

Direct Nitrosation of Aromatic Hydrocarbons and Ethers with the Electrophilic Nitrosonium Cation

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Various polymethylbenzenes and anisoles are selectively nitrosated with the electrophilic nitrosonium salt $\text{NO}^+ \text{BF}_4^-$ in good conversions and yields under mild conditions in which the conventional procedure (based on nitrite neutralization with strong acid) is ineffective. The reactivity patterns in acetonitrile deduced from the various time/conversions in Tables 2 and 3 indicate that aromatic nitrosation is distinctly different from those previously established for electrophilic aromatic nitration. The contrasting behavior of NO^+ in aromatic nitrosation is ascribed to a rate-limiting deprotonation of the reversibly formed Wheland intermediate, which in the case of aromatic nitration with NO_2^+ occurs with no deuterium kinetic isotope effect. Aromatic nitroso derivatives (unlike the nitro counterpart) are excellent electron donors that are subject to a reversible one-electron oxidation at positive potentials significantly less than that of the parent polymethylbenzene or anisole. As a result, the series of nitrosobenzenes are also much better Brønsted bases than the corresponding nitro derivatives, and this marked distinction, therefore, accounts for the large differentiation in the deprotonation rates of their respective conjugate acids (i.e. Wheland intermediates).

Introduction

Aromatic nitrosation unlike electrophilic aromatic nitration is, by and large, restricted to only the most reactive (electron-rich) substrates such as phenols and anilines.^{1,2} In the usual synthetic procedure, nitrous acid is generated *in situ* by the neutralization of nitrite salts with strong (aqueous) mineral acid which also promotes the production of the active nitrosating agents via the equilibria in eq 1. It is generally acknowledged that



nitrosonium (NO^+) and nitrous acidium (H_2ONO^+) ions formed in eq 1 are significantly poorer electrophiles than nitronium (NO_2^+) and nitric acidium (H_2ONO_2^+) ions responsible for aromatic nitration with nitric acid. [For example, NO^+ is estimated to be $<10^{14}$ times less effective than NO_2^+ which effects an encounter-control nitration of benzene.^{3]} However, the nitrosation of various aromatic and heteroaromatic donors (ArH) show substantial deuterium isotope effects^{4,5} to suggest that the deprotonation of the Wheland intermediate $\text{Ar}^+(\text{H})\text{NO}$ is rate-limiting in the presence of aqueous acids.⁶ It follows that the usual synthetic procedure based on acid catalysis according to eq 1 is thus self-defeating, and alternative

methodologies under basic, or at the very least, neutral conditions are clearly desirable.

The commercial availability of nitrosonium salts ($\text{NO}^+ \text{X}^-$)⁷ offers the opportunity to effect the direct nitrosation of various aromatic donors (ArH), particularly in non-aqueous solutions, *i.e.*



Since nitrosonium tetrafluoroborate is readily soluble in anhydrous acetonitrile, we examined its usage in the direct nitrosation according to eq 2 ($\text{X}^- = \text{BF}_4^-$) of two classes of aromatic donors: polymethylbenzenes and various methyl ethers (anisoles).

Results

1. Aromatic Nitrosation with Nitrosonium Tetrafluoroborate. The enhanced donor properties of anisole were initially exploited in order to establish the optimum reaction conditions to effect aromatic nitrosation with a solution of $\text{NO}^+ \text{BF}_4^-$ in acetonitrile. Thus the results in Table 1 show that more or less equimolar amounts of anisole and $\text{NO}^+ \text{BF}_4^-$ were converted (75%) at room temperature to *p*-nitrosoanisole in good yield within 0.5 h. Longer exposure times led to the complete conversion of anisole (entries 3 and 4), but at the expense of drastically reduced yields of the nitrosated product. An improvement in conversion/yield was obtained at higher temperature for short exposures (entry 6). Complete conversion of anisole was obtained in 30 min with a 3-fold molar excess of $\text{NO}^+ \text{BF}_4^-$ at 25 °C (last entry) to afford *p*-nitrosoanisole in quantitative yield according to the stoichiometry in eq 3. We thus concluded that the treatment of the aromatic donor with 3 equiv of $\text{NO}^+ \text{BF}_4^-$ dissolved in acetonitrile for 0.5 h at room temperature represented the most convenient and efficient procedure for nitrosation. Accordingly, a series of substituted anisoles and polymethylbenzenes were uniformly exposed to $\text{NO}^+ \text{BF}_4^-$ under these conditions as follows.

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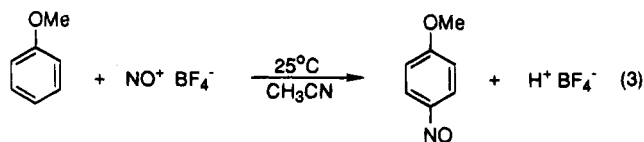
(6) The nitrosation of very reactive indoles and azulene shows minimal kinetic isotope effects in aqueous perchloric acid, and the reaction rates are considered to be encounter controlled. See Challis, B. C.; Higgins, R. J.; Lawson, A. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1223.

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Table 1. Optimal Conditions for the Nitrosation of Anisole with Nitrosonium Tetrafluoroborate in Acetonitrile Solution

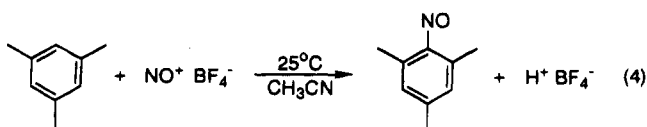
anisole (mmol)	NO ⁺ BF ₄ ⁻ (mmol)	CH ₃ CN (mL)	temp (°C)	time (h)	conv ^a (%)	yield ^b (%)
0.45	0.50	5	25	0.5	75	86
0.45	0.50	5	25	1.0	93	77 ^c
0.45	0.50	5	25	2.5	100	60 ^d
0.45	0.50	5	25	23	100	21 ^e
0.25	0.50	5	25	0.5	85	97
0.25	0.50	5	40	0.5	100	93
0.25	0.50	5	40	1.3	100	89
0.40	1.00	10	25	0.4	95	88
0.17	0.50	5	-40	3.0	10	82
0.17	0.50	5	25	0.5	100	100

^a Based on recovered anisole. ^b Based on consumed anisole. Determined by GC using the internal standard method. ^c In addition to 4-methoxy-1,4-quinoneanil, MQ, (10%); 4,4'-dimethoxyazoxybenzene, AZB, (5%); and 4,4'-dimethoxyazobenzene, AB, (2%), see Experimental Section. ^d In addition to MQ (11%), AZB (1%), and AB (13%). ^e In addition to MQ (9%) and AB (55%).



Substituted anisoles with one or two methyl substituents (see Table 2) were nitrosated in high yields, provided the *para* positions were unsubstituted. For example, *o*- and *m*-methylanisoles reacted with NO⁺ BF₄⁻ considerably faster than anisole, and even those reactions carried out at 0 °C afforded quantitative yields of the nitroso(methyl)anisoles within 30 min. By contrast, only 30% of *p*-methylanisole was consumed after 30 min at 25 °C (Table 2, entry 4), and it yielded a complex mixture consisting of only minor amounts of the *o*-nitroso(methyl)anisole (<3%) together with the corresponding *o*-nitro derivative (10%).⁸ The remainder was accounted for as the dimeric dimethoxybitolyl and other (unidentified) high molecular weight products. It is noteworthy that 2,6-dimethylanisole was nitrosated slower than anisole (entry 5), but the 3,5-isomer was considerably more reactive (entry 6). In both cases, selective nitrosation occurred in high yields at the *para* position relative to the methoxy substituent. Bromoanisoles were significantly less reactive to NO⁺ BF₄⁻, and the nitrosated products were obtained in mediocre yields from only the *ortho* and *meta* isomers after prolonged times (see last three entries).

Polymethylbenzenes were also treated with NO⁺ BF₄⁻ under the uniform conditions in Table 3. Relative to the anisoles, longer times were required to attain reasonable conversions of even the most reactive methylbenzene without significant deterioration of the nitrosated product. Thus, mesitylene was carried to 85% conversion over the course of 5 h to afford nitrosomesitylene in high yield, *i.e.*



(8) Previous workers suggested the nitroaromatic products to derive from further oxidation of the first formed nitroso derivatives. See Lobachev, V. L.; Savsunenko, O. B.; Rudakov, E. S. *Kinet. Catal. (USSR)* **1991**, *32*, 11.




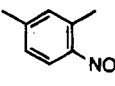


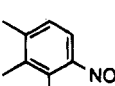

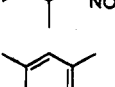

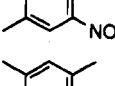

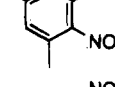



Table 2. Nitrosation of Substituted Anisoles with NO⁺ BF₄⁻

Substituted Anisole (ArH)	Temp. (°C)	Time (h)	Conv. ^b (%)	ArNO	Yield ^c (%)
	25	0.5	100		100 (87)
	0	0.5	100		100 (83)
	0	0.5	100		100 (82)
	25	0.5	30	— ^d	—
	25	1.5	72		83 (70)
	0	0.5	100		95 (84)
	25	30	50		50
	25	30	50		40
	25	30	10	—	—

^a All reactions with 1.33 mmol of arene and 4.00 mmol of NOBF₄ in 40 mL acetonitrile. ^b Based on recovered arene. ^c Based on consumed arene. Determined by GC using the internal standard method. Isolated yield in parenthesis. ^d Traces of a nitrosomethoxytoluene (~3%), a nitromethoxytoluene (10%), and a biaryl dimer (3%) identified by GC-MS.

The isomeric hemimellitene (entry 5) and pseudocumene (entry 6) similarly gave a single nitrosated trimethylbenzene in high yields. However, striking differences in reactivity were noted in the isomeric dimethyl- and tetramethylbenzenes—*m*-xylene (entry 3) being much more readily nitrosated than either *o*- or *p*-xylene and prehnitene (entry 8). It is particularly noteworthy that prehnitene was transformed to the corresponding nitrosotetramethylbenzene under conditions in which durene (entry 9) was essentially unreacted. With each polymethylbenzene, nitrosation always occurred selectively, with substitution occurring at a *para* position relative to a methyl substituent. In those instances where nitrosation was ineffective (toluene, *o/p*-xylene, durene, and pentamethylbenzene), the nitrosoarene was formed in low yield (or absent) and nitration was the predominant side reaction, as described in the Experimental Section. Interestingly, the electron-rich donors durene

Table 3. Nitrosation of Polymethylbenzenes with $\text{NO}^+ \text{BF}_4^-$ ^a

Polymethylbenzene (ArH)	Time (h)	Conv. ^b (%)	ArNO	Yield ^c (%)
	24	3	- ^d	-
	24	4.5	- ^e	42 (-)
	24	85		89 (70)
	24	3.0	- ^e	14 (-)
	5	65		85 (67)
	5	75		80 (65)
	5	85		85 (78)
	3	50		68 (55)
	5.5	13	- ^f	-
	8	13	- ^g	-
	5	3	- ^h	-

^a All reactions with 1.33 mmol of alkylbenzene and 4.00 mmol of NOBF_4 in 40 mL of acetonitrile at room temperature. ^b Based on recovered alkylbenzene. ^c Based on consumed alkylbenzene. Determined by GC using the internal standard method. Isolated yield in paranthesis. ^d The only products observed were *o*-nitrotoluene and *p*-nitrotoluene (2:1). ^e These nitrosoarenes not isolated. See Experimental Section. ^f 3-Nitroindurene (10%), 2,2',3,4,4',5,5'-heptamethyldiphenylmethane the only products detected. ^g Nitropentamethylbenzene (9%), 2,2',3,3',4,4',5,5',6-nonamethyldiphenylmethane the only products detected. ^h Pentamethylbenzylacetamide (2%) the sole product.

and pentamethylbenzene were relatively unreactive, and they afforded low yields of the corresponding nitro products together with the oxidative (diphenylmethane) dimers,⁹ *i.e.*



[Compare with the formation of the oxidative biaryl dimer¹⁰ during the nitrosation of *p*-methylanisole above.]

