Charge-Transfer Structures of Aromatic EDA Complexes Leading to Electron Transfer with the Electrophilic Nitrosonium Cation

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Abstract: Benzene and hexamethylbenzene partake in the rapid formation of unique electron donor–acceptor (EDA) complexes with the nitrosonium cation, as reflected in the association constants that vary markedly from $K = 0.5$ to 31 000 M^{-1}, respectively. The 1:1 EDA complexes of electron-rich arene donors exhibit particularly high degrees of charge transfer that are established by X-ray crystallography coupled to the infrared spectroscopic analysis of the N–O stretching frequencies. Thus the N–O bond distance undergoes a dramatic lengthening from 0.95 Å in the simple salt NO$^+$SbCl$_6^-$ to 1.12 Å in the hexamethylbenzene (HMB) complex. Such a bond elongation of the nitrosonium acceptor is equivalent to that extant in nitric oxide (1.15 Å), and it is accompanied by a corresponding change of the aromatic donor in the ground state of the EDA complex to that of the cation radical (HMB$^{•+}$), as deduced from the changes in the ^{13}C NMR and the IR spectra. The same structural and spectroscopic analysis of the other NO$^+$ complexes reveals a graded series of the EDA complexes in which the degree of charge transfer (Z) varies linearly with the donor strength as measured by the ionization potential of the arene (ArH). The increase of Z from benzene (0.52) to hexamethylbenzene (0.97) in the charge-transfer complex tracks their increasing proclivity to undergo electron transfer and afford arene cation radicals (ArH$^{•+}$) as reactive intermediates. A general mechanistic formulation based on electron transfer from the charge-transfer complex is developed, in which the facility of the followup reactions (such as fragmentation, cycloreversion, rearrangement, ion-pair annihilation, etc.) of the labile ArH$^{•+}$ is critical. When the electron transfer is reversible, this 1-electron mechanism is shown not to be readily distinguished from the more conventional electrophilic (2-electron) pathways.

Introduction

The nitrosonium cation NO$^+$ is the active electrophile in the nitrosation of phenols and anilines,[1] and it is also an effective oxidant in electron transfer from other electron-rich compounds.[2] Indeed such an ambivalent behavior of NO$^+$ is particularly relevant to the dichotomy between electrophiles and oxidants in 2-electron and 1-electron processes[3] that pertain to a variety of organic, inorganic, and organometallic transformations.[4] As such, the recent reports of NO$^+$ complexes with aromatic donors (ArH)[5] are especially noteworthy since arenes are known to be subject to both electrophilic attack to afford substitution products (Ar-NO)[1] as well as to one-electron oxidation to produce cation radicals (ArH$^{•+}$).[2,6] The [NO$^+$, ArH] complex is likely to be the active precursor to both processes.[7] Thus it is important to quantitatively delineate its structure and redox properties, particularly in the context of electron donor–acceptor (EDA) complexes in which

charge-transfer absorption bands are characteristic.[8] Accordingly, we have focussed in this study on (a) the structural variations of the arene donor in the formation of [ArH, NO$^+$] complexes in solution and (b) their spectroscopic relationship to the crystalline 1:1 complexes that are structurally established by X-ray crystallography.[9] The facile thermal decomposition of the NO$^+$ complexes with various aromatic donors via electron transfer to afford nitric oxide and a series of both persistent and transient aromatic cation radicals (ArH$^{•+}$) is also pertinent to this study, since they are highly competitive with the (electrophilic) reactions of aromatic and related donors in which cation radicals are not apparent as reactive intermediates.

Results

Formation of Electron Donor–Acceptor (EDA) Complexes of the Nitrosonium Acceptor with Arene Donors in Solution. An intense yellow-orange color developed spontaneously upon the addition of benzene to a solution of NO$^+$BF$_4^-$ in dry acetonitrile under an inert atmosphere. The spectral transformation accompanying this color change is shown in Figure 1A by the growth of a new absorption band brought about by the incremental additions of benzene. A closer inspection of the absorption band (non-Gaussian) with $\lambda_{max} = 343$ nm suggested the presence of an additional component tailing to beyond 500 nm. Indeed the low-energy band was clearly resolved in the absorption spectrum obtained from NO$^+$BF$_4^-$ and hexamethylbenzene (Figure 1B), and its progressive blue (hypsochromic) shift with the other arene donors such as pentamethylbenzene, durene, and mesitylene is shown in Figure 1C. The digital Gaussian deconvolution of the absorption spectra yielded the band maxima (Table I, column 4), the relative positions of which paralleled the increase in the ionization potentials of the arene donors that is predicted by the Mulliken charge-transfer formulation of electron donor–acceptor (EDA) complexes as intermediates.[10] Accordingly, the pair of new absorption bands resulting from the intermolecular interaction

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Table I. Charge-Transfer Spectra of Aromatic EDA Complexes with the Nitrosonium Cation[a]

R-substituted benzene, R =	IP, eV	$h\nu_{CT}(I)$,[b] eV	fwhm,[b,c] 10^{-2} cm^{-1}	$h\nu_{CT}(II)$,[b] eV	fwhm,[b,c] 10^{-2} cm^{-1}
H	9.23	3.61	85	3.1	60
chloro	9.08	3.62	92		
bromo	9.05	3.82	85	3.1	80
methyl	8.82	3.70 (3.5)	93 (130)	2.6 (2.3)	50 (80)
tert-butyl	8.65	3.59	80	2.8	50
1,2-dimethyl	8.56	3.64	77	2.8	60
1,4-dimethyl	8.44	3.65	69	2.4	60
1,2,4-trimethyl	8.27	3.59	74	2.5	45
1,3,5-trimethyl	8.42	3.55 (3.2)	76 (105)	2.6 (2.3)	50 (50)
1,3,5-tri-*tert*-butyl	8.19	3.55 (3.2)	73 (120)	2.6 (2.2)	40 (50)
1,2,4,5-tetramethyl	8.05	3.67 (3.5)	71 (130)	2.6 (2.3)	50 (60)
pentamethyl	7.92	3.70	70	2.5	50
hexamethyl	7.85	3.64 (3.2)	71 (120)	2.5 (2.2)	60
hexaethyl	7.71	3.64	81	2.3	45
1,2-DNP[d]	7.66	3.63 (3.4)	80 (120)	2.4 (2.2)	50 (50)
1,3-DNP[d]	7.72	3.63	86	2.4	30
1,4-DNP[d]	7.71	(3.3)	(50)	(2.4)	(50)

[a] In ~10^{-3} M NOBF$_4$ or NOPF$_6$ and excess arene in acetonitrile solution at 25 °C, unless indicated otherwise. [b] Diffuse reflectance spectrum in parentheses. [c] Full width at half maximum. [d] DNP = dineopentyltetramethyl.

Table II. Formation Constants of the Charge-Transfer Complexes of Benzenoid Donors with the Nitrosonium Cation[a]

R-substituted benzene, R =	concn,[b] 10^3 M	NOBF$_4$[c]	λ_{mon}[d]	K[e]	ϵ_{CT}[f]
H	41–580	9.8	346	0.46	780
			460	0.64	60
chloro	66–840	8.0	343	2.2	110
			500	2.0	6.4
methyl	45–75	6.0	342	5.0	400
tert-butyl	26–94	9.6	340	7.3	270
			460	10	52
1,2-dimethyl	4.8–18	1.5	338	31	2200
			500	46	180
1,4-dimethyl	3.9–14	1.5	336	31	1300
	13–93	6.3	520	27	81
1,3,5-trimethyl	3.1–23	0.8	345	56	2100
1,3,5-tri-*tert*-butyl	3.3–19	0.9	349	34	1700
1,2,4,5-tetramethyl	0.4–9.3	0.36	336	450	1100
	6.3–29	3.4	520	360	40
	9.4–21[g]	8.0	660	190	60
pentamethyl	0.3–1.5	0.20	337	5100	2400
hexamethyl	0.2–1.7	0.20	337	31000	3100

[a] In acetonitrile solution at room temperature. [b] Lower–upper concentration range. [c] 10^3 M. [d] Monitoring wavelength in nm. [e] M^{-1}. [f] M^{-1} cm^{-1}. [g] In the presence of 0.057 M n-Bu$_4$NClO$_4$.

Table III. Selected Bond Distances (Å) in the Mesitylene EDA Complex with NOSbCl$_6$

N/O(3)–N/O(4)	1.069 (13)	C(10)–C(11)	1.424 (18)
C(1)–C(6)	1.397 (23)	C(10)–C(16)	1.489 (21)
C(2)–C(3)	1.353 (18)	C(12)–C(13)	1.375 (21)
C(3)–C(8)	1.505 (17)	C(13)–C(14)	1.412 (19)
C(5)–C(6)	1.379 (19)	C(14)–C(18)	1.527 (24)

Table IV. Selected Bond Angles (deg) in the Mesitylene EDA Complex with NOSbCl$_6$

C(2)–C(1)–C(7)	121.1 (15)	C(11)–C(10)–C(16)	118.7 (14)
C(1)–C(2)–C(3)	120.2 (15)	C(10)–C(11)–C(12)	121.1 (13)
C(2)–C(3)–C(8)	121.1 (13)	C(11)–C(12)–C(17)	122.9 (13)
C(3)–C(4)–C(5)	121.2 (11)	C(12)–C(13)–C(14)	120.8 (13)
C(4)–C(5)–C(9)	121.7 (12)	C(13)–C(14)–C(18)	119.8 (13)
C(1)–C(6)–C(5)	120.2 (12)	C(10)–C(15)–C(14)	119.2 (13)

of various arenes with the NO$^+$ acceptor are designated as $h\nu_{CT}(II)$ and $h\nu_{CT}(I)$ in Table I to correspond with the charge-transfer (CT) absorption in the visible region between 400 and 500 nm and the UV region between 320 and 350 nm, respectively.[11] Both bands were more or less insensitive to the polarity of the solvent—typically varying from 498 and 337 nm for the hexamethylbenzene complex with NO$^+$BF$_4^-$ in acetonitrile to 495 and 333 nm, respectively, in dichloromethane.

The binding energies of the electron donor–acceptor complexes were evaluated spectrophotometrically in solution by the intensification of the charge-transfer bands attendant upon the successive addition of arene donor. Thus the concentration dependence of the charge-transfer absorption is given by the Benesi–Hildebrand relationship,[12]

$$\frac{[NO^+BF_4^-]}{A_{CT}} = \frac{1}{\epsilon_{CT}} + \frac{1}{K\epsilon_{CT}[ArH]} \quad (1)$$

where A_{CT} and ϵ_{CT} are the absorbance and extinction coefficient, respectively, at the spectral maxima under conditions in which the arene donor was present in excess. The values of the formation constants K and the extinction coefficients ϵ_{CT} were obtained from the slopes and intercepts, respectively, of the plots (eq 1) for the 1:1 complexes, i.e.[6]

$$ArH + NO^+BF_4^- \overset{K}{\rightleftharpoons} [ArH, NO^+BF_4^-] \quad (2)$$

at the monitoring wavelengths listed in Table II. As a measure of the experimental reliability, the saturation factors defined as $s = A_{CT}/(\epsilon_{CT}[NO^+BF_4^-])$ were evaluated at various concentrations and found to lie within the region $0.2 < s < 0.8$, for which the error in the determination of K is less than 4% according to Deranleau's criterion.[13] Importantly, the comparable values of K evaluated at each absorption band indicated that both bands, $h\nu_{CT}I$ and $h\nu_{CT}II$, are related to the formation of the same [ArH, NO$^+$] complex. Since the values of K and ϵ_{CT} in Table II were also found to be rather invariant with different nitrosonium salts, the counterion (e.g., BF$_4^-$, PF$_6^-$, SbCl$_6^-$, etc.) is omitted hereafter for the measurements carried out in solution.

Isolation and X-ray Crystallography of the NO$^+$ Complex with Mesitylene. Although the nitrosonium salt NO$^+$PF$_6^-$ was insoluble in dichloromethane, its dissolution occurred readily in the presence of an arene donor to afford a highly colored solution (vide supra), which deposited crystals of the EDA complex upon standing at −20 °C. In this manner, the crystalline 1:1 arene complexes [ArH, NO$^+$PF$_6^-$] were isolated with the more electron-rich arenes such as ArH = mesitylene, durene, pentamethylbenzene, and hexamethylbenzene. In particular, the quality of the single crystal obtained from the mesitylene complex with NO$^+$SbCl$_6^-$ was sufficiently high for the origin of the charge-transfer interaction extant in the EDA complex to be precisely revealed by X-ray crystallography. Thus the ORTEP diagram in Figure 2 shows the

(11) For multiple charge-transfer bands, see: Mataga, N.; Kubota, T. *Molecular Interactions and Electronic Spectra*; Dekker: New York, 1970.
(12) (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.

