Strong electronic coupling in intermolecular (charge-transfer) complexes. Mechanistic relevance to thermal and optical electron transfer from aromatic donors

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Intermolecular electron transfer from various arene donors (ArH) to the nitrosonium acceptor (NO^+) proceeds *via* a series of unusual [1:1] precursor complexes. Quantitative analysis of the accompanying pair of charge-transfer absorption bands ($h\nu_H$ and $h\nu_L$) reveals the presence of strong electronic interactions between the donor/acceptor moieties in [ArH,NO^+] complexes with the coupling elements lying in the range: $\mathbf{H}_{ab} = 1.4 \pm 0.5$ eV. In the context of Sutin's development of Marcus–Hush theory, these dyads represent a Robin–Day Class III system for the 2-step transformation of the reactant diabatic state $\{ArH + NO^+\}$ to the final diabatic state $\{ArH^{+\bullet} + NO^\bullet\}$, in which the unusually high values of $\mathbf{H}_{ab}$ characterize a series of intermolecular (precursor) complexes that lie in a single (potential-energy) minimum. As such, the thermal electron transfer between the arene donor and the nitrosonium acceptor occurs first *via* the redistribution of a pair of electrons in the formation of the $[ArH, NO]^+$ complex with $X_{min} = 1.0$, and then followed by its homolytic dissociation to the $\{ArH^{+\bullet}$ and $NO^\bullet\}$ products. This conclusion is experimentally confirmed by X-ray crystallographic and IR analyses of the precursor complexes that identify: (i) the strongly perturbed donor/acceptor moieties structurally akin to arene cation radicals ($ArH^{+\bullet}$) and the reduced nitric oxide ($NO^\bullet$), and (ii) the degree of charge transfer (Z) that is complete (100%). Optical electron transfer *via* the direct photoactivation of the precursor complex to the identical Franck–Condon state $\{ArH^{+\bullet}, NO^\bullet\}^*$ occurs independent of whether the high-energy ($h\nu_H$) or the low-energy ($h\nu_L$) absorption band is irradiated.

Introduction

Electron donor/acceptor interactions leading to characteristic charge-transfer absorption bands are relevant to many intermolecular electron-transfer processes of organic and organometallic origin.[1,2] As such, the quantitative evaluation of these redox systems is important to such divergent fields as the formulation of organic and organometallic reaction mechanisms[3] as well as the development of novel electronic materials.[4] Of particular interest to the present study is the role of *strong* donor/acceptor (or charge-transfer) interactions in thermal (adiabatic) and photoactivated (optical) electron transfers from various aromatic (ArH) donors.

Electron-transfer theories, mainly based on inorganic (coordination) compounds, identify the electronic (coupling) interaction $\mathbf{H}_{ab}$, together with the Marcus reorganization energy λ, and the free-energy change ΔG^0 as crucial factors in determining the kinetic and thermodynamic characteristics of a redox system.[5–8] Heretofore, particular attention has been devoted to weakly and moderately interacting donor/acceptor pairs with values of the electronic coupling element $\mathbf{H}_{ab}$ generally less than 200 cm^{-1},[5,6] and a somewhat minor (consequent) effect on the energy profile (along the reaction coordinate[9]) of the traditional two-state representation.[10] However, with increasingly strong electronic interactions in the donor/acceptor pair,[11] it is seen in Fig. 1 that the nuclear and electronic characteristics of the precursor complex are predicted to be more strongly perturbed relative to the non-interacting (diabatic) states,[8,12] and the activation free energy to be progressively lowered. Finally, in the limiting region with $\mathbf{H}_{ab} \geqslant \lambda/2$, the redox system is completely delocalized, with a single potential-energy minimum and no activation barrier for electron transfer. In the framework of the Robin–Day classification[13] of mixed-valence compounds, the increasing magnitudes of the electronic coupling reflect the progressive transition from Class I ($\mathbf{H}_{ab} = 0$, non-interacting redox centers) to Class II ($0 < \mathbf{H}_{ab} < \lambda/2$, weakly interacting) and to Class III ($\mathbf{H}_{ab} \geqslant \lambda/2$, delocalized) systems.[8]