Table 4. Effect of Added Bases on Mesitylene Nitrosation with $\text{NO}^+ \text{BF}_4^-$ ^a

added base	(mmol)	conv ^b (%)	yield ^c (%)
none	0.00	32	91
pyridine	0.71	31	93
2,6-lutidine	0.71	28	92
2,4,6-collidine	0.71	36	87
2,6-di- <i>tert</i> -butyl-4-methylpyridine	0.71	23	94
bis-1,8-(dimethylamino)pyridine	0.71	5	90
triethylamine	0.71	0	0
sodium carbonate	0.71	<1	50
calcium acetate	0.71	14	95
calcium oxide	0.71	10	95

^a All reactions with 0.71 mmol of mesitylene and 2.1 mmol of $\text{NO}^+ \text{BF}_4^-$ in 28 mL of acetonitrile for 1.5 h in the dark. ^b Based on unreacted mesitylene (determined by GC). ^c Based on consumed mesitylene (determined by GC).

2. Effect of Bases on Aromatic Nitrosation with Nitrosonium Salt. In order to obviate the (possible) deleterious effects of the acid ($\text{H}^+ \text{BF}_4^-$) formed in the course of aromatic nitrosation according to eqs 3 and 4, various organic and inorganic bases were examined as additives (Table 4). Since the nitrosonium cation is itself a (Lewis) acid,¹¹ care was exercised in the choice of soluble organic bases with graded degrees of steric hindrance (entries 2–6). The insoluble inorganic bases (entries 8–10) were intended to maximize any beneficial effects of heterogeneity.

Examination of the conversion/yield obtained in the nitrosation of mesitylene under these conditions (Table IV, columns 3/4) shows that the strong, relatively unhindered base triethylamine (entry 7) shut down the nitrosation completely. Moreover the proton sponge (entry 6) and the inorganic bases exerted a strong negative influence. Otherwise, the effect of added pyridine bases was at best a slight increase in conversion (for details, see the Experimental Section).

3. Deuterium Isotope Effect on Aromatic Nitrosation with Nitrosonium Tetrafluoroborate. The kinetic isotope effect in the nitrosation of anisole and mesitylene was examined by intermolecular competition. Initially, anisole-*d*₅ and mesitylene-*d*₃ were prepared in >99% isotopic purity by methylation of phenol-*d*₆ with dimethyl sulfate¹² and by multiple exchanges of mesitylene with trifluoroacetic acid-*d*₁₃ respectively. Equimolar amounts of the aromatic (protio/deuterio) donors were exposed in various amounts to nitrosonium tetrafluoroborate, and the nitrosations were carried out to low conversions by quenching the reaction at suitable times (see Table 5). The deuterium kinetic isotope effects determined by the mass spectral analysis of both the recovered aromatic donor as well as the nitrosoarene are listed in the last column of Table 5 (see Experimental Section for details).

4. Visual and Spectral Changes Observed in Aromatic Nitrosation with Nitrosonium Tetrafluoroborate. The straightforward stoichiometry, simply expressed by eqs 2–4, belies the complex series of intense color changes that accompanied aromatic nitrosation with $\text{NO}^+ \text{BF}_4^-$ in acetonitrile solution. For example, immediately upon the addition of anisole to the colorless

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Table 5. Deuterium Kinetic Isotope Effect on the Nitrosation of Mesitylene and Anisole with NO⁺ BF₄⁻ ^a

[ArH]/[ArD] ^a (mmol/mmol)	NOBF ₄ (mmol)	CH ₃ CN (mL)	time (h)	conv ^b (%)	yield ^c (%)	[ArH]/[ArD] ^{a,e}	[ArNO]/[Ar _d NO] ^{a,f}
MES/MES- <i>d</i> ₃							
(1.70/1.70)	0.34	10	3.25	2	90	0.94	3.8 (3.9)
(3.00/3.00)	1.06	10	4.50	3	95	0.97	3.6 (4.0)
(0.29/0.31)	2.00	10	0.75	11	93	0.81	3.8 (3.5)
AN/AN- <i>d</i> ₅							
(2.21/1.84)	0.30	5	0.40	7	100	1.05	7.4 (8.0)
(0.16/0.14)	1.00	10	0.16	55	95	0.26	6.1 (5.0)

^a Determined by GC-MS analysis. MES = mesitylene, AN = anisole. ^b Based on unreacted aromatic donor. ^c Based on consumed aromatic donor. ^e Isotopic composition of unreacted aromatic donor. ^f Isotopic composition of nitrosoarene. Value in parenthesis calculated from the change in isotopic ratio of the unreacted aromatic donor.

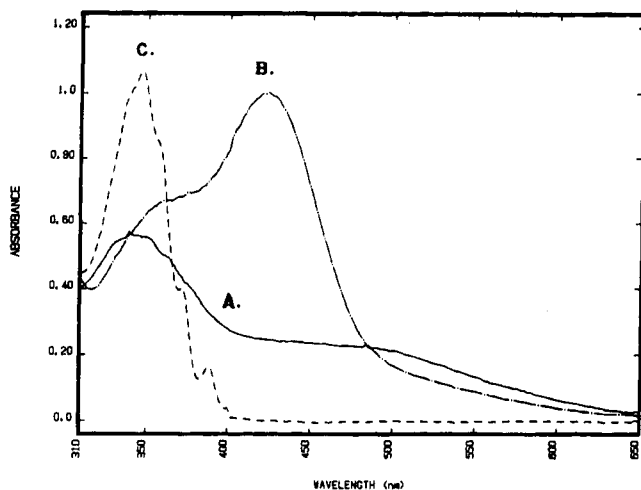


Figure 1. Spectral changes attendant upon the treatment of 2×10^{-2} M anisole with 7×10^{-3} M NO⁺ BF₄⁻ in acetonitrile at 0 °C: (A) immediately upon mixing, (B) after 10 min, and (C) upon the aqueous quench after 15 min.

solution of nitrosonium salt, a deep red coloration developed. As the solution was stirred at 25 °C, the red color faded and it was steadily replaced by a yellow component. The final bright yellow mixture rapidly yielded a completely colorless solution when it was quenched with water. Essentially the same series of the color changes occurred during the nitrosation of mesitylene with NO⁺ BF₄⁻ in acetonitrile.

The quantitative effects of the dramatic color changes are illustrated in Figure 1 by the series of three (typical) absorption spectra (A–C) which characterized the three distinct stages of aromatic nitrosation.

Spectrum A obtained initially was persistent when anisole and NO⁺ BF₄⁻ were mixed at low temperature (–40 °C). Figure 2A illustrates how the intensity of the red coloration was subject to progressive enhancement upon incremental additions of more anisole, and the corresponding spectral change monitored at the absorbance maximum (A_{342}) followed the Benesi–Hildebrand relationship, *i.e.*¹⁴

$$\frac{[\text{NO}^+ \text{BF}_4^-]}{A_{342}} = \frac{1}{K_{\text{EDA}} \epsilon_{342} [\text{ArH}]} + \frac{1}{\epsilon_{342}} \quad (5)$$

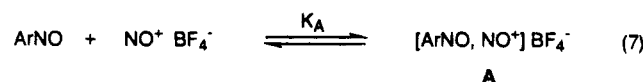
where ArH = anisole. The linear relationship shown in the inset of Figure 2A yielded values of $K_{\text{EDA}} = 2.5 \text{ M}^{-1}$ and $\epsilon_{342} = 1000 \text{ M}^{-1} \text{ cm}^{-1}$ at –40 °C. A close inspection of the spectra in Figure 2A indicated the presence of overlapping bands—a high-energy band with a distinct

maximum at ~350 nm and a second broad absorption extending beyond 700 nm. The digital (Gaussian) deconvolution in Figure 2B is indeed consistent with two components: band I with $\lambda_{\text{max}} = 342 \text{ nm}$ (full width at half maximum (fwhm) = 95 cm^{-1}) and band II with $\lambda_{\text{max}} = 467 \text{ nm}$ (fwhm = 77 cm^{-1}). A series of other substituted anisoles yielded similar colorations when treated with NO⁺ BF₄⁻ at –40 °C in acetonitrile solution. However, the color intensity was markedly dependent on the substituent. For example, the additions of anisole, 2-methylanisole and 3,5-dimethylanisole (in equiv amounts) to aliquots of a standard solution of NO⁺ BF₄⁻ at –40 °C resulted in very pale pink, light red, and dark red-brown solutions, respectively, the corresponding absorption spectra of which are shown in Figure 3. [Note that each absorption spectrum also consisted of the pair of overlapping components I and II (*vide supra*).] These qualitative color changes were quantified by evaluating the formation constant K_{EDA} in eq 6



by the application of the Benesi–Hildebrand relationship (eq 5). It is thus noteworthy that the formation constants listed in Table 6 increased by over 2 orders of magnitude from 4-bromoanisole to 4-methylanisole. Such a structural dependence of K_{EDA} in the NO⁺ complexes with substituted anisoles is also compared with that observed earlier with the series of polymethylbenzenes from *p*-xylene to pentamethylbenzene.¹⁵ Most importantly, the variation of the spectral band energies ($h\nu_{\text{CT}}$) in Table 7 (column 5) with the aromatic donor strength (column 2) established the formation of the electron donor–acceptor or EDA complex in eq 6 to be charge-transfer in character as described by Mulliken.¹⁶

Spectrum B of the yellow solution steadily increased in intensity with the increasing conversion of anisole, as illustrated by the series of time-lapse spectra in Figure 4. Interestingly, the same absorption spectrum with $\lambda_{\text{max}} = 422 \text{ nm}$ (see inset) was independently obtained when NO⁺ BF₄⁻ was added to a solution of pure 4-nitrosoanisole in acetonitrile solution. Spectral titration was consistent with a large association constant of $K_{\text{A}} > 40\,000 \text{ M}^{-1}$ and an enhanced extinction coefficient of $\epsilon_{\text{A}} = 25\,000 \text{ M}^{-1} \text{ cm}^{-1}$ for the 1:1 adduct A, *i.e.*



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

(14) (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.

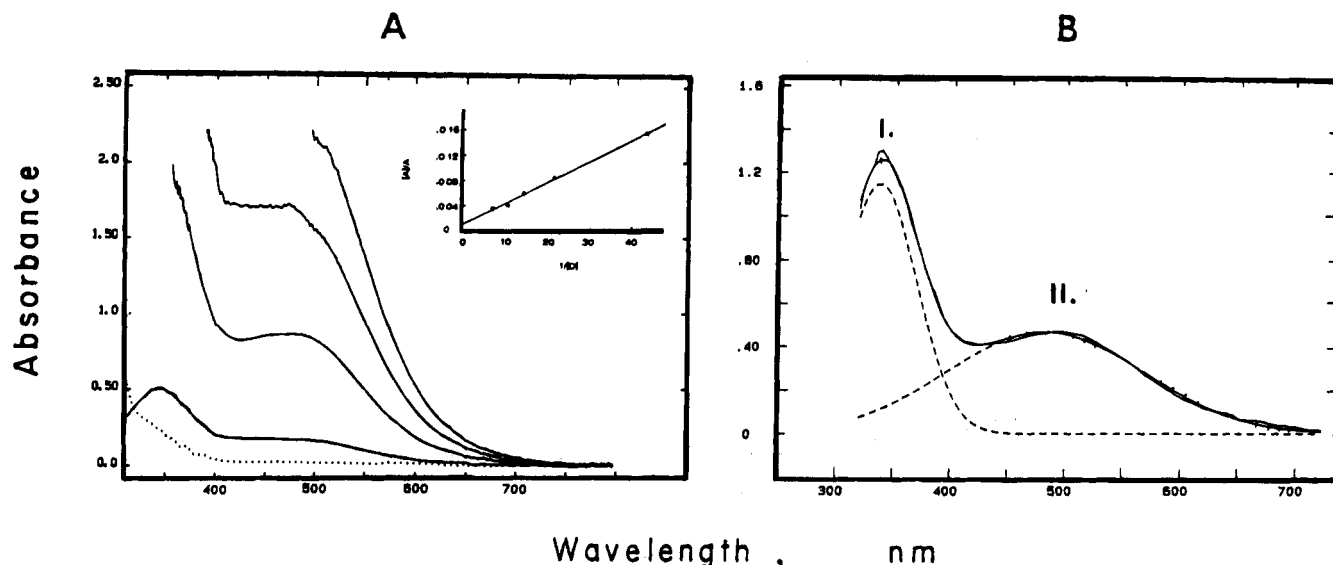


Figure 2. (A) Charge-transfer spectrum from 0.003 M $\text{NO}^+ \text{BF}_4^-$ and (bottom-to-top) 0, 0.028, 0.074, 0.12, and 0.166 M anisole in acetonitrile at -40°C . Inset: Benesi-Hildebrand plot of $[\text{NO}^+ \text{BF}_4^-]/A_{342}$ versus $[\text{anisole}]^{-1}$. (B) Charge-transfer spectrum of 0.004 M 4-methylanisole at 0.005 M $\text{NO}^+ \text{BF}_4^-$ in acetonitrile showing the Gaussian deconvolution into bands I and II (see Table 7).