(13) Deranleau, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 4044, 4050.
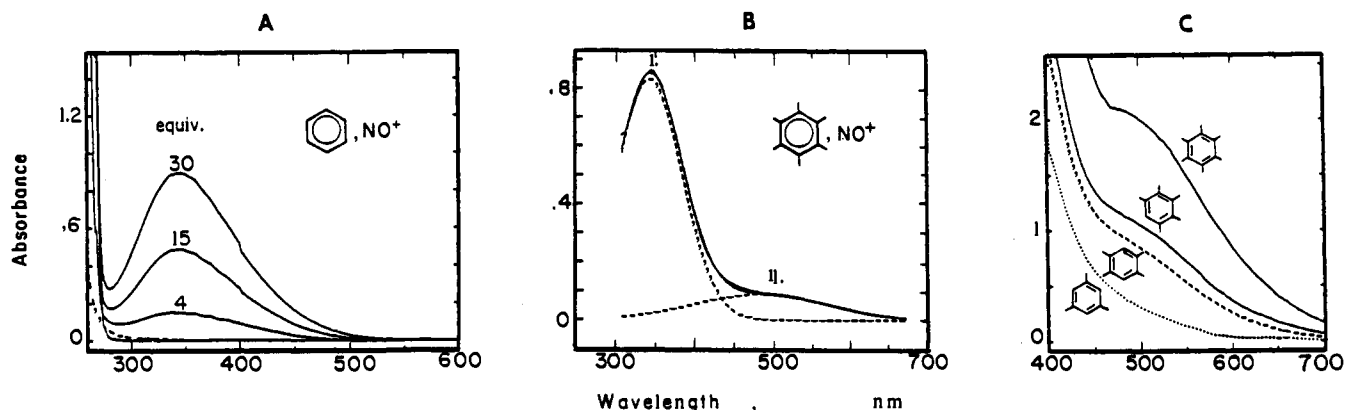
Figure 1. Charge-transfer spectrum of the NO⁺ complexes with (A) benzene and (B) hexamethylbenzene in acetonitrile at 25 °C. (C) Bathochromic shift of the low-energy band with increasing donor strength in the order hexamethylbenzene, pentamethylbenzene, durene, and mesitylene, as indicated in nitromethane.
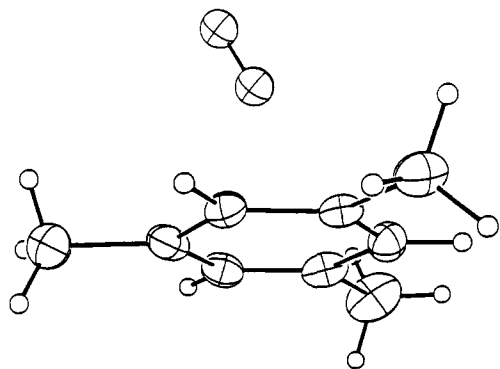

Figure 2. ORTEP diagram of the crystalline 1:1 EDA complex of mesitylene with NO⁺SbCl₆⁻, showing the central location of the NO⁺ acceptor over the benzene plane.

oblique (bent) orientation of the nitrosonium acceptor poised centrally over the mesitylene ring; and its nonbonded distance of closest approach to an aromatic carbon atom of 2.5 Å was only slightly less than the van der Waals contact.[14] The structural parameters of the crystalline EDA complex, as listed in Tables III and IV, indicted that the mesitylene donor was undistinguished from those found elsewhere.[15] Most notably, however, the N–O separation of 1.07 Å in the nitrosonium moiety of the mesitylene complex in Table III was significantly shorter than that in the analogous hexamethylbenzene (HMB) complex that has been reported variously as 1.36 Å for [HMB, NO⁺SbCl₆⁻] and 1.128 Å for [HMB, NO⁺AsF₆⁻].[9] However if the crystallographic analysis of the disordered [HMB, NO⁺SbCl₆⁻] was reconsidered in the light of the structure of the mesitylene complex as presented herein (see Experimental Section), the reconstructed value of 1.11 Å was obtained for the N–O bond distance, which placed it in acceptable agreement with that for [HMB, NO⁺AsF₆⁻]. Accordingly, the average distance of 1.12 Å can be taken to represent the N–O bond separation that is pertinent to the charge-transfer interaction of hexamethylbenzene with the nitrosonium acceptor.

Vibrational Spectra of Crystalline EDA Complexes of NO⁺Y⁻ with Arene Donors. To obtain an independent measure of the change in the N–O bond length accompanying the variation of the arene donor in the EDA complex, as provided by the X-ray crystallographic analysis above, a careful comparison of the vi-

(14) Compare: (a) Brock, C. P.; Dunitz, J. D. *Acta Crystallogr.* **1982**, *B38*, 2218. (b) Potenza, J.; Mastropaolo, D. *Acta Crystallogr.* **1975**, *B31*, 2527. (c) Iball, J.; Low, J. N. *Acta Crystallogr.* **1974**, *B30*, 2203. (d) Korp, J. D.; Bernal, I. *Cryst. Stuct. Commun.* **1980**, *9*, 821. (e) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. See also: Pauling, L. *Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1973.

(15) Compare: (a) Dahl, T. *Acta Chem. Scand.* **1971**, *25*, 1031. (b) Hanusa, T. P.; Huffman, J. C.; Todd, L. J. *Polyhedron* **1982**, *1*, 77. (c) Karl, R. R., Jr.; Wang, Y. C.; Bauer, S. H. *J. Mol. Struct.* **1975**, *25*, 17. (d) Broude, V. L. *Z. Eksp. Teor. Fiz. SSR* **1952**, *22*, 600.

Table V. Vibrational Spectra of Aromatic EDA Complexes with the Nitrosonium Cation[a]

R-substituted benzene, R =	NO⁺Y⁻	ν_{NO^+},[b] cm⁻¹	fwhm,[b,d] cm⁻¹	A_f[c]
none	NOBF₄	2290 (2348)		
none	NOPF₆	2290 (2340)	44 (100)	
none	NOAsF₆	(2338)		
none	NOSbCl₆	2270 (2210)	(100)	
H	NOPF₆	2075	100	2730
methyl	NOPF₆	2037 (2042)	91 (100)	3040
	NOSbCl₆	2030 (1992)	82 (160)	6100
1,2-dimethyl	NOPF₆	2000 (2040)	97	6540
1,4-dimethyl	NOPF₆	1998	92	3660
1,3,5-trimethyl	NOPF₆	1975 (2016)	74 (160)	7640
	NOSbCl₆	1964 (1983)	70 (100)	8160
1,3,5-tri-*tert*-butyl	NOPF₆	1964		
1,2,4,5-tetramethyl	NOPF₆	1933 (1986)	70 (190)	5660
pentamethyl	NOPF₆	1907 (1920)	65 (100)	6340
hexamethyl	NOPF₆	1885 (1899)	52 (150)	5590
	NOSbCl₆	1885 (1860)	52 (110)	7860
	NOAsF₆	(1895)	(104)	
hexaethyl	NOPF₆	1900	53	7310
1,3-DNP[e]	NOPF₆	1884		
1,4-DNP[e]	NOPF₆	1884		

[a]In nitromethane solution with ∼0.1 M NO⁺Y⁻ and arene at 25 °C. [b]Diffuse reflectance spectra in parentheses. [c]Molar integrated absorption intensity, cm⁻¹ M⁻¹ cm⁻². [d]Full width at half maximum. [e]DNP = dineopentyltetramethyl.

brational spectrum of the nitrosonium moiety in the parent salt (NO⁺Y⁻) relative to that in the arene complex [ArH, NO⁺Y⁻] was made, especially with respect to the single stretching frequency at ν_{NO} = 1876 cm⁻¹ in the neutral diatomic NO.[16] The stretching vibration of the nitrosonium salt NO⁺Y⁻ from the diffuse reflectance infrared spectrum of a crystalline sample (see Experimental Section) occurred at ν_{NO} = 2348, 2340, and 2338 ± 5 cm⁻¹ with a band width (fwhm) of ∼100 cm⁻¹ for Y = BF₄⁻, PF₆⁻, and AsF₆⁻, respectively. The stretching vibrations (ν_{NO}) of the nitrosonium acceptor in the EDA complexes were similarly obtained from the diffuse reflectance spectra of the crystalline 1:1 complexes of NO⁺Y⁻ with various arene donors. Most noteworthy of the results listed in Table V was the marked effect that the arene donor exerted on ν_{NO}, which dramatically decreased simply on going from the mesitylene complex (ν_{NO} = 1983 cm⁻¹) to the hexamethylbenzene complex (ν_{NO} = 1860 cm⁻¹) with NO⁺SbCl₆⁻. The change in the N–O stretching frequencies of $\Delta\nu_{NO}$ = 123 cm⁻¹ for this pair of EDA complexes compared with the frequency difference $\Delta\nu_{NO}$ = 334 cm⁻¹ between the uncomplexed nitrosonium hexafluorophosphate and free nitric oxide. Since the latter structures revealed an increase in the N–O bond separation from 0.95 Å (NO⁺SbCl₆⁻)[17] to 1.15 Å (NO),[16] a simple linear inter-

(16) (a) Keck, D. B.; Hause, C. D. *J. Mol. Spectrosc.* **1968**, *26*, 163. (b) Laane, J.; Ohlsen, J. R. *Prog. Inorg. Chem.* **1980**, *27*, 465.
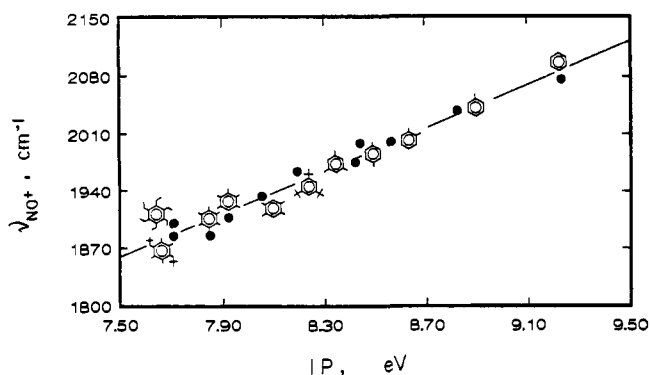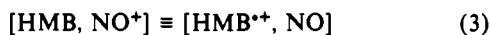
Charge-Transfer Structures of Aromatic EDA Complexes

J. Am. Chem. Soc., Vol. 113, No. 13, 1991 4965

Figure 3. Variation of the N–O stretching frequency in NO$^+$ complexes with the ionization potential of the arene donor (as indicated).

Table VI. ^{13}C and ^{1}H NMR Spectra of [ArH, NO$^+$] Complexes[a]

| | ^{13}C chemical shift | | | ^{1}H chemical shift | |
arene	Ar	Δδ[b]	Me	Ar	Me
hexamethyl-benzene	150.8 (133.2)	17.6	17.9 (17.0)		2.48 (2.18)
pentamethyl-benzene	141.5 (130.2)	11.3	21.1 (20.8)	7.66 (6.79)	2.46 (2.20)
	151.0 (133.6)	17.4	17.3 (16.4)		2.44 (2.16)
	151.5 (134.5)	17.0	16.9 (16.1)		
	152.8 (136.1)	16.7			
durene	142.9 (132.3)	10.7	19.7 (19.3)	7.67 (6.89)	2.48 (2.18)
	151.3 (135.1)	16.2			
mesitylene	137.8 (128.2)	9.6	21.6 (21.5)	7.49 (6.83)	2.52 (2.28)
	151.8 (139.3)	12.3			
toluene	132.5 (127.7)	4.8	21.7 (21.7)	7.57 (7.26)	2.52 (2.38)
	135.1 (130.0)	5.1			
	136.1 (130.4)	5.7			
	147.6 (139.6)	8.0			
benzene	131.0 (129.8)	1.2		7.49 (7.38)	

[a] Measured in solution (CD$_3$CN or CD$_3$NO$_2$). The free arene in parentheses. [b] Difference in chemical shift of the complexed and the free arene.

Table VII. Aromatic Vibrational Frequencies in the EDA Complexes with Nitrosonium Salts

R-substituted benzene, R =	NO$^+$Y$^-$	medium[a]	^{2}B$_{2g}$,[b] cm^{-1}
H	NOPF$_6$	CD$_3$CN	1581 (1595)
methyl	NOPF$_6$	DR	1573 (1604)
	NOSbCl$_6$	DR	1575 (1604)
1,2-dimethyl	NOPF$_6$	DR	1589 (1609)
1,3,5-trimethyl	NOPF$_6$	DR	1578 (1610)
	NOSbCl$_6$	DR	1571 (1610)
1,2,4,5-tetramethyl	NOPF$_6$	CD$_3$CN	1580, 1529 (1620, 1560)
	NOPF$_6$	DR	1586, 1532 (1620, 1560)
1,2,3,5-tetramethyl	NOPF$_6$	DR	1585, 1545 (1616, 1585)
pentamethyl	NOPF$_6$	DR	1567 (1608)

[a] Measured in solution (CD$_3$CN) or in the solid state (DR). [b] Q band of the EDA complex and the free arene (in parentheses) as assigned by Ohno.[23]

polation predicted the frequency change of Δν = 123 cm^{-1} to represent the difference of 0.07 Å between the N–O separations in the mesitylene and hexamethylbenzene complexes—in excellent accord with that revealed by X-ray crystallographic analysis (vide supra). Accordingly, we concluded that the monotonic variation of ν_{NO} with various donors in Table V pointed to the corresponding increases of the N–O bond separation in the crystalline EDA complexes.

Charge-Transfer Structures of the NO$^+$ Complexes with Arene Donors in Solution. The subtle structural changes in the nitrosonium acceptor, as detected in the vibrational spectra of the crystalline [ArH, NO$^+$Y$^-$] complexes, can also be employed for structure elucidation of the same complexes in solution. For example, the nitromethane solutions of the nitrosonium salts NO$^+$Y$^-$ showed the single stretching band at ν_{NO} = 2290 cm^{-1} (fwhm = 44 cm^{-1}) to be independent of the counterion with Y = BF$_4^-$, PF$_6^-$, or AsF$_6^-$ (with the slight exception of NO$^+$SbCl$_6^-$ with ν_{NO} = 2270 cm^{-1}). These aprotic solutions of NO$^+$Y$^-$ were well-behaved, since the molar integrated absorption intensity, defined as[18] $A_i = (Cl)^{-1}\int \ln (I_0/I)$ dν [where the incident irradiation (I_0) is attenuated to I upon the passage through distance l of a solution containing C molar NO$^+$Y$^-$] followed the Beer–Lambert relationship to beyond 1 M concentration. When benzene was added, the solutions turned orange and an additional strong band appeared at ν_{NO} = 2075 cm^{-1}, which continued to grow at the expense of the original 2290-cm^{-1} band with incremental additions of benzene. The Jobs' plot indicated that the appearance of the new nitrosyl band was directly associated with the formation of the 1:1 EDA complex of benzene and NO$^+$PF$_6^-$ (see eq 2). The N–O stretching frequencies of other arene complexes with NO$^+$Y$^-$ evaluated in solution by this procedure are listed in Table V, and their monotonic variation with the donor strength of the arene donor as given by their ionization potentials (IP) is shown in Figure 3. It is important to note that the values of ν_{NO} for these EDA complexes in solution showed the same decreasing trend with the number of methyl substituents on benzene as those measured in the crystalline 1:1 complexes (Table V). Most significant was the value of ν_{NO} = 1885 cm^{-1} for the hexamethylbenzene complexes [HMB, NO$^+$PF$_6^-$] and [HMB, NO$^+$SbCl$_6^-$], which was strikingly akin to the value of ν_{NO} = 1876 cm^{-1} for free nitric oxide. Such a coincidence of N–O stretching frequencies was symptomatic of an overall one-electron reduction of the nitrosonium moiety within the 1:1 EDA complex. If so, it must be accompanied by a charge transfer that is tantamount to the one-electron oxidation of the hexamethylbenzene donor, i.e.

$$[\text{HMB, NO}^+] \equiv [\text{HMB}^{\bullet+}, \text{NO}] \qquad (3)$$

Particularly diagnostic of this formulation would be the increased positive charge distribution onto the hexamethylbenzene moiety in the 1:1 complex to approach that of the free cation itself—as reflected by the changes in the NMR and IR spectra of the aromatic donor upon complexation, described below.