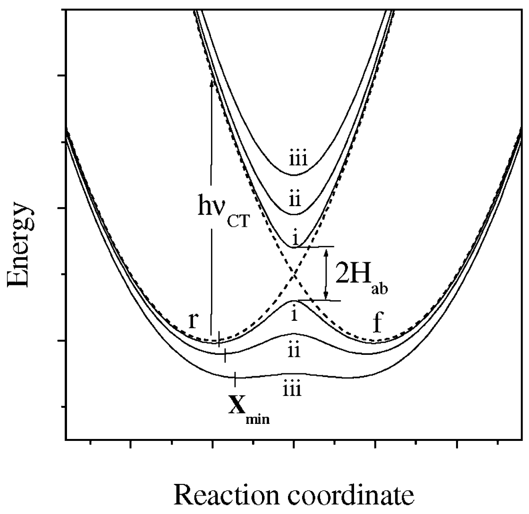


Fig. 1 Generalized plot of the free-energy changes along the reaction coordinate for an electron transfer reaction with $\Delta G^0 = 0$. The electronic coupling increases from the diabatic reactants (r) and final(f) states (dotted lines) with $\mathbf{H}_{ab}/\lambda = 0$ to various adiabatic states with $\mathbf{H}_{ab}/\lambda = 0.10$ (i), 0.23 (ii) and 0.33 (iii).

Although simple and well-behaved organic (redox) systems are rather unusual,[14] we recently identified the intermolecular electron-transfer between aromatic donors and the cationic nitrosonium acceptor to represent a reversible interchange that proceeds *via* the [1:1] donor/acceptor or charge-transfer complex as the direct precursor:[15]

$$\mathrm{ArH + NO^+ \rightleftarrows [ArH, NO^+] \rightleftarrows ArH^{+\bullet} + NO^\bullet} \qquad (1)$$

This organic system offers several unique advantages for the quantitative elucidation of electron-transfer processes with strongly interacting (redox) pairs,[16] since the nitrosonium cation moiety is a simple diatomic that allows the resident charge on a partially reduced moiety to be determined from its N–O stretching frequency and its bond length by infrared spectroscopy and X-ray crystallography.[17] Moreover, the thermodynamic driving force for electron transfer (from strongly endergonic to exergonic regions) is readily modulated by employing various benzene derivatives with comparable steric properties (see Table 1).[18] Finally, every species in eqn. (1) is sufficiently persistent to allow all quantitative measurements to be experimentally scrutinized.[19] Accordingly, our objective in this study is the verification of the semi-empirical theoretical approaches to electron transfer[6,8] as applied to strongly coupled organic systems for quantitative correctness, especially insofar as the electronic interaction energies, charge distributions, and ground-state and optical properties are concerned.[20,21] Experimental methodologies involving: (a) structural (X-ray crystallographic) analysis, (b) spectral (UV-Vis, IR) characteristics; and (c) photochemical (steady-state and time-resolved) probes will form the basis for evaluating specific features of the theoretical predictions.

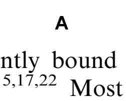
Results, theory and calculations

I Spontaneous complexation of aromatic donors with the nitrosonium acceptor

(A) Appearance of charge-transfer absorption bands. When aromatic donors (Table 1) are added to a solution of $\mathrm{NO^+SbCl_6^-}$, the instantaneous formation of electron donor/acceptor or EDA complexes is immediately revealed by distinctive yellow to red colorations. Spectral examination of the highly colored solutions indicates the appearance of two new absorption bands—an intense high-energy band (H) and a very weak low-energy band (L). The partially overlapping bands can be numerically deconvoluted into a pair of Gaussian components; and the absorption maxima of the prominent H bands are listed in Table 1, together with their bandwidths ($\Delta\nu_{1/2}$) and extinction coefficients ($\varepsilon_{\mathrm{CT}}$). Spectrophotometric analyses at various concentrations of arene and $\mathrm{NO^+SbCl_6^-}$ (according to the Job and Benesi–Hildebrand methodologies) also establish the formation of the [1:1] precursor complex, that is:[15,17]