Table 6. Formation of Aromatic EDA Complexes with Nitrosonium^a

aromatic donor	(10^3 M) ^b	$\text{NO}^+ \text{BF}_4^-$ (10^3 M)	λ_{mon}^c (nm)	K_{EDA} (M^{-1})	ϵ_{CT} ($\text{M}^{-1} \text{cm}^{-1}$)
4-methylanisole ^d	(4.0–16.0)	1.0	346	62	980
anisole ^d	(23–194)	5.0	506	63	370
			344	2.5	1000
4-bromoanisole ^d	(120–400)	28.0	480	1.5	635
			340	0.35	470
<i>p</i> -xylene	(3.9–1.4) ^e	1.5	500	0.6	100
			336	31	1300
mesitylene	(13–93) ^e	6.3	520	27	81
			345	56	2100
durene	(0.4–9.3) ^e	0.36	336	450	1100
pentamethylbenzene	(0.3–1.5) ^e	0.2	337	5100	2400

^a In acetonitrile solution at 25°C . ^b Lower–upper concentration range. ^c Monitoring wavelength. ^d At -40°C . ^e Data from ref 15.

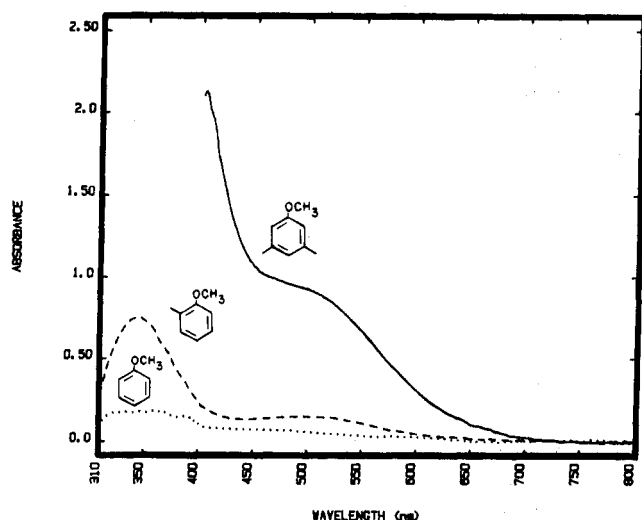


Figure 3. Bathochromic/hyperchromic shifts of the charge-transfer bands of aromatic EDA complexes with 0.005 M $\text{NO}^+ \text{BF}_4^-$ and 0.005 M anisole (—), 0.005 M 2-methylanisole (---), and 0.005 M 3,5-dimethylanisole (· · ·) at -40°C .

from $\text{ArNO} = 4\text{-nitrosoanisole}$ at 25°C . Indeed all the nitroso derivatives of the anisoles and polymethylbenzenes in Tables 2 and 3 exhibited similar spectral changes when treated with $\text{NO}^+ \text{BF}_4^-$ in acetonitrile solutions. The association constants and spectral pa-

Table 7. Charge-Transfer Spectra of Aromatic EDA Complexes with Nitrosonium^a

aromatic donor	IP^b (eV)	$h\nu_{\text{CT(I)}}$ (eV)	fwhm^c (10^2 cm^{-1})	$h\nu_{\text{CT(II)}}$ (eV)	fwhm^c (10^2 cm^{-1})
anisole	8.39	3.61	95	2.63	77
2-methylanisole	8.24	3.58	72	2.60	122
4-methylanisole	8.18	3.65	78	2.56	106
3,5-dimethylanisole	<i>d</i>	3.49	81	2.54	96
2-bromoanisole	<i>d</i>	3.51	87	2.68	119
4-bromoanisole	8.49	3.71	109	2.58	125
1,4-dimethylbenzene ^e	8.44	3.65	69	2.4	60
1,3,5-trimethylbenzene ^e	8.42	3.55	76	2.6	50
1,2,4-trimethylbenzene ^e	8.27	3.59	74	2.5	45
1,2,4,5-tetramethylbenzene ^e	8.05	3.67	71	2.6	50
pentamethylbenzene ^e	7.92	3.70	70	2.5	50

^a In acetonitrile solution with $\sim 10^{-3} \text{ M}$ $\text{NO}^+ \text{BF}_4^-$ and excess aromatic donor at -40°C . ^b Data from refs 25 and 64. ^c Full width at half maximum. ^d Not determined. ^e At 25°C . Data from ref 15.

rameters of some representative examples are collected in Table 8.

Spectrum C corresponded to that of 4-nitrosoanisole dissolved in acetonitrile. The fact that it derived from spectrum B by the addition of water confirmed the reversible formation of the nitrosonium adduct A in eq 7. Indeed, the presence of a single isosbestic point for the spectral changes in Figure 5 showed that 4-nitrosoanisole was quantitatively (re)generated from adduct A, presumably *via* the catalytic (irreversible) de-

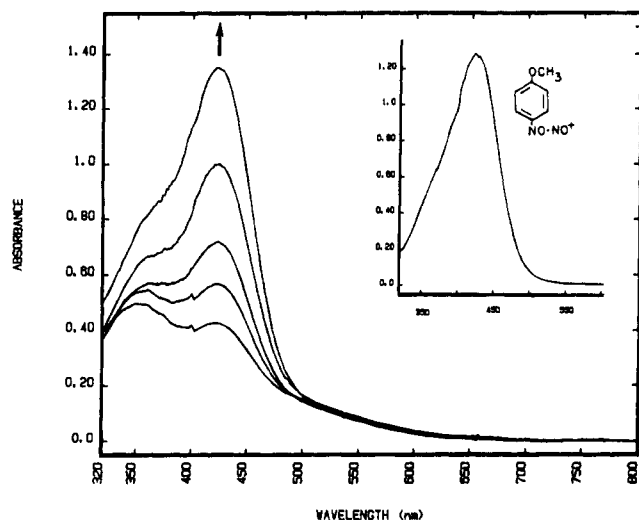

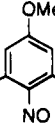
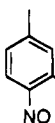
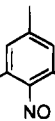


Figure 4. Growth of spectrum B at 2 min intervals (bottom-to-top) following the mixing of 2×10^{-3} M anisole and 7×10^{-3} M $\text{NO}^+ \text{BF}_4^-$ in acetonitrile solution at 0 °C. Inset: Absorption spectrum of adduct A from 7×10^{-5} M 4-nitrosoanisole and 0.003 M $\text{NO}^+ \text{BF}_4^-$ in acetonitrile at 25 °C.

Table 8. Association of Nitrosoarenes with the Nitrosonium Cation. Spectral Properties and Association Constants of Adducts A^a

Nitrosoarene	(10^5 M)	NOBF_4 (10^3 M)	λ_{max} (nm)	K_A^b (M^{-1})	ϵ^b ($\text{M}^{-1}\text{cm}^{-1}$)
	7.30	3.0 - 15.0	422	> 40,000	25,000
	3.45	3.0 - 15.0	398	^c	18,300
	5.50	3.0 - 15.0	382	^c	35,000
	8.39	3.0 - 15.0	389	2,000	11,500

^a In acetonitrile solution at 25 °C. ^b Evaluated at the maximum.

^c Not determined.

struction of NO^+ by water.¹⁷ [Note that nitrosoarenes show strong aromatic ($\pi-\pi^*$) absorptions in the UV region ($\lambda \sim 330$ nm, $\epsilon \sim 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), and the very weak (n,π^*) transitions at ~ 750 nm ($\epsilon < 50 \text{ M}^{-1} \text{ cm}^{-1}$) are responsible for the green to blue colors in solution.²⁰]

(17) The facile hydration of the nitrosonium cation is shown in spectrum C (Figure 1) by the vibrational fine structure of nitrous acid at $\lambda = 338, 348, 358, 372,$ and 389 nm.¹⁸ Water is regenerated by the subsequent conversion of nitrous acid to dinitrogen trioxide.¹⁹

(18) Kortum, G. Z. *Phys. Chem. B* **1939**, *43*, 418.

(19) Markovits, G. Y.; Schwartz, S. E.; Newman, L. *Inorg. Chem.* **1981**, *20*, 445.

(20) Mijs, W. J.; Hoekstra, S. E.; Ulman, R. M.; Havinga, E. *Rec. Trav. Chim. Pays-Bas* **1958**, *77*, 746.

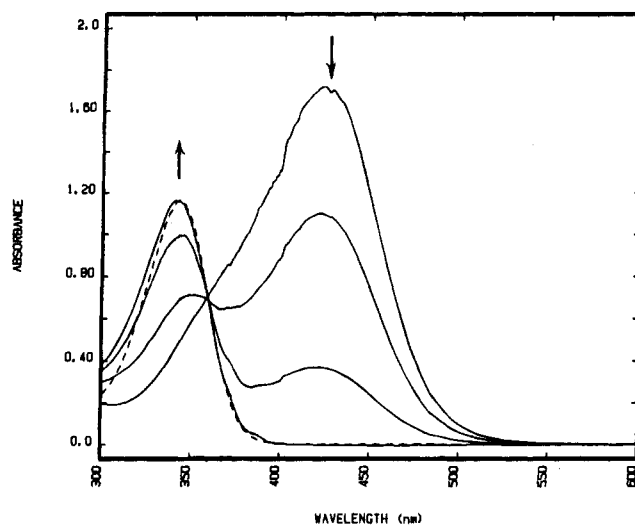
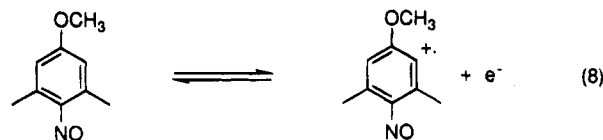


Figure 5. Spectral changes attendant upon the treatment of adduct A (formed from 7×10^{-5} M 4-nitrosoanisole and 0.003 M $\text{NO}^+ \text{BF}_4^-$) with incremental amounts of water relative to the absorption spectrum of 7×10^{-5} M 4-nitrosoanisole alone (---).

5. Nitrosoarenes as Electron Donors. The facile association of ArNO and NO^+ , with values of K_A in Table 8 that are substantially larger than the formation constants of the aromatic complexes [ArH, NO^+] in Table 6, suggested that the nitrosated products were better electron donors than the aromatic hydrocarbon or ether from whence they were derived! Indeed, most of the nitroso derivatives in Tables 9 and 10 were reversibly oxidized at moderate potentials of $E_{1/2} \sim 1.3 \pm 0.3$ V vs SCE. For example, the initial positive-scan cyclic voltammogram (CV) of 4-nitrosoanisole at a platinum electrode in acetonitrile containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) showed a well-defined anodic peak at $E_p = 1.50$ V vs SCE and a coupled cathodic peak at 1.44 V on the reverse scan, with the cathodic/anodic peak current ratio $i_c/i_a > 0.6$ at a scan rate of $v = 100 \text{ mV s}^{-1}$. The peak current ratio of unity was approached for 4-nitrosoanisole at higher scan rates, and a theoretical value²¹ of $i_c/i_a = 1.0$ was attained with the 3,5-dimethyl analogue at $v = 500 \text{ mV s}^{-1}$ (see Figure 6). Calibration of the peak currents with the aid of a ferrocene internal standard indicated a one-electron oxidation to the cation-radical, *e.g.*



Under the same electrochemical conditions, the parent polymethylbenzenes and substituted anisoles were oxidized irreversibly, with anodic peak potentials that were significantly more positive than those of the nitroso derivatives, as shown by the results in Tables 9 and 10.

Discussion

Various polymethylbenzenes and anisoles are selectively nitrosated with the nitrosonium salt $\text{NO}^+ \text{BF}_4^-$ in acetonitrile solution at room temperature or below.