A. NMR Spectra of Aromatic Complexes with the Nitrosonium Cation. Since the gross changes in the charge distribution of aromatic cations are acutely reflected in the NMR spectra,[19] we examined the resting state of the hexamethylbenzene moiety in the 1:1 complex by first measuring the ^{13}C chemical shifts, both in solution and in the crystalline solid state.[20] Indeed the pair of sharp ^{13}C resonances at δ 17.0 and 133.2 for the methyl and aromatic carbons of hexamethylbenzene dissolved in nitromethane were substantially shifted downfield to δ 17.9 and 150.8, respectively, in the red-brown solution containing 0.1 M NO$^+$PF$_6^-$ and an equimolar amount of hexamethylbenzene. [Note that at

(17) Estimated value from: (a) Mootz, D.; Poll, W. *Z. Naturforsch.* **1984**, *39b*, 1300. (b) Toogood, G. E.; Chieh, C. *Can. J. Chem.* **1975**, *53*, 831. (c) Barbier, P.; Mairesse, G.; Wignacourt, J. P.; Baert, F. *Cryst. Struct. Commun.* **1976**, *5*, 633. (d) Höhle, T.; Mijlhoff, F. C. *Recl. Trav. Chim.* **1967**, *86*, 1153.

(18) (a) Yarwood, I. *Spectroscopy and Structure of Molecular Complexes*; Plenum: London, 1973; p 105. (b) Alpert, N. L.; Keiser, W. E.; Szymanski, H. A. *Theory and Practice of Infrared Spectroscopy*; Plenum: New York, 1970; p 83. (c) Ramsay, D. A. *J. Am. Chem. Soc.* **1952**, *74*, 72.

(19) (a) Spiesecke, H.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468 and references therein. (b) Grutzner, J. B. In *Recent Advances in Organic NMR Spectroscopy*; Lambert, J. D., Rittner, R., Eds.; Norell Press: Landisville, NJ, 1987; Chapter 2. (c) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Wiley: New York, 1980; p 177. See also: (d) Prakash, G. K. S.; Iyer, P. S. *Rev. Chem. Intermed.* **1988**, *9*, 65. (e) Fraenkel, G.; Carter, R. E.; McLachlan, A.; Richards, J. H. *J. Am. Chem. Soc.* **1960**, *82*, 5846. (f) Tokuhiro, T.; Fraenkel, G. *J. Am. Chem. Soc.* **1969**, *91*, 5005. (g) Forsyth, D. A.; Olah, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 4086. (h) Olah, G. A.; Mateescu, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1430. (i) Pines, A.; Gibby, M. G.; Waugh, J. S. *Chem. Phys. Lett.* **1972**, *15*, 373. (j) Morozov, S. V.; Shubin, V. G.; Koptyug, V. A. *Zh. Org. Khim.* **1989**, *25*, 889. (k) Mamatyuk, V. I.; Detsina, A. N.; Koptyug, V. A. *Zh. Org. Khim.* **1976**, *12*, 739. (l) Bakhmutov, V. I.; Galakhov, M. V. *Russ. Chem. Rev.* **1988**, *57*, 839. (m) Hunadi, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 6889. (n) O'Brien, D. H.; Hart, A. J.; Russell, C. R. *J. Am. Chem. Soc.* **1975**, *97*, 4410. (o) Mayr, H.; Förner, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 6032. (p) Oth, J. F. M.; Muellen, K.; Koenigshofen, H.; Wassen, J.; Vogel, E. *Helv. Chim. Acta* **1974**, *57*, 2387.

(20) (a) Fyfe, C. A. *Molecular Complexes*; Foster, R., Ed.; Elek Science: London, 1973; Vol. 1, p 209ff. (b) Blann, W. G.; Fyfe, C. A.; Lyerla, J. R.; Yannoni, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 4030.

these concentrations the complexation of hexamethylbenzene at NO^+ was essentially complete ($>98\%$), as judged by the value of K in Table II.] Similarly, the pair of ^{13}C resonances for hexamethylbenzene by solid-state (MAS/CP) NMR spectroscopy were shifted to 20.5 and 151.9 in the crystalline 1:1 complex [HMB, $NO^+SbCl_6^-$] isolated by the procedure described above. Such a downfield shift of $\Delta\delta(^{13}C)$ for the methyl resonance in the [HMB, NO^+] complex relative to that in the uncomplexed HMB was also reflected in a corresponding small, but experimentally significant shift of $\Delta\delta(^1H) \simeq 0.3$ in the proton NMR spectrum (nitromethane-d_3 solution). The analogous changes in the ^{13}C and ^1H chemical shifts of the other arene complexes with NO^+ are compared in Table VI. Most importantly, the large variations of the relative ^{13}C chemical shifts ($\Delta\delta$) for the ring carbons in column 4 were particularly diagnostic of the increased cationic character of the aromatic moiety ($ArH^{\bullet+}$) in the EDA complexes of the electron-rich aromatic donors.

B. IR Spectra of Aromatic Complexes with the Nitrosonium Cation. The variation in the infrared spectrum of the aromatic donor is known to occur upon its oxidation to the cation radical,[21] principally as a result of the changes in the C–C bond distances.[22] We have also observed significant shifts in the C–C stretching vibrations in the [ArH, NO^+] complex relative to that of the free arene donor in the diagnostic spectral region around 1600 cm^{-1}.[23] The consistent red shifts of the relevant IR bands listed in Table VII accorded with the increased cationic character of the aromatic moiety as $ArH^{\bullet+}$ for the EDA complex in the following way. The degenerate ground state ($^2E_{1g}$) of the cation radical of the parent benzene donor is predicted to undergo a Jahn–Teller distortion.[24] The elongated and compressed structures of D_{2h} symmetry corresponding to the $^2B_{2g}$ and $^2B_{3g}$ electronic states, respectively, are shown below with their optimized (carbon bond distance) geometries computed by ab initio molecular orbital theory (6-31G basis set) for static Jahn–Teller contributions.[25] The $^2B_{2g}$ state is calculated to be more stable than the $^2B_{3g}$ state by ~2.0 kcal
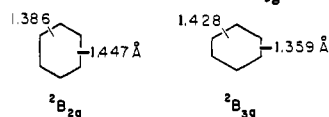

mol^{-1},[25] and the skeletal stretching modes associated with the elongated benzenoid structures have been assigned in the IR spectrum to the 1600-cm^{-1} region.[23] Indeed, the predicted red shift of this stretching vibration in the conversion of the neutral benzenoid donor to its cation radical has been experimentally observed in the oxidation of C_6F_6 (1530 cm^{-1}) to $C_6F_6^{\bullet+}$ (1490 cm^{-1}).[26] If the frequency shift of $\Delta\nu = 40$ cm^{-1} is roughly taken as the full measure of electron removal, the red shifts in Table VII[27] reflect the significant charge transfer in the ground state of the aromatic EDA complexes in the manner described by the

^{13}C NMR chemical shifts in Table VI.

Oxidation of Arene Donors by the Nitrosonium Cation. The high degree of charge transfer in the ground state of the nitrosonium complex with hexamethylbenzene, as described by the equivalency depicted in eq 3, augured well for a chemical process involving the actual transfer of one electron to NO^+ from other well-endowed aromatic donors. Indeed, the direct oxidation of an electron-rich arene by the nitrosonium cation was observed in the spontaneous production of the cation radical of octamethyl-biphenylene (OMB) simply upon mixing the aromatic donor with $NO^+BF_4^-$ in acetonitrile solution under an argon atmosphere. The straightforward 1:1 stoichiometry in eq 4 was readily established
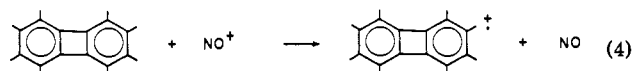
by the microvoltammetric analysis of the liberated NO^{28} and the spectrophotometric analysis of the cation radical $OMB^{\bullet+}$ by its characteristic absorption band at $\lambda_{max} = 600$ nm (ϵ 2000 M^{-1} cm^{-1}).[29]

The exposure of anthracene (AnH) to $NO^+PF_6^-$ in dichloromethane similarly led to the rapid evolution of nitric oxide, even at -78 °C. This resultant dark green solution contained black crystals of the anthracene cation radical as its π-dimer,[6] i.e.
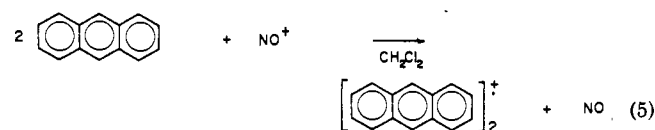
When anthracene was added to a solution containing excess $NO^+BF_4^-$ in the more polar solvent acetonitrile, the transient yellow-green color of the charge-transfer complex was followed by the rapid libertion of 2 mol of nitric oxide that were quantitatively analyzed by microvoltammetry.[28] The treatment of anthracene with a stoichiometric amount of $NO^+BF_4^-$ in acetonitrile yielded primarily N-9-anthrylacetamide[30] upon aqueous workup, together with a small amount of anthraquinone[31] and 9-nitroanthracene (see Experimental Section), i.e.

$$AnH + 2NO^+ \xrightarrow[\text{(H}_2\text{O)}]{CH_3CN} 9\text{-AnNHAc} + 2NO, \text{ etc.} \quad (6)$$
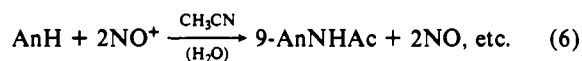
The σ-bonded dimer of anthracene otherwise known as the photodimer dianthracene[32] σ-$(ArH)_2$ also reacted rapidly with $NO^+BF_4^-$ at 25 °C in dichloromethane to afford the same dark green solution as that obtained from anthracene (vide supra), and it contained the black crystals of the anthracene cation radical as its π-dimer, i.e.

Likewise, the oxidation of dianthracene by the nitrosonium cation in acetonitrile solution afforded anthraquinone and 9-nitroanthracene, as described above.

The charge-transfer complex preceding the electron transfer from an aromatic donor could be observed in the exposure of 4-methoxytoluene (MT) to $NO^+BF_4^-$ in dichloromethane at -78 °C. The yellow solution containing partially dissolved $NO^+BF_4^-$ showed the prominent high-energy band at $\lambda_{max} = 334$ nm of the

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(22) See: (a) Bews, J. R.; Glidewell, C. *J. Mol. Struct. (THEOCHEM)* **1982**, *3*, 197, 205. (b) Coulson, C. A.; Golebiewski, A. *Mol. Phys.* **1962**, *5*, 71. (c) Fritz, H. P.; Gebauer, H.; Friedrich, P.; Ecker, P.; Artes, R.; Schubert, U. *Z. Naturforsch.* **1978**, *33b*, 498. (d) Pearson, W. B. *Struct. Rep.* **1957**, *21*, 603.

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(24) (a) Liehr, A. D. *Rev. Mod. Phys.* **1960**, *32*, 436. (b) Snyder, L. C. *J. Chem. Phys.* **1960**, *33*, 619. (c) Hobey, W. D.; McLachlan, A. D. *J. Chem. Phys.* **1960**, *33*, 1695. (d) See also Coulson, C. A.; Golebiewski, A. in ref 22b.

(25) Raghavachari, K.; Haddon, R. C.; Miller, T. A.; Bondybey, V. E. *J. Chem. Phys.* **1983**, *79*, 1387.

(26) (a) Richardson, T. J.; Tanzella, F. L.; Bartlett, N. *J. Am. Chem. Soc.* **1986**, *108*, 4937. (b) Conversely, the calculated foreshortening of the relevant C–C bonds in the cation radical of p-dimethoxybenzene is observed as a blue shift in the Raman spectra. [Ernstbrunner, E.; Girling, R. B.; Grossman, W. E. L.; Hester, R. E. *J. Chem. Soc., Perkin Trans. 2* **1978**, 177.]

(27) The 1600-cm^{-1} band of the symmetrical hexamethylbenzene was not observed in either the IR spectrum of the solution (absorption) or the crystalline complex (diffuse reflectance).
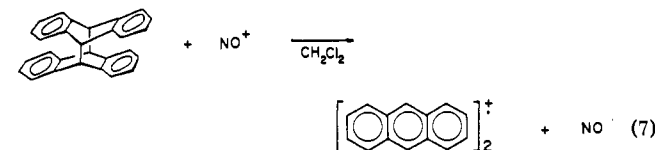
(28) Karpinski, Z. J.; Kochi, J. K. To be submitted.

(29) Hart, H.; Teuerstein, A.; Babin, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 903.

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(32) Bouas-Laurent, H.; Castellan, A.; Desvergne, J. P. *Pure Appl. Chem.* **1980**, *52*, 2633.

