (compare Figure 4).

[22] Dean, J. A. *Lange's Handbook of Chemistry*, 3rd ed.; McGraw-Hill: New York, 1985.

[23] For the identification of these byproducts, see the Experimental Section.

[24] Olah, G. A.; Olah, J. A.; Overchuk, N. A. *J. Org. Chem.* **1965**, *30*, 3373.

[25] Cf. Benoit, R. L.; Frêchette, M.; Lefebvre, D. *Can. J. Chem.* **1988**, *66*, 1159.

Table IV. Oxidative Aromatic Nitration in the Presence of DBMP[a]

arene (10 mmol)	$NO^+PF_6^-$ (10 mmol)	DBMP[b] (10 mmol)	solv, mL	time, h	$ArNO_2$[c] (10^2 mmol)	$Ar'CH_2NO_2$[d] (10^2 mmol)	BH^+[e] (10^2 mmol)
durene (2.6)	3.1	3.2	10	12	3-nitro (5.5)	A (8.7)	31
durene (5.1)	4.1	7.2	23	3	3-nitro (7.4)	A (14)[f]	36
pentamethylbenzene (2.7)	3.3	3.6	15	3.5	1-nitro (6.7)	B (14)[g]	11
pentamethylbenzene (21.4)	20.9	21.9	90	3	1-nitro (10)	B (103)[h]	190
hexamethylbenzene (4.4)	4.6	3.6	30	2	-	C (27)[i]	
1,4-dimethylnaphthalene (10.2)	7.4	6.2	20	12	2-nitro (11)	D (20)[j]	61

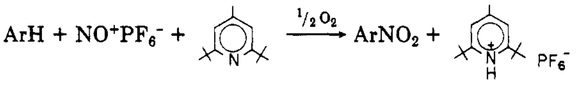
[a] Under 1 atom of O_2 in CH_2Cl_2 at 3 °C in the dark. [b] 2,6-Di-*tert*-butyl-4-methylpyridine. [c] Isolated yield, unless indicated otherwise. [d] A = α-nitrodurene, B = 1-nitromethyl-2,3,4,5-tetramethylbenzene, C = α-nitrohexamethylbenzene, D = α-nitro-1,4-dimethylnaphthalene. [e] 2,6-Di-*tert*-butyl-4-methylpyridinium hexafluorophosphate isolated. [f] Plus nitro dimer (~0.01 mmol). [g] Recovered arene (0.05 mmol). [h] Recovered arene (1.00 mmol). [i] Pentamethylbenzaldehyde (0.028 mmol), pentamethylbenzyl alcohol (~0.005 mmol), recovered arene (0.27 mmol). [j] Diaryl (~0.1 mmol), recovered arene (0.35 mmol).

Table V. Photoinduced Oxidative Aromatic Nitration with NO^+ Charge-Transfer Complexes[a]

arene (10 mmol)	$NO^+PF_6^-$ (10 mmol)	temp, °C	time, h	$ArNO_2$ (10^2 mmol)	ArH[b] (10 mmol)	conv,[c] %
toluene (6.8)	2.7	0	3	2-, 4-NO_2 (2.6/1.1)	6.2	14
		15	40	2-, 4-NO_2 (3.8/2.5)	5.4	23
toluene (8.2)	3.7	0	3[d]	2-NO_2 (1.1)	8.0	3.2
		15	40[d]	2-, 4-NO_2 (3.8/1.9)	6.9	15
durene (8.3)	1.7	−20	3[e]	3-NO_2 (11)[f]	5.2	65
durene (0.9)	0.19	−20	48[d]	3-NO_2 (0.12)	0.75	6.5

[a] Under 1 atom of O_2 in nitromethane with constant irradiation at $\lambda > 415$ nm, unless indicated otherwise. [b] Recovered arene. [c] Conversion of arene based on $NO^+PF_6^-$ charged. [d] In the dark. [e] Irradiation at $\lambda > 480$ nm. [f] Nitro dimer (~0.01 mmol) trimethylbenzaldehyde (~0.01 mmol), diaryl (0.04 mmol).

arene was the last component to be added to the three-phase mixture. Under these conditions, the decoloration of the reddish CT color was accompanied by the precipitation of the pyridinium salt in quantitative yields according to the stoichiometry

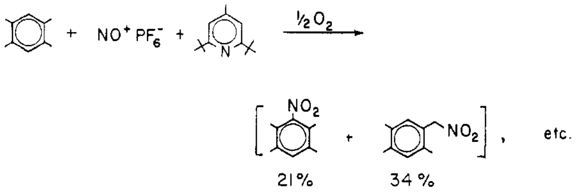


(10)

It is noteworthy that the addition of DBMP directly to the solution of the preformed charge-transfer complex in dichloromethane led to only poor conversions of durene according to eq 10. The latter can be attributed to competitive deactivation of the solubilized nitrosonium ion (as the CT complex) by the hindered base.[24]

The rate of oxidative nitration also occurred more slowly in the presence of the pyridine base. Thus Figure 5 shows that the consumption of 0.5 equiv of dioxygen by even one of the most electron-rich arenes (pentamethylbenzene) required several hours (compare Figure 4). Such a retardation could have arisen from the partial neutralization of the nitrosonium ion (vide supra) by the hindered base DBMP. If so, the process was probably reversible owing to the ultimate consumption of dioxygen in stoichiometric amounts.

Analysis of the reaction mixture from the methyl-substituted arenes revealed that two types of nitrated aromatic products were produced. On one hand, the yields of the nitroarenes described in Tables II and III were markedly diminished, but in their place significant amounts of side-chain (benzylic) nitro compounds were produced, e.g.



(11)

The analogous bifurcation of the pathway leading to oxidative nitration by the hindered base is described for the related methylarenes in Table IV. Otherwise the reaction mixtures were rather bereft of other products, producing only small amounts of the nitro dimer (<3%) from durene (vide supra) and the benzaldehyde (8%) from hexamethylbenzene.

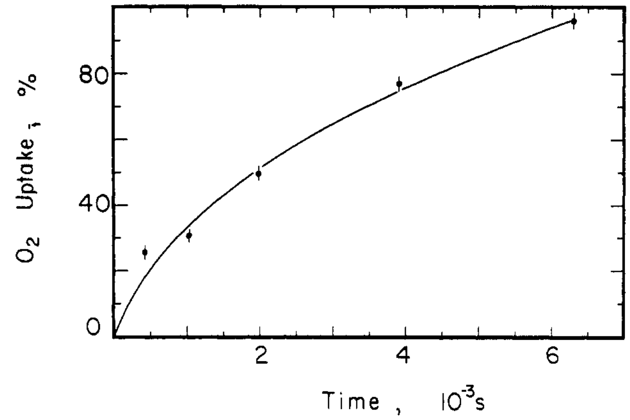


Figure 5. Effect of the hindered base DBMP (1 equiv) on the uptake of dioxygen by the pentamethylbenzene CT complex with $NO^+PF_6^-$ at 3 °C in dichloromethane solution.