(21) See Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

Table 9. Substituted Anisoles and Their Nitroso Derivatives as Electron Donors^a

Anisole (ArH)	E_p^b	ArNO	E_p^b	$E_{1/2}^b$	ΔE_p (mV)
	1.72		1.50	1.47	220
	1.61		1.46	1.42	150
	1.68		1.38	1.34	300
	1.55		1.19	1.15	360
	1.72		1.51	1.47	210
	1.87		1.73	1.62	140
	1.58				
	1.83				

^a In acetonitrile containing 0.1 M Bu₄N⁺PF₆⁻ at $v = 100 \text{ mV s}^{-1}$ and 25 °C.

^b V vs. SCE.

Table 10. Electrochemical Oxidation of Polymethylbenzenes and Their Nitroso Derivatives^a

Methylbenzene (ArH)	E_p^b	ArNO	E_p^b	$E_{1/2}^b$	ΔE_p (mV)
	2.62		1.85	-	770
	2.25		1.80	-	425
	2.11		1.78	-	330
	2.09		1.57	1.53	520
	1.90		1.58	1.53	320
	2.02		1.42	1.38	600
	1.76		1.53	1.44	230
	1.79		1.41	1.37	380

^a In acetonitrile containing 0.1 M Bu₄⁺PF₆⁻ at $v = 100 \text{ mV s}^{-1}$ and 25 °C.

^b V vs. SCE.

1. Anomalous Reactivity of Aromatic Donors in Nitrosations with the Nitrosonium Salt NO⁺BF₄⁻.

Although no attempt was made to carry out a detailed kinetic study of aromatic nitrosation with NO⁺BF₄⁻, the time/conversions in Tables 2 and 3 are sufficient to provide an adequate guide for assessing the reactivity of the various aromatic donors toward nitrosonium cation. For example, anisole, *o*- and *m*-methylanisole, and 3,5-dimethylanisole are the most reactive substrates, as judged by the complete conversions that can be achieved within 30 min even at 0 °C. By comparison, the most reactive polymethylbenzenes, *viz.* *m*-xylene and mesitylene, require 24 h to attain 85% conversion at 25 °C. Such a differentiation in aromatic reactivity with variation of the donor strength (as evaluated by the ionization potential in Table 7)²² does not generally accord with the pattern established in other electrophilic aromatic substitutions,²³ including nitration.²⁴ Indeed, a closer inspection of the reactivity trends in Tables 2 and 3 reveals some distinctive anomalies in aromatic nitrosation. For example, *m*-xylene is substantially more reactive than the *para* isomer, and the same is true for the isomeric

(22) Foster, R. *Organic Charge-Transfer Complexes*; Academic: New York, 1969.

(23) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 7240. See also Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1227.

(24) Kim, E. K.; Lee, K. Y.; Kochi, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 1756.

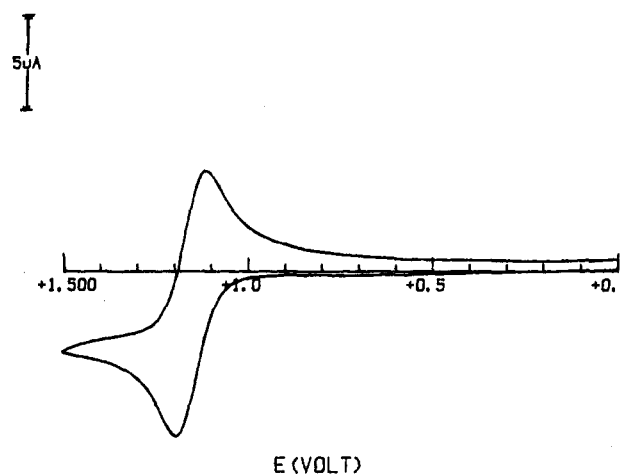
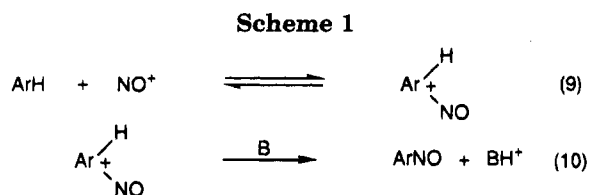


Figure 6. Initial positive scan cyclic voltammogram of $5 \times 10^{-3} \text{ M}$ 3,5-dimethyl-4-nitrosoanisole in acetonitrile containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate at $v = 100 \text{ mV s}^{-1}$.

m- and *p*-methylanisoles, as well as *m*- and *p*-bromoanisoles. Furthermore, the *ortho* isomer has comparable reactivity in the case of *m*-methylanisole and *m*-bromoanisole, but it is significantly less reactive than *m*-xylene. [Note that aromatic donor strengths are generally rather insensitive to the substitution pattern;

for example, the ionization potentials of *o*-, *m*- and *p*-xylenes are 8.56, 8.56 and 8.44 eV, respectively.^{25]} Finally, the best aromatic donors examined in this study, *viz.* durene, pentamethylbenzene, and hexamethylbenzene, are essentially unreactive to $\text{NO}^+ \text{BF}_4^-$ in acetonitrile solution.

2. Deprotonation as a Critical Step in Aromatic Nitrosation. In aromatic nitration, the linear variation of the second-order rate constant ($\log k_2$) with the strength of the aromatic donor accords with the rate-limiting formation of the Wheland intermediate.^{24,26} The subsequent proton loss is fast and occurs with no kinetic deuterium isotope effect.²⁸ By contrast, the results in Table 5 show that the nitrosation of mesitylene and anisole proceeds with a substantial deuterium kinetic isotope effect. If aromatic nitrosation is considered to proceed via an analogous pathway involving NO^+ addition to the aromatic π -donor, there is no spectroscopic evidence for the buildup of the Wheland intermediate.¹⁵ Accordingly, the most economical formulation consistent with the observed kinetic isotope effect includes a reversible addition process. In aromatic nitrosations with $\text{NO}^+ \text{BF}_4^-$, the solvent is most likely to be the Brønsted base (*i.e.* $\text{B} = \text{CH}_3\text{CN}$) required for the (slow) deprotonation of the Wheland intermediate.^{29,30} According to Scheme 1, the reactivity and positional selectivity of various



aromatic donors, as described in Tables 2 and 3, are both critically dependent on the facility of the deprotonation step (eq 10).³¹ On this basis, we attribute the low reactivity of $\text{NO}^+ \text{BF}_4^-$ toward the electron-rich donors durene and pentamethylbenzene to the relatively slow deprotonation rate from the heavily methylated Wheland intermediates in acetonitrile solutions. Likewise, the strong propensity for the nitrosation of the various anisoles to occur selectively at the *para* position can be ascribed to the preferential formation of the *para*-Wheland intermediate, which may also undergo a faster rate of deprotonation relative to *ortho* attack.

(25) Howell, J. D.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

(26) Note that the rates of aromatic nitration carried out with the nitronium salt $\text{NO}_2^+ \text{BF}_4^-$ are leveled, since benzene nitration is diffusion controlled.²⁷

(27) Ridd, J. H. *Adv. Phys. Org. Chem.* **1968**, *16*, 1.

(28) Melander, L. *Arkiv. Kemi.* **1950**, *2*, 211. Melander, L. *Isotope Effects on Reaction Rates*; Ronald: New York, 1960.

(29) Although others³⁻⁶ have discussed the slow deprotonation of the Wheland intermediate, the possibility of its reversible formation, as in Scheme 1, has not been addressed (probably owing to the strong acid conditions employed heretofore).

(30) Deprotonation of the Wheland intermediate in eq 10 is irreversible since control experiments demonstrate that nitrosoarenes do not revert to the starting materials in the presence of added acid ($\text{H}^+ \text{BF}_4^-$); see Experimental Section for details.

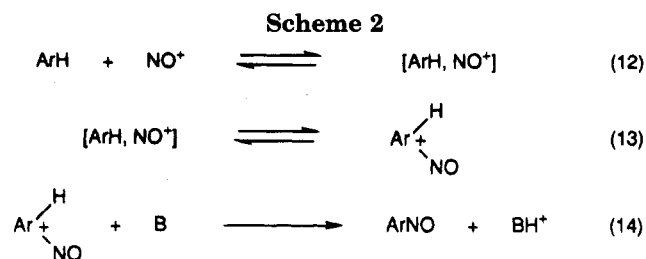
(31) (a) It is important to note that aromatic nitrosation is facile when the leaving group is not a proton but a relatively stabilized metal cation such as $(\text{CH}_3)_3\text{Si}^+$, CH_3Hg^+ , Ph_3Sn^+ , ClMg^+ , $(\text{CF}_3\text{CO}_2)_2\text{Tl}^+$, *etc.*³² For example, nitrosobenzene is readily formed in excellent yields via *ipso* attack during the nitrosation of phenylmercuric chloride with sodium nitrite and trifluoroacetic acid.^{32b} (b) The lower (overall) reactivity of some electron-rich polymethylbenzenes and anisoles may also be due to the enhanced stability of the precursor EDA complexes (see Kim, E. K., *et al.* in ref 15). The extent to which *ipso* adducts of NO^+ contributes is undetermined.

Attempts to enhance the nitrosation rates with added bases (see Table 4) are futile, unless they can selectively discriminate between the desired H^+ removal in eq 10 and the inadvertent (nucleophilic) complexation of NO^+ ,^{11,33} *i.e.*



Indeed the steric requirements for both processes are practically indistinguishable, and even the most sterically hindered base we had available, *viz.* 2,6-di-*tert*-butyl-4-methylpyridine, is unable to effect a significant enhancement in either the conversion or yield (Table 4). We thus conclude that if a more efficient procedure is to be developed for the nitrosation of those aromatic donors that are incompletely converted in Tables 2 and 3, it will require a solvent (or added base) more basic than acetonitrile,³⁴ yet able to leave the reactive nitrosonium electrophile unfettered.¹¹ This conclusion readily accounts for the limited effectiveness of the conventional procedure (based on nitrite salt and mineral acid) to nitrosate the polymethylbenzenes and anisoles with the high conversions and yields in Tables 2 and 3.³⁵ In other words, the optimum conditions (strong acid) required to generate the active electrophile in eq 1 effectively counteracts the beneficial effects of any base for the deprotonation of the Wheland intermediate in eq 10.

3. Polymethylbenzenes and Anisoles as Electron Donors with Nitrosonium Acceptor. As aromatic compounds, the polymethylbenzenes and anisoles in Tables 2 and 3 are among the most electron-rich donors available.^{25,36} As such, the charge-transfer spectrum, illustrated in Figure 2 and tabulated in Tables 6 and 7, represents the rapid, preequilibrium formation of the EDA complex according to eq 6. With the inclusion of the EDA complex, the more general mechanism for electrophilic aromatic nitrosation with $\text{NO}^+ \text{BF}_4^-$ can be presented as³⁰ in Scheme 2.



Mulliken theory predicts that the degree of charge transfer in EDA complexes depends on the ionization potential of the donor and the electron affinity of the acceptor.^{16,22} For the series of $[\text{ArH}, \text{NO}^+]$ complexes in eq 12, complete electron transfer from ArH to NO^+ will

(32) (a) Coombes, R. G. In *Comprehensive Organic Chemistry*; Sutherland, I. O., Ed.; Pergamon: Oxford, 1979; Vol. 2, p 310. See also under nitrosodemercuration, nitrosodethallation, nitrosodesilylation, nitrosodestannylation, *etc.* in Taylor, R. in ref 2. (b) Uemura, S.; Toshimatsu, A.; Okano, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1076; *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2582.

(33) Lee, K. Y.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1994**, 237 and references therein.

(34) For the proton affinities of other weak bases like acetonitrile, see Ford, G. P.; Scribner, J. D. *J. Comput. Chem.* **1983**, *4*, 594 and Knight, J. S.; Freeman, C. G.; McEwan, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1404.

(35) The nitrosation of only a few anisoles in moderate yield (and no methylbenzene) with nitrite/acid are reported. See, *e.g.* Hodgson, H. H.; Crouch, E. A. C. *J. Chem. Soc.* **1943**, 221 and Radner, F.; Wall, A.; Loncar, M. *Acta Chem. Scand.* **1990**, *44*, 152.

