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Redox Equilibria of the Nitrosonium Cation and of Its Nonbonded Complexes

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The coordinatively unsaturated nitrosonium cation is reduced at the reversible redox potential of $E° = 1.28$ V vs SCE, as determined by the cyclic voltammetry of either the salt $NO^+BF_4^-$ on the initial negative scan or nitric oxide on the initial positive scan in acetonitrile. The marked solvent dependence of $E°$ in other aprotic media (such as dichloromethane and nitromethane) correlates linearly with Gutmann's DN parameter for solvent donicity. Solvation as the critical factor in the stabilization of NO^+ is akin to its formation of charge-transfer complexes with various aromatic donors. In the latter case, the analytical solution of the electrode kinetics for NO^+ in the presence of arenes (Ar) by digital simulation of the cyclic voltammograms yields the reversible reduction potentials of a series of 1:1 complexes [NO^+,Ar], in which $E_c°$ also varies linearly with the oxidation potential of the arene ligand. This, coupled with the notable 260-mV shift in the nitrosonium reduction potential to $E_c° = 1.02$ V (for Ar = hexamethylbenzene), underscores the importance of electron donation in the stabilization of NO^+ by nonbonded ligands. The rate constant for NO^+ reduction is 100 times slower than that for the related dioxygen/superoxide couple. The relatively large reorganization energy for electron transfer is readily identified with the force constant and bond distance change inherent to this simple diatomic redox couple, and it accords with the theoretical predictions of Marcus.

Introduction

Nitrosonium (NO^+) is a versatile diatomic cation that has found extensive use in inorganic and organometallic as well as in organic synthesis.[1] Being isoelectronic with carbon monoxide, NO^+ is an excellent ligand.[2] Although NO^+ has been used as an electrophile,[3] particularly with substitution-inert donors,[4] its electron-transfer reactions are generally lacking. Thus there are different reports for the reversible reduction of NO^+ occurring at positive potentials as varied as $E_{1/2} = 1.25$, 0.39, and 1.22 V vs SCE.[5-7] Moreover the *microscopic reverse* process with nitric oxide is purported to occur at the separate oxidation potential of $E_{1/2} = 1.32$ V.[7] Part of the ambiguity stems from the questionable purity of NO^+ and NO sources, as well as the absence of a rigorous delineation of solvent effects on the redox equilibrium, i.e.

$$NO^+ + e \xrightleftharpoons{E°} NO \tag{1}$$

Table I. Electrochemical Parameters for the Reduction of the Nitrosonium Cation[a]

solvent	v, V s^{-1}	E_p, V	ΔE_p, mV	$E_{1/2}$,[b] V	$i_p^c/\sqrt{v}$[c]
MeCN	0.1	1.220	132	1.286	59.2
	0.3	1.207	150	1.282	57.7
	0.5	1.202	161	1.283	57.3
	0.7	1.199	169	1.284	55.6
	0.9	1.192	181	1.283	55.9
$MeNO_2$	0.1	1.280	123	1.342	47.5
	0.3	1.275	130	1.340	45.8
	0.5	1.267	138	1.336	57.9
	0.7	1.263	140	1.333	59.6
	0.9	1.253	149	1.328	60.6

[a] Solutions of 1×10^{-2} M $NO^+BF_4^-$ containing 0.1 M TBAH at 23 °C. All potentials measured relative to SCE with $E_{1/2} = 0.41$ and 0.35 V for Cp_2Fe standard in MeCN and $MeNO_2$, respectively. [b] $E_{1/2} = (E_p^c + E_p^a)/2 = E°$. [c] In units of $\mu A\ s^{1/2}\ V^{-1/2}$.

These factors are understandable if one considers that NO^+, being a small, coordinatively unsaturated cation, is highly susceptible to stabilization via coordination with various types of σ-donors including aprotic solvents, e.g., acetonitrile, ether, and even such a nonpolar medium as dichloromethane, which is generally considered to be noncoordinating.[8] Accordingly, our objective in this study is to establish reliable values for the thermodynamic potential $E°$ and the kinetics of the electron transfer in eq 1, especially by taking cognizance of medium effects. Furthermore, the influence of coordination on the redox properties of NO^+ is examined in two types of nonbonded complexes, namely, charge-transfer complexes with arenes[9] and crown ether complexes.[10] Three representative aprotic solvents (acetonitrile, nitromethane, and dichloromethane) were selected to evaluate the medium effects on the NO^+/NO redox couple owing to their distinctive polar character.[11]

Results

Among the various techniques available for the measurement of reversible redox potentials, cyclic voltammetry (CV) was considered the method of choice for the transient electrochemistry

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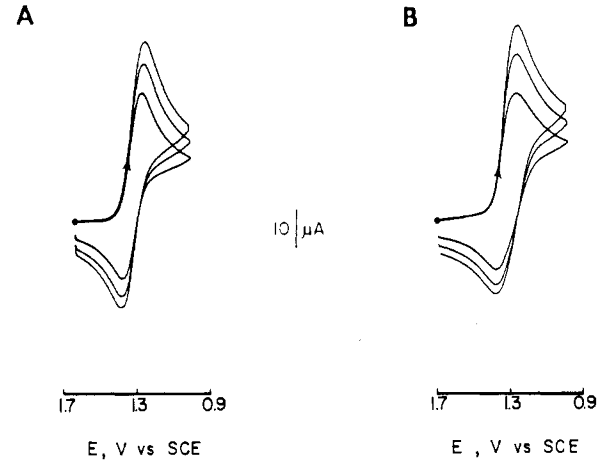

Figure 1. Initial negative-scan cyclic voltammetry of 10 mM $NO^+BF_4^-$ in (A) acetonitrile and (B) nitromethane containing 0.1 M TBAH at $v = 0.3$, 0.5, and 0.7 V s^{-1} at 23 °C.

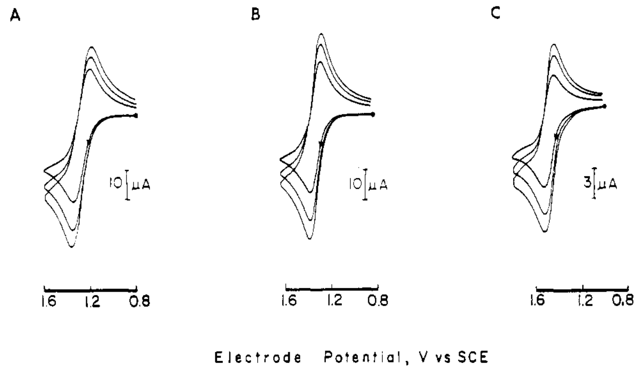

Figure 2. Initial positive-scan cyclic voltammograms of ~10 mM nitric oxide in (A) acetonitrile, (B) nitromethane, and (C) ~3 mM NO in dichloromethane containing 0.1 M TBAH at $v = 0.3$, 0.5, and 0.7 V s^{-1} at 23 °C.

of the highly sensitive nitrosonium cation. Of utmost importance for these studies was the rigorous purification of both NO^+ and NO (see Experimental Section for details) prior to their electrochemical reduction and oxidation, respectively. Moisture and all protic adulterants were rigorously excluded in order to avoid the neutralization of NO^+ and to dispel any doubt regarding the identity of the electroactive substrate.

Redox Equilibrium of the Nitrosonium/Nitric Oxide Couple. The cyclic voltammogram of the nitrosonium salt $NO^+BF_4^-$ on the initial negative scan showed a well-defined cathodic peak at $E_p^c = 1.20$ V vs SCE and the coupled anodic wave at $E_p^a = 1.36$ V on the return positive scan in acetonitrile solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. Chemical reversibility of the redox equilibrium in eq 1 was achieved at relatively slow CV scan rates (v) as indicated in Figure 1A by the ratio of the cathodic/anodic peak currents i_p^c/i_p^a of unity.[12] Furthermore, the constant values of the current function $i_p^c/\sqrt{v}$ in Table I point to diffusive CV waves without any indication of adsorption.[13] The standard reduction potential for the redox couple in eq 1 was evaluated as $E° = 1.28$ V vs SCE from the constancy of the values of $(E_p^a + E_p^c)/2$ at the various CV scan rates in Table I.[14] Essentially the same cyclic voltammetric behavior was observed in nitromethane (Figure 1B); but the initial reductive process could not be examined in dichloromethane owing to the insolubility of $NO^+BF_4^-$ in this solvent.