V. Photoinduced Oxidative Aromatic Nitration with NO^+ Charge-Transfer Complexes. Oxidative aromatic nitration of the selected arenes, toluene and durene, was examined by the deliberate excitation of the charge-transfer absorption band with actinic radiation of $\lambda > 415$ nm from a Hg–Xe lamp. The use of a sharp cutoff filter ensured that only the CT band was irradiated (see Figure 1), and there was thus no ambiguity about the adventitious local excitation of complexed (or uncomplexed) chromophores.[8] Furthermore, in order to minimize competition from the thermal process (vide supra), the photoinduced oxidative nitration was carried out at either 0 or −20 °C. Indeed the comparative results presented in Table V show that both toluene and durene were oxidatively nitrated under these conditions. Although the quantum yields for nitration were not measured, we qualitatively judged from the prolonged photolysis times required to achieve even low conversions that $\Phi < 10^{-1}$. Inspection of the aromatic products such as the o/p ratio of nitrotoluene and the durene byproducts (aldehyde, nitro dimer, etc.), that essentially the same products were de-

Table VI. Comparative Nitration of Durene and Pentamethylbenzene

nitration procedure[a]	arene	product distribution, %: nuclear	side chain	byprod	ref[b]
HNO_3, Ac_2O, 0 °C	PMB	55	37	8[i]	*c*
HNO_3, Ac_2O, 0 °C	DUR	52	12	42[j]	*c*
HNO_3/H_2SO_4, NM, RT	PMB	69	–	31[k]	*d*
HNO_3/H_2SO_4, NM, RT	DUR	76	–	24[k]	*e*
$NO_2PF_6 \cdot 2H_2O$, NM, RT	DUR	69	22	24[m]	*e*
NO_2PF_6, NM, RT	DUR	6.7	15	42[n]	*e*
HNO_3, $Ac_2O/CH_2Cl_2/HOAc$, –55 °C	DUR	(67)	(33)		*f*
HNO_3, H_2SO_4, 25 °C	DUR	37	–	8[p]	*g*
HNO_3/AN, Ac_2O, RT	DUR	65	35[q]	*q*	*h*
$NOBF_4/O_2$, AN, 3 °C	PMB	100	0		this work
$NOBF_4/O_2$, AN, 3 °C	DUR	100	0		this work
$NOPF_6/O_2$/DBMP, MC, 3 °C	PMB	10	90		this work
$NOPF_6/O_2$/DBMP, MC, 3 °C	DUR	31	60		this work

[a] Nitrating agent, solvent (MN = nitromethane, AN = acetonitrile, MC = dichloromethane), temperature (RT = room temperature) for durene (DUR) and pentamethylbenzene (PMB). [b] As given in ref 26 for footnotes *c–h*. [i] 2,3,4,5-Tetramethylbenzaldehyde. [j] ArOAc (33%), 2,4,5-trimethylbenzaldehyde (3%), alcohol (6%). [k] Undescribed. [m] 2,4,5-Trimethylbenzaldehyde and 2,3,5,6,2′,4′,5′-heptamethyldiphenylmethane (22%), dinitration (2%). [n] Dinitration. [p] Dinitration isolated. [q] Includes aldehyde and dimer.

rived by the photoinduced (CT) promotion of oxidative aromatic nitration as those produced thermally in Table II.

Discussion

Oxidative nitration as effected by the autoxidation of the charge-transfer complexes of nitrosonium salts successfully complements the long list of available methods for arene nitration employing various types of nitrating agents.[26] The unique character of the oxidative aromatic nitration in this study is sharply focused on the electron-rich methylarenes in which a variety of side reactions are known to readily compete—such as side-chain nitration and substitution, oxidation to benzaldehydes and quinones, nitrative coupling, multiple nitration, etc.[27]

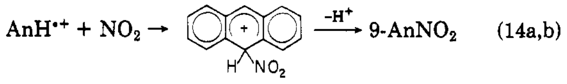
I. Comparative Procedures for the Nitration of Methylbenzenes. Table VI presents a short summary of how the competition among nuclear, side-chain and multiple nitration is affected in some representative nitration procedures for a pair of particularly susceptible methylarenes, viz., durene and pentamethylbenzene.[28] Indeed the comparative results in Table V show that oxidative aromatic nitration with NO^+ is the only method in which (a) nuclear nitration proceeds in high yields and (b) without contamination by multiple substitution, and (c) the ratio of nuclear/side-chain nitration can be deliberately manipulated. Such an unusual selectivity and flexibility doubtlessly derives from the unique pathway by which nitration occurs, involving as it does the overall 2-electron oxidation of the (NO^+) reagent.

II. Mechanism of the Oxidative Nitration of Anthracene. Since the nitrosonium ion is completely inert to dioxygen under the reaction conditions, the formal transformation of the nitrogen(III) reagent NO^+ to nitrogen(V) product $ArNO_2$ must occur via a reactive intermediate. Furthermore a nitrosoarene (such as that potentially formed according to eq 2) is not a relevant intermediate since it cannot be converted to $ArNO_2$ under these conditions. Indeed the ready oxidation of anthracene by NO^+ as described in eq 8 provides the means to produce nitric oxide, which is known to be highly susceptible to autoxidation (eq 7).[16] The subsequent coupling of the anthracene cation radical with NO_2 will lead to the nitration of anthracene (AnH, Table III), as outlined in Scheme I.[29]

Scheme I

$$AnH + NO^+ \rightarrow AnH^{\bullet +} + NO \qquad (12)$$

$$NO + {}^1/{}_2O_2 \rightarrow NO_2 \qquad (13)$$



(14a,b)

The key steps in Scheme I (eq 12 and 13) are independently documented as eq 8 and 7, respectively, eq 12 being carried out under the same reaction conditions without dioxygen. Furthermore we have previously established the rapid interception of such arene cation radicals by NO_2 to afford the Wheland intermediate (eq 14a) that leads to aromatic nitration by proton loss (eq 14b) without a deuterium kinetic isotope effect.[29,30] The key role played by anthracene cation radical in Scheme I is also supported by its autoxidation to anthraquinone, which can be detected in small but significant amounts in the course of oxidative nitration (Table III).

III. Selectivity and Side-Chain Substitution during Oxidative Aromatic Nitration. The identification of arene cation radicals and nitric oxide as the seminal intermediates in Scheme I provides a ready explanation for two important facets of oxidative aromatic nitration, namely, the selectivity and the variable side-chain attack.[30,31] Thus the high selectivity derives in Scheme I from the specific homolytic coupling of the reactive arene cation radical with the paramagnetic nitrogen dioxide (see eq 14a).[13,28] Moreover, multiple nitration is strongly disfavored by the presence of an electronegative nitro sub-

---

(26) (a) For a recent general review, see: Schofield, K. *Aromatic Nitration*; Cambridge University Press: Cambridge, 1980. (b) *Industrial and Laboratory Nitrations*; Albright, L. F., Hanson, C., Eds.; Am. Chem. Soc. Sym. Ser. **1976**, 22, Washington, DC. (c) Blackstock, D. J.; Fischer, A.; Richards, K. E.; Wright, G. J. *Aust. J. Chem.* **1973**, *26*, 775. (d) Hunziker, E.; Myhre, P. C.; Penton, J. R.; Zollinger, H. *Helv. Chim. Acta* **1975**, *58*, 230. (e) Hanna, S. B.; Hunziker, E.; Saito, T.; Zollinger, H. *Helv. Chim. Acta.* **1969**, *52*, 1537. Compare also: Bloom, A. J.; Fleischmann, M.; Mellor, J. M. *Electrochim. Acta* **1987**, *32*(5), 785 for the electrosynthesis of NO_2BF_4 from N_2O_4. (f) Fischer, A.; Leonard, D. R. *Can. J. Chem.* **1976**, *54*, 1795. (Relative yields reported in parentheses.) (g) Manglik, A. K.; Moodie, R. B.; Schofield, K.; Dedeoglu, E.; Dutly, A.; Rys, P. *J. Chem. Soc., Perkin Trans. 2* **1981**, *10*, 1358. (h) Wright, O. L.; Cleary, J. J.; Dickason, W. C. *Proc. La. Acad. Sci.* **1968**, *31*, 126.

(27) Suzuki, H. *Synthesis* **1977**, 217.

(28) Fischer, A.; Wright, G. J. *Austr. J. Chem.* **1974**, *27*, 217.

(29) (a) Sankararaman, S.; Haney, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7824. See also ref. 12 (b) Note that the homolytic coupling of $AnH^{\bullet +}$ and NO_2 in eq 14a is likely to proceed by second-order kinetics in a manner similar to the behavior of the *p*-methoxyanisole cation radicals owing to their similar thermodynamic stabilities (i.e., $E_{ox}{}^0$ of AnH and $C_6H_6(OMe)_2$ are 1.49 and 1.50 V, respectively). See also ref 17.

(30) Masnovi, J. M.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.*, in press.