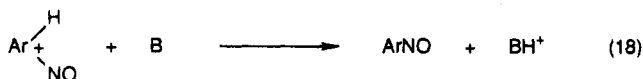
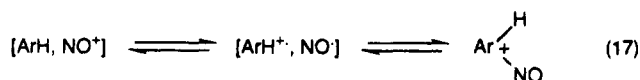
(36) Rathore, R.; Bosch, E.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1157.

lead to the donor cation radical $\text{ArH}^{\bullet+}$ and nitric oxide (NO). The driving force for such an electron transfer, *i.e.*



is evaluated in solution by the reversible oxidation potential of ArH and the reduction potential of NO^+ . For the most electron-rich donor hexamethylbenzene with $E_{\text{ox}} = 1.58 \text{ V vs SCE}$,²⁵ the driving force for electron transfer in eq 12 is evaluated as $-\Delta G_0 = 12 \text{ kcal mol}^{-1}$ ³⁷ based on $E_{\text{red}} = 1.28 \text{ V vs SCE}$ for the reduction of NO^+ .³⁸ Such an exergonic driving force for electron transfer predicts that a substantial concentration of aromatic cation radicals can exist in solution. Indeed, the small but discrete amounts of oxidative dimeric biphenyls and diphenylmethanes formed as byproducts from the treatment of *p*-methylanisole, durene, and pentamethylbenzene (see Tables 2 and 3) are symptomatic of cation radical intermediates during aromatic nitrosation.^{9,10} Such an observation raises the possibility that NO^+ attack on the aromatic donor is a two-step process,³⁹ as shown in Scheme 3. The extent to which the radical ion

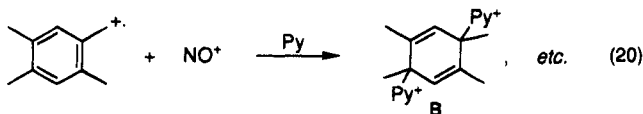
Scheme 3



pair in eq 17 suffers diffusive separation can lead to dimeric byproducts,⁴⁰ *e.g.*



The two-step mechanism in eq 17 also accounts for the unusual behavior of durene toward NO^+ . For example, the results in Table 3 show that a mixture of durene and $\text{NO}^+ \text{BF}_4^-$ is essentially unreactive. However, a recent study³³ describes how the same mixture of durene and $\text{NO}^+ \text{BF}_4^-$ with added pyridine leads to the *ipso* adduct **B** in excellent yield. According to Scheme 3, the *ipso* adduct **B** derives from the irreversible (nucleophilic) addition of pyridine (Py) to the durene cation radical, *i.e.*



which otherwise undergoes reversible back electron transfer (eq 17) when the rate of deprotonation is too slow

(37) Bockman, T. M.; Karpinski, Z.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 1970.

(38) Lee, K. Y.; Kuchynka, D. J.; Kochi, J. K. *Inorg. Chem.* **1990**, *29*, 4196. For the corresponding properties of NO_2^+ , see Lee, K. Y.; Amatore, C.; Kochi, J. K. *J. Phys. Chem.* **1991**, *95*, 1285.

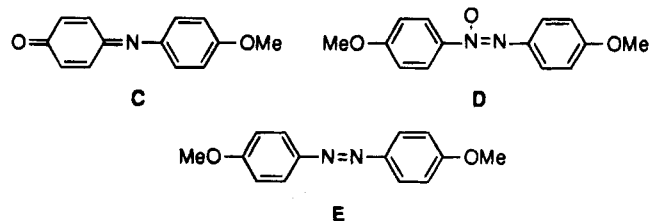
(39) The formation of aromatic cation radicals *via* the adiabatic electron transfer in eq 17 is akin to the photochemical activation of the EDA complex formed in eq 6.³⁷ Thus our inability to promote aromatic nitrosation by the direct irradiation of the charge-transfer absorption band (see Experimental Section) is attributed to the slow deprotonation rate in eq 18 relative to fast back electron transfer in eq 17.³⁷

(40) Yoshida, S. *Electrooxidation in Organic Chemistry*; Wiley: New York, 1984. For a discussion, see also Kim, E. K. *et al.* in ref 15.

to compete. On the other hand, the electrophilic mechanism in Scheme 2 cannot easily account for the ready formation of the *ipso* adduct **B** from durene and $\text{NO}^+ \text{BF}_4^-$ in the presence of added pyridine.

4. Nitrosoaromatic Products as Electron Donors with the Nitrosonium Acceptor. The comparative electrochemical behavior of polymethylbenzenes and anisoles in Tables 9 and 10 establish the relative donor properties of the nitrosated products. Most importantly, the difference in donor properties are reflected in association constants of the $[\text{ArNO}, \text{NO}^+]$ complex in Table 8 which are about 2 orders of magnitude larger than the formation constant of the precursor (EDA) complex in Table 6.

The strong association of the nitrosoaromatic product with the nitrosonium cation in eq 7 is observed as a bright yellow color (spectrum B) of the final reaction mixture. It thus accounts for the requirement of excess $\text{NO}^+ \text{BF}_4^-$ to effect the maximum conversion of the aromatic donor in the nitrosation procedure (see Table 1). Although we have been unable to grow a single crystal of adduct **A** suitable for X-ray crystallography, we tentatively suggest that NO^+ is σ -bound to the nitroso group rather than π -bound to the aromatic ring in a manner previously established for the precursor (EDA) complex.¹⁵ Furthermore, it is not known whether NO^+ bonding occurs before or after the nitrosoaromatic product is formed. If the binding occurs at the earlier stage it could aid in the deprotonation of the Wheland intermediate.⁴¹ Moreover, NO^+ binding to the nitrosoanisoles is responsible for the decreased yields of nitrosoanisoles upon the prolonged exposures described in Table 1 (especially entry 4) that lead to the condensation products identified as



(see Experimental Section for details). Thus, quinoneanil **C** compares with an authentic sample prepared from benzoquinone and anisidine,⁴² and it clearly derives from the oxidative demethylation of the first-formed nitrosoanisole probably *via* adduct **A**.⁴³ Analogously, the azoxybenzene **D** and azobenzene **E** that result from the facile dimerization of nitrosoanisole⁴⁴ (followed by successive deoxygenations) have been previously reported as byproducts of anisole nitrosation with sodium nitrite and sulfuric acid.⁴⁵

Summary and Conclusions

A series of polymethylbenzenes and anisoles are readily nitrosated with the nitrosonium salt $\text{NO}^+ \text{BF}_4^-$ in aceto-

(41) In this case, the acidity of the Wheland intermediate is enhanced owing to its dipositive charge. Formation of such an intermediate would also drive the aromatic nitrosation more quickly to completion in the presence of excess $\text{NO}^+ \text{BF}_4^-$.

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(43) For oxidative demethylation of methoxybenzenes with NO^+ , see Rathore, R. *et al.*, in ref 36.

(44) Boyer, J. H. In *The Chemistry of the Nitro and Nitroso Group*; Feuer, H., Ed.; Interscience Pub: New York: 1969; Part I, p 215.

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nitrile at room temperature and below. The reactivity pattern deduced from the time/conversions in Tables 2 and 3 indicate that aromatic nitrosations with the electrophilic NO^+ are distinctly different from those previously established for the related electrophilic aromatic nitration. The sizeable (deuterium) kinetic isotope effects measured for the nitrosation of mesitylene and anisole point to the rate-limiting deprotonation of the reversibly formed Wheland intermediate, unlike the conventional mechanism for aromatic nitration. An alternative two-step mechanism in Scheme 3 for the addition of NO^+ to aromatic donors is consistent with the previous evidence for electron transfer between aromatic donors and the nitrosonium cation.⁴⁶

In contrast to aromatic nitration, nitrosation leads to nitrosoaromatic products that are significantly better electron donors than the polymethylbenzene and anisole donors from whence they are derived. As a result, the presence of an extra NO^+ is desirable in the preparative procedure to accommodate the formation of the $[\text{ArNO}, \text{NO}^+]$ adduct. The strong association also leads to a slow oxidative degradation of the nitrosoanisoles. Most importantly, the enhanced donor properties of nitrosoarenes indicates that they are also effective Brønsted bases,⁴⁷ certainly by comparison with the limited base strengths of the corresponding nitro analogues. Such a marked distinction in the base strengths of ArNO and ArNO_2 thus accounts for the strong differentiation in the deprotonation rates of their conjugate acids (*i.e.* Wheland intermediates) $\text{Ar}^+(\text{H})\text{NO}$ and $\text{Ar}^+(\text{H})\text{NO}_2$, respectively. Finally, this conclusion resolves the classical ambiguity¹ in the differences in reactivity and positional selectivity of various aromatic donors in nitrosation *versus* nitration, despite the comparable (thermodynamic) stabilities of the active electrophiles (NO^+ and NO_2^+).³⁸

Experimental Section

Materials. Nitrosonium tetrafluoroborate (Strem) was stored in a Vacuum Atmospheres HE-493 dry box free from traces of oxygen, moisture, and solvent vapors. Acetonitrile (Fisher) was stirred over potassium permanganate for 24 h and then refluxed for 1 h. The solid was filtered and the clear solvent distilled from phosphorus pentoxide under an argon atmosphere. The distillate was refluxed over calcium hydride for 6 h and then distilled under a flow of argon. The purified solvent was stored under an argon atmosphere in a Schlenk flask fitted with a Teflon stopcock. The aromatic hydrocarbons anisole, 2-methylanisole, 3-methylanisole, 4-methylanisole, 2,6-dimethylanisole, 3,5-dimethylanisole, 2-bromoanisole, 3-bromoanisole, 4-bromoanisole, *o*-xylene, *m*-xylene, *p*-xylene, mesitylene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1,2,3,4-tetramethylbenzene, nitrosobenzene, *o*-nitrosotoluene, 4-nitro-*o*-xylene, and *o*- and *p*-nitrotoluene (Aldrich) were used as received. Toluene (Fisher) was distilled from sodium. Durene, pentamethylbenzene and hexamethylbenzene (Aldrich) were recrystallized from ethanol before use. Pyridine, 2,6-lutidine, and 2,4,6-collidine (Aldrich) were refluxed over barium oxide and then distilled before use. 2,6-Di-*tert*-butyl-4-methylpyri-

dine and *bis*-1,8-(dimethylamino)naphthalene (Aldrich) were used as received. Triethylamine (Fisher) was distilled from potassium hydroxide before use. Sodium carbonate, calcium acetate, and calcium oxide were dried *in vacuo* at 100 °C for 4 h before use. Anisole-*d*₅ (>99%) was prepared by the alkylation of phenol-*d*₆ (MSD Isotopes) with potassium hydroxide and dimethyl sulfate.¹² Mesitylene-*d*₃ (>99%) was prepared according to the literature procedure.¹³ The isomeric purity was estimated by GC-MS and ¹H NMR spectroscopy.¹³ Nitropentamethylbenzene, 3-nitrodurene, and nitro-*p*-xylene were available from previous studies.⁴⁸ Nitrosodurene was prepared according to the literature procedure.⁴⁹ An acetonitrile solution of fluoroboric acid (HBF_4) was prepared by bubbling dry HCl into a solution of silver tetrafluoroborate in dry acetonitrile. The precipitated silver chloride was filtered, the excess HCl removed with a stream of argon, and the concentration determined by titration with a standard solution of sodium hydroxide.

Instrumentation. ¹H and ¹³C NMR spectra were recorded in CDCl_3 on a General Electric QE-300 NMR spectrometer and the chemical shifts are reported in ppm units downfield from tetramethylsilane. UV-vis absorption spectra were recorded on a Hewlett-Packard 8450A diode-array spectrometer. Infrared spectra were recorded on a Nicolet 10DX FT spectrometer. Gas chromatography was performed on a Hewlett-Packard 5890A series gas chromatograph equipped with a HP 3392 integrator. GC-MS analyses were carried out on a Hewlett-Packard 5890 chromatograph interfaced to a HP 5970 mass spectrometer (EI, 70 eV). HPLC analyses were performed with an LDC system comprised of a Constameric 3500 solvent delivery pump coupled to a Spectromonitor 3100 variable wavelength detector with a Hewlett-Packard HP 3390 integrator. An Alltech 5- μm Hypersil BDS column was used. Melting points were performed on a Mel-Temp (Laboratory Devices) apparatus and are uncorrected. Cyclic voltammetry (CV) was performed on a BAS-100A Electrochemical Analyzer. The CV cell was of an airtight design with high vacuum Teflon valves and Viton O-ring seals to allow an inert atmosphere to be maintained without contamination by grease. The working electrode consisted of an adjustable platinum disc embedded in a glass seal to allow periodic polishing (with a fine emery cloth) without changing the surface area ($\sim 1 \text{ mm}^2$) significantly. The SCE reference electrode and associated salt bridge were separated from the catholyte by a sintered glass frit. The counter electrode consisted of a platinum gauze that was placed $\sim 3 \text{ mm}$ from the working electrode. Low-temperature photolyses were performed in a custom-made Dewar flask maintained at constant temperature with a Cryocool CC-65A immersion cooler. Elemental analysis was performed by Atlantic Microlab Inc., Norcross, GA.