Charge-Transfer Structures of Aromatic EDA Complexes

J. Am. Chem. Soc., Vol. 113, No. 13, 1991 4967

Table VIII. Oxidative Coupling of *p*-Methoxytoluene by the Nitrosonium Cation and Metal Oxidants

oxidant[a,b]	biaryl[c]	diphenylmethane[d]
NOBF$_4$	0.72	
{Mn$_3$O(OAc)$_6$(AcOH)$_3$}OAc	0.75	0.08 (0.04)
{Fe$_3$O(OAc)$_6$(H$_2$O)$_3$}OAc		0.88 (0.17)
Cu(OAc)$_2$		0.58 (0.06)
{Co$_3$O(OAc)$_6$(AcOH)$_3$}OAc	0.28	0.03 (0.01)
Pb(OAc)$_4$	0.38	0.05 (0.01)
Tl(OAc)$_3$		0.08 (0.09)

[a] With 1.61 mmol of NOBF$_4$ and 3.69 mmol of MT in dichloromethane. [b] With 1 mmol of metal acetate and 40 mmol of MT in HClO$_4$/HOAc according to ref 35. [c] Mixture of dimethoxydimethylbiphenyls in mmols (see Experimental Section). [d] 2,4′-Dimethoxy-5-methyldiphenylmethane and 3,4′-dimethoxy-6-methyl isomer (in parentheses) in mmols.

[MT, NO$^+$] complex, which persisted for days at −78 °C. The methoxytoluene donor was intact at this temperature, as judged by the persistence of its characteristic ^{1}H resonances at δ 2.28 and 3.75 in the NMR spectrum and by the quantitative recovery of MT upon workup without warning. When the mixture was allowed to warm to room temperature, gas evolution was observed, and the solution gradually turned purple. The UV–vis spectrum revealed the presence of absorption bands at λ = 286, 402, 440, and 538 nm which were strongly reminiscent of those previously observed with aromatic cation radicals.[33] Indeed, the aqueous workup of the purple solution afforded the dimeric dimethyldimethoxybiphenyl as a mixture of two isomers[34] in 39% yield, in addition to a small amount (∼3%) of the trimeric analogues (see Experimental Section). It was noteworthy that the isomeric methyldimethoxydiphenylmethanes formed in the oxidation of methoxytoluenes by various metal oxidants (see Table VIII)[35] were absent. This, coupled with the presence of nitric oxide in the liberated gas (as detected by the characteristic band at 1876 cm^{-1} in the IR spectrum), supported the initial electron transfer from MT followed by the coupling of the cation radical to afford the biaryl, i.e.

$$MT + NO^+ \rightarrow NO + MT^{\cdot+} \xrightarrow{MT} [CH_3OC_6H_3CH_3]_2, \text{ etc.}$$
(8)
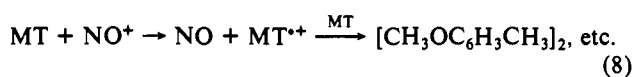
The stable product derived from the transient aromatic cation radical was also observed from the interaction of hexamethylbenzene and NO$^+$BF$_4^-$. For example, when an anaerobic solution containing equimolar amounts of hexamethylbenzene and NO$^+$-BF$_4^-$ in acetonitrile was allowed to stand at room temperature in the dark, it gradually liberated nitric oxide. Workup of the dark red-brown solution by the addition of water after 10 days led to pentamethylbenzylacetamide (see Experimental Section), i.e.

(9)
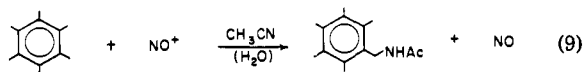
Such a side chain acetamidation was however not an important process, as indicated by the recovery of large amounts of hexamethylbenzene (96%). The latter accorded with the ready isolation of the stable [HMB, NO$^+$PF$_6^-$] complex in the crystalline solid state from dichloromethane solution under an inert atmosphere (vide supra).

The formation of the charge-transfer complex followed by electron transfer could also be inferred from the behavior of NO$^+$BF$_4^-$ toward the aromatic donor bicumene. Typically, the solution of bicumene and NO$^+$BF$_4^-$ in acetonitrile showed the pair of charge-transfer bands with λ$_{max}$ = 338 and 420 nm that were

characteristic of the other [ArH, NO$^+$] complexes listed in Table I. Moreover, evaluation of the formation constant of K = 11 M^{-1} (ε$_{CT}$ = 295 M^{-1} cm^{-1}) and the nitrosyl stretching band at ν_{NO} = 2027 cm^{-1} in the IR spectrum indicated the properties of the 1:1 bicumene complex to be indistinguishable from those of other NO$^+$ complexes derived from monoalkylbenzenes (Table V), i.e.

(10)
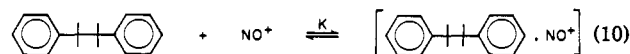
The orange solution of bicumene and NO$^+$BF$_4^-$ in either acetonitrile or nitromethane persisted at 25 °C for a few hours. However upon standing for 4 days protected from light and air (dioxygen),[6] it slowly evolved nitric oxide to afford a pale yellow solution which contained 1,1,3-trimethyl-3-phenylindane as the major component[36] in 10% conversion, together with minor

(11)

amounts of cumene, cumyl alcohol, and an unidentified biphenyl derivative (see Experimental Section).

Donor Rearrangements Induced by the Nitrosonium Cation. The cycloreversion of dianthracene by the nitrosonium cation in eq 7 was reminiscent of the valence isomerization of the olefinic donor hexamethyl(Dewar benzene) promoted by NO$^+$PF$_6^-$. Thus a colorless mixture of NO$^+$PF$_6^-$ in dichloromethane immediately took on a red-brown color upon the addition of an equimolar amount of HMDB at 25 °C under an argon atmosphere. The complete dissolution of NO$^+$BF$_4^-$ occurred within 2 h, and the UV–vis spectrum of the highly colored solution showed a pair of absorption bands centered at λ$_{max}$ 326 and 486 nm that were highly diagnostic of the charge-transfer complex of hexamethylbenzene and NO$^+$ (see Table I), i.e.

(12)
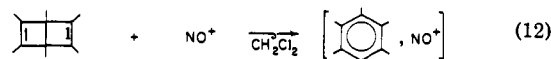
The rate of aromatization of HMDB as described in eq 12 was subject to temperature control, and it could be retarded indefinitely at −78 °C, provided the colorless solution of HMDB and NO$^+$PF$_6^-$ (showing only UV absorption at λ < 300 nm) was protected from adventitious light. The catalytic nature of the aromatization of HMDB (1.04 mmol) was demonstrated in the dissolution of a small amount of NO$^+$PF$_6^-$ (0.061 mmol) in nitromethane-d_3, followed by the observation of the gradual change in the ^{1}H NMR spectrum of HMDB, with diagnostic resonances at δ 1.08 and 1.59,[37] to a single sharp resonance at δ 2.20 of hexamethylbenzene, i.e.

(13)
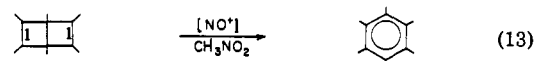
Hexamethylbenzene could be readily isolated in high yields (1700% based on NO$^+$) by sublimation from the reaction mixture.

Oxidative rearrangement induced by NO$^+$ was observed with such structurally diverse donors as cycloheptatriene, homobenzvalene, and cyclopropylbenzene. Thus a mixture of cycloheptatriene and NO$^+$BF$_4^-$ in acetonitrile turned from yellow to orange upon standing at room temperature for an hour. Removal of the solvent in vacuo afforded tropylium tetrafluoroborate[38] (with a single sharp resonance at δ 9.36 for the ^{1}H NMR spectrum in CD$_3$NO$_2$),[39] i.e.

(14)

Similarly, a transient yellow color was observed when homobenzvalene was added to a colorless solution of NO$^+$BF$_4^-$ in nitromethane-d_3. The change in color to dark brown within 10 min was accompanied by the vigorous evolution of gas, and the

(33) (a) Sankararaman, S.; Haney, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5235, 7824. (b) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: New York, 1988.

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Table IX. Formation of 5-Phenylisoxazoline from Cyclopropylbenzene with Various Nitrosating Agents

cyclopropyl-benzene, mmol	reagent, mmol	solvent	temp, °C	isoxazoline,[a] mmol
2.86	$NOBF_4$ (0.74)	CH_3CN	25	0.51 (<0.001)
0.17	$NOBF_4$ (0.13)	$CDCl_3$	25	0.11 (0.004)
0.80	$NOBF_4/O_2$ (0.58)	CH_3CN	25	0.18 (0.008)
0.80	$NOBF_4$ (0.54)	CH_3CN	25	0.18 (0.075)
0.64	$NOBF_4$ (0.46)	CH_2Cl_2	25	0.23
10[b]	N_2O_4 (20)	CH_2Cl_2	−30	2.5 (5.0)[e]
c	$NaNO_2/TFA$	CH_2Cl_2	−35	(80%)[f]
d	$Cu(NO_3)_2$	Ac_2O	0–10	(55%)[f]

[a] 5-Phenylisoxazoline and *trans*-cinnamaldehyde (in parentheses). [b] From ref 40c. [c] TFA = trifluoroacetic acid in ref 40d. [d] From 1,2-diphenylcyclopropane in ref 40b. [e] Benzaldehyde (2.0 mmol) was also obtained. [f] Only the % yield of product was reported.

¹H NMR spectrum of the solution showed only a single sharp resonance of the tropylium cation at δ 9.35, i.e.

$$\square \xrightarrow[CH_3NO_2]{NO^+} \; \textcircled{+} \; , \; etc. \qquad (15)$$

The yellow color obtained upon the treatment of cyclopropylbenzene with $NO^+BF_4^-$ in acetonitrile at −40 °C intensified upon allowing the solution to warm to room temperature with stirring. Aqueous workup of the solution afforded 5-phenylisoxazoline[40] according to the presumed stoichiometry
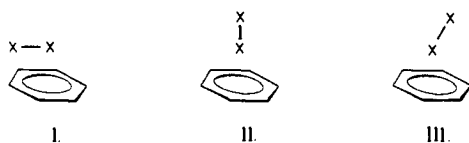
$$\bigcirc\!\!-\!\!\triangleleft \; + \; NO^+ \xrightarrow{CH_3CN} \bigcirc\!\!-\!\!\langle \; + \; H^+ \qquad (16)$$
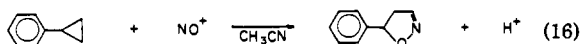
When the course of the oxidative rearrangement was examined directly at 25 °C in CD_3NO_2 solution, by following the change in the ¹H NMR spectrum, the growth of the characteristic resonances of the protonated isoxazoline was observed immediately after mixing of the components (see Experimental Section). The facility with which the reaction occurred was evident by the dissolution of $NO^+BF_4^-$ upon standing with cyclopropylbenzene in dichloromethane to afford a bright yellow solution from which 5-phenylisoxazoline was isolated in 50% yields. Indeed the high yields of the isoxazoline consistently obtained (together with varying amounts of *trans*-cinnamaldehyde) by the action of the various nitrosating agents listed in Table IX directly on phenylcyclopropane is noteworthy.

Discussion

The nitrosonium cation bears a formal relationship to the well-studied halogens (i.e., $X_2 = I_2$, Br_2, and Cl_2)[41]—with both classes of structurally simple diatomic electron acceptors forming an extensive series of intermolecular electron donor–acceptor (EDA) complexes that show well-defined charge-transfer absorption bands in the UV–vis spectral region.

Axial and Oblique Structures of Aromatic EDA Complexes with Diatomic Acceptors. Mulliken originally identified the three possible nonbonded structures of the halogen complexes as[42]

        X—X   X   X
                          | /
                          X   X

    ◁▱▷   ◁▱▷   ◁▱▷

      I   II   III

and the subsequent X-ray studies established the axial form II to be extant in the crystals of the benzene complexes with Cl_2 and Br_2.[43] In these 1:1 molecular complexes, the closest approach

Figure 4. Direct relationship of the charge-transfer excitation energies ($h\, v_{CT}$) of iodine[41] and nitrosonium EDA complexes with the same series of arene donors.

of the halogen to the benzene (ring) carbon of 3.3 Å exceeds the distance for conventional bonding, and it is obtained by charge-transfer interactions involving the benzene HOMO and the halogen LUMO.[44] As such, the linear arrangement of the two halogen atoms of X_2 in the EDA complex of C_{6v} symmetry can be simply depicted as a weak π–σ^* interaction.[45] On the other hand, X-ray crystallography of the NO^+ complex of either hexamethylbenzene[9] or mesitylene (Figure 2) shows the diatomic NO moiety to be tilted by ~30° away from the vertical projection (and slightly displaced by ~0.03 Å from the centroid).[46] The additional π–π^* contribution to the oblique structure III is reminiscent of back-bonding that leads to the ligand bending in metal nitrosyls.[47] Despite any detailed differences of the HOMO–LUMO interactions in the X_2 and NO^+ complexes with arene donors, however, the linear correlation ($r = 0.95$) shown in Figure 4 can be expressed analytically as

$$h v_{CT}[ArH, NO^+] = 0.7 h v_{CT}[ArH, I_2] + 0.1 \qquad (17)$$

to underscore the essential unity in the variations of the charge-transfer interaction energies ($h v_{CT}$) as they are affected by the different strengths of arene donors.

Charge Transfer in Weak and Strong Aromatic EDA Complexes. Recent time-resolved spectroscopic studies have identified the charge-transfer excitation ($h v_{CT}$) of aromatic EDA complexes with various types of acceptors (A) to their ion–radical pairs [$ArH^{•+}$, $A^{•-}$].[48] Such electronic transitions in weak EDA complexes, like those of the halogen acceptors, are mainly associated with the excited states, e.g.

$$ArH + Br_2 \underset{}{\overset{K}{\rightleftharpoons}} [ArH, Br_2] \xrightarrow{h v_{CT}} [ArH^{•+}, Br_2^{•-}] \qquad (18)$$

(40) (a) Huisgen, R.; Christl. M. *Chem. Ber.* **1973**, *106*, 3291. (b) Sychkova, L. D.; Shabarov, Yu. S. *J. Org. Chem. (USSR)* **1976**, *12*, 2538. (c) Smirnova, M. M.; Geiderikh, A. V.; Mochalov, S. S.; Shabarov, Yu. S. *J. Org. Chem. (USSR)* **1988**, *24*, 1070. (d) Shabarov, Yu. S.; Saginova, L. G.; Gazzaeva, R. A. *J. Org. Chem. (USSR)* **1982**, *18*, 2319.