Table II. Electrochemical Parameters for the Oxidation of Nitric Oxide[a]

solvent	v, V s^{-1}	E_p^a, V	ΔE_p, mV	$E_{1/2}$,[b] V	$i_p^a/\sqrt{v}$[c]
MeCN	0.1	1.356	131	1.291	58.5
	0.3	1.360	155	1.283	58.0
	0.5	1.363	165	1.281	55.8
	0.7	1.366	174	1.279	59.0
	0.9	1.372	184	1.280	54.5
$MeNO_2$	0.1	1.397	122	1.336	54.0
	0.3	1.405	133	1.338	56.5
	0.5	1.400	137	1.332	58.1
	0.7	1.403	150	1.328	52.8
	0.9	1.413	163	1.332	50.1
CH_2Cl_2	0.3	1.533	125	1.470	20.0
	0.5	1.537	120	1.477	17.5
	0.7	1.542	129	1.478	16.2
	0.9	1.552	135	1.484	15.5

[a] Solutions of ~10^{-2} M nitric oxide in MeCN and $MeNO_2$ or ~3×10^{-3} M NO in CH_2Cl_2 and 0.1 M TBAH at 23 °C. All potentials measured relative to SCE with $E_{1/2} = 0.48$ V for Cp_2Fe in CH_2Cl_2. [b] $E_{1/2} = (E_p^a + E_p^c)/2 = E°$. [c] In units of μA $s^{1/2}$ $V^{-1/2}$.

Solvent effects on the redox equilibrium however could be determined from the microscopic reverse oxidation of nitric oxide. Thus the initial positive-scan cyclic voltammogram of NO in Figure 2 showed the well-defined anodic peak at $E_p^a = 1.54$ V vs SCE and the coupled cathodic wave at $E_p^c = 1.42$ V on the return negative scan in dichloromethane solution containing 0.1 M TBAH. It is noteworthy that the electrochemical parameters for the oxidation of NO in acetonitrile and nitromethane (Table II) were essentially the same as those obtained from the reduction of NO^+ (Table I) in the same solvent. We conclude therefore that there is no ambiguity[15] in the standard potentials for the NO^+/NO redox couple in solvents of different polarity, as listed in either Table I or II.

Electron-Transfer Kinetics for the Reduction of NO^+. An indication of the rates of electron transfer inherent to the NO^+/NO redox couple can be obtained from an inspection of the values of the cathodic/anodic peak separation $\Delta E_p = E_p^c - E_p^a$. Thus Tables I and II reveal magnitudes of ΔE_p that are considerably larger than 60 mV predicted for a Nernstian process, i.e. fast heterogeneous rate of electron transfer.[16] Moreover, the sweep rate dependence of the peak potential for both the reduction of NO^+ and the oxidation of NO resulted in slopes of ~30 mV/log v.[17] We note further that all of the cyclic voltammograms shown in Figures 1 and 2 are quite symmetrical, more or less independent of the solvent polarity. Such coupled cathodic and anodic waves of the same shapes were suggestive of the electrochemical transfer coefficient α of 0.5.[18] Indeed the latter could be quantitatively evaluated from the CV peak width taken as $|E_p - E_{p/2}| = 47.7/\alpha$, where $E_{p/2}$ represented the potential at the half-height of the CV wave.[12] The values of the transfer coefficient evaluated in this manner (Table III) were found in the three solvents to be constant at $\alpha = 0.50$ within the experimental error of ±0.03.[19]

The heterogeneous rate constant k_s for the reduction of NO^+ at the Pt electrode was evaluated from the transfer coefficient α, the diffusion coefficient D, and the separation of the CV peak potentials at different scan rates by three independent procedures.

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(19) For $v > 400$ mV s^{-1} in dichloromethane, the slight variations (<10%) in α may be due to adsorption effects.

Table III. Kinetics Parameters for the Heterogeneous Reduction of the Nitrosonium Cation[a]

electroactive species	solvent	α	$10^5 D$, cm^2 s^{-1}	$10^3 k_s$, cm s^{-1} [b] eq 3	eq 4	eq 5
NO^+	MeCN	0.49 ± 0.03	1.43 ± 0.02	4.6	5.8	6.1 (2)[d]
NO	MeCN	0.50 ± 0.02	1.43 ± 0.02	5.1	3.5	5.0
NO^+	$MeNO_2$	0.50 ± 0.03	0.99 ± 0.05	2.0	5.5	6.0
NO	$MeNO_2$	0.51 ± 0.03	0.99 ± 0.05	3.7	6.1	7.2
NO	CH_2Cl_2	0.49 ± 0.03	~1.2	*c*	7.1 ± 0.8	9.1 ± 0.7

[a] At a Pt electrode in solutions containing 0.1 M TBAH at 23 °C. [b] Error estimated as ±10%. [c] Large scatter in sweep rate dependence of E_p^a. [d] At a glassy carbon electrode with $r = 1.5$ mm.

In the first method,[20] the scan rate parameter v_{60} necessary to effect the peak separation of $\Delta E_p = 60$ mV was obtained by the extrapolation of the experimental plot of ΔE_p versus log v, so that

$$(\log k_s)/\sqrt{D} = \tfrac{1}{2} \log v_{60} - \alpha(1 - \alpha) + \tfrac{1}{2}[(1 - \alpha) \log \alpha + \alpha \log (1 - \alpha)] + C \quad (2)$$

where $C = 0.783/\ln 10 + {}^1/_2 \log (n\mathcal{F}/RT)$, $\mathcal{F}$ is the Faraday constant, and D is the average diffusion coefficient of NO^+ and NO.[21] Since the plots of ΔE_p versus log v for $NO^+BF_4^-$ were found to be linear in acetonitrile and nitromethane at scan rates $v > 0.2$ V s^{-1}, eq 2 with $\alpha = 0.50$ and $T = 23$ °C could be reexpressed simply as[22]

$$(\log k_s)/\sqrt{D} = \tfrac{1}{2} \log v_{60} + 0.736 \quad (3)$$

The second method[23] derives from the scan rate dependence of the peak shift for the quasi-reversible charge transfer to NO^+ given as

$$E_p^c - E^\circ = -\frac{RT}{\alpha n\mathcal{F}} [0.78 + \ln (\alpha D a)^{1/2} - \ln k_s] \quad (4)$$

where $a = n\mathcal{F}v/RT$ and the other terms are as given above. The third method is based on the working curve[16] derived from eq 4, in which the scan rate function Ψ for $\alpha = 0.5$ can be expressed as

$$\Psi = k_s/(Dbv)^{1/2} \quad (5)$$

where $b = \pi n\mathcal{F}/RT$. The original tabulation[16] of Ψ with the peak separation ΔE_p was replotted as a function of the experimental variable v (vide supra). Since this and the second method allowed the heterogeneous rate constant to be obtained from a single cyclic voltammogram, the values of k_s presented in Table III are the averages obtained from a series of CV curves measured in the range $0.05 < v < 1.00$ V s^{-1}.

Reductive Behavior of NO^+ Complexes with Aromatic Donors. In order to extend the solvent-induced shift of E° in Tables I and II, the cyclic voltammetric behavior of NO^+ was examined in the presence of strong aromatic donors (Ar) capable of forming nonbonded complexes, i.e.

$$NO^+ + Ar \overset{K}{\rightleftharpoons} [NO^+,Ar] \quad (6)$$

Thus, upon the addition of arene to the acetonitrile solution of $NO^+BF_4^-$ containing 0.1 M TBAH, the colorless solution immediately took on the dark brown hue characteristic of the charge-transfer complex[9] $[NO^+,Ar]$ according to eq 6. With such strong aromatic donors as hexamethylbenzene, the nitrosonium cation can exist in solution largely in the form of the charge-transfer complex in eq 6 as a direct result of the large formation constant of $K = 3 \times 10^4$ M^{-1}.[23] This simplification allowed the complex electrode kinetics (inherent to the multiple redox processes stemming from eq 6) to be more readily dissected with the aid of digital simulation of the cyclic voltammograms.[24] Accordingly, the cyclic voltammetry of NO^+ with hexamethylbenzene (Ar_6) was initially examined in detail, and the essential redox parameters were then substantiated by further cyclic voltammetric examination of the weaker donors pentamethylbenzene (Ar_5) and durene (Ar_4) with the more limited formation constants of $K = 5 \times 10^3$ and 3×10^2 M^{-1}, respectively,[23] as follows.

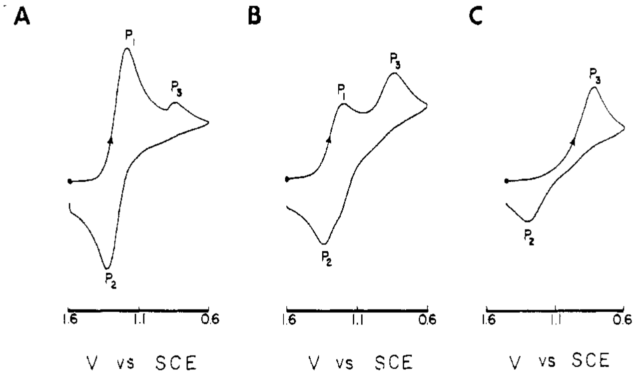

Figure 3. Cyclic voltammograms of 10 mM $NO^+BF_4^-$ with (A) 2.0, (B) 5.0, and (C) 10 mM hexamethylbenzene in acetonitrile containing 0.1 M TBAH at $v = 0.5$ V s^{-1} at 23 °C.