Nitrosation of Arene Donors with Nitrosonium Tetrafluoroborate. Optimization of Reaction Conditions.

Reaction of Anisole. In each reaction a Schlenk tube fitted with a magnetic stirrer was charged with $\text{NO}^+ \text{BF}_4^-$ (0.50 mmol, see Table 1) in the dry box and sealed with a Teflon stopcock. Acetonitrile (5 mL) was added under a flow of argon and the mixture stirred until the salt was completely dissolved. Anisole (49 mg, 0.45 mmol) was added, the tube sealed, and the dark brown reaction mixture stirred in the dark for the time specified in Table 1. The solution was rapidly transferred by cannula to a vigorously stirred mixture of dichloromethane (75 mL) and water (50 mL) containing mesitylene (20 μL) as internal standard. The organic layer was separated and washed twice with water ($2 \times 50 \text{ mL}$). The extract was analyzed by GC and NMR spectroscopy using mesitylene as internal standard. Reactions at 25 °C for longer than 1 h led to intense red colorations and the organic extract was dark red/brown after aqueous workup. The red/brown coloration was due to the formation of several high molecular weight products. These were separated by flash chromatography and identified as the following: **4-methoxy-1,4-quinoneanil**,^{42b}

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λ_{\max} (log ϵ , Et₂O) 259 (4.32), 312 (4.08), 486 (3.81); IR ν (KBr) 1640, 1620, 1600, 1575, 1498, 1478, 850 cm⁻¹; ¹H NMR 3.77 (s, 3), 6.48 (dd, $J = 2.1, 10.2$ Hz, 1), 6.60 (dd, $J = 2.1, 9.9$ Hz, 1), 6.88 (br s, 4), 7.14 (dd, $J = 2.7, 10.2$ Hz, 1), 7.23 (dd, $J = 2.7, 10.2$ Hz, 1); ¹³C NMR 55.51, 114.44, 123.63, 128.25, 132.28, 132.98, 142.05, 142.61, 156.40, 158.94, 187.80; GC-MS 213 (M⁺); **4,4'-dimethoxyazoxybenzene**,⁵⁰ GC-MS 258 (M⁺); and **4,4'-dimethoxyazobenzene**,⁵¹ ¹H NMR δ 3.79 (s, 6), 6.90 (d, $J = 9$ Hz, 4), 7.78 ($J = 9$ Hz, 4); ¹³C NMR 114.05, 144.22, 146.87, 161.45; GC-MS 242 (M⁺). Thus after reaction of anisole with NO⁺ BF₄⁻ for 0.5 h at 25 °C the mixture was worked up and analyzed by quantitative GC. The mixture contained anisole (25%), 4-nitrosoanisole (69%), and 4-methoxy-1,4-quinoneanil (10%). After 1 h only 7% of the anisole remained unreacted and the yield of nitrosoanisole was 72%. In addition 4-methoxy-1,4-quinoneanil (10%), 4,4'-dimethoxyazoxybenzene (5%), and 4,4'-dimethoxyazobenzene (2%) were detected. After 2.5 h the anisole was totally consumed; however, the yield of 4-nitrosoanisole was only 60%. 4-Methoxy-1,4-quinoneanil (10%), 4,4'-dimethoxyazoxybenzene (1%), and 4,4'-dimethoxyazobenzene (13%) were also detected. After 23 h the yield of 4-nitrosoanisole was reduced to 21% and the yield of 4,4'-dimethoxyazobenzene increased to 55%. In addition 4-methoxy-1,4-quinoneanil (9%) was detected. When the reaction was performed with 2 equiv of NO⁺ BF₄⁻ at 25 °C for 0.5 h the conversion (85%) and the yield of 4-nitrosoanisole (82%) was higher than that obtained with 1 equiv of NO⁺ BF₄⁻. The best conversion/yield was obtained on reaction of anisole with 3 equiv of NO⁺ BF₄⁻ for 0.5 h at room temperature. With these conditions there was essentially quantitative conversion of anisole to 4-nitrosoanisole. Indeed an isolated yield of 87% was obtained. The reaction conditions and the corresponding yields of *p*-nitrosoanisole are recorded in Table 1. Based on these results the following procedure for nitrosation was adopted.

General Procedure: Nitrosation of Anisole. A Schlenk tube, equipped with a magnetic stir bar, was charged with NO⁺ BF₄⁻ (468 mg, 4.0 mmol) in the dry box and sealed with the aid of a Teflon stopcock. Acetonitrile (40 mL) was added under a flow of argon, and the mixture was stirred until the nitrosonium salt was completely dissolved. Anisole (144 μ L, 1.33 mmol) was added with a hypodermic syringe under a flow of argon. The tube was sealed, and the contents were stirred in the dark for 30 min. The dark brown reaction mixture was poured into a vigorously stirred mixture of dichloromethane (75 mL) and water (50 mL). The organic layer was washed with water (3 \times 50 mL aliquots) until the aqueous layer remained clear. The pale green-brown organic solution was dried over magnesium sulfate and the solvent removed *in vacuo*. [The yield of nitrosoanisole and the unreacted anisole were estimated by quantitative GC and HPLC analysis using the internal standard method.] The crude residue was rapidly filtered through a short column of silica gel, with hexane/dichloromethane (4/1, v/v) as eluant, and the pale blue solution of nitrosoanisole collected. The nitrosoanisole was further purified by crystallization from hexane. The yields estimated by gas chromatography and the yields of isolated pure compounds are presented in Tables 2 and 3. **4-Nitrosoanisole:** deep blue crystals (hexane), mp 22–23 °C (lit.⁵² 23 °C); IR ν (film) 1601, 1585, 1504, 1450, 1413, 1332, 1295, 1262 vs, 1193, 1182, 1112, 1021, 838, 763 cm⁻¹; ¹H NMR δ 3.86 (s, 3), 6.94 (d, $J = 8.7$ Hz, 2), 7.83 (d, $J = 8.7$ Hz, 2); ¹³C NMR δ 55.94, 113.81, 124.56 br, 163.92, 165.57; GC-MS 137 (M⁺), 107, 92, 78, 77, 64, 63. The following nitrosoarenes were prepared using this procedure with the reaction times and temperatures specified in Tables 2 and 3. **2-Methyl-4-nitrosoanisole:** blue crystals (hexane), mp 53–54 °C (lit.⁵³ 53.5 °C); IR ν 1601, 1488, 1472, 1434, 1402, 1348, 1252 vs, 1203, 1150, 1096, 1042, 1021, 951, 902, 817, 741 cm⁻¹; ¹H NMR δ 2.21 (s, 3), 3.92 (s, 3), 6.95 (d, $J = 8.7$ Hz, 1), 7.31 (br s, 1), 8.13 (br d, $J = 8.7$ Hz, 1); ¹³C NMR δ 16.09, 55.96, 109.05, 119.87, 127.38, 163.68, 164.07;

GC-MS 151 (M⁺), 136, 108, 106, 91, 78, 77. **3-Methyl-4-nitrosoanisole:** greenish-blue crystals (hexane) mp 21–22 °C (lit.⁵³ 22 °C); IR ν 3013, 2970, 2943, 2927, 2847, 1601, 1574, 1493, 1456, 1445, 1398, 1348, 1327, 1289, 1246 vs, 1176, 1096, 1085, 1037, 994, 854, 811 cm⁻¹; ¹H NMR δ 3.10 (s, 3), 3.76 (s, 3), 6.30 (d, $J = 9.0$ Hz, 1), 6.46 (dd, $J = 2.7$ and 9.0 Hz, 1), 6.75 (d, $J = 2.7$ Hz, 1); ¹³C NMR δ 17.41, 55.62, 110.71, 111.77, 115.00, 146.29, 163.14, 165.93; GC-MS 151 (M⁺). **2,6-Dimethyl-4-nitrosoanisole:** blue crystals (hexane), mp 53–55 °C (lit.⁵⁴ 51 °C); IR ν (Nujol) 1595, 1483, 1332, 1295, 1256, 1200, 1139, 1058, 881, 843, 806 cm⁻¹; ¹H NMR δ 2.36 (s, 6), 3.78 (s, 3), 7.56 (s, 2); ¹³C NMR δ 16.27, 59.67, 122.46, 131.97, 163.51, 163.80; GC-MS 165 (M⁺). **3,5-Dimethyl-4-nitrosoanisole:** colorless crystals (hexane), mp 121–122 °C (lit.²⁰ 120 °C); IR ν (Nujol) 1595, 1477, 1461, 1445, 1332, 1295, 1257, 1198, 1176, 1139, 1064, 999, 940, 881, 865, 849, 800, 714 cm⁻¹; ¹H NMR δ 2.67 (s, 6), 3.91 (s, 3), 6.63 (s, 2); ¹³C NMR δ 20.25, 56.67, 114.36, 134.36, 137.19, 164.30; GC-MS 165 (M⁺). **4-Nitroso-2-bromoanisole:** blue crystals (hexane), mp 83–84 °C (lit.⁵⁴ 85 °C); IR ν 1590, 1568, 1483, 1461, 1445, 1402, 1386, 1338, 1278, 1246, 1130, 1037, 1010, 897, 817, 768, 735 cm⁻¹; ¹H NMR δ 3.98 (s, 3), 7.06 (d, $J = 9.0$ Hz, 1), 7.67 (s, 1), 8.26 (d, $J = 9.0$ Hz, 1); GC-MS 215 (M⁺, ⁷⁹Br), 217 (M⁺, ⁸¹Br). **4-Nitroso-3-bromoanisole:** green crystals (hexane), mp 66–67 °C (lit.⁵⁵ 69 °C); ¹H NMR 3.91 (s, 3), 6.37 (d, $J = 9.0$, 1), 6.74 (dd, $J = 2.7, 9.0$, 1), 7.40 (d, $J = 2.7$, 1); GC-MS 215 (M⁺, ⁷⁹Br), 217 (M⁺, ⁸¹Br). **2,4-Dimethylnitrosobenzene:** colorless crystals (hexane), mp 42 °C (lit.⁵⁶ 44 °C); ¹H NMR δ 2.38 (s, 3), 3.29 (s, 6), 6.28 (d, $J = 8.4$ Hz, 1), 6.95 (d, $J = 8.4$ Hz, 1), 7.32 (s, 1); ¹³C NMR δ 17.23, 21.90, 107.80, 126.44, 133.00, 142.65, 147.86, 164.74; GC-MS 135 (M⁺). **2,4,6-Trimethylnitrosobenzene:** colorless crystals (methanol), mp 121–122 °C (lit.⁵⁷ 122 °C); IR ν (Nujol) 1606, 1477, 1445, 1311, 1262 vs, 1252, 1193, 1037, 1015, 886, 854, 806, 714 cm⁻¹; ¹H NMR δ 2.26 (s, 3), 2.33 (s, 6), 6.93 (s, 2); ¹³C NMR δ 18.24, 20.71, 129.41, 130.43, 132.17, 138.86, 140.32; GC-MS 149 (M⁺). **2,4,5-Trimethylnitrosobenzene:** colorless crystals (methanol), mp 62–63 °C (lit.⁵⁸ 65 °C); green crystals (dichloromethane), mp 43–44 °C (lit.⁵⁸ 45–46 °C); IR ν (Nujol) 1499, 1450, 1295, 1273, 1252 vs, 1026, 1005, 886, 870, 833, 752, 720, 688 cm⁻¹; ¹H NMR δ 2.17 (s, 3), 2.26 (s, 3), 3.21 (s, 3), 6.13 (s, 1), 7.25 (s, 1); ¹³C NMR δ 16.64, 19.15, 20.41, 108.51, 133.52, 140.28, 146.89, 148.48, 164.99; GC-MS 149 (M⁺). **2,3,4-Trimethylnitrosobenzene:** cream-colored crystals (methanol), mp 79–80 °C; IR ν (Nujol) 1595, 1466, 1445, 1386, 1381, 1268 vs, 1230, 827, 774 cm⁻¹; ¹H NMR δ 2.31 (s, 3), 2.36 (s, 3), 3.32 (s, 3), 5.95 (d, $J = 8.4$ Hz, 1), 6.88 (d, $J = 8.4$ Hz, 1); ¹³C NMR δ 13.18, 15.20, 21.43, 103.34, 126.82, 137.90, 142.80, 146.23, 165.69; GC-MS 149 (M⁺). Anal. Calcd for C₉H₁₁NO: C, 72.48; H, 7.38; N, 9.40. Found: C, 72.39; H, 7.43; N, 9.43. **2,3,4,5-Tetramethylnitrosobenzene:** green crystals (methanol), mp 69–71 °C (lit.⁴⁹ 72 °C); IR ν (Nujol) 1597, 1515, 1477, 1450, 1386, 1311, 1257, 1187, 1074, 1037, 897, 838 cm⁻¹; ¹H NMR δ 2.10 (s, 3), 2.13 (s, 3), 2.29 (s, 3), 3.21 (s, 3), 5.77 (s, 1); ¹³C NMR δ 13.09, 15.65, 17.09, 20.49, 104.43, 133.50, 137.72, 140.50, 145.33, 165.15; GC-MS 163 (M⁺). **Reaction of 4-Methoxytoluene with NO⁺ BF₄⁻.** Reactions carried out under the standard conditions at 25 °C for 30 min followed by the usual workup yielded a red residue which was analyzed by quantitative GC and GC-MS. The residue contained unreacted 4-methoxytoluene (0.93 mmol, 70%), a nitrosomethoxytoluene (0.04 mmol, 3%), a nitromethoxytoluene (0.13 mmol, 10%), a binary dimer (0.04 mmol, 3%), and several other unidentified high molecular weight products. **Reaction of 4-Bromoanisole with NO⁺ BF₄⁻.** Reaction according to the standard conditions at 25 °C for 30 h yielded, after workup, a pale yellow residue which was analyzed by quantitative GC and GC-MS. The residue contained unreacted 4-bromoanisole (1.20 mmol, 90%) and several other unidentified products. **Reaction of Toluene with NO⁺ BF₄⁻.** Reaction under the standard conditions for