(31) Hartshorn, S. R. *Chem. Soc. Rev.* **1974**, *3*, 167. See also Suzuki in ref 27.

stituent to discourage further oxidation of the first-formed $ArNO_2$ to its cation radical. According to Scheme I, side-chain nitration results from the interception of the methylarene cation radical by the added base (Scheme II)

Scheme II

$$ArCH_3^{\bullet+} + B \xrightarrow{k_H} ArCH_2^{\bullet} + BH^+ \quad (15)$$

$$ArCH_2^{\bullet} + NO_2 \rightarrow ArCH_2NO_2 \quad (16)$$

where B is 2,6-di-*tert*-butyl-4-methylpyridine in this study. The kinetics of such a proton transfer from methylarene cation radicals by pyridine bases (eq 15) has been examined earlier.[32] Indeed the kinetic isotope effect of $k_H/k_D \sim 3^{30}$ for this process is wholly consistent with the absence of side-chain substitution during oxidative aromatic substitution without added base (Table II). By the same token, we anticipate that the relative amounts of side-chain/nuclear nitration in Table IV can be continuously tuned by the judicious adjustment of the pyridine (DBMP) concentration.

IV. Some Solvent Effects in Oxidative Aromatic Nitration. Proton transfer as described in eq 15 is also favored in nonpolar solvents such as dichloromethane.[30] Such ionic processes can contribute to byproduct formation, which become increasingly more important in dichloromethane (Table III) relative to that observed in the more polar acetonitrile (Table II).[33] Thus independent studies[30] have shown the competition for homolytic coupling in eq 14a relative to proton transfer in eq 15 to be favored in acetonitrile. Accordingly, we anticipate polar aprotic solvents to provide an optimum medium for nuclear nitration by the autoxidation of NO^+ charge-transfer complexes.

V. Mechanism for the Oxidative Nitration of Nonactivated Arenes. As appealing as the formulation in Scheme I may be for oxidative aromatic nitration, it leaves open the question as to why the rather unactivated arenes such as toluene and xylene readily participate in oxidative aromatic nitration (Table II). Thus such arenes in contact with $NO^+PF_6^-$ show no evidence of undergoing electron transfer, certainly within the time span shown by anthracene in eq 8.[35] It is possible, however, for electron transfer to occur without apparently affecting the persistence of the charge-transfer absorption bands in Table I, if it were *highly* reversible. In such an event, the limited redox equilibrium (k_1/k_{-1}) would be pulled by the facile and irreversible autoxidation (k_2) of nitric oxide[36] (Scheme III).

Scheme III

$$ArH + NO^+ \overset{K}{\rightleftharpoons} [ArH,NO^+] \quad (17)$$

$$[ArH,NO^+] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [ArH^{\bullet+},NO] \quad (18)$$

$$[ArH^{\bullet+},NO] + 1/2O_2 \xrightarrow{\text{fast}} ArH^{\bullet+} + NO_2\text{, etc.} \quad (19)$$

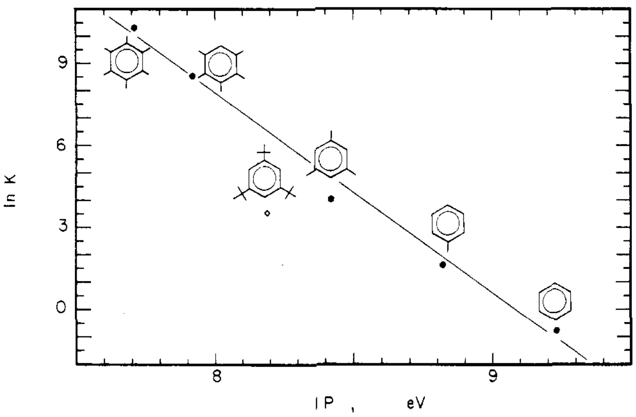


Figure 6. Marked variation of the formation constants of $[ArH,NO^+]$ complexes in acetonitrile solution with the ionization potentials of the arene donor.

The magnitude of such a redox equilibrium is expected to be highly dependent on the arene oxidation potential E_{ox}^0,[37] which mediates the electron-transfer rate constant k_1 as well as that (k_{-1}) for back-electron transfer.[38] On this basis, it is possible to account of the oxidation of anthracene ($E_{ox}^0 = 1.49$ V)[39] in eq 8, under conditions in which neither toluene nor xylene ($E_{ox}^0 = 2.25$ and 2.16 V)[40] shows any signs of oxidation. Nonetheless this formulation requires that in the absence of dioxygen, the corresponding cation radicals do not spontaneously leak from the solvent cage in eq 18, either by diffusive separation or by a fast irreversible reaction.

VI. Direct Activation of the Arene CT Complexes with NO^+. Contrariwise, the oxidation potential of toluene ($E_{ox}^0 = 2.25$ V) may be too prohibitive for electron transfer to occur in eq 18,[41] however limited its extent. If so, the autoxidation of the arene charge-transfer complex itself (Scheme IV, eq 21) will provide a more direct pathway for oxidative aromatic nitration. We are unaware of any precedent for electron transfer to occur directly from charge-transfer complexes.[42] However, the characteristics of the series of $[ArH,NO^+]$ complexes as a general class are somewhat unusual. First, the charge-transfer spectra always consist of a pair of absorption bands—the position of the more intense, higher energy band being rather invariant at $\lambda_{CT_1} = 350 \pm 10$ nm ($\epsilon \cong 10^2$–10^3 M^{-1} cm^{-1}) with the arene donor, whereas the weaker, low-energy band varies with the arene donor more in the expected manner [e.g., $\lambda_{CT_2} = \sim 450$ ($\epsilon = 60$ M^{-1} cm^{-1}) and ~ 480 nm ($\epsilon =$

Scheme IV

$$ArH + NO^+ \rightleftharpoons [ArH,NO^+] \quad (20)$$

$$[ArH,NO^+] + \tfrac{1}{2}O_2 \rightarrow ArH^{\bullet+} + NO_2\text{, etc.} \quad (21)$$

---

[32] Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7472.

[33] The increase of byproducts in dichloromethane is parallel to the increased rate of proton transfer to yield benzylic radicals which are readily oxidized and capable of arene addition to afford dimers, benzaldehydes, etc.[30,34] For solvent effects on the competition between ionic (proton transfer) and radical (coupling) processes in the reactions of arene cation radicals, see Sankararaman, et al. in ref 29.

[34] See (a) Rollick, K. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 1319. (b) Rollick, K. L.; Kochi, J. K. *J. Org. Chem.* **1982**, *47*, 435. (c) See also ref 13b.

[35] For NO^+, the values of E_{red}^0 are 1.48, 1.33, and 1.28 V vs SCE in dichloromethane, nitromethane, and acetonitrile, respectively (Lee, K. Y., unpublished results). Thus the oxidation of anthracene is roughly isoergonic. See also Radner in ref 10.

[36] The mechanism of the autoxidation of nitric oxide in eq 19 is thoroughly reviewed by Heicklen, J.; Cohen, N. *Adv. Photochem.* **1968**, *5*, 203. The dioxygen is indicated as $1/2O_2$ for the stoichiometry only, and is not intended to convey any mechanistic connotations.

[37] For the one-electron process E_{ox}^0 is for the process: $ArH \rightleftharpoons ArH^{\bullet+} + e$.

[38] For the related oxidation with NO_2^+, see: Eberson, L.; Radner, F. *Acc. Chem. Res.* **1987**, *20*, 53.

[39] Masnovi, J. M.; Seddon, E. A.; Kochi, J. K. *Can. J. Chem.* **1984**, *61*, 2552. See ref 35.

[40] Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

[41] Owing to the endergonic driving force of $\Delta G \simeq 17$ kcal mol^{-1}.

[42] See, e.g., (a) Foster, R. F. *Molecular Complexes*; Elek Science: London, 1973; Vol. I and II, p 1974. (b) Foster, R. F. *Molecular Association*; Academic: New York, **1975**, **1979** and ref 8.