(A) Hexamethylbenzene (Ar_6). The cyclic voltammogram of the acetonitrile solution containing 10 mM $NO^+BF_4^-$ and 0.2 equiv of hexamethylbenzene showed a new cathodic peak P_3 at $E_p^c = 0.81$ V (Figure 3A) in addition to the cathodic peak P_1 and the anodic peak P_2 of the NO^+/NO couple (compare Figure 1A). With the addition of 0.5 equiv of Ar_6, the solution became darker and the cathodic current of P_3 increased at the expense of the P_1 current (Figure 3B). The latter disappeared completely upon the addition of 1 equiv of hexamethylbenzene (Figure 3C). The new cathodic peak P_3 was thus readily assigned to the reduction of the charge-transfer complex, i.e.

$$[NO^+,Ar_6] \xrightarrow{P_3} [NO,Ar_6] \quad (7)$$

The invariance of the peak potential of P_3 with added hexamethylbenzene in Figures 3 indicated that NO^+ was always complexed with Ar_6, in accord with expectations based on the magnitude of the formation constant (vide supra). Furthermore, the presence of added hexamethylbenzene had essentially no effect on the cathodic reduction of NO^+ (up to 1 equiv), as indicated by the unshifted potential of P_1 (Figure 3A,B) and the scan rate dependence $\partial E_p/\partial \log v$, both of which were the same as those obtained in the absence of Ar_6. However, the anodic peak P_2 of NO on the return scan was shifted to the more negative potentials of 1.35 and 1.29 V upon the incremental addition of 0.5 and 3.0 equiv, respectively, of hexamethylbenzene, owing to the presence of the neutral complex, i.e.

$$[NO,Ar] \overset{K'}{\rightleftharpoons} NO + Ar \quad (8)$$

The latter was also revealed in the anodic oxidation of nitric oxide

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(20) Nadjo, L.; Saveant, J. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1973**, *48*, 113.

(21) See Experimental Section for details.

(22) The values of C and $\alpha = 0.5$ in eq 2 are incorporated into the constant term (0.736).

(23) Kim, E. K. Unpublished results quoted by: Kochi, J. K. *Acta Chem. Scand.* **1990**, *44*, 409. See also: Kim, E. K.; Kochi, J. K. *J. Org. Chem.* **1989**, *54*, 1692.

(24) For previous mechanistic studies, compare: Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61. Kochi, J. K. *J. Organomet. Chem.* **1986**, *300*, 139. See also related papers.

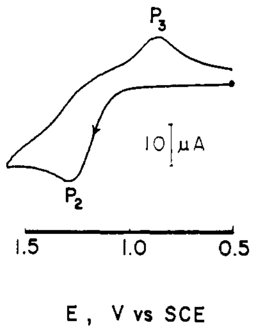

Figure 4. Initial positive-scan cyclic voltammogram of ~5 mM nitric oxide with 5 mM hexamethylbenzene in acetonitrile containing 0.1 M TBAH at v = 0.5 V s^{-1}. Note the absence of the cathodic peak P_1 on the return scan.

Table IV. Electrochemical and Kinetics Data for CV Simulation of NO^+ Reduction with Arene Donors

		arene donor		
equilibrium process	param	Ar_6	Ar_5	Ar_4
$[NO^+,Ar] \overset{e^-}{\rightleftharpoons} [NO,Ar]$	$E_c°$, V	1.02	1.10	1.13
	k_s', cm s^{-1}	0.001	0.003	0.0025
	α'	0.4	0.4	0.4
$NO^+ + Ar \rightleftharpoons [NO^+,Ar]$	K, M^{-1}	5×10^4	5×10^3	3×10^2
	k_1, M^{-1} s^{-1}	1×10^7	1×10^7	
	k_2, s^{-1}	2×10^2	2×10^3	
$[NO,Ar] \rightleftharpoons NO + Ar$	K', M	0.1	0.1	0.7
	k_3, s^{-1}	10^4	10^4	
	k_4, M^{-1} s^{-1}	10^5	10^5	

in the presence of added hexamethylbenzene. Thus, Figure 4 depicts a typical initial positive-scan cyclic voltammogram of NO in acetonitrile containing Ar_6, in which the cathodic peak P_1 of free NO^+ is missing on the return scan (compare Figure 2) and simply replaced by P_3 of the charge-transfer complex $[NO^+,Ar_6]$.[25]

In order to obtain the quantitative assessment of the pertinent redox potential ($E_C°$) and the formation constant (K') for eqs 7 and 8, the cyclic voltammograms in Figure 3B,C were reconstructed analytically by digital simulation using the expanded space–time grid to describe diffusion of all electroactive species at the Pt electrode.[26,27] The electrode kinetics were based on the mechanism shown in Scheme I deduced from the qualitative behavior of the CV peaks P_1, P_2, and P_3 outlined above.

Scheme I

$$NO^+ \overset{E°}{\rightleftharpoons} NO \tag{9}$$

$$NO^+ + Ar \overset{K}{\rightleftharpoons} [NO^+,Ar] \tag{10}$$

$$[NO^+,Ar] \overset{E_c°}{\rightleftharpoons} [NO,Ar] \tag{11}$$

$$[NO,Ar] \overset{K'}{\rightleftharpoons} NO + Ar \tag{12}$$

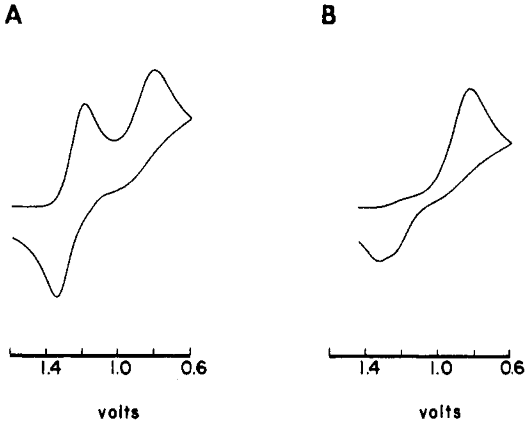

Figure 5. (A) Computer simulation of the experimental cyclic voltammogram shown in Figure 3B. (B) Simulation of Figure 3C.

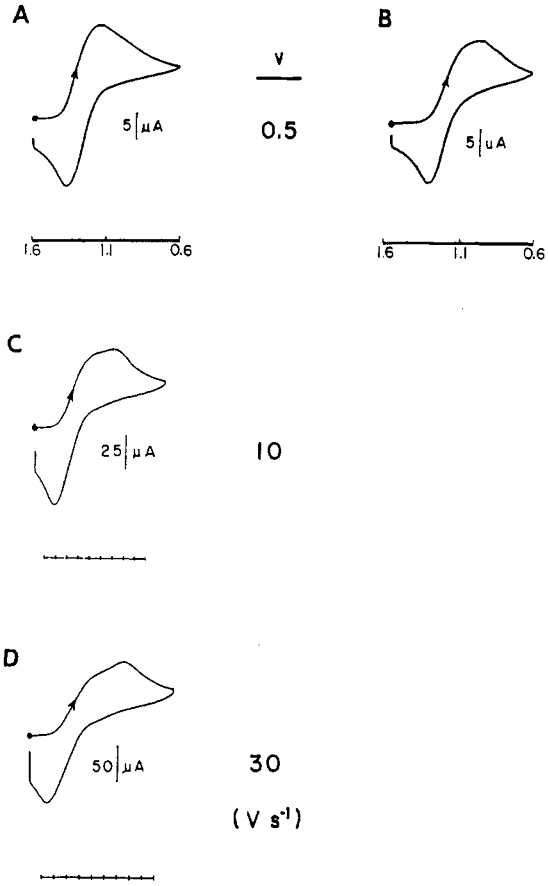

Figure 6. Cyclic voltammograms of 10 mM $NO^+BF_4^-$ with (A) 5 and (B) 10 mM pentamethylbenzene in acetonitrile containing 0.1 M TBAH at v = 0.5, (C) 10, and (D) 30 V s^{-1}.

For aid in the computer simulation of the cyclic voltammograms according to Scheme I, the electrochemical parameters for NO^+ in eq 9, namely, $E°$, k_s, and α, were taken from Tables I and III. The formation constant for the charge-transfer complex in eq 10, described as $K = k_1/k_2$, was based on an earlier spectrophotometric determination.[23] These together with optimized electrochemical parameters for eq 11, namely, $E_c°$, k_s', and α' in Table IV, were critical for the accurate simulation of the cathodic current and peak potential of CV waves P_1 and P_3 with the variation in hexamethylbenzene concentration. The equilibrium constant for the neutral complex in eq 12, described as $K' = k_3/k_4$, was important in the establishment of the anodic peak potential of P_2 at various concentrations of hexamethylbenzene. The diffusion coefficients of NO^+ and NO were taken as 1.4×10^{-5} cm^2 s^{-1} (Table III) and that for the charge-transfer complex was estimated as 1×10^{-5} cm^2 s^{-1}, although precise values were not critical for

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(25) These experiments do not delineate the contributions from the direct oxidation of the neutral complex, i.e.

$$[NO,Ar] \xrightarrow{-e} [NO^+,Ar] \tag{a}$$

and/or the oxidation of free NO followed by rapid complex formation, i.e.

$$NO \xrightarrow{-e} NO^+ \xrightarrow[fast]{Ar} [NO^+,Ar] \tag{b}$$

The fast-scan cyclic voltammetric studies required to resolve this mechanistic dichotomy were discouraged by our inability to accurately prepare solutions of gaseous NO with known concentrations.