$$\mathrm{ArH + NO^+ \xrightleftharpoons{K_{et}} [ArH, NO^+]} \qquad (2)$$

(B) Structural characterization of the [ArH,NO$^+$] complexes. Isolation and X-ray crystallography at low temperatures reveal a common family of charge-transfer complexes with the general structure **A**,



A

in which the non-covalently bound NO moiety lies directly over the aromatic ring.[15,17,22] Most importantly, the inner-sphere character of these precursor complexes is in accord with the intermolecular separations (r_{DA}, Table 1) that are significantly smaller than the sum of the van der Waals radii of 3.25 Å.

(C) Reversible (charge-transfer) complexation followed by electron transfer. The charge-transfer absorption bands in Table 1 are transient and when the solutions are scrutinized, the reversible equilibration of the precursor complex with the paramagnetic products of electron transfer is apparent:

$$\mathrm{ArH + NO^+ \rightleftarrows [ArH, NO^+] \xrightleftharpoons{K_{CT}} ArH^{+\cdot} + NO^\cdot} \qquad (3)$$

Although the formation constant (K_{et}^{-1}) of the complex is pertinent to the overall electron-transfer process, it is of secondary importance here and the earlier description[15] is sufficient for this study.

II Electronic coupling elements for arene/nitrosonium complexes

(A) Evaluation of the electronic coupling element from the charge-transfer spectral data. Experimentally, the electronic coupling element (**H**) in the precursor complex is evaluated from the spectral data in Table 1 by using the Hush expression based on the Mulliken formalism:[20,21]

$$\mathbf{H}_{\mathrm{MH}} = 0.0206(\nu_{\mathrm{CT}}\Delta\nu_{1/2}\varepsilon_{\mathrm{CT}})^{1/2}/r_{\mathrm{AD}} \qquad (4)$$

where ν_{CT} and $\Delta\nu_{1/2}$ are the spectral maximum and full-width at half maximum (cm^{-1}), respectively, of the charge-transfer absorption band, $\varepsilon_{\mathrm{CT}}$ is the extinction coefficient (M^{-1} cm^{-1}) of this precursor complex, and r_{AD} is the separation (Å) between the redox centers. Although the Mulliken–Hush (MH) expression in eqn. (4) was originally derived for precursors in the limit of weak interactions, it was subsequently shown by Creutz, Newton and Sutin to also be applicable (within the two-state model) to strongly interacting systems.[23,24]

The electronic coupling elements $\mathbf{H}_{\mathrm{MH}}$ calculated from the CT spectral data with the aid of eqn. (4)[25] are listed in Table 1 (last column). For the somewhat ambiguous separation parameter r_{DA}, we initially utilized the vertical distance of N to the mean (aromatic) plane in structure **A** as directly evaluated from the X-ray crystallographic data.[26]