420 M^{-1} cm^{-1}) for benzene and hexamethylbenzene, respectively].[43] Second, the magnitudes of the formation constant K for the charge-transfer complex in Table I are strongly dependent on the arene donor. Indeed the unusually large factor of 10^6 that separates benzene from hexamethylbenzene (Figure 6) can be interpreted in terms of the valence-bond description[44] as an increased contribution of the electron-transfer component to the ground-state of the complex.[44b] If so, the redox properties of the ground-state complex could vary with the donor strength of the arene moiety—in accord with the expectations of eq 21. Be that as it may, the results in Table V show that the deliberate excitation of the charge-transfer band ($h\nu_{CT_2}$) that varies with arene donor effectively achieves the same oxidative aromatic nitration. Such a photoactivation of the charge-transfer complex represents the alternative means to induce electron transfer with the complex[45] (Scheme V).

Scheme V

$$\mathrm{ArH} + \mathrm{NO}^+ \rightleftharpoons [\mathrm{ArH,NO}^+] \qquad (22)$$

$$[\mathrm{ArH,NO}^+] \xrightarrow{h\nu_{CT}} [\mathrm{ArH}^{\bullet+},\mathrm{NO}] \qquad (23)$$

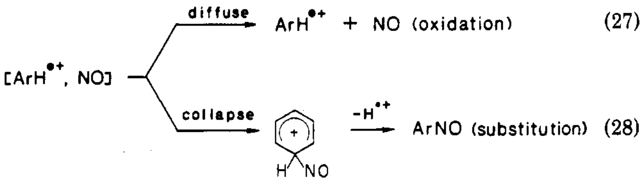
$$[\mathrm{ArH}^{\bullet+},\mathrm{NO}] + \tfrac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{ArH}^{\bullet+} + \mathrm{NO}_2, \text{ etc.} \qquad (24)$$

VII. Comments on Aromatic Oxidation and Substitution with NO$^+$ (Nitrous Acid). The foregoing mechanistic analysis shows that oxidative aromatic nitration has the distinct earmarks of the dual role played by NO$^+$ in aromatic oxidation and substitution as described in eq 1 and 2. Since the polynuclear arenes, as well as the phenols and anilines pertinent to the latter, are merely extended examples of the aromatic donors (ArH) described in this study,[8] it follows that the analogous charge-transfer complexes are also intermediates in aromatic oxidation and substitution. Moreover, it may not be surprising that the characteristic colors associated with such CT complexes would not have been routinely reported. Thus polynuclear arenes, phenols, anilines, etc. are substantially more electron rich than either hexamethylbenzene or naphthalene, as indicated by the reduced values of their ionization potentials.[46] Such potentials (that are actually less than that of anthracene) should provide driving forces that lead to electron-transfer rates that are faster than that reported for eq 8. Accordingly the colors of the charge-transfer complexes could have, at best, been only observed fleetingly. Electron transfer in this manner also provides a basis for unifying the mechanisms of oxidation and substitution, as outlined in Scheme VI.

Scheme VI

$$\mathrm{ArH} + \mathrm{NO}^+ \rightleftharpoons [\mathrm{ArH,NO}^+] \qquad (25)$$

$$[\mathrm{ArH,NO}^+] \rightarrow [\mathrm{ArH}^{\bullet+},\mathrm{NO}] \qquad (26)$$



According to Scheme VI, aromatic oxidation and substitution by NO$^+$ share the charge-transfer complex [ArH,NO$^+$] and the ensuing ion radical pair [ArH$^{\bullet+}$,NO] in common with oxidative aromatic nitration. The critical divergence of pathways is promoted by dioxygen (which scavenges nitric oxide according to Scheme I, III, or IV and thus leads to oxidative aromatic nitration). In the absence of dioxygen, we would expect the dichotomy between oxidation and substitution to be largely controlled by the stability of the aromatic ion radical—the highly stabilized ones enjoying diffusive separation (eq 27). Although the kinetics of ion radical collapse (eq 28) have not as yet been examined, the newer developments in time-resolved spectroscopy of the related system [ArH$^{\bullet+}$,NO$_2$] will hopefully shed light on this problem.[29] Furthermore in a more general context, the close relationship between the ion radical pairs [ArH$^{\bullet+}$,NO] and [ArH$^{\bullet+}$,NO$_2$] bears directly on the role of NO$^+$ (or nitrous acid) catalysis[47] in electrophilic aromatic nitration.

Experimental Section

Materials. NOBF$_4$ (Pfaltz and Bauer) was recrystallized from acetonitrile at −20 °C, followed by filtration in a drybox. Vacuum drying yielded a colorless crystalline powder. NOPF$_6$ (Pfaltz and Bauer) was used without purification. The aromatic hydrocarbons were obtained from commercial sources and repurified as follows. Toluene (Matheson), *p*-xylene (Matheson), and mesitylene (J. T. Baker) were refluxed over and distilled from sodium. 4-Methoxytoluene (Aldrich) was vaccum distilled and passed through activated alumina (Woelm N-Super 1) under an argon atmosphere. Durene (Aldrich), pentamethylbenzene (Aldrich), naphthalene (Matheson, Coleman, Bell), and hexamethylbenzene (Fluka) were recrystallized from ethanol and sublimed in vacuo. 1,4-Dimethylnaphthalene (Aldrich) and anthracene (Aldrich, gold) were used as received. 2,6-Di-*tert*-butyl-4-methylpyridine (DBMP, Aldrich) was sublimed in vacuo. Authentic nitro compounds were obtained from the following sources: 4-methoxy-3-nitrotoluene, 2-nitrotoluene, and 4-nitrotoluene from Eastman; 1-nitronaphthalene, 2-nitronaphthalene, 9-nitroanthracene, and anthraquinone from Aldrich. Isolated reaction products were identified by comparison of their ^{1}H NMR spectra and their retention times on gas chromatography with those of authentic samples. Tetrabutylammonium iodide (Eastman) and nitrite (Fluka) were dried over P$_2$O$_5$ in vacuo. Adamantane (Aldrich) was used as received. Dioxygen was purified by passing it through a 30-cm tube packed with anhydrous CaSO$_4$ and molecular seive (4 Å). It was then passed through a cold trap (−78 °C) and into the reaction flask via a gas burette filled with mineral oil. Before introduction of dioxygen, the apparatus was evacuated for 10 min. Solvents were dried as follows. Acetonitrile (HPLC grade, Fisher Scientific) was initially stirred over KMnO$_4$ for 12 h, and the mixture was refluxed for an additional hour. After filtration, the colorless liquid was treated with diethylenetriamine, and the mixture was refiltered. Acetonitrile was finally refractionated from P$_2$O$_5$ under an argon atmosphere. Dichloromethane (J. T. Baker) was initially stirred with concentrated sulfuric acid. The separated layer was neutralized and dried over anhydrous Na$_2$CO$_3$. It was finally distilled from anhydrous P$_2$O$_5$ under an argon atmosphere. Nitromethane (Fisher, 96%) was crystallized at −78 °C until most of it was frozen. The slightly pale yellow liquid was cannulated, and the colorless solid was recrystallized three times. The resulting nitromethane was warmed to room temperature and treated with CaCl$_2$. Distillation at reduced pressure at 150 mmHg (bp 49–50 °C) afforded colorless nitromethane that was stored under argon in a Schlenk flask in the dark. Nitro-

---

(43) Since the low-energy band appears as a shoulder, the values of λ_{CT_2} are approximate.

(44) (a) In the limiting case for the ground-state wave function $\Psi_{CT} = a\Psi_1 + b\Psi_2$, where Ψ_1 is the no-bond function representing [ArH,NO$^+$] and Φ_2 is the dative function representing [ArH$^{\bullet+}$,NO].[8] (b) The coefficient b for benzene is smaller than that for hexamethylbenzene to accord with the differences in their ionization potentials.