(26) Gosser, D. K.; Rieger, P. H. *Anal. Chem.* **1988**, *60*, 1159.

(27) Compare Feldberg, S. W. *Electroanal. Chem.* **1969**, *3*, 199; *J. Electroanal. Chem.* **1981**, *127*, 1. Feldberg, S. W.; Jeftic, L. *J. Phys. Chem.* **1972**, *76*, 2439.

(28) The value of $k_1 = 10^7$ M^{-1} s^{-1} in Table IV represented the upper limit of the computer program and indicates that the rate of complex formation is probably close to the diffusion-controlled limit.

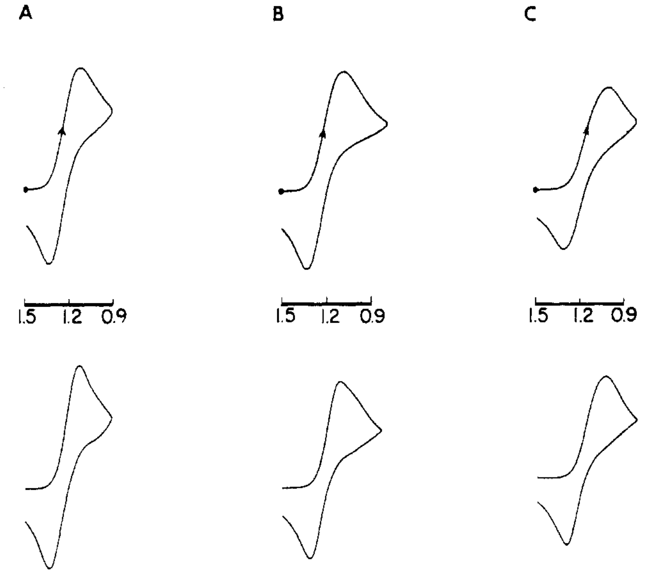


Figure 7. First row: Reductive cyclic voltammograms of 10 mM $NO^+BF_4^-$ with (A) 20, (B) 50, and (C) 100 mM durene in acetonitrile containing 0.1 M TBAH at $v = 0.5$ V s^{-1}. Second row: Computer simulation of the experimental cyclic voltammogram directly above.

the digital simulation. The final simulations shown in Figure 5 were based on the optimized parameters listed in Table IV. Particularly pertinent were the values of K, $E_c°$, and k_s' for the charge-transfer complex. The second-order rate constant for the formation of the complex did not materially affect the CV simulation, provided the value $k_1 > 10^3$ M^{-1} s^{-1} was employed.[28] Similarly, the equilibrium of the neutral complex in eq 12 was not sufficient to distinguish the CE mechanism for the electrochemical process occurring at the anode (P_2) from the EC alternative.[29,30]

(B) Pentamethylbenzene (Ar_5). The cyclic voltammograms shown in Figure 6 of NO^+ in the presence of pentamethylbenzene appeared to be distinctively different from those obtained from hexamethylbenzene under the same conditions (compare Figure 3). In particular, the initial cathodic process for the brown acetonitrile solution was revealed as a single broad wave that shifted negative in the presence of increasing amounts of Ar_5, and the coupled anodic wave remained relatively invariant. However, closer CV scrutiny evoked a partial resolution of the cathodic wave into two components at higher scan rates (see Figure 6C,D), in a manner reminiscent of that observed with hexamethylbenzene in Figure 3B. This revelation suggested the reduction of NO^+ and Ar_5 to occur by an electrochemical process similar to that in Scheme I. Indeed, the adjustment of merely two parameters, namely, (a) the formation constant to $K = 5 \times 10^3$ M^{-1} (to accord with the independent spectrophotometric determination[23]) and (b) the reduction potential $E_c°$ to the values listed in Table IV, led to simulations in excellent agreement with the experimental cyclic voltammograms shown in Figure 6A,B.

(C) Durene (Ar_4). The presence of 1 equiv of durene showed little effect on the shape of cyclic voltammogram of NO^+ in Figure 1. However, the addition of more Ar_4 (up to 10 equiv) led to a progressive shift of both the cathodic and anodic peaks to more negative potentials and an accompanying slight increase in the cathodic/anodic peak separation, as illustrated in Figure 7 (upper). These subtle features were readily accommodated in the CV simulation of NO^+ and Ar_4 by extending the adjustment of the formation constant and the reduction potential of the charge-transfer complex, as described above, to even lower values. Indeed, the optimized parameters in Table IV provided the series of simulated cyclic voltammograms that were adequately fitted to their experimental counterparts, as shown by a direct comparison of the upper and lower cyclic voltammograms in Figure 7.

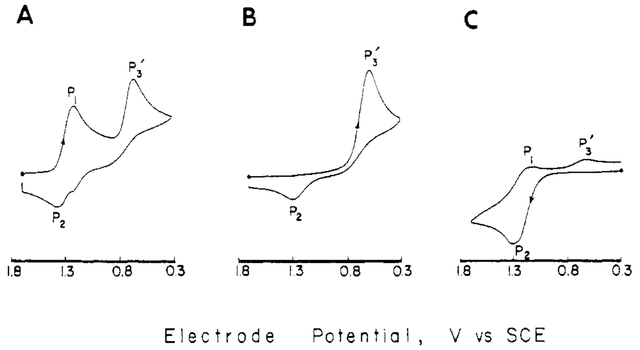
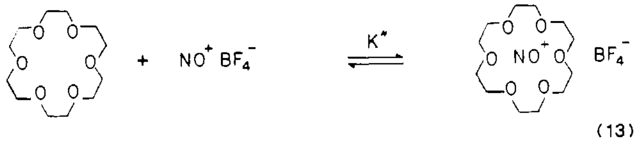


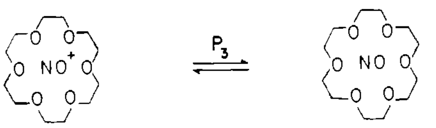
Figure 8. (A, B) Initial negative-scan cyclic voltammograms of 10 mM $NO^+BF_4^-$ respectively with 5 and 10 mM 18-crown-6 in acetonitrile containing 0.1 M TBAH at $v = 0.5$ V s^{-1}. (C) Initial positive-scan cyclic voltammogram of ~5 mM nitric oxide with 5 mM 18-crown-6 in acetonitrile under the same conditions.

Effect of Crown Ether on the Reduction of NO^+. The addition of 0.5 equiv of crown ether (18-crown-6) to the colorless solution of 10 mM $NO^+BF_4^-$ in acetonitrile caused an immediate change to the yellow coloration characteristic of the charge-transfer complex, i.e.[10]



(13)

The general appearance of the initial negative-scan cyclic voltammogram of this solution resembled that in Figure 3B of hexamethylbenzene under the same conditions. Thus, a distinctive new cathodic wave P_3' appeared at $E_p = 0.64$ V vs SCE (Figure 8A), together with the unchanged cathodic peak P_1 and the anodic peak P_2 of the NO^+/NO couple. Upon the addition of more crown ether (1 equiv relative to NO^+), only the cathodic peak P_3' remained at $E_p = 0.64$ V in Figure 8B at the expense of cathodic peak P_1. This CV behavior is diagnostic of the reduction of the strong complex of NO^+ with 18-crown-6, i.e.



(14)

in a manner similar to that described for hexamethylbenzene above. A closer inspection of the cyclic voltammograms in Figure 8A,B however reveals the anodic wave P_2 on the return scan to be significantly smaller than that expected for the reoxidation of NO. Such a cyclic voltammogram for the chemically irreversible reduction of the crown ether complex of NO^+ suggested that the nitric oxide was being generated in a form only partially available for reoxidation to the NO^+ complex in eq 14. The control experiments such as that shown in Figure 8C established the stability of NO in the presence of crown ether, as shown in the initial positive-scan cyclic voltammogram by the appearance of the anodic wave P_2 as well as the cathodic waves P_1 and P_3' on the return scan. However, the diminished cathodic currents of the latter again suggested that only part of the NO converted to NO^+ and its crown ether complex.[31]

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(29) Simulation of the EC process (eq b in footnote 25) based on $k_4 = 0$ failed to predict the observed shifts in E_p^a with the concentration variation of hexamethylbenzene. However, the program-imposed upper limit of 10^7 M^{-1} s^{-1} for the second-order rate constant k_1 could be insufficient to shift the equilibrium in eq 12.

(30) Spectral examination of concentrated arene solutions of nitric oxide have failed to reveal any new absorption band attributable to the weak complex [NO,Ar] predicted by the value of K' in Table IV: Kim, E. K. Unpublished results.