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24 h at 25 °C yielded, after workup, a red oily residue which was analyzed by quantitative GC and GC-MS. The residue contained unreacted toluene (1.29 mmol, 97%), 4-nitrotoluene (0.016 mmol), and 2-nitrotoluene (0.024 mmol). **Reaction of *o*-Xylene with NO⁺ BF₄⁻.** Reaction under the standard conditions for 24 h at 25 °C yielded, after workup, a deep red oily residue which was analyzed by quantitative GC and GC-MS. The residue contained unreacted *o*-xylene (1.27 mmol, 95%); 4-nitroso-*o*-xylene (tentative assignment, 0.025 mmol, 2%), GC-MS (*m/z*) 135 (M⁺, 40), 105 (44), 103 (28), 77 (100), 65 (21), 63 (30); and 4-nitro-*o*-xylene (0.031 mmol, 2%), GC-MS (*m/z*) 151 (M⁺, 4), 134 (31), 106 (20), 103 (25), 79 (94), 78 (35), 77 (100), 65 (23), 63 (32). **Reaction of *p*-Xylene with NO⁺ BF₄⁻.** Reaction under the standard conditions at 25 °C for 24 h yielded, after workup, a deep red oily residue which was analyzed by quantitative GC and GC-MS. The residue contained unreacted *p*-xylene (1.29 mmol, 97%); 2-nitroso-*p*-xylene (tentative assignment, 0.01 mmol, 1%), GC-MS (*m/z*) 135 (M⁺, 35), 105 (44), 103 (54), 79 (100), 78 (35), 77 (66), 65 (30), 63 (37); and 2-nitro-*p*-xylene (0.03 mmol, 2%), GC-MS (*m/z*) 151 (M⁺, 6), 134 (34), 106 (26), 103 (26), 79 (80), 78 (35), 77 (100), 63 (28). **Reaction of Durene with NO⁺ BF₄⁻.** Reaction under the standard conditions for 5.5 h at 25 °C yielded, after workup, a pale yellow crystalline residue which was analyzed by GC, GC-MS, HPLC, and NMR spectroscopy. The solid contained unreacted durene (1.16 mmol, 87%), 3-nitrodurene (0.13 mmol), and 2,2',3,4',5,5',6-heptamethyldiphenylmethane⁵⁹ (0.02 mmol). Nitrosodurene was not detected (HPLC). **Reaction of Pentamethylbenzene with NO⁺ BF₄⁻.** Reaction under the standard conditions for 8 h at 25 °C yielded, after workup, a pale yellow crystalline residue which was analyzed by quantitative GC and GC-MS. The residue contained unreacted pentamethylbenzene (1.16 mmol, 87%), nitropentamethylbenzene (0.11 mmol, 9%), and 2,2',3,3',4,4',5,5',6-nonamethyldiphenylmethane⁶⁰ (0.02 mmol). **Reaction of Hexamethylbenzene with NO⁺ BF₄⁻.** Reaction under the standard conditions for 5 h yielded, after workup, a white crystalline residue which was analyzed by quantitative GC and GC-MS. The residue contained unreacted hexamethylbenzene (1.29 mmol, 97%) and *N*-pentamethylbenzylacetamide⁶¹ (0.03 mmol, 2%).

The Effect of Base on the Nitrosation of Mesitylene with NO⁺ BF₄⁻. The nitrosation of mesitylene in the presence of added base was investigated under standard conditions. Thus a Schlenk tube, equipped with a magnetic stir bar, was charged with NO⁺ BF₄⁻ (2.1 mmol) in the dry box and sealed with a Teflon stopcock. Acetonitrile (28 mL) was added under a flow of argon and the mixture stirred until homogeneous. The base (0.71 mmol) was added, followed by the mesitylene (0.71 mmol). The resultant mixture was stirred in the dark for 1.5 h, diluted with dichloromethane (75 mL), and washed with water (3 × 50 mL). The organic solution was analyzed by quantitative GC and GC-MS using the internal standard method.

When each of the pyridine bases (pyridine, 2,6-lutidine, 2,4,6-collidine, and 2,6-di-*tert*-butyl-4-methylpyridine) was added to the solution of nitrosonium salt, a pale green color formed indicative of the formation of nitrosopyridinium salts.³³ After the addition of mesitylene, the solution became dark red-brown. Over the course of 1.5 h, each of these became dark brown. By contrast, the addition of triethylamine to the solution of NO⁺ BF₄⁻ gave rise to an orange-brown solution which was not appreciably changed upon the addition of the mesitylene. Furthermore, the color did not change over the course of 1.5 h. Bis-1,8-(dimethylamino)naphthalene appeared to react with the nitrosonium salt, since a dark red-brown solution formed immediately upon mixing with NO⁺ BF₄⁻. Each of the inorganic bases (sodium carbonate, calcium acetate, and calcium oxide) formed heterogeneous, colorless

solutions with NO⁺ BF₄⁻ in acetonitrile. After the addition of mesitylene, the mixtures became orange-brown. The mixtures containing calcium salts remained heterogeneous and dark brown over the 1.5 h. However the mixture containing sodium carbonate became homogeneous and lighter brown. For each of the bases, the conversion of mesitylene and yield of nitrosomesitylene (in parenthesis) were the following: pyridine, 31% (93%); 2,6-lutidine, 28% (92%); 2,4,6-collidine, 36% (87%); 2,6-di-*tert*-butyl-4-methylpyridine, 23% (94%); triethylamine, 0% (0%); bis-1,8-(dimethylamino)naphthalene, 5% (90%); sodium carbonate, <1% (50%); calcium acetate, 14% (95%); calcium oxide, 10% (95%); without added base, 32% (91%).

Deuterium Kinetic Isotope Effect. General Procedure: A Schlenk tube, equipped with a magnetic stir bar, was charged with NO⁺ BF₄⁻ (40 mg, 0.34 mmol) in the dry box and sealed with the aid of a Teflon stopcock. Acetonitrile (8 mL) was added under a flow of argon and the mixture stirred until the solution was homogeneous. Mesitylene (236 μL, 1.70 mmol) and mesitylene-*d*₃ (236 μL) were added to acetonitrile (2 mL) in a separate Schlenk tube under a flow of argon. The exact ratio of mesitylene to deuteriomesitylene (ArH/ArD = 1.00, Table 5, column 1) was determined by GC-MS analysis of this solution. The solution was transferred by cannula into the solution of NO⁺ BF₄⁻. The resultant red-brown solution was stirred in the dark for 3 h 15 min and worked up as described in the general nitrosation procedure. The crude organic extracts were analyzed by quantitative GC and GC-MS. Anisole was used as internal standard to estimate the conversion of mesitylenes (2%) and the yield of nitrosomesitylenes based on consumed mesitylenes (90%). The isotopic ratio of the unreacted mesitylenes (ArH/ArD = 0.94, Table 5, column 7) and the product nitrosomesitylene (ArNO/Ar₂NO = 3.8, Table 5, column 8) was recorded. [Authentic nitrosomesitylene-*d*₂ was prepared by reaction of mesitylene-*d*₃ with NO⁺ BF₄⁻ according to the general procedure.] The conversion, yield, and ratio are recorded in Table 5. The same general procedure was used for each of the competitive reactions listed in Table 5.

Charge-Transfer Absorption Spectra of the EDA Complexes of Arene Donors with the Nitrosonium Cation. Standard stock solutions of NO⁺ BF₄⁻ in dry acetonitrile were prepared under an argon atmosphere, in Schlenk tubes fitted with Teflon stopcocks. A 2-mL aliquot of a standard stock solution of NO⁺ BF₄⁻ was added with the aid of an all glass syringe to a quartz cuvette fitted with a Teflon stopcock under an argon atmosphere. The cuvette was cooled in a dry ice/acetone bath to -40 °C and the UV-vis absorption spectrum of the nitrosonium solution recorded at -40 °C. A known amount of the aromatic donor was added to the cold solution under a flow of argon and the cuvette sealed with the aid of a Teflon stopcock. The red/orange solution was briefly mixed at -40 °C and the UV-vis absorption spectrum recorded at -40 °C. The absorption spectrum of the nitrosonium acceptor alone was then digitally subtracted from the spectrum of the red EDA complex and the difference is referred to as the charge-transfer (CT) absorption spectrum. [After recording the CT absorption spectrum, the red solution was rapidly transferred, with the aid of a Teflon cannula, into a vigorously stirred mixture of dichloromethane and water. The colorless organic layer was separated, washed with water, dried over MgSO₄, and analyzed by quantitative HPLC and GC. The aromatic donor was recovered quantitatively.] The CT absorption spectra obtained in this way were digitally deconvoluted by assuming the superposition of a pair of Gaussian bands. The absorption maxima and the full width at half maximum (fwhm) of the component bands were recorded and are listed in Table 7.

In order to determine the formation constant of the [aromatic donor-NO⁺] complexes, the concentration of the standard solution of nitrosonium cation and the aromatic donor were chosen such that the donor could be added in large excess. For anisole a nitrosonium salt concentration of 5 × 10⁻³ M was chosen. Known amounts of anisole (from 2.3 × 10⁻³ M to 1.94 × 10⁻¹ M) were successively added, at -40 °C, to the solution of the nitrosonium salt and the UV-vis absorption spectra recorded at -40 °C. The charge-transfer absorbances

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at the spectral maxima (A_{CT}) were determined and the Benesi-Hildebrand procedure applied to calculate the formation constant, K_{CT} , and the extinction coefficient, ϵ_{CT} , of the CT complex formation. The quotient of the nitrosonium cation concentration and the absorbance at the maximum was plotted against the reciprocal of the donor concentration. The intercept was equated to $(\epsilon_{CT})^{-1}$ and the slope to $(K\epsilon_{CT})^{-1}$. The exact concentrations used and the calculated formation constants and extinction coefficients are listed in Table 6.