(45) For the time-resolved spectroscopy of charge-transfer complexes to yield the ArH$^{\bullet+}$ transients as in eq 23, see Sankararaman et al. in ref 13, 29a, and 30.

(46) Klasinc, L.; Kovac, B.; Güsten, H. *Pure Appl. Chem.* **1983**, *55*, 289.

(47) See (a) Leis, J. R.; Pĕna, M. E.; Ridd, J. H. *J. Chem. Soc., Chem. Commun.* **1988**, 670. (b) Ali, M.; Ridd, J. H. *J. Chem. Soc., Perkin Trans. 2* **1986**, 327 and related papers.

Table VII. Infrared Spectral Data of Arene CT Complexes with $NO^+PF_6^-$

$[ArH,NO^+PF_6^-]$ ArH	solid, cm^{-1} NO^+ (fwhm)[b]	Δ[c]	solution,[a] cm^{-1} NO^+ (fwhm)
hexamethylbenzene	1899 (152)	441	1880 (49)
pentamethylbenzene	1927 (196)	413	1904 (59)
durene	1986 (191)	355	1929 (60)
mesitylene	2016 (157)	324	1967 (93)

[a] In dichloromethane. [b] Full width half maximum. [c] Shift from free $NO^+PF_6^-$ at 2340 cm^{-1}.

Table VIII. Electronic Spectral Data of Arene CT Complexes with $NO^+PF_6^-$

	solid (λ, nm)			solution (λ, nm)[a]		
$[ArH,NO^+PF_6-]$ ArH	CT_1	CT_2	A_1/A_2[b]	CT_1	CT_2	A_1/A_2[b]
hexamethylbenzene	360	520	0.81	337	~500	15
durene	340	510	0.85	335	~500	10
mesitylene	380	*c*	-	335	*c*	-

[a] In dichloromethane. [b] Area ratio of CT_1/CT_2. [c] CT_2 not resolved.

methane-d_3 (Aldrich, 99 atm % D, Gold label) received in a sealed ampule was opened in a drybox, stored in a Schlenk flask equipped with Teflon stopcocks. It was always used under a dry dinitrogen atmosphere. Trifluoroacetic acid (Mallinckrodt) was refluxed with and then distilled from P_2O_5 under an argon atmosphere.

Instrumentation. UV–vis absorption spectra were measured on a Hewlett-Packard 8450A diode-array spectrometer with 2-cm^{-1} resolution. Reflectance UV–vis spectra were recorded on Perkin-Elmer 330 spectrometer equipped with a Hitachi Model H210-2101 integrating sphere accessory. ^1H and ^{13}C NMR spectra in solution were obtained on either a JEOL FX 90Q or a General Electric QE 300 FT NMR spectrometer. IR spectra were recorded on a Nicolet 10DX FT spectrometer equipped with the collector DRIFT accessory with blocker device (Spectra-Tech). Gas chromatography was performed on a Hewlett-Packard 5790A series FID gas chromatograph with a 3392 integrator. Correction factors (*f*) for the arenes and the nitration products were calibrated with authentic samples (vide infra). All inert atmosphere manipulations were carried out in a Vacuum Atmospheres MO-41 drybox. GC–MS analyses were carried out on a Hewlett-Packard 5890 chromatograph interfaced to a HP 5970 mass spectrometer (EI, 70 eV).

Charge-Transfer Absorption Spectra of Arene CT Complexes with NO^+. All operations were performed in a glovebox using Teflon-topped UV cells equipped with a side arm. The stock solution of $NOBF_4$ in CH_3CN was transferred to the UV cell, and a known amount of aromatic donor was added prior to the measurement of the absorption spectrum. The spectrum in dichloromethane was measured as follows. A weighed amount of $NOBF_4$ was transferred to a preweighed UV cell, and dichloromethane together with a known amount of aromatic donor were added. $NOBF_4$, which was insoluble in dichloromethane, was dissolved in the course of complex formation with aromatic donors such as durene, pentamethylbenzene, and hexamethylbenzene to produce a homogeneous solution.

Formation Constants of Arene CT Complexes with NO^+. In a typical procedure, an 8-mL aliquot of a standard stock solution of nitrosonium salt in acetonitrile was transferred to a 1-cm quartz cuvette. A weighed amount of arene was added incrementally under an argon atmosphere. The absorbance changes were measured at the spectral maxima as well as at other wavelengths close to the absorption maxima. From a plot of $[NO^+](A_{CT})^{-1}$ against $(\text{arene})^{-1}$, consisting of six data points, the slope was estimated as $(K\epsilon_{CT})^{-1}$ and the intercept as $\epsilon_{CT}{}^{-1}$.[8] Generally the formation constant obtained from the peak maxima showed the best correlation coefficient for linearity. In the case of hexamethylbenzene and pentamethylbenzene only four or five data points were taken, owing to the extremely high formation constants ($K > 1000$).

Isolation of Crystalline Charge-Transfer Complexes of Arenes with $NOPF_6$. Typically, the arene was added to a flask that contained $NOPF_6$ (drybox). A minimum amount of dichloromethane was added to the colorless mixture and undissolved solid was removed by filtration. The resulting reddish solution was chilled to −20 °C in the dark. After 48 h, the crystals were collected and dried under an argon stream. The sample for the diffuse reflectance IR spectrum was prepared in the drybox by using small portions of the ground crystals. The reflectance measurements were made with the collector DRIFT accessory with the block device. Solution IR spectra were recorded by dissolving the crystals in dichloromethane and introducing into a sealed (0.1 cm) NaCl or AgCl cell (Table VII). Diffuse reflectance UV–vis spectra of the crystals were taken on crystals ground with either adamantane or powdered quartz in a drybox. Spectra were measured in a circular sealed quartz cell against an alumina disk, as the reference (Table VIII). Quantitative analysis of the complexes was carried out by ^1H NMR spectroscopy with CH_3NO_2 as the internal standard and by gas chromatographic analysis with nonane as the internal standard. [Hexamethylbenzene, $NOPF_6$]: Black shiny crystals (0.297 g, 74%) were isolated from 0.203 g of hexamethylbenzene and 0.193 g of $NOPF_6$ in 9 mL of CH_2Cl_2. ^1H NMR (CD_3CN): δ 2.48. Molecular weight calcd for $[C_6(CH_3)_6, NOPF_6]$ 337.3, found 334. [Pentamethylbenzene, $NOPF_6$]: Black crystals (0.350 g, 65%) were isolated from 0.289 g of pentamethylbenzene and 0.249 g of $NOPF_6$ in 7.0 mL of CH_2Cl_2. ^1H NMR (CD_3NO_2): δ 2.44 (9 H), 2.51 (6 H), 7.66 (1 H). Molecular weight calcd for $[C_6H(CH_3)_5, NOPF_6]$ 323.2, found 326. [Durene, $NOPF_6$]: Brown crystals (0.341 g, 68%) were obtained from 0.200 g of durene and 0.204 g of $NOPF_6$ in 5 mL of CH_2Cl_2. ^1H NMR (CD_3NO_2): δ 2.43 (12 H), 7.56 (2 H). Molecular weight calcd for $[C_6H_2(CH_3)_4, NOPF_6]$ 309.2, found 311. [Mesitylene, $NOPF_6$]: yellow-orange crystals (0.089 g, 34%) were isolated from 0.121 g of mesitylene and 0.139 g of $NOPF_6$ in 3 mL CH_2Cl_2. ^1H NMR (CD_3NO_2): δ 2.51 (9 H), 7.50 (3 H).