(31) The "missing" NO and NO^+ in the cyclic voltammograms of 18-crown-6 with NO^+ and NO, respectively, may be due to their rapid encapsulation by the polyether ligand. Repeated attempts to crystallize the CT complex [NO^+,18-crown-6] merely yielded an amorphous, intractable yellow mass, suggestive of mixtures.

Table V. Reversible Reduction Potentials of the Nitrosonium Cation and of Its Complexes[a]

cation	solvent	$E°$ or $E_c°$,[b] V vs SCE
NO^+	MeCN	1.28 (0.87)
	$MeNO_2$	1.33 (0.98)
	CH_2Cl_2	1.48 (1.00)
$[NO^+,Ar_6]$	MeCN	1.02 (0.61)
$[NO^+,Ar_5]$	MeCN	1.10 (0.69)
$[NO^+,Ar_4]$	MeCN	1.13 (0.72)
$[NO^+$,18-crown-6$]$	MeCN	~0.9

[a] By cyclic voltammetry at a platinum electrode in solutions containing 0.1 M TBAH at 25 °C. [b] $E°$ in eq 1 and $E_c°$ in eq 11. Values in parentheses (corrected for junction and reference potentials) relative to ferrocene with $E_{1/2}$ = 0.41 (MeCN), 0.35 ($MeNO_2$), and 0.48 (CH_2Cl_2) V vs SCE, according to ref 34.

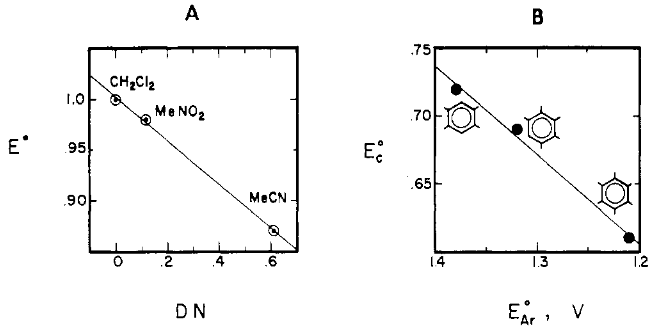

Figure 9. Free energy correlations of the reduction potentials (A) $E°$ of NO^+ with the Gutmann solvent donor number DN and (B) $E_c°$ of the NO^+/arene complex with the oxidation potential ($E_{Ar}°$) of the uncoordinated arene. (Note the values of $E°$, $E_c°$, and $E_{Ar}°$ are referenced to ferrocene, and DN is referenced to dichloroethane and normalized to volts.)

Discussion

The nitrosonium/nitric oxide redox couple is reversible and well-behaved in aprotic solvents, in which cyclic voltammetry establishes the NO^+ reduction to always occur at the same potential as the NO oxidation (see Tables I and II).

Redox Potential of the Nitrosonium Cation. Effects of Solvation and Complex Formation. The reversible redox potential of $E°$ = 1.28 V vs SCE for the NO^+/NO couple determined by cyclic voltammetry in acetonitrile solution (Table V) compares with the value of $E°$ = 1.48 V merely by a change to the less polar dichloromethane (Table V). The rather pronounced positive shift in $E°$ is most readily accounted for by the relative stabilization of the nitrosonium cation by its differential interaction with this pair of solvents.[32] Indeed, the quantitative measure of such solvent effects is shown in Figure 9A by the linear correlation (eq 15)

$$E° = -0.22\mathrm{DN} + 1.00 \qquad (15)$$

of the redox potential $E°$ for the NO^+/NO couple (after correction for the junction and reference potentials[34]) with the solvent donicity (DN) as defined by Gutmann.[35,36]

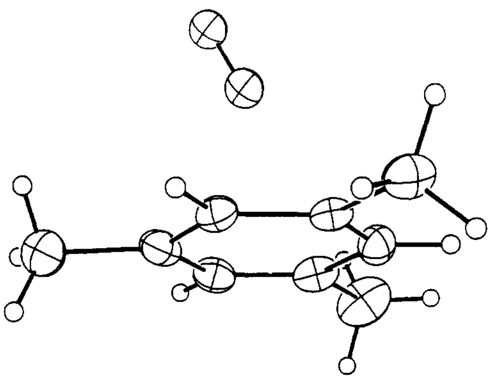

Figure 10. ORTEP diagram of the charge-transfer complex of the nitrosonium ion and mesitylene.

The solvation of NO^+ leading to diffuse ionic stabilization compares with the nonbonded, but unidirectional, interaction of arene donors with NO^+ in charge-transfer complexes. Thus, X-ray crystallography of a series of such complexes has established the centrosymmetric (η^6) structure[37] shown in Figure 10 for the mesitylene derivative,[23] in which the closest NO^+ distance to the arene centroid of 2.2 Å is determined solely by charge-transfer interactions.[38] Nonetheless, the powerful stabilizing effect on the nitrosonium moiety is shown by the remarkable shift of its reversible redox potential to $E_c°$ = 1.02 V in the hexamethylbenzene complex (Table V). Moreover, the magnitude of the donor effect on the reduction of NO^+ can be quantitatively evaluated by the direct relationship of $E_c°$ with the oxidation potential of the free uncoordinated arene ($E_{Ar}°$) in Figure 9B. Indeed, the sizable slope of the relationship expressed as

$$E_c° = 0.66E_{Ar}° - 0.18 \qquad (16)$$

points to the strong contribution of arene, via electron donation, to the stabilization of the nitrosonium moiety.[39] This conclusion suggests that even such nonpolar, aprotic solvents as dichloromethane are likely to be involved in the stabilization[8] of NO^+—to a degree sufficient to exert a negative shift of the peak potential of the cathodic CV wave P_1 during the cyclic voltammetric examination of nitric oxide (see Figure 2C).[40]

The marked effect of nonbonded donors on the stabilization of the nitrosonium cation is shown to an even greater degree by crown ethers (Figure 8). The formation constant of $K'' > 10^4$ M^{-1} for the crown ether complex in eq 13 is estimated from the unshifted potentials of the cathodic and anodic waves P_1 and P_2, respectively, by assuming the same rapid complexation as observed with the hexamethylbenzene complex. Most importantly, the peak potential of the new cathodic wave P_3' assigned in eq 14 to the reduction of the complex $[NO^+$,18-crown-6$]$ occurs at the most negative potential of E_p^c = 0.64 V. Although the unexplained behavior of the anodic wave P_2 (vide supra) prevented the CV simulations necessary to rigorously evaluate the reversible reduction potential of the complex, the value of $E_c° \sim 0.9$ V vs SCE can be readily estimated from the comparison of the P_1/P_3' peak widths relative to those in the cyclic voltammograms (Figure 3)

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(32) Solvation energies of the uncharged NO are negligible in comparison to those of the cationic NO^+.[33]

(33) See for example: (a) Abraham, N. H. *J. Am. Chem. Soc.* **1982**, *104*, 2085. (b) Lofti, M.; Roberts, R. M. G. *Tetrahedron* **1979**, *35*, 2137. (c) Peover, M. E. *J. Electroanal. Chem. Interfacial Electrochem.* **1967**, *2*, 1. (d) Case, B. In *Reactions of molecules and Electrodes*; Hush, N. W., Ed.; Wiley: New York, 1971.

(34) (a) The value of $E°$ in eq 15 is based on the ferrocene couple in various solvents taken as the reference standard according to: Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854. See also: (b) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461. (c) Kadish, K. M.; Corrilon, J.-L.; Yao, C.-L.; Malinski, T.; Gritzner, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, *235*, 189.

(35) (a) Gutmann, V. *CHEMTECH* **1977**, 255. (b) Note that the value of DN in kcal mol^{-1} has been normalized to eV units in eq 15.

(36) In this regard, the reported values of $E°$ = 0.39 and 1.24 V in sulfuric acid could be ascribed to the varying water content of the acidic medium.[6]

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

(38) The vertical distance from the nitrogen atom (in NO^+) to the arene plane varies from 2.04,[37] to 2.20,[23] to 2.49 Å[37] in the hexamethylbenzene, mesitylene, and toluene complexes, respectively, of $NO^+SbCl_6^-$.

(39) (a) Similarly in the gas phase, the effect of donicity on arene complexation is indicated by the linear correlation of the NO^+ affinity (expressed in volts) and the arene ionization potential with a slope of -0.5. (b) See Reents, W. D., Jr.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 2791. (c) The values of $E_{Ar}°$ for eq 16 are from: Amatore, C. Unpublished results.

(40) (a) The association of NO^+ with various weak neutral donors has been established in the gas phase: Williamson, A. D.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 5714. Moreover, the NO^+ affinities of acetonitrile and ethyl acetate are only slightly less than that of toluene,[39] for which the EDA complex has been isolated.[37] (b) Note that the ionization potential of NO in the gas phase of IP = 9.26 eV is comparable to that of benzene: Lias, S. G. *Chem. Phys. Lett.* **1978**, *54*, 147.