Spectral Characterization of the Nitrosation of Aromatic Donors. A striking feature of the nitrosation of anisoles and methylbenzenes with $\text{NO}^+ \text{BF}_4^-$ is the progressive darkening of the reaction mixture with time. This phenomenon is best characterized by UV-vis spectroscopy using very dilute solutions since the colors generated are very intense. Typically, a stock solution of $\text{NO}^+ \text{BF}_4^-$ in dry acetonitrile (7×10^{-3} M) was prepared, under an argon atmosphere, as described above. This solution (2 mL) was transferred with the aid of a cannula into a quartz cuvette fitted with a Schlenk adaptor. The cuvette was cooled to -40°C in a dry ice/acetone bath and the UV-vis absorption spectrum measured. Anisole (2×10^{-3} M) was added under a flow of argon, and the spectrum of the resultant red solution was recorded at -40°C . This charge-transfer spectrum is labeled A in Figure 1. The red solution was warmed to 0°C , and the UV-vis absorption spectrum was recorded (at 0°C) at 2 min intervals. During this time, the solution first turned orange-red, orange, and finally canary yellow. The family of spectra shown in Figure 4 show that these color changes are due to the growth of an absorbance with $\lambda_{\text{max}} = 422$ nm (referred to as spectrum B in Figure 1). When water (20 μL) was added to the solution, the color was immediately bleached. The UV-vis absorption spectrum of the bleached solution exhibited an absorption at 345 nm due to nitrosoanisole²⁰ and the overlapping fine structure of the absorption due to nitrous acid at 338, 348, 358, 372, and 389 nm.¹⁸ Note that prolonged reaction of anisole with $\text{NO}^+ \text{BF}_4^-$ at higher concentrations led to the formation of trace amounts of high molecular weight red/brown products (*vide supra*) and colorless solutions were not always obtained after the aqueous workup. The same series of color changes was observed in the reactions of the substituted anisoles and the polymethylbenzenes.

Spectral Characterization of the Nitrosoarene-Nitrosonium Complexes. The concentrations for these determinations were chosen such that the acceptor ($\text{NO}^+ \text{BF}_4^-$) was present in large excess relative to the nitrosoarene donor. Thus, four stock solutions of $\text{NO}^+ \text{BF}_4^-$ in dry acetonitrile (0.003, 0.006, 0.010, and 0.015 M) were prepared as described above. Stock solutions of nitrosoanisole and nitrosomesitylene ($\sim 10^{-3}$ M) in dry acetonitrile were also prepared in Schlenk tubes under an argon atmosphere. [These solutions were essentially colorless since the absorption bands responsible for the pale blue/green color of solutions of nitrosoarenes have low extinction coefficients $\epsilon = 50 \text{ M}^{-1} \text{ cm}^{-1}$.] A solution of $\text{NO}^+ \text{BF}_4^-$ (2 mL) was transferred with a glass-tip syringe to a quartz cuvette fitted with a Teflon stopcock, and the UV-vis absorption spectrum of the colorless solution measured. An aliquot of the nitrosomesitylene solution (25 μL) was added to the cuvette under a flow of argon and the UV-vis absorption spectra of the pale yellow solution recorded. This procedure was repeated (with the same concentration of nitrosomesitylene) with each of the stock solutions of $\text{NO}^+ \text{BF}_4^-$. The absorbance at the spectral maximum was determined from each of the spectra and the Benesi-Hildebrand relationship¹⁴ was used to determine the formation constant and the extinction coefficient for formation of adduct A. For nitrosomesitylene $K = 2000$, and $\epsilon_{CT} = 11\,500$, were determined. For nitrosoanisole the extinction coefficient ($\epsilon = 25\,000$) was obtained from the intercept $[(\epsilon_{CT})^{-1}]$ of the plot of $[\text{nitrosoanisole}]/(A_{CT})^{-1}$ versus $[\text{NO}^+]^{-1}$; however, K could not be determined accurately since the slope $[(K\epsilon_{CT})^{-1}]$ was 0. Since the slope was $< 10^{-9}$ (the lower limit of our calculation) we estimated $K\epsilon_{CT} > 10^9$ and we estimated a lower limit for K is 4×10^4 .

The extinction coefficient was also estimated using a simplified approach. Thus the UV-vis absorption spectrum of a

mixture of nitrosoanisole and $\text{NO}^+ \text{BF}_4^-$ was recorded under conditions where no absorption due to uncomplexed nitrosoanisole was observed. Complete complexation was assumed and the absorbance, A_c , at the maximum was thus that of the complex at a concentration equal to the initial nitrosoarene concentration. The absorbance (A_n) and extinction coefficient (ϵ_n) of the nitrosoarene under identical conditions without $\text{NO}^+ \text{BF}_4^-$ was determined. The extinction coefficient of the nitrosoanisole-nitrosonium complex was estimated by the relation: $\epsilon_c = \epsilon_n A_n / A_c$. With this approach the extinction coefficient of the [nitrosoanisole, NO^+] complex was estimated to be $19\,000 \text{ M}^{-1} \text{ cm}^{-1}$. The extinction coefficients for nitrosonium complex formation with 3,5-dimethyl-4-nitrosoanisole and 4-nitroso-*m*-xylene were also determined (see Table 8).

Reversibility of the Nitrosoarene-Nitrosonium Complexation. The reversible nature of the complexation of the nitrosoarenes 4-nitrosoanisole, 3,5-dimethyl-4-nitrosoanisole, nitrosomesitylene, and 2,4-dimethylnitrosobenzene was studied spectroscopically. Typically, a dry acetonitrile solution of the pure nitrosoanisole ($\sim 10^{-5}$ M, see Table 8 for appropriate concentrations) and $\text{NO}^+ \text{BF}_4^-$ (3×10^{-3} M) was prepared, under an argon atmosphere, in quartz cuvette fitted with a Teflon stopcock. The UV-vis absorption spectrum corresponded to that of nitrosonium complexed nitrosoanisole (see Figure 5, initial spectrum). Water was added incrementally and the UV-vis absorption spectrum recorded after each addition. A clear isosbestic point was observed and the final UV-vis absorption spectrum corresponded to that of the nitrosoanisole with the overlapping fine structure due to the absorbance of nitrous acid at 338, 348, 358, 372, and 389 nm.¹⁸ The UV-vis absorption spectrum of an acetonitrile solution of the nitrosoanisole was recorded at the same initial concentration (see Figure 5, dashed line). This spectrum was identical to the final spectrum obtained after addition of water to the nitrosonium complexed nitrosoarene (see Figure 5) thus confirming that the nitrosoarene was recovered intact.

Cyclic Voltammetry of Anisoles, Methylbenzenes, and Nitrosoarenes. The cyclic voltammetric measurements were carried out in dry acetonitrile containing 0.1 M supporting electrolyte (tetra-*n*-butylammonium hexafluorophosphate) and 5×10^{-3} M arene, under an argon atmosphere. All cyclic voltammograms were recorded at the sweep rate of 100 mV s^{-1} and were IR compensated. The potentials were referenced to SCE which was calibrated with added ferrocene (5×10^{-3} M) as internal standard. The oxidation potentials ($E_{1/2}$) were calculated by taking the average of the anodic and cathodic peak potentials.⁶²

Stability of Nitrosoarenes. Nitrosonium Salts. A solution of $\text{NO}^+ \text{BF}_4^-$ (0.3 mmol) in dry acetonitrile (3 mL) was prepared, under an argon atmosphere, as described in the general nitrosation procedure. Nitrosoanisole (0.2 mmol) was added and the resultant dark brown solution stirred in the dark for 8 h. After workup the reaction mixture was analyzed by GC (using mesitylene as internal standard) and found to contain only nitrosoanisole (0.2 mmol). **Protic Acid: TFA.** A solution of nitrosoanisole (0.2 mmol) and trifluoroacetic acid (0.4 mmol) in dry acetonitrile (2 mL) was stirred, under argon, in the dark for 3 h. The solution remained pale green-blue throughout the time and after aqueous workup the nitrosoanisole was recovered intact. **HBFA.** A pale green solution of nitrosoanisole (0.3 mmol) and tetrafluoroboric acid (0.3 mmol) in dry acetonitrile (2 mL) was stirred, under an argon atmosphere in the dark for 1 h. After aqueous workup, the nitrosoanisole was recovered intact. A similar experiment was allowed to stir in the dark at 25°C for 8 h and analyzed by quantitative GC-MS. In addition to nitrosoanisole (0.27 mmol) there were traces of 4-nitrosophenol⁵⁹ (< 0.01 mmol) and 4,4'-dimethoxyazoxybenzene⁵⁰ (< 0.01 mmol), 4,4'-dimethoxyazobenzene⁶¹ (< 0.01 mmol). In a third experiment, a dark

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brown solution of nitrosoanisole (0.3 mmol) and tetrafluoroboric acid (1.5 mmol) in dry acetonitrile (3 mL) was stirred in the dark for 12 h. The brown solution was worked up as usual and analyzed by quantitative GC. 4-Nitrosophenol (0.20 mmol), 4-nitrosoanisole (0.02 mmol), 4,4'-dimethoxyazoxybenzene (<0.01 mmol), and 4,4'-dimethoxyazobenzene (0.01 mmol) were detected. The possibility that nitrosation was reversible under our reaction conditions was addressed by treating nitrosoanisole with HBF_4 in the presence of *o*-methylanisole. Thus, *o*-methylanisole (0.86 mmol) was added to a solution of *p*-nitrosoanisole (0.43 mmol) and tetrafluoroboric acid (0.43 mmol) in dry acetonitrile. The resultant solution was stirred at room temperature for 2 h. After aqueous workup the reaction mixture was analyzed by quantitative GC and contained only *p*-nitrosoanisole (0.40 mmol) and *o*-methylanisole (0.86 mmol).

Photochemical Activation of the Charge-Transfer Complexes of Aromatic Donors with $\text{NO}^+ \text{BF}_4^-$. Since previous studies³⁷ have clearly demonstrated that the direct irradiation of the charge-transfer bands of the $[\text{ArH}, \text{NO}^+]$ complexes generated the cation radical pair $[\text{ArH}^+, \text{NO}^\cdot]$ several attempts were made to photoinitiate the nitrosation of anisole and mesitylene with $\text{NO}^+ \text{BF}_4^-$ by actinic irradiation of the charge-transfer bands of the $[\text{ArH}, \text{NO}^+]$ complexes. The following general procedure was followed. **General Procedure:** Two identical 25-mL Schlenk tubes were charged with $\text{NO}^+ \text{BF}_4^-$ (175 mg, 1.50 mmol) in the dry box and sealed with the aid of a Teflon. Acetonitrile (15 mL) was added under a flow of argon, and the mixture stirred until the solutions became homogeneous. The solutions were cooled to -40°C in a dry ice/acetone bath and mesitylene (69 μL , 0.50 mmol) was added to each under a flow of argon. Both tubes were sealed with Teflon stopcocks and one was wrapped in aluminum foil to serve as the unirradiated control. The tubes were placed in an unsilvered Dewar (filled with acetone) maintained at $-40^\circ\text{C} \pm 2^\circ\text{C}$ with an immersion cooler. The unwrapped solution was irradiated with focused light from a medium pressure 450-W mercury lamp passed through an aqueous IR filter and a 340-nm cut-off filter. This procedure ensured that

only the CT band was irradiated (see Figure 2). After 5 h, the irradiated and control solutions were simultaneously worked up as described for the thermal nitrosation. Quantitative GC indicated that there was no reaction in either mixture and the mesitylene was recovered intact. The same result was obtained at this temperature for extended times (up to 72 h). The reaction was repeated at -5°C in an otherwise identical manner. There was a 5% conversion to nitrosomesitylene in both the irradiated solution and the unirradiated control. When the reaction was repeated at 15°C for 2 h there was a 30% conversion to nitrosomesitylene in both solutions. A series of reaction was performed under the conditions described above with a 366 ± 4 nm interference filter. In each reaction the same conversion and yield of nitrosomesitylene was obtained. Photochemical induction in the presence of added base was also attempted according to the general procedure. In each reaction, at least 3 equiv of the nitrosonium salt was used with 1 mL of acetonitrile for each 0.1 mmol of $\text{NO}^+ \text{BF}_4^-$. Reactions were performed with 2,6-di-*tert*-butyl-4-methylpyridine (1 equiv) at temperatures from -40°C to 25°C and times from 1.5 to 48 h. No photochemically enhanced reaction could be detected under these conditions. A similar series of reactions was performed with 2,4,6-collidine with 1–5 equiv at similar temperatures and times. In all reactions, the conversion of mesitylene (to nitrosomesitylene) was the same. In a reaction using a 366 ± 4 nm interference filter with 1 equiv of collidine and irradiation at -20°C for 34 h a selective 1% conversion to nitrosomesitylene was obtained. A similar set of reactions was performed with anisole (with and without added base) in an otherwise identical manner, *i.e.* range of temperature and time. No photochemically enhanced reaction was detected.

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