Oxidative Aromatic Nitration in CH_3CN and CH_3NO_2. In a typical procedure, a Schlenk flask charged with a preweighed amount of nitrosonium salt was evacuated and filled with dioxygen. The solvent was added with the aid of a hypodermic syringe under a dioxygen atmosphere. The subsequent addition of the aromatic donor to the solution cooled in an ice bath (3 °C) yielded a strongly colored solution. The progress of reaction was followed in the dark either by the color change or by the dioxygen consumption. For product analysis, a small aliquot of the reaction mixture was periodically extracted under dioxygen, diluted with CH_2Cl_2, and quenched with water. After drying with $MgSO_4$, it was analyzed by gas chromatography using the internal standard method. After the reaction was complete, the solvent was removed, and the crude mixture was analyzed by ^1H NMR spectroscopy using an internal standard. For the isolation of products, the column chromatography of the reaction mixture (after solvent removal) adsorbed on a silica gel column was eluted with hexane–ether mixtures. ***p*-Xylene**: From the orange solution of 0.568 mmol of $NOBF_4$ with 0.473 mmol of *p*-xylene in 20 mL of acetonitrile, 0.076 mmol of dioxygen uptake was observed within 30 min. Dioxygen uptake (0.21 mmol) was completed after 7.5 h. The starting orange color was only slightly discharged even after 75 h. No starting material was observed at this time. Column chromatography yielded 48 mg (68%) of 2-nitro-*p*-xylene. GC–MS: M^+, 151. ^1H NMR ($CDCl_3$): δ 2.38 (3 H, s), 2.53 (3 H, s), 7.23, 7.27 (2 H, dd), 7.76 (1 H, s) [lit.[48] 2.35, 2.47, 7.12, 7.65]. **Mesitylene**: The orange solution from 1.22 mmol of mesitylene

---

(48) Fischer, A.; Ramsay, J. N. *Can. J. Chem.* **1974**, *52*, 3960.

and 1.02 mmol of $NOBF_4$ in 15 mL of CH_3CN reacted with dioxygen for 42 h. Column chromatography gave 0.69 mmol of unreacted mesitylene, 2-nitromesitylene (0.13 mmol), and a trace amount of orange material, which was not identified. Mass balance, 67%. 2-Nitromesitylene: Mp: 44 °C (lit.[26c] mp 44 °C) GC-MS: M^+ 165. ^1H NMR ($CDCl_3$): δ 2.28 (6 H, s), 2.31 (3 H, s), 6.91 (2 H, 2). **Durene**: Within 45 min of stirring, 0.5 equiv of dioxygen was consumed by the solution of 0.32 mmol of durene and 0.42 mmol of $NOBF_4$ in 20 mL of CH_3CN. After 3.5 h, the solution was orange, and after 7 h it was light yellow. Column chromatography yielded 48 mg (84%) of 3-nitrodurene. Mp: 113 °C (lit.[26g] mp 113 °C). GC-MS: M^+ 179. ^1H NMR ($CDCl_3$): δ 2.11 (6 H, s), 2.25 (6 H, s), 7.05 (1 H, s). IR (KBr): 2973, 2952, 2868, 2748, 1518, 1363, 1018, 899, 765, 618, 527 cm^{-1}. The reaction in nitromethane was carried out similarly. Within 45 min, 0.5 equiv of dioxygen was consumed from the solution of 0.48 mmol of $NOBF_4$ in 20 mL of CH_3NO_2 and 0.41 mmol of durene. Only 3-nitrodurene (0.37 mmol, 92%) was observed by ^1H NMR and GC analysis. **Pentamethylbenzene**: The red-brown solution of 0.47 mmol of pentamethylbenzene and 0.36 mmol of $NOBF_4$ in 25 mL of CH_3CN was bleached within 3 h. The crude reaction mixture consisted of 0.36 mmol of 1-nitropentamethylbenzene and 0.07 mmol of unreacted pentamethylbenzene. Nitropentamethylbenzene was isolated by column chromatography with hexane, and it was recrystallized from ethanol at −20 °C. Mp: 162 °C (lit.[49] mp 158–159 °C). ^1H NMR ($CDCl_3$): δ 2.15 (6 H, s), 2.22 (9 H, s). IR (KBr): 3009, 2973, 2868, 1525, 1265 cm^{-1}. GC-MS: M^+ 193. **1,4-Dimethylnaphthalene**: The dark brown solution from 0.28 mmol of 1-4-dimethylnaphthalene and 0.43 mmol of $NOBF_4$ in 20 mL of CH_3CN was stirred for 3.5 h. At this time the color of the reaction mixture was green, and no starting material was apparent by GC analysis. The evaporation of reaction mixture led to a dark syrupy residue, which was redissolved in dichloromethane and passed through a short silica gel column to give 36 mg (68%) of 2-nitro-1,4-dimethylnaphthalene. Mp: 68–70 °C (lit.[50a] 67–68 °C). ^1H NMR ($CDCl_3$): δ 2.65 (3 H), 2.71 (3 H), 7.48 (1 H, s), 7.5 (2 H, m), 7.99 (2 H, m). ***p*-Methoxytoluene**: A red-purple solution was observed when 0.75 mmol of *p*-methoxytoluene was mixed with 0.79 mmol of $NOBF_4$ in 30 mL of CH_3CN; within 30 min of stirring, 0.18 mmol of dioxygen was consumed, but there was no apparent color change. After 8 h, no arene reactant was apparent and 0.70 mmol of 3-nitro-4-methoxytoluene was obtained as an orange liquid (76.9 mg, 62%). It was identical with an authentic sample (vide supra). **Toluene**: A yellow color developed with 0.19 mmol of $NOPF_6$ and 0.085 mmol of toluene in 4 mL of nitromethane. The color was not discharged after 9 h. The analysis for the reaction mixture indicated mainly starting material, and the conversion to *o*- and *p*-nitrotoluene was 20%. After 21 h of stirring at 15 °C, the combined yields of *o*-nitrotoluene (0.053 mmol), *p*-nitrotoluene (0.031 mmol), and *m*-nitrotoluene (0.003 mmol) were essentially quantitative.

Oxidative Aromatic Nitration in Dichloromethane. In a typical procedure, a Schlenk flask was charged with nitrosonium salt, and CH_2Cl_2 was added with the aid of a hypodermic syringe under a dioxygen atmosphere. Nitrosonium salt was not soluble, and there was no color development. To the above mixture at 3 °C, the aromatic donor was added to give a colored solution. The reaction mixture was periodically analyzed by ^1H NMR spectroscopy and gas chromatography. The products were usually isolated by column chromatography on a silica gel. **Durene**: A red-brown solution of 0.11 mmol of durene and 0.08 mmol of $NOPF_6$ in CH_2Cl_2 changed to a purple solution within 1 h, and finally to a light red-purple solution after 4.5 h. Thin-layer chromatography (Whatman, silica gel) gave 0.008 mmol of unreacted durene, 0.04 mmol of 3-nitrodurene, 0.016 mmol of 2,4,5-trimethylbenzaldehyde, and nitro dimer (vide infra) by elution with a hexane ether (2:1 v/v) mixture. 2,4,5-Trimethylbenzaldehyde;[26c] GC-MS: M^+ 148. ^1H NMR ($CDCl_3$): δ 2.29 (6 H, s), 2.59 (3 H, s), 7.03 (s, 1 H), 7.55 (1 H, s), 10.19 (1 H, s). IR (CH_2Cl_2): 1700 cm^{-1}. 1-Nitro-2,3,5,6,2′,4′,5′-heptamethyldiphenylmethane (nitro dimer of durene), GC-MS: M^+ 311. ^1H NMR ($CDCl_3$):[51] δ 2.05 (3 H, s), 2.11 (6 H, s), 2.19 (9 H, s), 2.36 (3 H, s), 3.93 (2 H, s), 6.27 (1 H, s), 6.92 (1 H, s). **Pentamethylbenzene**: Pentamethylbenzene (0.70 mmol) was treated with 0.77 mmol of $NOBF_4$ in 28 mL of CH_2Cl_2 to give a red-brown solution at 3 °C. Analysis after 9 h indicated 0.29 mmol of unreacted pentamethylbenzene and 0.32 mmol of 1-nitropentamethylbenzene. The solution was still red brown. Further reaction at room temperature for 15 h yielded an orange solution that afforded 0.63 mmol of 1-nitropentamethylbenzene. **Naphthalene**: A yellow color developed when 0.301 mmol of $NOPF_6$ and 0.822 mmol of naphthalene was mixed with CH_2Cl_2 under dioxygen. The green solution yielded a small amount of black deposit. GC analysis after 39 h indicated the presence of 0.54 mmol of naphthalene, 0.185 mmol of 1-nitronaphthalene, and 0.11 mmol of 2-nitronaphthalene. Column chromatography yielded 38 mg of unreacted naphthalene and 28 mg of 1-nitronaphthalene. **Anthracene**: $NOPF_6$ (0.71 mmol) and 0.73 mmol of anthracene in CH_2Cl_2 was cooled to 3 °C under a dioxygen atmosphere. The resulting green solution contained some black solid. After 4 h, the dark solution was filtered and washed with water, to yield 5.9 mg of unreacted anthracene, 93.3 mg of 9-nitroanthracene, and 10 mg of anthraquinone by column chromatography.