Table VI. Free Energy of Formation of [NO^+,Ar] Complexes in Acetonitrile

arene donor	IP,[a] eV	$E_{Ar}°$,[b] V	ΔG, kcal mol^{-1}		K, M^{-1}	
			calcd[c]	spectro[d]	calcd[c]	spectro[e]
Ar_6	7.85	1.65	−6.3	−7.3	5 × 10^4	31000
Ar_5	7.92	1.76	−5.0	−5.5	5 × 10^3	5100
Ar_4	8.05	1.82	−3.8	−3.7	3 × 10^2	450 (192)[f]

[a] Ionization potential from ref 14. [b] Oxidation potential in MeCN in volts vs SCE from ref 39. [c] From eq 19. [d] From data in column 6. [e] From ref 23. [f] In the presence of 0.1 M TBAH.

of the hexamethylbenzene complex.

Formation Constants of Nitrosonium Complexes. The structural simplicity of NO^+ complexes with various arenes also provides an opportunity to quantitatively examine donor effects on the stabilization of the nitrosonium cation, as qualitatively indicated by the marked but pervasive influence of solvent. Thus, the free energy change ΔG of NO^+ upon its complexation with a generalized donor D (eq 17) can be considered within the context of the following thermochemical cycle:

Scheme II

$$\begin{tikzcd}
NO^+ + D \arrow[r, shift left, "\Delta G"] \arrow[d, "E°"'] & {[NO^+,D]} \arrow[l, shift left] \arrow[d, "E_c°"] & (17) \\
NO + D \arrow[r, shift left, "\Delta G'"] & {[NO,D]} \arrow[l, shift left] & (18)
\end{tikzcd}$$

For the arene donors pertinent to the charge-transfer complex [NO^+,Ar], this free energy change is represented as

$$\Delta G = -\mathcal{F}(E° - E_c°) - RT \ln K' \tag{19}$$

with the values of $E°$, $E_c°$, and K' evaluated by the cyclic voltammetric methods listed in Tables IV and V. The comparison in Table VI of ΔG obtained from eq 19 with that independently determined by the spectrophotometric method[23] provides strong confirmation of the validity of the electrochemical analysis in Scheme I. Furthermore, since the equilibrium constant for the neutral complex [NO,Ar] is small and likely to be solvent insensitive, the measurement of $E_c°$ is alone sufficient to assess donor stabilization of the nitrosonium cation, whether D is an additive or the medium itself.

Activation Barriers for the Reduction of the Nitrosonium Cation. Despite the uncommonly high positive values of $E°$ (see Table V) that should easily place the nitrosonium cation among other strong oxidants,[41] it is not generally regarded to be unusually effective, especially in a synthetic capacity. Indeed, NO^+ is a unique cation, being the only diatomic oxidant known to be capable of a chemically reversible redox change in an accessible potential range.[42] Since the dioxygen/superoxide couple is the closest commonly available diatomic analogue,[43] the direct comparison of their intrinsic activation parameters is desirable. As such, the application of transient electrochemical methods such as cyclic voltammetry provides the means (eqs 2–5) to measure the heterogeneous rate constants k_s for the reduction of NO^+ at the Pt electrode.[44] It is noteworthy that the value of $k_s = 5 \times 10^{-3}$ cm s^{-1} for $NO^+ \rightarrow NO$ in Table IV is 2 orders of magnitude slower than that observed for $O_2 \rightarrow O_2^-$ in the same medium (acetonitrile).[45] The corresponding activation free energy evaluated as $\Delta G_{el}^{\ddagger} \simeq 11$ kcal mol^{-1} (see Experimental Section) is also substantially larger than that ($\Delta G_{el}^{\ddagger} = 7.6$ kcal mol^{-1}) for the dioxygen/superoxide couple.[46] In these diatomic systems, the inner-sphere reorganization energies for electron transfer are clearly associated with the change in bond length (r) accompanying the reduction. (For example, $r = 1.06$ and 1.15 Å for NO^+ and NO,[47] and $r = 1.21$ and 1.28 Å for O_2 and O_2^-[48]). However, it is the magnitude of the stretching force constants of 23.9 and 15.9 mdyn Å^{-1} for NO^+ and NO[49] relative to 11.8 and 7.72 mdyn Å^{-1} for O_2 and O_2^-[50] that is the critical factor leading to the higher activation barrier of the cationic nitrosonium couple.[51] It is interesting to note that the measured (uncorrected) barrier of $\Delta G_{el}^{\ddagger} = 11$ kcal mol^{-1} for heterogeneous electron transfer[53] is about half the barrier of $\Delta G_{ex}^{\ddagger} = 17.5$ kcal mol^{-1} calculated for the homogeneous self-exchange of NO^+ and NO,[56] in accord with the predictions of Marcus' theory.[57,58]

Experimental Section

Materials. The nitrosonium salt $NO^+BF_4^-$ (Pfaltz and Bauer) was repeatedly recrystallized from pure acetonitrile at −20 °C until colorless under an argon atmosphere. All further manipulations were carried out in a Vacuum Atmospheres MO-41 inert-atmosphere box equipped with a Dri-Train inert-gas circulator to maintain <1 ppm of dioxygen and water. The purity of $NO^+BF_4^-$ was assayed by the IR spectrum of the complex with 18-crown-6 in dichloromethane showing a single band at $\nu = 2250$ cm^{-1} (AgCl).[61] Nitric oxide (reagent grade) was further purified[62] by slowly passing a stream of the gas via glass frits serially through aqueous 12 M NaOH, followed by 50% v/v H_2SO_4 in water,

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(41) Particularly in aprotic solvents in which oxidants with $E° > 1$ V are considered strong, e.g., $E° = 1.1$ V for $Fe(phen)_3^{3+}$: Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Phys. Chem.* **1986**, *90*, 3747.

(42) For example, the $O_2^+ \rightarrow O_2$ couple is likely to be chemically reversible, but the value of $E \sim 5$ V is outside the potential range for use with most solvents: Dinnocenzo, J. P.; Banach, T. E. *J. Am. Chem. Soc.* **1986**, *108*, 6063.

(43) Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393.

(44) (a) Compare: Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 5839. (b) The heterogeneous rate constant for the reduction of NO^+ at a glassy carbon electrode was found to be essentially the same ($k_s = 2 \times 10^{-3}$ cm s^{-1} in acetonitrile). Electrode pollution precluded an accurate measurement on a gold surface.

(45) For $O_2 \rightarrow O_2^{\bullet-}$, the value of $k_s = 0.8$ cm s^{-1}: Peover, M. E.; Powell, J. S. *J. Polarogr. Soc.* **1966**, *12*, 108. For the measurement of the reorganization energies, see: Lind, J.; Shen, X.; Merenyi, G.; Jonsson, B. O. *J. Am. Chem. Soc.* **1989**, *111*, 7654.

(46) Hale, J. M. In *Reactions of Molecules at Electrodes*; Hush, N. S., Ed.; Wiley-Interscience: New York, 1971; Chapter 4.

(47) (a) Field, R. W. *J. Mol. Spectrosc.* **1973**, *47*, 194. (b) Nichols, N. L.; Hause, C. D.; Noble, R. H. *J. Chem. Phys.* **1955**, *23*, 57.

(48) (a) Herzberg, G. *Molecular Spectra and Molecular Structure*, 2nd ed.; D. Van Nostrand: Princeton, NJ, 1965; Vol. 1, p 560. (b) Abrahams, S. C.; Kalnajs, J. *Acta Crystallogr.* **1955**, 8, 503.

(49) Lane, J.; Ohlsen, J. R. *Prog. Inorg. Chem.* **1980**, *27*, 465.

(50) (a) Linnett, J. W. *J. Chem. Soc.* **1956**, 275. (b) Herzberg, G. In ref 48a.

(51) For example, the inner-sphere reorganization energies of $\lambda_i = 21$ and 6.4 kcal mol^{-1} are calculated for the NO^+/NO and O_2/O_2^- couples, respectively, solely on the basis of the bond distances and the stretching force constants listed above.[52] The difference of $\Delta\lambda_i \cong 15$ kcal mol^{-1} compares with the experimental value of 12 kcal mol^{-1}.

(52) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(53) The uncorrected value of $\Delta G_{el}^{\ddagger} \approx 11$ kcal mol^{-1} neglects the charging of the double layer for the work term.[54] If the double-layer potential of Pt is taken as that of Hg[55] and the potential of zero charge is shifted by 0.1 V, the value of $\Delta G_{el}^{\ddagger}$ is estimated to be reduced by less than 0.8 kcal mol^{-1}.

(54) See: (a) Petersen, R. A.; Evans, D. H. *J. Electroanal. Chem. Interfacial Electrochem.* **1987** *222*, 129. (b) Sharp, M.; Petersson, M.; Edström, K. *J. Electroanal. Chem. Interfacial Electrochem.* **1980**, *109*, 271. (c) Britton, W. E.; Ferraris, J. P.; Soulen, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 5322.