(41) Andrews, L. J.; Keefer, R. M. *Molecular Complexes in Organic Chemistry*; Holden-Day: San Francisco, 1964.

(42) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811. (b) Mulliken, R. S. *J. Chim. Phys.* **1964**, *61*, 20. Mulliken, R. S. *J. Phys. Chem.* **1952**, *56*, 801. See also ref 10.

(43) (a) Hassel, O.; Stromme, K. O. *Acta Chem. Scand.* **1959**, *13*, 1781. (b) Hassel, O.; Stromme, K. O. *Acta Chem. Scand.* **1958**, *12*, 1146.
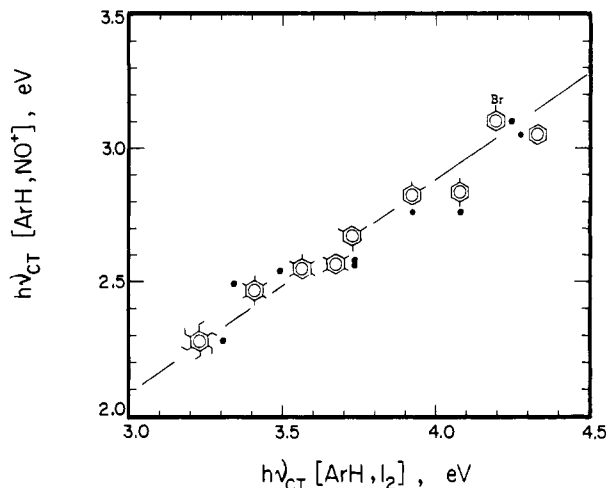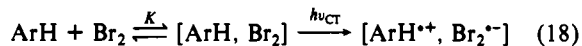
(44) (a) Flurry, R. L., Jr. *J. Phys. Chem.* **1965**, *69*, 1927; **1969**, *73*, 2111. (b) Flurry, R. L., Jr.; Politzer, P. *J. Phys. Chem.* **1969**, *73*, 2787. See also: (c) Gur'yanova, E. N.; Gol'dshtein, I. P.; Romm, I. P. *Donor–Acceptor Bond*; Wiley: New York, 1975. (d) Mataga, N.; Kubota, T. in ref 11, p 205ff.

(45) Compare Aono, S. *Prog. Theor. Phys.* **1959**, *22*, 313.

(46) (a) Although X-ray crystallography does not distinguish N from O, the greater electron polarization of nitrogen favors its closer approach to the arene donor. [Raghavachari, K.; Reents, W. D., Jr.; Haddon, R. C. *J. Comput. Chem.* **1986**, *7*, 265.] (b) IR studies of the [ArH, NO^+] complexes show no evidence for the formation of σ-adducts such as that modeled by either the heptamethylbenzenonium ion or the HF–ArH adducts. [See: Koptyug, V. A. *Top. Curr. Chem.* **1984**, *122*, 106. See also Reents, W. D., Jr.; Freiser, B. S. in ref 5. For theoretical studies, see: Minkin, V. I.; Minyaev, R. M.; Yudilevich, I. A.; Kletskii, M. E. *J. Org. Chem. (USSR)* **1985**, *21*, 842.]

(47) Hoffmann, R.; Chen, M. M. L.; Elian, M.; Rossi, A. R.; Mingos, D. M. P. *Inorg. Chem.* **1974**, *13*, 2666. See also: Kravtsova, E. A.; Mazalov, L. N. *J. Struct. Chem.* **1987**, *28*, 691. Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.

(48) (a) Jones, G., II in *Photoinduced Electron Transfer*, Part A; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; p 245ff. (b) Mataga, N. *Pure Appl. Chem.* **1984**, *56*, 1255. (c) Hilinski, E. F.; Masnovi, J. M.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 8071.
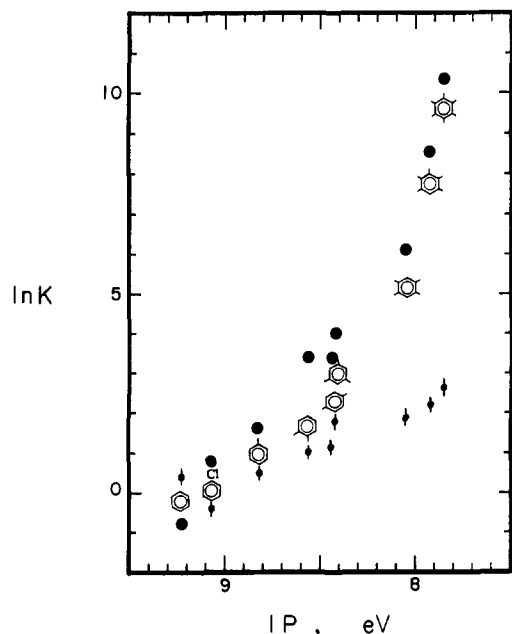
Figure 5. Weak and strong EDA complexes with iodine[51] (Φ) and nitrosoniun ion (●), respectively, as evaluated by the variation of their formation constants with different arene donors.

Figure 6. Degree of charge transfer in NO^+ complexes with the variation in the ionization potential of the arene donor, as evaluated by eq 20.

since the variations in the ground state are minor owing to the formation constants K that are not strongly dependent on the arene donor.[49] The same conclusion is not applicable to the NO^+ complexes, in which the magnitudes of the formation constants are much more strongly dependent on the ionization potential of the arene donor (see Figure 5). Thus the factor of $>10^4$ in Table II that separates the formation constant of the benzene complex with NO^+ from that of the hexamethylbenzene complex corresponds to more than 5 kcal mol^{-1} of extra stabilization energy in the [HMB, NO^+] complex. Indeed the unusually large slope in Figure 5 for the [ArH, NO^+] complexes is the distinguishing criterion for the existence of strong charge-transfer complexes.[10,44,50]

Generally the binding of electron donors (D) to electron acceptors (A) in EDA complexes can be conveniently described in qualitative valence-bond terms as[10,51]

$$\Psi_{GS} = \frac{1}{N}[a\phi_0 + b\phi_1 + ...] \tag{19}$$

where the ground-state wave function Ψ_{GS} mainly contains contributions from ϕ_0 and ϕ_1 representing the weak van der Waals or no-bond interaction of D,A and the dative or charge-transfer component $D^{\bullet+}A^{\bullet-}$, respectively, and N is the normalization factor. In *weak* EDA complexes such as [ArH, I_2], the binding derives largely from the first term with $a^2 \gg b^2$,[42] whereas the binding in *strong* EDA complexes such as [ArH, NO^+] depends largely on the ionization potential of the donor owing to the relatively increased importance of the charge-transfer contribution (i.e., $b^2 > a^2$).[52]

The Charge-Transfer Structures of Aromatic Complexes with the Nitrosonium Cation. The importance of ground-state charge transfer is observed experimentally in the [ArH, NO^+] complexes by the marked structural change in the nitrosonium moiety upon complexation to the arene donor. Thus the X-ray crystallographic analysis in Table III establishes the lengthening of the N–O bond distance that occurs concomitantly with the vibrational (infrared)
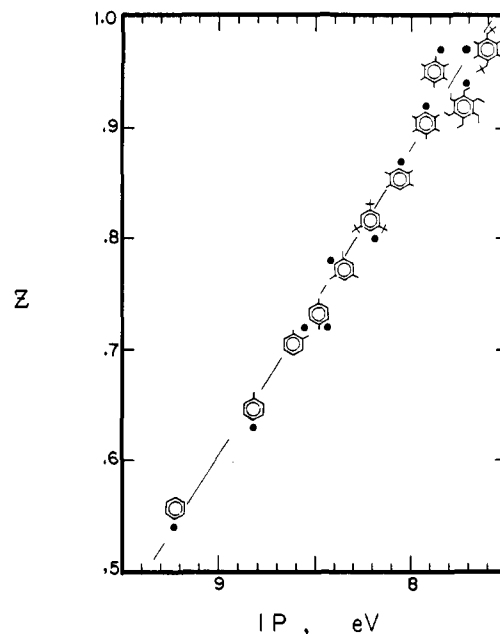
Table X. Degree of Charge Transfer in the Aromatic EDA Complexes with the Nitrosonium Cation

R-substituted benzene, R =	medium[a]	$\Delta\nu^b$	Z^c
H	NM	0.09	0.52
methyl	NM	0.11	0.61
	DR	0.13	0.65
BC^d	NM	0.12	0.66
1,2-dimethyl	NM	0.13	0.69
1,4-dimethyl	NM	0.13	0.70
1,3,5-trimethyl	NM	0.14	0.75
	DR	0.14	0.71
1,3,5-tri-*tert*-butyl	NM	0.14	0.80
1,2,4,5-tetramethyl	NM	0.16	0.86
	DR	0.15	0.77
pentamethyl	NM	0.17	0.92
	DR	0.18	0.91
hexamethyl	NM	0.18	0.97
	DR	0.19	0.97
hexaethyl	NM	0.17	0.93
1,3-DNP^e	NM	0.18	0.97
1,4-DNP^e	NM	0.18	0.97

[a] Measured in nitromethane solution (NM) or diffuse reflectance (DR). [b] Relative frequency shift, where $\Delta\nu = (\nu_{NO^+} - \nu_C)/\nu_{NO^+}$. [c] Degree of charge transfer is defined in eq 20. [d] BC = (2,3-dimethyl-3-phenyl)-2-butyl. [e] DNP = dineopentyltetramethyl.

decrease in the stretching frequency of the N–O bond (Table V) to closely approach that of nitric oxide.[53] Both of these experimental manifestations of the significant alteration of the nitrosonium moiety within the hexamethylbenzene complex relate to the general theory of the structural changes due to charge transfer, as evaluated by the parameter Z.[54] As a reflection of the degree of charge transfer, Z is well accommodated in nitrosonium complexes in which the variations in the vibrational frequencies of the simple diatomic acceptor are rather unambiguous measures of the structural change developed by Friedrich and Person,[55] i.e.

$$Z \simeq (\nu_{NO^+}^2 - \nu_C^2)/(\nu_{NO^+}^2 - \nu_{NO}^2) \tag{20}$$

(49) Briegleb, G. *Elektronen-Donator-Acceptor-Komplexe*; Springer: Heidelberg, 1961; p 106ff.

(50) Kosower, E. M. *Prog. Phys. Org. Chem.* **1965**, *3*, 81. See also Foster, R. in ref 8.

(51) Hanna, M. W.; Lippert, J. L. *Molecular Complexes*; Foster, R., Ed.; Elek Science: London, 1973; Vol. 1, p 6ff.

(52) See: Mataga, N.; Kubota, T., ref 44d, p 214. Yada, H.; Tanaka, J.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1660.

(53) By comparison, the frequency shift of Cl_2 in weak [C_6H_6, Cl_2] complexes is minor. See: (a) Person, W. B.; Erickson, R. E.; Buckles, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 29. (b) Collin, J.; D'Or, L. *J. Chem. Phys.* **1955**, *23*, 397.

(54) (a) Kampar, V. E.; Neilands, O. Ya. *Russ. Chem. Rev.* **1986**, *55*, 334. (b) Kampar, V. E.; Gudele, I. Ya.; Neilands, O. Ya. *Theor. Exper. Chem.* **1980**, *16*, 321. (c) Szczepaniak, K.; Tramer, A. *J. Phys. Chem.* **1967**, *71*, 3035. See also ref 18a.

Table XI. Aromatic Cationic Character in the EDA Complexes with the Nitrosonium Cation from Their ^{13}C NMR Spectra

R-substituted benzene donor, R =	$\rho_i{}^a$	q^b
1,3,5-trimethyl	0.86	0.55
	0.96	
1,2,4,5-tetramethyl	0.92	0.71
	0.86	
pentamethyl	0.93	0.77
	0.86	
	0.86	
	0.85	
hexamethyl	0.87	0.80
hexaethyl	0.85	0.89

^{a} From the ^{13}C NMR chemical shift at the ring carbon atom (C$_i$) according to eq 22. ^{b} Calculated total positive charge on the aromatic moiety of the [ArH, NO$^+$] complex.

where v_{NO^+}, v_C, and v_{NO} refer to N–O frequencies listed in Table V for the free nitrosonium cation, the EDA complex, and nitric oxide, respectively (see Appendix). As expected for degree of charge transfer, the values of Z for various [ArH, NO$^+$] complexes increase linearly with decreasing ionization potential of the arene donor (Figure 6). It is particularly noteworthy that the values of Z in Table X span the range from 0.52 for the benzene complex to 0.97 for the hexamethylbenzene analogue to reflect the reasonably large and almost complete charge transfer, respectively, that can occur in the ground states of these nitrosonium complexes (compare Figure 3).

The essential correctness of the charge-transfer formulation for the series of strong [ArH, NO$^+$] complexes is well supported by the accompanying measures of structural change in the aromatic donors. Thus the extent to which charge transfer is relevant to the alteration of the nitrosonium moiety within the [ArH, NO$^+$] complex to that of nitric oxide, as described above, must coincide with the arene moiety taking on an equal measure of cationic character, i.e.

$$[ArH, NO^+] \equiv [ArH^{\cdot+}, NO] \qquad (21)$$

The comparable energetics of these structural forms is underscored by the ionization potential of benzene (9.23 eV)[56] which is essentially the same as that of nitric oxide (9.26 eV).[57]

Since the local π-electron density ρ_i based on the Hückel model of aromatic hydrocarbons[58] is well correlated with the ^{13}C NMR chemical shifts according to the relationship[19]

$$\delta(^{13}C) = -142\rho_i + 274 \qquad (22)$$

(as described in the Appendix), the total cationic charge q on the donor can be represented as the sum of the π-electron deficiency at each carbon center, i.e., $q = \sum(1 - \rho_i)$. As applied to the ^{13}C NMR shifts listed in Table VI, the total charge on the aromatic moiety of [ArH, NO$^+$] complexes is given by the values of q in Table XI, column 3. The parallel trend of the aromatic cationic charge q evaluated in this manner with the degree of charge-transfer Z evaluated from the vibrational changes of the nitrosonium acceptor in the series of [ArH, NO$^+$] complexes in Table X is unmistakable. Although the corresponding changes in the vibrational frequencies of the aromatic donor also support the same general conclusion (see Table VII), the complex vibrational modes of the polyatomic donors discourage a quantitative analysis of the arene changes at this juncture.