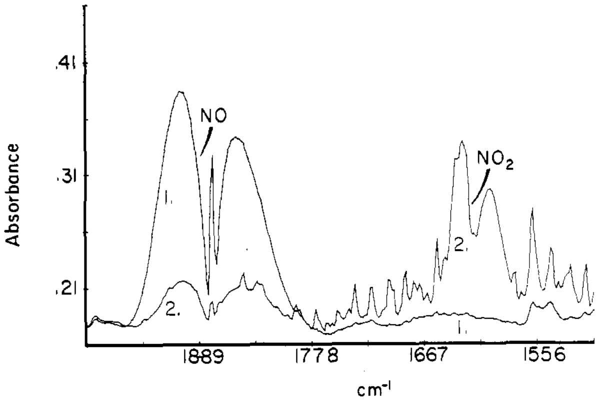


Figure 7. Infrared spectrum of nitric oxide evolved (curve 1) from anthracene and $NOPF_6$ in dichloromethane. Curve 2 is the IR spectrum of NO_2 after the introduction of dioxygen.

Oxidative Aromatic Nitration in the Presence of Hindered Base. The order of mixing the components was important for optimum yields of side-chain nitration product. Typically, dichloromethane was added to a Schlenk flask charged with nitrosonium salt under a dioxygen atmosphere, and 2,6-di-*tert*-butyl-4-methylpyridine was added. $NOPF_6$ was not soluble, and there was no color development at this stage. The aromatic donor was added to give a colored solution, and most of the nitrosonium salt dissolved. At 3 °C the color was bleached within 15 to 60 min, followed by a white precipitate. Diethyl ether was added, and the white solid was removed by filtration. The reaction products were separated by column chromatography and/or analyzed by ^1H NMR spectroscopy and gas chromatography. An authentic sample of the white solid 2-6-di-*tert*-butyl-4-methylpyridinium hexafluorophosphate was prepared from 59.7 mg (0.29 mmol) of DBMP and 100 μL of 60% of HPF_6 in 5 mL of CH_2Cl_2 at room temperature. After 2 h, the white solid was filtered and washed with water, cold (−20 °C) ethanol, and dichloromethane. It was dried in vacuo for 3 h. Mp: 212–215 °C dec. IR (KBr): 3395, 3093, 2973, 2952, 2882, 1638, 1616, 1490, 1462, 1377, 1328, 1293, 1250, 1223, 1040, 948, 913, 885, ~850 (br), 800, 737, 555 cm^{-1}. ^1H NMR (CD_3NO_2):[52] δ 1.55 (18 H, s), 2.21 (1 H, s), 2.62 (3 H, s), 7.81 (2 H, s). ^{19}F NMR (CD_3NO_2, $CFCl_3$ ref): −71.85 (d, J = 708). For the tetrafluoroborate salt, ^1H NMR (CD_3NO_2): δ 1.55 (18 H, s), 2.00 (1 H, br), 2.68 (3 H, s), 7.81 (2 H, s). ^{19}F NMR (CD_3NO_2, $CFCl_3$ ref): −151.0 (s). **Durene**: A red-brown mixture of 0.41 mmol of $NOPF_6$, 0.72 mmol of DBMP, and 0.51 mmol of durene was converted in 15 min to an orange solution and to a

---

[49] Suzuki, H.; Nakamura, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*(2), 473.

[50] (a) Fischer, A.; Wilkinson, A. L. *Can. J. Chem.* **1972**, *50*, 3988. (b) Suzuki, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 879.

[51] Clemens, A. H.; Ridd, J. H. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1227.

[52] (a) Anderson, A. G.; Stang, P. J. *Org. Synth.* **1981**, *60*, 34. (b) Weber, H.; Pant, J.; Liedigk, M.; Wunderlich, H. *Chem. Ber.* **1981**, *114*, 1455.