(55) (a) Grzeszczuk, M.; Smith, D. E. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *157*, 205. (b) Lexa, D.; Saveant, J. M.; Su, K. B.; Wang, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 6464.

(56) (a) Eberson, L.; Radner, F. *Acta Chem. Scand.* **1984**, *B38*, 861. (b) Eberson, L.; Radner, F. *Acc. Chem. Res.* **1987**, *20*, 53. (c) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987.

(57) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 4966; **1965**, *43*, 679.

(58) However, the theoretical treatment of Hush[59] predicts $\Delta G_{el}^{\ddagger} = \Delta G_{ex}^{\ddagger}$. See also: Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317. Furthermore, recent studies suggest that the Marcus and Hush predictions depend on the absolute magnitude of k_s.[60] However, at this juncture we cannot eliminate the possibility of an inner-sphere component to the electron-transfer mechanism, since the value of k_s could not be shown to be completely independent of the electrode surface (compare footnote 44b).

(59) Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1005.

(60) (a) Saji, T.; Maruyama, Y.; Aoyagui, S. *J. Electroanal. Chem. Interfacial Electrochem.* **1978**, *86*, 219. (b) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J.-M.; Saveant, J.-M. *J. Am. Chem. Soc.* **1979**, *101*, 3431.

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phosphorus pentoxide suspended on glass wool, and then a cold trap maintained at −100 °C. Acetonitrile (Fisher) was stirred with $KMnO_4$ for 24 h at 25 °C and the mixture refluxed until the liquid was colorless. After removal of the brown MnO_2 by filtration, the acetonitrile was fractionated from P_2O_5 under an argon atmosphere. Acetonitrile was again fractionated from CaH_2 and stored under argon in Schlenk flasks equipped with Teflon stopcocks. Dichloromethane (Fisher) was stirred with successive portions of 98% sulfuric acid until the acid layer was colorless. The resulting dichloromethane was washed with 5% aqueous $NaHCO_3$ and water. After drying with $CaCl_2$, the dichloromethane was refluxed from P_5O_5 and distilled under an argon atomosphere. Pure dichloromethane was subjected to a second fractionation from CaH_2 and the distillate stored in Schlenk flasks. Nitromethane (Fisher, 96%) was fractionally recrystallized at −78 °C from a partially frozen mixture. The pale yellow liquid was decanted, and the colorless crystals were recrystallized three times in this manner. The resulting nitromethane was treated with $CaCl_2$ followed by fractionation in vacuo at 150 mmHg. The fraction boiling in the range 49–50 °C was collected and stored in a Schlenk flask in the dark. Durene (Aldrich), pentamethylbenzene (Aldrich), hexamethylbenzene (Fluka), and hexaethylbenzene (Kodak) were recrystallized from ethanol and sublimed in vacuo. Mesitylene (J. T. Baker) was refluxed over and distilled from sodium. 1-Methylnaphthalene (Aldrich) was used as received. 18-Crown-6 (Aldrich) was dried in vacuo prior to use. Tetrabutylammonium hexafluorophosphate (TBAH, Aldrich) was recrystallized from a mixture of ethyl acetate and hexane followed by vacuum-drying at 140 °C. It was stored in a desiccator over P_2O_5 until used.

Electrochemical Instrumentation and Measurements. Cyclic voltammetry was performed on an iR-compensated potentiostat[63] driven by a Princeton Applied Research (PAR) 175 Universal Programmer. The high-impedence voltage follower amplifier was mounted external to the potentiostat to minimize the length of the connection to the reference electrode for low noise pickup. Current–voltage curves were plotted on a Houston Series 2000 X-Y recorder. Alternatively they were displayed on either a Tektronix 5115 storage oscilloscope or a Gould Biomation 4500 digital oscilloscope. The cyclic voltammetric cell was of airtight design with high-vacuum Teflon stopcocks and viton O-ring seals to allow an inert atmosphere to be maintained without contamination by grease. The working electrode consisted of a platform disk ($A = 7.85 \times 10^{-3}$ cm^2) embedded in glass. Periodic polishing was performed on a soft velvet cloth. The counter electrode consisted of a platinum-gauze sheet that was separated from the working electrode by ~0.75 cm. The SCE reference electrode and its salt bridge were separated from the working electrode compartment by a sintered-glass frit positioned as close as possible. The SCE reference electrode was connected to the counter electrode via a 0.02-μF capacitor to aid in the compensation of iR drop. All potentials are reported vs SCE, and $E°$ values for the ferrocene/ferrocenium couple were measured as 0.41 (acetonitrile), 0.35 (nitromethane), and 0.48 V (dichloromethane) relative to SCE.[34,35] The platinum microelectrode for the determination of D was constructed from platinum wire of radius $r = 5$ μM (Goodfellows) sealed in soft glass. Calibration of the electrode area was carried out with ferrocene by using the relationship[64] of the limiting current as $i_{\lim} = 4n\mathcal{F}DrC$, where $D = 2.4 \times 10^{-5}$ cm^2 s^{-1} for ferrocene[65] ($n = 1$) at the concentration of $C \cong 5$ mM. Solutions of $NO^+BF_4^-$ in acetonitrile and nitromethane yielded values of D in Table III. The diffusion coefficient of nitric oxide was assumed to be the same.[66] The diffusion coefficients of NO^+ and NO in dichloromethane were estimated on the basis of its viscosity being slightly greater than that of acetonitrile but less than the viscosity of nitromethane.[67]

Cyclic Voltammetry of the Nitrosonium Cation. In the drybox, $NO^+BF_4^-$ (7 mg, 6×10^{-5} mol) was weighed and placed in the working-electrode compartment of the cell and the cell sealed and removed from the glovebox. In a separate Schlenk flask, a 0.1 M stock solution of TBAH in acetonitrile was prepared. With the aid of a hypodermic syringe, 6 mL of the stock solution was added to the working-electrode compartment and 4 mL to the reference compartment. The calomel and working electrodes were inserted, and the cell was sealed. Voltammograms were recorded at various sweep rates. In the case of acetonitrile and nitromethane, no other CV waves were observed within the potential range screened for the solvent/electrolyte system. Furthermore, no adsorption effects could be observed in this media. Both the cathodic and anodic waves maintained their CV peak shapes and the current function, $i_p/\sqrt{v}$, remained relatively constant at all scan rates. For quasi-reversible systems, as in the present context, the values of $i_p/\sqrt{v}$ are predicted to show slight variations.[68] (Compare Table I.)

Cyclic Voltammetry of NO^+ Complexes with Arenes. For the cyclic voltammetry of the charge-transfer complex of NO^+ and arene, incremental mounts of donor were added to the acetonitrile solution of $NO^+BF_4^-$ in the cell described above against a countercurrent of argon. The solutions were always carefully protected from air, since the complexes of NO^+ and arene are known to be easily deteriorated by contact with air.[23,69] The unresolved cyclic voltammograms in acetonitrile solutions of 10 mM NO^+ in the presence of added durene at $v = 0.5$ V s^{-1} (see Figure 7) showed the following peak shifts as millimolar amounts of Ar_4, E_p^c (E_p^c/log v), E_p^a (E_p^a/log v): 0, 1.19 (−), 1.37 (−); 5, 1.17 (41.4), 1.36 (38.1); 10, 1.15 (45.3), 1.35 (28.5); 20, 1.13 (51.0), 1.33 (35.5); 30, 1.08 (71.9), 1.32 (34.5); 50, 1.06 (79.6), 1.31 (32.5); 100, 1.00 (93.4), 1.30 (41.9) [in units of V vs SCE and mV/log (V s^{-1})]. The cyclic voltammograms of NO^+ and hexaethylbenzene resembled those of Ar_5 (Figure 6) more than Ar_6 (Figure 3). The cyclic voltammographic behavior of NO^+ and mesitylene was roughly akin to that of durene. Solutions of α-methylnaphthalene and NO^+ turned green upon the passage of cathodic current and were not examined further. When 6×10^{-5} mol of $NOBF_4$ was added to dichloromethane containing 0.1 M TBAH, the crystals of $NOBF_4$ remained undissolved and the cyclic voltammogram showed no CV wave on either the negative or positive scan. However, when 3×10^{-5} mol of HMB was added, the crystals of $NOBF_4$ dissolved and the solution became dark brown. A cathodic wave at 0.80 V was observed on the initial negative scan and the coupled anodic wave occurred at 1.29 V on the return scan. On the initial positive scan, the anodic wave of Ar_6 was observed at 1.66 V. With incremental addition of Ar_6, the CV pattern did not change. Similar behavior was observed with the other arenes, and the shifts (in V vs SCE) at $v = 500$ mV s^{-1} are reported as donor, E_p^c, and E_p^a: none, 1.42, 1.54; Ar_4, 1.20, 1.34; Ar_5, 0.98, 1.32; Ar_6, 0.76, 1.35; 18-crown-6, 0.68, 1.10. For comparison, the corresponding values in acetonitrile (compare Figures 3, 6, and 7) were as follows: none, 1.20, 1.36; Ar_4, 1.15, 1.35; Ar_5, 0.94, 1.30; Ar_6, 0.81, 1.30; 18-crown-6, 0.60, 1.30. The anodic behavior of the arene was observed beyond +1.5 V.[14] No distinctive one-electron waves were observed for Ar_6, but Ar_5 and Ar_4 showed minor waves (unresolved) owing to their limited values of K.