Charge Transfer versus Electron Transfer in the Interaction of Aromatic Donors with the Nitrosonium Cation. The increased importance of charge transfer in proceeding up the series of NO$^+$ complexes with the enhanced donor strength of arenes that vary from benzene (IP = 9.23 eV) to the electron-rich hexamethylbenzene (IP = 7.85 eV) has its chemical consequences with respect to thermal (adiabatic) electron transfer. Thus the benzene complex with Z = 0.52 is persistent in acetonitrile solution for long periods, provided the solution is protected from adventitious moisture and light.[6] By contrast, the hexamethylbenzene complex with Z = 0.97 slowly liberates nitric oxide under the same conditions; and the corresponding amount of the N-benzylacetamide described in eq 9 is isolated upon the workup of the acetonitrile mixture. Since the acetamide product is known to derive from the sequestration of the transient hexamethylbenzene cation radical by the polar solvent,[59] the temporal evolution of the first-formed EDA complex (Tables I and II) to the radical ion pair is readily inferred, e.g.

Scheme I

$$HMB + NO^+ \xrightleftharpoons{K} [HMB, NO^+] \qquad (23)$$

$$[HMB, NO^+] \xrightleftharpoons[k_{-1}]{k_1} NO + HMB^{\cdot+} \qquad (24)$$

$$HMB^{\cdot+} \xrightarrow{k_2} etc. \qquad (25)$$

The electron-transfer step (k_1) in Scheme I is endergonic by ~8 kcal mol^{-1},[60] and it is likely to be reversible ($k_{-1} > k_1$). Accordingly, the electron-transfer equilibrium in eq 24 must be driven further by the followup reactions (k_2) of the HMB$^{\cdot+}$ cation radical.[61] This formulation is consistent with the *complete* conversion of the very strong aromatic donor octamethylbiphenylene with $E_{ox}{}^0$ = 0.78 V vs SCE[29] by the nitrosonium cation ($E_{red}{}^0$ = 1.28 V)[60] to yield the persistent cation radical in eq 4 as a result of the highly exergonic electron transfer of ΔG = –11.5 kcal mol^{-1}.

It is important to emphasize that the nitrosonium cation is not a strong oxidant, and there are few arene donors that are extant with reversible oxidation potentials of sufficient magnitude ($E_{ox}{}^0$ < 1.28 V)[56] to enable an exergonic electron transfer to occur commonly. Nevertheless, the oxidation of various arenes by nitrosonium cation may be readily effected if the endergonic electron-transfer equilibrium is followed by a facile followup transformation.[62] For example, the electron transfer to NO$^+$ from the intermediate donor anthracene with $E_{ox}{}^0$ = 1.49 V (and IP = 7.85 eV)[63] is driven to completion by the crystallization of the anthracene π-dimer salt from the dichloromethane solution in eq 5. It is particularly noteworthy that dianthracene, despite its limited donor properties of $E_{ox}{}^0 \sim$ 1.8 V, is easily converted to the same anthracene π-dimer salt by the nitrosonium cation in eq 7. In this case, the highly endergonic electron-transfer equilibrium is driven by the rapid fragmentation (cycloreversion) of the cation radical, i.e.

$$(26)$$
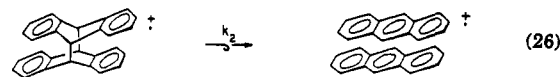
which is known to occur with a first-order rate constant of $K_2 \simeq$ 10^8 s^{-1}.[64] The facile scission of the carbon–carbon σ-bonds in aromatic cation radicals also accounts for the unusual oxidative
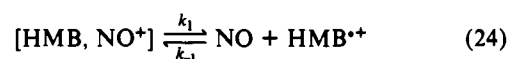
(55) (a) Friedrich, H. B.; Person, W. B. *J. Chem. Phys.* **1966**, *44*, 2161. (b) The evaluation of the degree of charge transfer by IR changes in the diatomic NO$^+$ is straightforward in comparison to most polyatomic acceptors in which the rigorous normal coordinate analysis of the complex vibrations is difficult. [Compare: Chappell, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442. Kampar, V. E.; Valtere, S. P.; Neilands, O. Ya. *Theor. Exper. Chem.* **1978**, *14*, 288.]

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

(57) Lias, S. G. *Chem. Phys. Lett.* **1978**, *54*, 147.

(58) Koptyug, V. A.; Mamatyuk, V. I.; Detsina, A. N. *Zh. Org. Khim.* **1976**, *12*, 739.

(59) (a) Bewick, A.; Edwards, G. J.; Mellor, J. M.; Pons, S. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1952. (b) Eberson, L.; Nyberg, K. *Tetrahedron Lett.* **1966**, 2389.

(60) Based on $E_{ox}{}^0$ = 1.62 V for hexamethylbenzene [Amatore, C. Private Communication] and $E_{red}{}^0$ = 1.28 V for NO$^+$ in acetonitrile [Lee, K. Y.; Kuchynka, D. J.; Kochi, J. K. *Inorg. Chem.* **1990**, *29*, 4196].

(61) Masnovi, J. M.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 2263.

(62) See: Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3567.

(63) Masnovi, J. M.; Seddon, E. A.; Kochi, J. K. *Can. J. Chem.* **1984**, *62*, 2552.

(64) Masnovi, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 6781.

rearrangement of bicumene induced by the nitrosonium cation in eq 11 to the hydrindane derivative (which structurally corresponds to the acid-catalyzed dimer of α-methylstyrene).[36] Thus the rapid cleavage of the bicumene cation radical reported earlier[65] may be followed by the oxidation and the head-to-tail recombination of the fragments, e.g.[66]

$$\text{(27)}$$

$$\text{(28)}$$
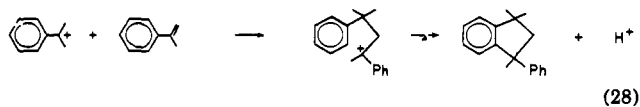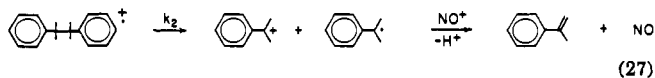
If so, the fragmentation rate (k_2) must be sufficiently rapid to drive the highly endergonic electron transfer equilibrium with ΔG > 20 kcal mol^{-1} based on an estimated oxidation potential of E_{ox}^0 ~ 2.2 V for bicumene.[56] Basically the same electron-transfer formulation is also applicable to the oxidative coupling of *p*-methoxytoluene (E_{ox}^0 = 1.67 V)[33] to the biaryls in eq 8, owing to the rapid collapse of the π-dimer to the σ-adduct, e.g.[67]

$$\text{(29)}$$
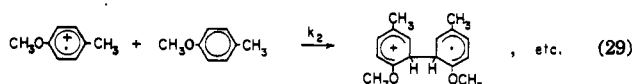
The oxidative conversions of the aromatic donors hexamethylbenzene, anthracene, dianthracene, bicumene, and methoxytoluene by the nitrosonium cation, as described above, are rather unequivocal examples[68] in which the establishment of an electron-transfer equilibrium is a clear prerequisite for the further (followup) reactions. There are other donors, including arenes and alkenes, in which the electron-transfer pathway is not readily distinguished from a more conventional electrophilic mechanism. For example, the aromatization of hexamethyl(Dewar benzene) (HMDB) in eq 12 via the labile cation radical has been established for photoinduced electron transfer,[69] and the corresponding adiabatic electron transfer to NO$^+$ can represent a viable mechanism,[70] as described above. In the absence of direct evidence for the cation radical HMDB$^{\bullet+}$ as the vital intermediate, however, the one-electron mechanism cannot be distinguished from the direct two-electron process induced by electrophilic addition,[71c] e.g.

$$\text{(30)}$$
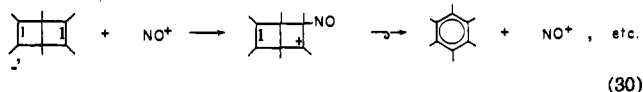
The same mechanistic ambiguity applies to the oxidative aromatization of cycloheptatriene in eq 14, the oxidative rearrangement of homobenzvalene in eq 15, as well as the insertion of NO$^+$ into cyclopropylbenzene in eq 16. Although the cation radicals are energetically accessible via an endergonic electron-transfer equilibrium with the nitrosonium cation,[71] each of these donors is also susceptible to electrophilic addition.[72]

Electron Transfer from Charge-Transfer Complexes as a General Formulation. The mechanistic conundrum presented by such a dichotomy between electron-transfer and electrophilic processes can only be rigorously resolved by the experimental proof of whether the cation radical (or the electrophilic adduct) is or is not the vital reactive intermediate. However in a thermal (adiabatic) reaction between arene donors and the nitrosonium cation, such reactive intermediates cannot be formed in sufficient concentrations to be directly observed by conventional experimental methods since their rates of followup reactions must perforce always be faster than their rates of formation—except when they are formed in a reversible equilibrium like the highly relevant EDA complexes [ArH, NO$^+$] described in this study. Indeed the formation of such charge-transfer complexes as reactive intermediates represents the unifying theme for both electron-transfer and electrophilic processes whenever arene and alkene donors (D) are exposed to various types of electron-poor species (A) that include electron acceptors, electrophiles, oxidants, etc.[3] Accordingly, let us proceed with the general mechanistic formulation as follows.

Scheme II

$$D + A \underset{}{\overset{K}{\rightleftharpoons}} [D, A] \qquad (31)$$

$$[D, A] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [D^{\bullet+}, A^{\bullet-}] \qquad (32)$$

$$[D^{\bullet+}, A^{\bullet-}] \overset{k_2}{\longrightarrow} \text{products} \qquad (33)$$

For the electron-transfer mechanism in Scheme II, the charge-transfer complex (eq 31) and the radical ion pair (eq 32) are both formed reversibly, and the critical transformation resides with the followup processes (k_2) in eq 33. Any unimolecular transformation of either D$^{\bullet+}$ or A$^{\bullet-}$ such as fragmentation, cycloreversion, rearrangement, etc., or their mutual (first-order) annihilation within the radical ion pair [D$^{\bullet+}$, A$^{\bullet-}$],[73] must be sufficiently rapid to compete with back electron transfer (k_{-1}) to drive both equilibria onward. Such a one-electron process is indistinguishable from a two-electron process (such as electrophilic addition),[74] i.e.

Scheme III

$$D + A \overset{K}{\rightleftharpoons} [D, A] \qquad (34)$$

$$[D, A] \overset{k_3}{\longrightarrow} \text{products} \qquad (35)$$
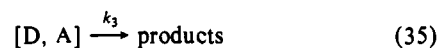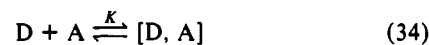
and the mechanistic equivalency is clearly delineated in the kinetic limits where the ion radical pair is short-lived, either due to a rapid followup reaction ($k_2 > k_{-1}$) and $k_3 = k_1$ or a rapid back electron transfer ($k_{-1} \gg k_2$) and $k_3 = k_1 k_2/k_{-1}$. In both cases the relative reactivities of a series of donors interacting with a common acceptor (or vice versa) will strongly depend on the variation of their oxidation (reduction) potentials. In addition, there is a third

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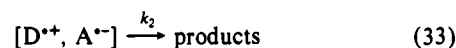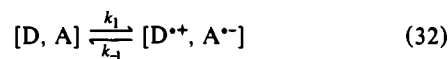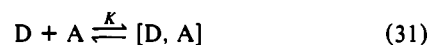(70) See: Roth, H. D.; Schilling, M. L. M.; Raghavachari, K. *J. Am. Chem. Soc.* **1984**, *106*, 253.
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(74) (a) For a discussion of charge-transfer complexes as obligatory intermediates in such processes, see: Colter, A. K.; Dack, M. R. J. In *Molecular Complexes*; Foster, R., Ed.; Elek Science: London, 1974; Vol. 2, p 2. (b) It is interesting to note that the linear correlation of the formation constants of [ArH, NO$^+$] and the σ-adducts [ArH$_2^+$F$^-$] (Kilpatrick, M.; Luborsky, F. E. *J. Am. Chem. Soc.* **1953**, *75*, 577) can be expressed as ln K[NO$^+$] = 0.46 ln K[H$^+$] + 8.9.