pale yellow solution within 3 h. Durene (0.26 mmol), 3-nitrodurene (0.074 mmol), and (2,4,5-trimethylphenyl)nitromethane (0.14 mmol) with trace amount of durene dimer (vide infra) were observed in the crude reaction mixture. Similarly, from the reaction of 0.26 mmol durene and 0.31 mmol of $NOBF_4$ with 0.32 mmol of DBMP in 10 mL of CH_2Cl_2 (24 h), 15.6 mg of (2,4,5-trimethylphenyl)nitromethane (34%) was isolated by column chromatography together with 2.7 mg of unreacted durene and 9.85 mg of 3-nitrodurene. (2,4,5-Trimethylphenyl)nitromethane, mp: 50–51 °C (lit.[26c] mp 50–51 °C). ^1H NMR ($CDCl_3$): δ 2.24 (6 H, s), 2.32 (3 H, s), 5.43 (2 H, s), 7.04 (1 H, s), 7.11 (1 H, s). IR (KBr): 1545, 1365 cm^{-1}. 2,3,5,6,2′,4′,5′-Heptamethyldiphenylmethane, GC–MS: M$^+$ 266. ^1H NMR ($CDCl_3$):[26e] δ 2.05 (9 H, s), 2.13 (3 H, s), 2.20 (6 H, s), 2.38 (3 H, s), 3.86 (2 H, s), 6.33 (1 H, s), 6.98 (2 H, s). On the other hand, when the Schlenk flask was initially charged with 0.24 mmol of $NOBF_4$ in CH_2Cl_2 under oxygen and then 0.23 mmol of durene added, it gave a red-brown solution. DBMP (0.21 mmol) was added quickly, and the bleaching of the color was observed upon stirring. The pale yellow reaction mixture after 7 h yielded 0.16 mmol (71%) of 3-nitrodurene, 0.039 mmol of durene, and 0.027 mmol (12%) of (2,4,5-trimethylphenyl)nitromethane. **Pentamethylbenzene**: From the reaction of 2.09 mmol of $NOPF_6$ 2.19 mmol of DBMP and 2.14 mmol of pentamethylbenzene in 90 mL of CH_2Cl_2 at 3 °C, 1.0 mmol of dioxygen consumption was observed. The color of the solution was pale yellow within 105 min. After 3 h, 1.01 mmol of unreacted pentamethylbenzene, 0.102 mmol of nitropentamethylbenzene, and 1.034 mmol of (2,3,4,5-tetramethylphenyl)nitromethane was detected by GC analysis. The colorless pyridinium salt (660 mg, 1.88 mmol) was removed. The mother liquor afforded 465 mg of pale yellow solid consisting of unreacted pentamethylbenzene (148 mg), 35 mg of nitropentamethylbenzene, and 165 mg of (tetramethylphenyl)nitromethane. (2,3,4,5-Tetramethylphenyl)nitromethane, Mp: 61 °C (lit.[53] mp 62–63 °C). ^1H NMR ($CDCl_3$): δ 2.23 (3 H, s), 2.24 (3 H, s), 2.26 (3 H, s), 2.29 (3 H, s), 5.46 (2 H, s), 7.00 (1 H, s). ^{13}C NMR ($CDCl_3$): δ 15.96, 16.38, 16.41, 20.58 (m), 78.6 (t, d, J = 146, 5.2), 125.4 (m), 130.6 (d, m, J = 151, 3–6), 133.9 (m), 134.3 (m), 136.3 (m), 137.5 (m). IR (KBr): 1546, 1370 cm^{-1}. GC–MS: M$^+$ 193. Similarly, from the reaction of 0.33 mmol of $NOBF_4$, 0.36 mmol of DBMP, and 0.27 mmol of pentamethylbenzene in 15 mL of CH_2Cl_2 under dioxygen, 35.8 mg of pyridinium salt was isolated after 3.5 h, together with 0.0047 mmol of pentamethylbenzene, 0.067 mmol of nitropentamethylbenzene, and 0.14 mmol of (2,3,4,5-tetramethylphenyl)nitromethane. **Hexamethylbenzene**: A red-brown mixture of 0.46 mmol of $NOBF_4$, 0.36 mmol of DBMP, and 0.44 mmol of hexamethylbenzene in 30 mL of CH_2Cl_2 was converted to a pale yellow solution within 30 min. After 2 h, 0.27 mmol of (pentamethylphenyl)nitromethane, 0.028 mmol of pentamethylbenzaldehyde, and trace amount (~0.005 mmol) of pentamethylbenzyl alcohol was observed. After removal of the pyridinium salt, the products were isolated by column chromatography with a mixture of methylene chloride–petroleum ether (1:10, v/v) as the eluent to give 35 mg of (pentamethylphenyl)nitromethane, 7.4 mg of pentamethylbenzyl alcohol, and 3 mg of pentamethylbenzaldehyde. Pentamethylphenylnitromethane, Mp: 84–86 °C (lit.[50b] mp 86–88 °C). ^1H NMR ($CDCl_3$): δ 2.25 (9 H, s), 2.30 (6 H, s), 5.57 (2 H, s). IR (KBr): 1553, 1379, 709 cm^{-1}. GC–MS: 207 (M$^+$, 1), 161 (100). Pentamethylbenzyl alcohol, ^1H NMR ($CDCl_3$):[50a] δ 2.24 (9 H), 2.36 (6 H), 4.78 (2 H). IR (KBr): 3290, 1448, 1420, 998, 653 cm^{-1}. GC–MS: 179 (M$^+$, 5), 178 (51). Pentamethylbenzaldehyde, ^1H NMR ($CDCl_3$):[50b] δ 2.21 (9 H, s), 2.39 (6 H, s) 10.60 (1 H, s). GC–MS: 176 (M$^+$, 85), 175 (100). **1,4-Dimethylnaphthalene**: From the reaction of 0.74 mmol of $NOBF_4$, 0.62 mmol of DBMP, and 1.02 mmol of 1,4-dimethylnaphthalene in 20 mL of CH_2Cl_2, a green color was observed during the reaction. This color was slightly discharged after 12 h. The colorless pyridinium salt (157 mg) was removed by filtration. Upon column chromatography, 54 mg of unreacted 1,4-dimethylnaphthalene, 40.3 mg of 1-methyl-4-(nitromethyl)-naphthalene, and 22 mg of 2-nitronaphthalene were obtained, together with 6 mg of an unidentified solid, which was assumed to be the dimer by GC–MS analysis. 1-Methyl-4-(nitromethyl)naphthalene, ^1H NMR ($CDCl_3$):[50a] δ 2.73 (3 H, s), 5.89 (2 H, s), 7.46 (4 H, m), 8.03 (2 H, m).

Measurement of Dioxygen Consumption. Typically, a Schlenk flask containing the nitrosonium salt was connected to a three-way stopcock, one of which was connected to an argon line and the other was to the dioxygen source. In order to maintain constant vapor pressure during the reaction, the temperature was maintained by an ice bath at 3 °C. For example, from 0.74 mmol of mesitylene and 0.22 mmol of $NOPF_6$ in 20 mL of CH_2Cl_2, the temporal consumption of O_2 was (s, mmol): 40, 0.036; 165, 0.063; 315, 0.080; 775, 0.089; 1655, 0.11, as presented in Figure 4.

Anaerobic Treatment of Aromatic Donors with Nitrosonium Salts in the Dark. Typically the arene donor was added to a Schlenk flask charged with a preweighed amount of nitrosonium salt in a solvent under an argon or dinitrogen atmosphere in the dark. The colored solution was stirred at 25 °C for a specified period, and then quenched with deoxygenated water. The colorless solution was extracted with diethyl ether, which was subsequently analyzed for the unreacted arene by ^1H NMR spectroscopy and/or gas chromatography. The amounts of toluene, xylene and mesitylene were unchanged for more than 2 days. Durene and pentamethylbenzene persisted intact for more than 6 h. Naphthalene was recovered in 98% yield after 6 h, but traces of 1-nitronaphthalene (<1%) were detected together with a residual thin black film on the flask wall. 1,4-Dimethylnaphthalene was recovered in 95% after 6 h at 25 °C, but no product was identified.

Under an anaerobic atmosphere, a solution of anthracene (0.061 mmol) in 4 mL of CH_2Cl_2 was added to $NOPF_6$ (0.53 mmol) at −78 °C to afford a green solution together with a black precipitate. In order to identify the gas bubbles that were clearly visible during this transformation, the same reaction was carried out directly in an IR cell (5-cm path length) at 25 °C under dinitrogen. The IR spectrum of the colorless gas shown as curve 1 in Figure 7 was the same as that of an authentic sample of nitric oxide.[15] When dioxygen was introduced into the cell, the atmosphere immediately turned yellow, and the new IR spectrum (curve 2) was readily assigned to that of nitrogen dioxide.[14] The green solution showed a broad absorption band at λ_{max} = 740 nm, reminiscent of the anthracene π-dimer cation.[18c] Dissolution of a small amount of the black crystal in dichloromethane afforded a similar green solution, but with a slightly shifted λ_{max} = 726 nm that was characteristic of anthracene cation radical formed upon dissociation.[54] The ESR spectrum of this solution indeed showed the characteristic well-resolved hyperfine splittings of anthracene cation radical.[55] The black crystals were quantitatively analyzed by iodometric reduction with tetrabutylammonium iodide in nitromethane using the unique diiodine absorption at λ_{max} = 484 nm (ϵ = 804 M^{-1} cm^{-1}).[56] Molecular weight calcd for $(C_{14}H_{10})_2PF_6$ 502, found 528.

Photoinduced Oxidative Aromatic Nitration. Toluene (0.68 mmol) and $NOPF_6$ (0.27 mmol) in 20 mL of $MeNO_2$ afforded a yellow solution that was cooled to −15 °C, and dioxygen was introduced. Irradiation was effected by the output of a 1-kW Hg–Xe lamp (Hanovia 977-B1), which was passed through a 415-nm sharp cutoff filter (Corning 415) to eliminate radiation with energy more than the CT band (Table I).[57] The thermal control was carried out under similar conditions, but in the dark (see Table V). Durene (0.83 mmol) and $NOPF_6$ (0.17 mmol) in 18 mL of $MeNO_2$ were similarly treated with dioxygen at −20 °C, but a sharp cutoff filter at $\lambda > 480$ nm was used. The identification of 2,4,5-trimethylbenzaldehyde and the nitro dimer was described above.

Acknowledgment. We thank S. Sankararaman and T. M. Bockman for helpful discussions and the National Science Foundation and the Robert A. Welch Foundation for financial support.

---

(53) Mishina, T. *J. Sci. Hiroshima Univ. Ser. A* **1980**, *441*(*1*), 157.

(54) Masnovi, J. M.; Kochi, J. K.; Hilinski, E. F.; Rentzepis, P. M. *J. Phys. Chem.* **1985**, *89*, 5387 and ref 18c.

(55) Cf. Howarth, O. W.; Fraenkel, G. K. *J. Chem. Phys.* **1970**, *52*, 6258.

(56) Cf. Benesi and Hildebrand in ref 11a.

(57) Sankararaman, S.; Kochi, J. K. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 278.