The CV simulations were carried out on the Fortran version of the Gosser–Rieger program[26] with a Compaq Deskpro personal computer. The simulations were based on the mechanism in Scheme I with the following electrochemical parameters for eq 9 designated as $E°$, k_s, and α, for eq 10 as $K = k_1/k_2$, for eq 11 as $E_c°$, k_s', and α', and for eq 12 as $K' = k_3/k_4$. The values of $E°$, k_s, and α for the NO^+/NO couple were initially taken from Tables I–III, and those for K from the independent spectrophotometric determination.[23] In order to establish the general voltammetric behavior with each arene, the potential variation of the cathodic peaks P_1 and P_3 for hexamethylbenzene (Ar_6), the broad unresolved cathodic peak for pentamethylbenzene (Ar_5), and the relatively sharp cathodic peak for durene (Ar_4) were examined with changes in K. Subsequently the values of $E°$ and k_s were optimized as a function of the arene concentration. The peak separation of P_1 and P_2 was especially sensitive to k_s, and E_p^c was used in the optimization of $E_c°$. The variation of the transfer coefficient in the range $0.3 < \alpha < 0.7$ optimized the shape of P_1. The shift in P_2 with the concentration of Ar_6 and Ar_5 was obtained from the combination of k_3 and k_4 (10^{-4} M $< K' <$ 10 M). For durene, the shift of the anodic peak potential with Ar_4 concentration was insensitive to k_3 and k_4, and thus only K' was optimized. The peak currents were then otpimized by tuning the values of K and $E_c°$. Although the EC mechanism for NO oxidation is included in Scheme I, the alternative CE process was considered.[25,29] However, the CV simulation with $k_4 = 0$ and more negative values of $E_c°$ failed to yield the observed shifts of P_2 with changes in the arene concentration. Also, the CE process cannot be completely discounted owing to the program-imposed limit of the first-order rate constant $k_1 < 10^5$ s^{-1}.[28] It is clear however from the spectral study[30] that the [NO,Ar] complex is at best very weak; and thus the distinction between the EC and CE processes of NO oxidation represents a fine mechanistic point.

Cyclic Voltammetry of Nitric Oxide. Cyclic voltammetry of nitric oxide was performed by bubbling the pure gas directly into the electrolytic solution contained in the CV cell for a period of approximately 10

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min. Solutions (and the atmosphere above them) of NO were colorless in the three solvents used. After the introduction of NO, the platinum working electrode was inserted and the cell sealed. The gain on the potentiostat was set to that of the known concentration of $NO^+BF_4^-$ in the particular solvent. At these settings, the concentration of NO was adjusted to give currents nearly the same as that obtained from a 1×10^{-2} M NO^+ solution. Decreasing the concentration of NO was simply performed by allowing argon to flow through the CV cell for a short period of time. This process was repeated until the currents were roughly similar to those of the NO^+ solutions in a given solvent and at the same scan rate. For the solvents CH_3CN and NO_2Me, the voltammograms showed clean diffusive behavior (see Table II). However, in the cyclic voltammogram of NO in dichloromethane, adsorption at the platinum working electrode was apparent for both the oxidation of NO and the return NO^+ reduction waves at concentrations greater than $\sim 5 \times 10^{-3}$ M. Even at concentrations of $<5 \times 10^{-3}$ M, slight adsorption effects were indicated by the nonconstant $i_p/\sqrt{v}$ values shown in Table II. The adsorption was only minor, since the CV waves continued to be rather diffusive in character, as shown in Figure 2C. The adsorption effects were not taken into account in the calculation of the heterogeneous charge-transfer rate, k_s. Thus, these values in Table III must be accepted with some caution.

Activation Barriers for Electron Transfer. The heterogeneous rate constants k_s in Table III were related to the activation free energy[52] as $k_s = \kappa A \exp(-\Delta G_{el}^{*}/kT)$, where κ for the transmission coefficient is taken as unity, and the preexponential factor $A = (\delta r_e)\Gamma_n \nu_n$ was evaluated as 3×10^5 cm s^{-1} for $\Gamma_n = 1$, $\delta r_e = 1 \times 10^{-8}$ cm, and $\nu_n = 3 \times 10^{13}$ s^{-1}.[70] The correction for the charging of the double layer[71] was neglected by assuming that the electrode potential was close to the bulk potential,[46,54] the difference being approximated as no more than 15%.[58,72] The inner-sphere reorganization energy was approximated by the Marcus relationship[73,74] $\lambda_i = [\sum_j f_j^{O} f_j^{R}/(f_j^{O} + f_j^{R})](\Delta r)^2$, where f_j^{O} and f_j^{R} are the force constants of the oxidized NO^+ (O_2) and the reduced NO (O_2^-) respectively.

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Reaction of (Dioxygen)(dithiocarbamato)rhodium Complexes with Carbon Dioxide. Formation and Chemical Cleavage of Rhodium Peroxycarbonato and Carbonato Rings

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Dioxygen complexes of bis(triphenylphosphine)(dithiocarbamato)rhodium and its analogue have been prepared. The structure determined by NMR spectroscopy was interpreted by the strong electron-accepting nature of the dioxygen ligand. The complex reacts with carbon dioxide at room temperature to give the peroxycarbonato complex $Rh(S_2CNMe_2)(CO_4)(PPh_3)_2$. The structure of this complex, in which the oxygen atom originating from carbon dioxide occupies the position trans to one of the S atoms of the chelating S_2CNMe_2 while the oxygen originating from the dioxygen is trans to one of the PPh_3 ligands, is proposed on the basis of its successive reactions. In the presence of excess triphenylphosphine, the peroxycarbonate was deoxygenated to give a yellow carbonato complex, $Rh(S_2CNMe_2)(CO_3)(PPh_3)_2$, which has two trans(S,O) pairs and trans triphenylphosphines, as characterized by crystallographic analysis. The complex crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 12.634$ (5) Å, $b = 17.681$ (4) Å, $c = 10.449$ (4) Å, $\alpha = 98.97$ (3)°, $\beta = 109.27$ (4)°, $\gamma = 99.27$ (2)°, and $Z = 2$. When heated to 70 °C, this complex isomerizes to the thermodynamically stable form with an orange-red color. After being heated for a prolonged time in the presence of triphenylphosphine, the carbonate complex was further deoxygenated to give the carbon dioxide adduct of $Ru(S_2CNMe_2)(PPh_3)_2$, which was not isolated but characterized by NMR spectroscopy.

Introduction

Although a variety of group VIII metal peroxy complexes have been prepared from dioxygen, they are in general reluctant to react with simple olefins by nonradical pathways. A notable exception is the case of rhodium: $[Rh(O_2)(AsPh_3)_4]^+$ can transfer its oxygen ligand to terminal olefins, producing ketones.[1] The combination of rhodium chloride and cupric perchlorate in alcohol catalyzes oxidation of terminal olefins by O_2 at room temperature.[2] It appears, therefore, important to understand the reactivity of the dioxygen molecule coordinated to rhodium. To our knowledge, only two mononuclear rhodium–dioxygen complexes, $[Rh(O_2)(AsMe_2Ph)_4]ClO_4$[1] and $RhCl(O_2)(^tBuNC)(PPh_3)_2$,[3] and two dinuclear complexes, $[RhCl(O_2)(PPh_3)_2]_2$[4] and $[Rh(cod)]_2(O_2)$,[5] have been known, but reactivity of the coordinating dioxygen has not been fully examined. In this report we describe the preparation of a mononuclear rhodium–dioxygen complex having dithiocarbamate and triphenylphosphine as ancillary ligands. Its reaction with carbon dioxide is fairly facile and provides information concerning reactivity and bonding of the oxygen atoms bound to rhodium. The present work is also relevant to the recent literature that addition of carbon dioxide affects the product distribution in the Rh(I)-catalyzed oxidation of styrene by O_2.[6]

Experimental Section

^1H and ^{31}P NMR spectra were recorded on a JEOL JNM-GX-400 spectrometer in CD_2Cl_2 using $SiMe_4$ and H_3PO_4 as internal and external standards, respectively. IR spectra were obtained on a Shimadzu IR-27G spectrometer using the KBr pellet method. For column chromatography, Sumitomo activated alumina KCG-30, deactivated beforehand by 10 wt % of water, or WAKOGEL C-200 was used.

Preparation of $Rh(S_2CNMe_2)(O_2)(PPh_3)_2$ (2a). A mixture of $RhCl(PPh_3)_3$ (1 g, 1.2 mmol), Na(dtc) (dtc = dimethyldithiocarbamate; 194 mg, 1.1 mmol), and triphenylphosphine (288 mg, 1.1 mmol) in THF

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