4972 *J. Am. Chem. Soc., Vol. 113, No. 13, 1991*

Kim and Kochi

limiting situation, observed with arene donors and the nitrosonium cation, in which the large variation in the formation constants K is diagnostic of a high degree of charge transfer in the ground state of the EDA complex. Mechanistically, this structural situation translates to $[D, A] \equiv [D^{\bullet+}, A^{\bullet-}]$ in Scheme II. The latter is tantamount to the irrelevancy of the electron-transfer equilibrium (eq 32), so that $k_3 = k_2$. The interrelationship between the charge-transfer complex and the radical ion pair is critical to the understanding of the electron-transfer mechanism presented in Scheme II. Such a focus however requires the direct observation of the charge transfer that it not allowed in donor–acceptor systems undergoing adiabatic changes. As such, we hope to present time-resolved spectroscopic studies of the microdynamical behavior of the radical ion pair $[D^{\bullet+}, A^{\bullet-}]$. These reactive intermediates can be generated by the vertical (nonadiabatic) processes involving the direct charge-transfer photoexcitation of NO^+ complexes with the aromatic donors relevant to this study.[75]

Experimental Section

Materials. NOBF$_4$ (Pfaltz and Bauer) was recrystallized from acetonitrile at -20 °C, followed by filtration in a dry box and vacuum drying to yield colorless crystals. NOPF$_6$ (Pfaltz and Bauer) was used without purification. NOSbCl$_6$ was prepared from SbCl$_5$ and NOCl[76] in dichloromethane at -20 °C under an argon atmosphere. The pale yellow crystals obtained after removal of solvent were dried in vacuo at room temperature. NOAsF$_6$ was prepared by ion exchange of n-Bu$_4$NAsF$_6$ and NOSbCl$_6$ in a mixture of nitromethane and dichloromethane at -20 °C to give colorless crystals. n-Bu$_4$NAsF$_6$ was obtained in quantitative yields from the reaction of n-Bu$_4$NI (Eastman) and (C$_6$H$_5$)$_3$CAsF$_6$ (Ozark Mahoning) at room temperature. The solutions of the nitrosonium salts were always transferred with the aid of a glass hypodermic syringe equipped with a Teflon needle. The aromatic hydrocarbons were reagent grade, commercial samples that were purified by distillation or recrystallization from alcohol: benzene, bromobenzene, toluene, and *tert*-butylbenzene (Eastman), chlorobenzene, iodobenzene, and biphenyl (Matheson), ethylbenzene, o- and p-xylene, 1,3,5-tri-*tert*-butylbenzene, durene, and pentamethylbenzene (Aldrich), hexamethylbenzene (Fluka), mesitylene (Baker), 4-methoxytoluene (Aldrich), and naphthalene (Matheson). Anthracene (Aldrich), hexamethyl(Dewar benzene), and cycloheptatriene (Aldrich) were used as received. 1,2-, 1,3-, and 1,4-dineopentyltetramethylbenzene were obtained as gifts from M. S. Newman; and homobenzvalene from M. Christl was distilled in vacuo (20 °C at 3 Torr). Adamantane (Aldrich) was sublimed prior to use. Powdered quartz was washed and dried at 200 °C for 24 h. Acetonitrile (HPLC grade, Fisher) 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 refiltered acetonitrile was finally refractionated from P$_2$O$_5$ under an argon atmosphere. Dichloromethane (Baker) was initially stirred with concentrated sulfuric acid; the separated layer was neutralized, dried over anhydrous Na$_2$CO$_3$, and finally distilled from anhydrous P$_2$O$_5$ under an argon atmosphere. Nitromethane (Fisher) was chilled at -78 °C until most of it was frozen and the slightly pale yellow liquid was removed with the aid of a cannula. The colorless solid was resubjected to the same treatment three times, and after the resulting nitromethane was treated with CaCl$_2$ it was distilled at reduced pressure (150 mmHg, bp 49–50 °C) to afford colorless nitromethane that was stored under argon in a Schlenk flask in the dark. Dichloromethane-d_2 (Cambridge Isotopes 99.3% D) and nitromethane-d_3 (Aldrich, 99% D) were stored under nitrogen in a Schlenk flask equipped with Teflon stopcocks. Trifluoroacetic acid (Mallinckrodt) was distilled from P$_2$O$_5$ 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 a Perkin-Elmer 330 spectrometer equipped with a Hitachi Model H210-2101 integrating sphere accessory. The ^{1}H 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 and the diffuse reflectance spectra of solid samples were obtained with the collector DRIFT accessory and blocker device (Spectra-Tech). Gas chromatography was performed on a Hewlett-Packard 5790A series FID gas chromatography equipped with a 3392 integrator.

All inert atmosphere manipulations were carried out in a Vacuum Atmospheres MO-41 dry box. GC-MS analyses were carried out on a Hewlett-Packard 5890 chromatograph interfaced to a HP 5970 mass spectrometer (EI, 70 eV). ASYST 2.0 Software was employed for the deconvolution data processing with an AT&T 6300 plus computer.

Isolation of Crystalline Charge-Transfer Complexes of Arenes with Nitrosonium Salts. Typically, the arene was added to a flask that contained the nitrosonium salts (dry box) and a minimum amount of dichloromethane was added to the colorless mixture. The undissolved solid was removed by filtration and the resulting red solution was chilled to -20 °C in the dark. After 48 h, the crystals were collected and dried under a stream of argon. Quantitative analysis of the complexes was carried out by ^{1}H NMR spectrometry with nitromethane or 1,2-dichloromethane as the internal standard and by gas chromatography with nonane as the internal standard. [**Hexamethylbenzene, NOPF$_6$**]: Black shiny crystals (0.30 g, 74%) were isolated from 0.20 g of hexamethylbenzene and 0.19 g of NOPF$_6$ in 9 mL of CH$_2$Cl$_2$. ^{1}H NMR (CD$_3$CN): δ 2.48. Molecular weight calculated for [C$_6$(CH$_3$)$_6$,NOPF$_6$] 337, found 334. [**Pentamethylbenzene, NOPF$_6$**]: Black crystals (0.35 g, 65%) were isolated from 0.29 g of pentamethylbenzene and 0.25 g of NOPF$_6$ in 7 mL of CH$_2$Cl$_2$. ^{1}H NMR (CD$_3$NO$_2$): δ 2.44 (9 H), 2.51 (6 H), 7.66 (1 H). Molecular weight calculated for [C$_6$H(CH$_3$)$_5$, NOPF$_6$] 323, found 326. [**Durene, NOPF$_6$**]: Brown crystals (0.34 g, 68%) were obtained from 0.20 g of durene and 0.20 g of NOPF$_6$ in 5 mL of CH$_2$Cl$_2$. ^{1}H NMR (CD$_3$NO$_2$): δ 2.43 (12 H), 7.56 (2 H). Molecular weight calculated for [C$_6$H$_2$(CH$_3$)$_4$, NOPF$_6$] 309, found 311. [**Mesitylene, NOPF$_6$**]: yellow-orange crystals (0.089 g, 34%) were isolated from 0.12 g of mesitylene and 0.14 g of NOPF$_6$ in 3 mL of CH$_2$Cl$_2$. ^{1}H NMR (CD$_3$NO$_2$): δ 2.51 (9 H), 7.50 (3 H). [(**Toluene**)$_2$, **NOSbCl$_6$**]: Brown crystals were isolated from 32 mg of NOSbCl$_6$ and 87 mg of toluene in 2 mL of CH$_2$Cl$_2$.[13] [**Mesitylene, NOSbCl$_6$**]: Black cherry crystals (0.17 g, 90% yield) were obtained from 0.14 g of NOSbCl$_6$ and 0.35 g of mesitylene in 5 mL of CH$_2$Cl$_2$. [**Hexamethylbenzene, NOSbCl$_6$**]: Black brown crystals (0.10 g, 77%) were isolated from 0.087 g of NoSbCl$_6$ and 0.047 g of hexamethylbenzene in 3 mL of CH$_2$Cl$_2$. [**Hexamethylbenzene, NOAsF$_6$**]: Black brown crystals (0.020 g, 79%) were obtained from 0.015 g of NOAsF$_6$ and 0.027 g of hexamethylbenzene in 2 mL of CH$_2$Cl$_2$ and 5 mL of hexane. ^{19}F NMR (CFCl$_3$ reference): δ -65.0 (q, J = 933 Hz).

Charge-Transfer Absorption Spectra of Arene CT Complexes with NO$^+$. All operations were performed in an inert atmosphere box in a Teflon-capped cuvette equipped with a side arm. The stock solution of NOBF$_4$ in CH$_3$CN was transferred to the cuvette 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 nitrosonium salt was transferred to a preweighed cuvette, and dichloromethane together with a known amount of aromatic donor were added. NOBF$_4$ or NOPF$_6$, which was initially insoluble in dichloromethane, dissolved in the course of complex formation with aromatic donors such as durene, pentamethylbenzene, and hexamethylbenzene to produce a homogeneous red solution. The spectra of the crystalline complexes were obtained by dissolving them in CH$_2$Cl$_2$ under argon atmosphere. The diffuse reflectance UV–vis spectra were taken on crystals that were ground with either adamantane or powdered quartz (dry box) as the diluent against an alumina reference. Solution and solid spectra measured on the wavelength (nm) scale were converted to the energy scale and deconvoluted by assuming the superposition of a pair of Gaussian bands.

The formation constants of arene CT complexes with NO$^+$ were determined as follows: An 8-mL aliquot of a standard stock solution of nitrosonium salt in acetonitrile was transferred to a 1-cm quartz cuvette and a weighed amount of arene was added incrementally under an argon atmosphere. The absorbances (A_{CT}) were measured at the spectral maxima and at other wavelengths close to the absorption maxima. From the plots of $[NO^+](A_{CT})^{-1}$ against $[arene]^{-1}$, consisting of six data points, the slopes were equated to $(K\epsilon_{CT})^{-1}$ and the intercept of ϵ_{CT}^{-1}.[12]

Vibrational Spectra of the Aromatic EDA Complexes with the Nitrosonium Cation. The samples for the diffuse reflectance IR spectra were prepared in the dry box with either the powdered crystals or the ground mixtures of the arene donor with the nitrosonium salt. Solution IR spectra were recorded in a sealed (0.1 cm) AgCl cell by dissolving the crystals in dichloromethane. Alternatively, the preweighed nitrosonium salt was dissolved in nitromethane and a known amount of arene (0.05–0.5 M) was added (glove box). The spectral assignments for the nitrosonium salts were based on the literature values.[17,76] The integrated absorptivity (A) was calculated from the area under an absorption band with a computer program.[77] The molar integrated intensity (A_i) of the NO$^+$ vibration frequency was determined from the integrated absorption in the concentration range of 0.47–1.0 M NOPF$_6$ in CH$_3$NO$_2$. The

(75) Preliminary results indicate that the same products are formed in the charge-transfer photoexcitation of the EDA complexes.

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Charge-Transfer Structures of Aromatic EDA Complexes

J. Am. Chem. Soc., Vol. 113, No. 13, 1991 4973

molar integrated intensity A_i of the EDA complexes in Table V was evaluated in nitromethane solution from the formation constants listed in Table II.[78] In the Jobs' plot for the determination of the 1:1 complex formation, the sum of the arene and nitrosonium concentration was fixed to 0.5 M. In the mixture of benzene and NOPF$_6$ in nitromethane the integrated absorbance of the complexed NO$^+$ plotted against the concentration resulted in a maximum at the 1:1 benzene:NOSbCl$_6$ ratio. Similarly, the formation of a 1:1 complex in the mixture of toluene with NOPF$_6$ was determined in nitromethane solution.

NMR Spectra of the Aromatic EDA Complexes with the Nitrosonium Cation. A preweighed sample of the nitrosonium salt was dissolved in nitromethane (dry box) and a known amount of the arene was added together with an internal standard. The low-temperature ^{1}H and ^{13}C NMR spectra were measured for the complexes dissolved in CD$_2$Cl$_2$ at −75 °C. For the low-temperature NMR study in sulfur dioxide, a weighed amount of nitrosonium salt was transferred to an NMR tube containing a sealed capillary tube of acetone-d_6 and TMS. The mixture was cooled to −78 °C and the arene was added under an argon atmosphere. Finally SO$_2$ was condensed into the mixture and the NMR tube was sealed. The NMR spectra at temperatures down to −78 °C were not significantly different from those obtained at 25 °C. The σ-complex was not observed. The ^{13}C NMR spectra of crystalline EDA complexes were measured at 50 MHz on a Bruker MSL 200 spectrometer by using magic angle spinning (MAS)/cross polarization (CP) with a Macor rotor spun at 2.5 kHz.

X-ray Crystallography of the [Mesitylene, NOSbCl$_6$] Complex. A thin cherry-black plate having approximate dimensions $0.62 \times 0.16 \times 0.06$ mm was mounted (glove box) in a glass capillary in random orientation on a Nicolet R3m/V automatic diffractometer. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. The final cell constants, as well as other information pertinent to data collection and refinement, were the following: space group $P1$, triclinic; cell constants $a = 11.386$ (3) Å, $b = 11.933$ (3) Å, $c = 13.190$ (4) Å, $\alpha = 74.41$ (2)°, $\beta = 84.04$ (2)°, $\gamma = 83.56$ (2)°, $V = 1710$ Å^3; molecular formula C$_9$H$_{12}$ NO$^+$ SbCl$_6^-$; formula weight 484.67; formula units per cell $Z = 4$; density $\rho = 1.88$ g cm^{-3}; absorption coefficient $\mu = 25.6$ cm^{-1}; radiation (Mo Kα) $\lambda = 0.71073$ Å; collection range $4 < 2\theta < 45°$; scan width $\Delta\theta = 1.40 + (K\alpha_2 - K\alpha_1)°$; scan speed range 2.5–15.0 deg. min^{-1}; total number of data collected 4466; independent data $I > 3\sigma(I) = 2517$; $R = \sum ||F_o| - |F_c||/\sum|F_o| = 0.040$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.033$; weights $w = \sigma(F)^{-2}$. The Laue symmetry was determined to be 1′, and the space group was shown to be either $P1$ of $P1'$. Intensities were measured with the ω scan technique, with the scan rate depending on the count obtained in rapid prescans of each reflection. Two standard reflections were monitored after every 2 h or every 100 data points collected, and these showed only a 10% decay over the 3 days of the experiment. In reducing the data, Lorentz and polarization corrections were applied, as well as an empirical absorption correction based on ψ scans of ten reflections having χ values between 70 and 90°. The structure was solved by the SHELXTL Patterson interpretation program, which revealed the position of the two independent Sb atoms in the asymmetric unit, consisting of two complete formula units. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single nonvariable isotropic temperature factor. On the sole basis of analysis of isotropic temperature factors, it was concluded that both nitrosonium cations were disordered, with each atomic site being half populated by nitrogen and half by oxygen. Accordingly, each site was refined as a 50:50 N:O ratio, with the isotropic temperature factors within each molecule constrained to be equal. After all shift/esd ratios were less than 0.5, convergence was reached at the agreement factors listed above. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed a maximum peak of about 0.4 e Å^{-3}. All calculations were made with Nicolet's SHELXTL PLUS (1987) series of crystallographic programs. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table XII (supplementary materials) for the mesitylene EDA complex with NOSbCl$_6$. By comparison, the N–O bond distance of 1.36 Å in the corresponding hexamethylbenzene complex previously reported by Brownstein et al.[9] was unusually long. We therefore concluded that this model with the nitrogen fixed on the mirror plane was incorrect and considered the simplest change to involve a slight shift (by 0.03 Å) along the z direction perpendicular to the mirror. The shift to z = 0.22 (when the atom is centered on the mirror plane z = 0.25), to accord with the acentric structure of the

mesitylene complex determined in this study, resulted in the N–O bond distance of 1.11 Å.

Thermal Reactions of Aromatic Donors with the Nitrosonium Cation. A solution of 0.02 M NOBF$_4$ (0.060 mmol) in acetonitrile was transferred to a specifically designed dual spectroelectrochemical cell (quartz) under an argon atmosphere. The addition of octamethylbiphenylene (OMB, 0.018 mmol) immediately led to a dark blue solution, the spectrophotometric analysis ($\lambda_{max} \sim 600$ nm, $\epsilon = 2000$ M^{-1} cm^{-1})[29] of which indicated the presence of 0.019 mmol of the OMB^{*+} cation radical. The subsequent voltammetric analysis of the blue solution indicated the presence of 0.017 mmol of nitric oxide and 0.037 mmol of unreacted NOBF$_4$.

Anthracene (0.055 mmol) was added to a 0.036 M solution of NOBF$_4$ in 2 mL of acetonitrile under an argon atmosphere. The yellow solution turned dark within an hour and afforded upon an aqueous quench N-9-anthracenylacetamide (0.008 mmol) which was identified by GC-MS analysis: m/z 235 (M$^+$, 53), 194 (38), 193 (100), 192 (38), 165 (36).[30] Anthraquinone (0.0015 mmol) and small amounts of 9-nitroanthracene and an unidentified material (which afforded anthraquinone on standing) were also observed, together with 0.030 mmol of unreacted anthracene. The voltammetric analysis of a solution of anthracene (0.010 M) and NO$^+$BF$_4^-$ (0.033 M) in acetonitrile revealed the presence of nitric oxide (0.018 M) and unreacted NO$^+$BF$_4^-$ (0.006 M). The oxidation of anthracene by NOBF$_4$ in dichloromethane was described previously.[6]

Dianthracene (7.9 mg) was added to a mixture of NOBF$_4$ (3.9 mg, 0.022 mmol) and 2 mL of dichloromethane at −78 °C. The yellow solution was allowed to warm to −20 °C whereupon it turned green (λ_{max} 726 nm) and precipitated the black crystals of π-(C$_{14}$H$_{10}$)$_2$BF$_4$.[6] When the same components were treated in acetonitrile solution for 12 h at 25 °C, it yielded (after an aqueous quench) 0.0011 mmol of 9-nitroanthracene and 9.5 × 10^{-4} mmol of anthraquinone.

To a solution of NOBF$_4$ (0.27 mmol) in nitromethane was added 0.072 mmol of bicumene (dry box). Analysis of the yellow solution after 3.5 days indicated the presence of 1,1,3-trimethyl-3-phenylindane in 8% yield, together with 78% of unreacted bicumene. ^{1}H NMR (CDCl$_3$):[36] δ 1.03 (s, 3 H), 1.35 (s, 3 H), 1.69 (s, 3 H), 2.19 (d, 1 H), 2.42 (d, 1 H), 7.1–7.3 (m, 9 H). GC-MS, m/z 236 (15, M$^+$), 226 (26), 221 (100), 143 (52), 91 (35). In addition, cumene (0.002 mmol), cumyl alcohol (<0.001 mmol), and an unidentified biaryl were detected by GC-MS analysis.

The addition of hexamethylbenzene (0.117 mmol) to a solution of NOBF$_4$ (0.100 mmol) in 8 mL of acetonitrile under an argon atmosphere afforded a deep red solution. No visible change in color was observed for 10 days if the solution was protected from light. Evaporation of the solvent in vacuo gave a red solid which upon aqueous workup afforded N-pentamethylbenzylacetamide.[59] ^{1}H NMR (CDCl$_3$): δ 1.96 (s, 3 H), 2.23 (s, 9 H), 2.27 (s, 6 H), 4.50 (d, 2 H). IR (KBr): 3310, 2917, 1645, 1539, 1441, 1397, 1272, 1061, 702, 597 cm^{-1}. GC-MS, m/z 219 (18, M$^+$), 162 (18), 161 (16), 160 (100), 145 (33), 91 (12). Hexamethylbenzene (0.112 mmol) was largely recovered (96%) intact.

Hexamethyl(Dewar benzene) (1.04 mmol) was treated with 0.061 mmol of NOPF$_6$ in 1.6 mL of nitromethane-d_3 at −78 °C in a sealed tube in vacuo. Upon warming to room temperature, the pale yellow solution clearly revealed the presence of hexamethylbenzene (^{1}H NMR, δ 2.20) which continued to increase to 0.50 mmol (825% based on NOPF$_6$) after 3 h and 1.02 mmol (1700%) after 24 h. The UV–vis of the final red solution was that of [HMB, NO$^+$] in Table I.

Cycloheptatriene (0.097 mmol) was added to a solution of NOPF$_6$ (0.053 mmol) in 7 mL of acetonitrile at room temperature under an argon atmosphere to yield an orange solution. After 3 h, the solvent was removed in vacuo, and the solid (10.6 mg, 85%) was identified as tropylium hexafluorophosphate by its characteristic ^{1}H NMR spectrum (δ 9.36) in nitromethane-d_3. The similar treatment of homobenzvalene (0.072 mmol) with 0.038 mmol of NOPF$_6$ in nitromethane-d_3 afforded a yellow solution which turned red within 10 min. The ^{1}H NMR spectrum showed only a single resonance of tropylium (hexafluorophosphate, 0.07 mmol).

The addition of p-methoxytoluene (MT, 3.69 mmol) to a mixture of NOBF$_4$ (1.61 mmol) and dichloromethane (25 mL) at −78 °C under an argon atmosphere resulted in a yellow solution. (UV–vis: λ_{max} 334 nm) containing some undissolved salt. Complete dissolution occurred at 25 °C, and the highly colored mixture (λ 286, 402, 440, and 538 nm) evolved gas (76 mL, 3.4 mmol) consisting of nitric oxide ($\nu_{NO} = 1876$ cm^{-1}) together with an unidentified species ($\nu = 3550$ cm^{-1}). Aqueous workup of the purple reaction mixture led to the discharge of the color, and it yielded after silica gel chromatography a mixture (0.72 mmol) of 6,6′-dimethoxy-3,3′-dimethylbiphenyl [^{1}H NMR (CDCl$_3$):[35] δ 2.29 (s, 6 H), 3.67 (s, 6 H), 6.7–7.2 (m, 6 H)] and 5,6′-dimethoxy-2,3′-dimethylbiphenyl [^{1}H NMR (CDCl$_3$):[35] δ 2.03 (s, 6 H), 3.70 (s, 6 H), 6.7~7.2 (m, 6 H)], together with 0.05 mmol of trimers (GC-MS). The recovered MT was 2.0 mmol by gas chromatographic analysis. A similar

(78) For details see: Kim, E. K. Doctoral Dissertation, University of Houston, 1990.

reaction of MT (3.57 mmol) and $NOBF_4$ (0.73 mmol) in 20 mL of acetonitrile at 25 °C afforded 0.24 mmol of biaryls and 3.24 mmol of recovered MT.

Cyclopropylbenzene (2.86 mmol) was added to a solution (0.74 mmol) of $NO^+BF_4^-$ in 40 mL of acetonitrile at 25 °C under an argon atmosphere. The resultant yellow solution was stirred for 7 h at 25 °C in the dark, quenched with 10% $NaHCO_3$, and extracted with diethyl ether to afford 5-phenylisoxazoline (0.51 mmol) by column chromatography with silica gel. ^1H NMR ($CDCl_3$): δ 2.94 (d, d, d, J = 17.6, 8.2, 1.7 Hz), 3.43 (d, d, d, J = 17.6, 11, 1.7 Hz), 5.51 (d, d, J = 8.2, 10.9 Hz), 7.18 (br t), 7.32 (m). ^{13}C NMR ($CDCl_3$): δ 43.7 (t, J = 38 Hz), 79.8 (d, J = 29 Hz), 125.7 (d, J = 23 Hz), 128.1, 128.7 (d, J = 22 Hz), 139.8 (s), 145.5 (d, J = 23 Hz). IR (neat liquid):[40a] 3065, 3030, 2924, 2854, 1673, 1602, 1497, 1455, 1434, 1363, 1286, 1265, 1209, 1075, 1026, 920, 850, 759, 702 cm^{-1}. GC-MS, m/z (%) 147 (M^+, 15), 146 (10), 130 (5), 116 (5), 115 (17), 105 (23), 104 (100), 91 (18), 78 (49), 77 (43), 76 (6), 69 (25), 65 (12), 63 (12), 51 (47), 50 (25), 42 (33), 41 (12). Anal. Calcd for C_9H_9NO: C, 73.44; H, 6.16; N, 9.52. Found: C, 72.81; H, 6.18; N, 9.29. Protonated 5-phenylisoxazoline was obtained from the mixture of $NOPF_6$ with cyclopropylbenzene in CD_3NO_2. ^1H NMR: δ 3.9 (d, d, d, J = 21.5, 10.5, 1.96 Hz), 4.38 (d, d, d, J = 21.5, 10.5, 2.3 Hz), 6.32 (t, J = 10.5 Hz), 7.53 (m), 8.85 (d, d, J = 2.22, 1.95 Hz). ^{13}C NMR: δ 42.4, 87.6, 128.4, 130.6, 131.7, 159.0.

Appendix

The degree of charge transfer in the EDA complexes as described in eq 20 was developed from the relationship[55]

$$Z = (\Delta k/k)/(1 - k'/k) \tag{36}$$

where k and k' are the force constants for NO^+Y^- and NO, respectively, and Δk is the force-constant difference between the free nitrosonium salt and that of the EDA complex (k_c). The force constants for the diatomic species are related to the N–O vibrational frequencies by the general expression $k_i = 4\pi^2 c^2 \mu v_i^2$, where c is the speed of light and μ the reduced mass.[79] If the N–O vibrational frequency (v_C) in the EDA complex is also approximated by the diatomic molecule expression, i.e., $v_C = (2\pi c)^{-1} \cdot (k_c/\mu)^{1/2}$, then $\Delta k \simeq 4\pi^2 c^2 \mu (v_{NO}^{+2} - v_C^2)$. Substitution into eq 36 yields eq 20.

The relationship between the ^{13}C chemical shift ($\delta(^{13}C)$) and the π-electron density (ρ_i) on a carbon atom in eq 22 was obtained from the plot of known $\delta(^{13}C)$ values from conjugated systems[19]

against the calculated π-electron densities of the corresponding carbon atom. The latter were obtained from the simple relationship between the Hückel charge density (ρ_{av}) and the number of electrons per ring carbon atom. The ^{13}C chemical shifts used in the correlation were[19] [^{13}C ppm (averaged), π-electron density] 1,2,3,4-tetramethylcyclobutadiene dication [209.7, 0.5], 1,3,5,7-tetramethylcyclooctatraene dication [176.7, 0.5], 1,2-dimethyl-3,4-benzocyclobutene dication [167.9, 0.75], anthracene dication [159.1, 0.857], tropylium [155.4, 0.857], benzotropenium [146.9, 0.909], benzenonium [165.02, 0.80], heptamethylbenzenonium [172.98, 0.80], biphenylene dication [160.9, 0.833], pyrene dication [156.0, 0.875], tetracene dication [150.6, 0.888], perylene dication [144.8, 0.900], octalene [132.6, 1], anthracene [128.0, 1], naphthalene [128.5, 1], benzene [129.8, 1], biphenylene [132.5, 1], 1,3-cyclohexadiene [125.45, 1], cyclohexadienyl anion [98.64, 1.2], 1,1-dimethylcyclohexadienyl anion [102.76, 1.2], fluorenyl anion [116.7, 1.08], indenyl anion [113.5, 1.111], anthracene dianion [115.1, 1.143], benzocycloheptatrienyl dianion [103.7; 1.167], octalene dianion [111.9, 1.143], octalene tetraanion [88.0, 1.286]. From the correlation of C^{13} chemical shift with the π-electron density at a carbon atom, the linear relationship (r = 0.97) in eq 22[80] was obtained. The π-electron densities of the aromatic carbon atoms in the [ArH, NO^+] complexes were obtained from eq 22. The total charge (q) was taken as the sum of π-electron deficiency at each carbon atom [$\sum(1 - \rho_i)$], which was equivalent to the positive charge density on the arene ring of the [ArH, NO^+] complexes.

Supplementary Material Available: Tables of complete bond lengths, bond angles, and atomic coordinates and the numbering scheme for [mesitylene, $NOSbCl_6$] (3 pages). Ordering information is given on any current masthead page.

(79) Herzberg, G. L. *Infrared and Raman Spectra*; van Nostrand: Princeton, NJ, 1945; p 62.

(80) Such a relationship was originally established by Spiesecke and Schneider[19a] on the basis of fewer cations. For the extensive use of the correlation, see refs 19b–p.

Excited-State and Ground-State Reactivities of Para-Substituted Benzyl Radicals toward Molecular Oxygen

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Abstract: The quenching rates of the $1A_2$ fluorescence-state p-X-benzyls (X = F, Cl, OCH_3, and OCH_2ph) by molecular oxygen were determined to be (1.8–2.3) × 10^{10} M^{-1} s^{-1}, which are about 1 order of magnitude higher than the ground-state oxygenation rates. Physical quenching at the diffusion-limited rate and oxygenation reaction at a lower rate were demonstrated for the reactivities of the excited state ($1A_2$) and the ground state ($1B_2$) toward molecular oxygen, respectively. A poor quenching rate of 6.7 × 10^9 M^{-1} s^{-1} for p-cyanobenzyl in the $2B_2$ fluorescent state implies that the excited-state oxygenation competes with the physical quenching. The oxygenation rate of benzyl radical in the ground state ($1B_2$) was reduced by the introduction of stabilizing substituents (Cl, phenyl, Br, NO_2, and CN) at the para position. A good correlation was found between the oxygenation rate and the free radical substituent parameter (σ^*) based upon the NBS bromination of 4-substituted 3-cyanotoluene.

The oxygenation of benzyl radical to form benzylperoxy radical has been studied[1-5] previously in order to elucidate the primary

process of liquid-phase autoxidation and gas-phase photochemical smog. By monitoring the decay of the transient $D_n \leftarrow D_0$ ab-