(B) Strongly coupled arene/nitrosonium dyads as a Robin–Day Class III redox system. Examination of the electronic coupling elements listed in Table 1 indicates the presence of uniformly large values with $\mathbf{H}_{\mathrm{MH}}$ that exceed 1.3 eV in many of the precursor complexes. By the same token, the Marcus reorganization energies for the oxidation (*i.e.*, $\mathrm{ArH \rightleftarrows ArH^{+\bullet} + e}$) of the same donors are: $\lambda_{\mathrm{ArH}} = 2.0 \pm 0.2$ eV.[27] Coupled with the reorganization energy of the nitrosonium cation: $\lambda_{\mathrm{NO}} = 3.0$ eV,[27a] we find the reorganization energies of the cross reactions to lie in the range: $\lambda_{\mathrm{CR}} = 2.5 \pm 0.1$ eV, which is less than twice the value of the electronic coupling elements in Table 1. According to Sutin *et al.*,[8] such redox systems with $\mathbf{H}_{\mathrm{ab}} > \lambda/2$ fall into Class III, as based on the classical Robin–Day categories for mixed-valence complexes.[13] As such, the lowest potential-energy surface (consisting of a broad single minimum) in Fig. 1 provides a useful guide for the further examination these interesting redox dyads.

III Experimental validation of the electronic coupling elements

The electronic coupling elements evaluated by the semi-empirical theoretical treatment according to the Mulliken–Hush formulation in eqn. (4) bear directly on their prediction of the spectral as well as structural properties of the precursor com-

Table 1 Oxidation potentials of the donors, E^0_{ox}, characteristics of the high-energy band (ν_{H}, $\Delta\nu_{1/2}$ and ε) in their complexes with nitrosonium, distance between nitrogen and aromatic plane, r_{DA} (from X-ray analysis) and electronic coupling elements $\mathbf{H}_{\mathrm{MH}}$ based on the Mulliken model

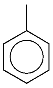
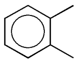
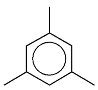
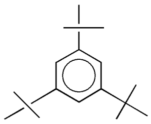
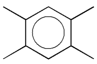
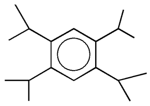
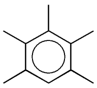
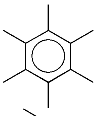
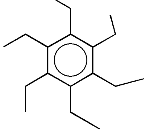
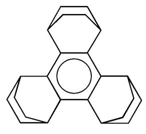
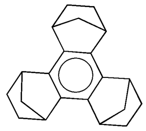
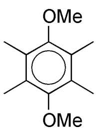
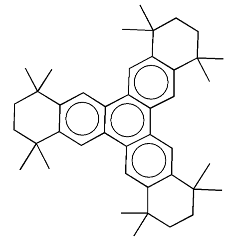
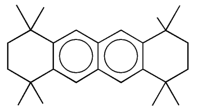
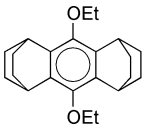
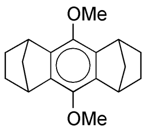
Aromatic donor			$E^0_{\mathrm{ox}}{}^a$/V	$\nu_H{}^b$/10^3 cm^{-1}	$\Delta\nu_{1/2}{}^b$/10^3 cm^{-1}	ε^c/10^3 M^{-1} cm^{-1}	$r_{\mathrm{DA}}{}^d$/Å	$\mathbf{H}_{\mathrm{MH}}$/eV
1	BEN		2.70	29.8	6.0	1.6	2.1^e	~0.7
2	TOL		2.42	29.6	6.5	3.5	2.1^e	~1.0
3	*o*-XY		2.13	29.8	6.1	3.5	2.192(2)	0.97
4	*p*-XY		2.06	30.2	6.8	4.0	2.155(2)	1.10
5	MES		2.11	29.5	5.9	5.8	2.185(4)	1.22
6	TBB		2.01	29.4	6.6	4.0	2.1^e	~1.1
7	DUR		1.83	30.3	5.9	7.0	2.092(2)	1.36
8	TPB		1.80	29.5	6.0	6.8	2.1^e	~1.3
9	PMB		1.75	30.1	6.0	8.1	2.049(2)	1.48
10	HMB		1.62	30.1	6.0	8.0	2.093(2)	1.47
11	HEB		1.59	29.5	6.1	7.0	2.080(2)	1.36
12	TET		1.55	28.8	5.9	7.7	2.097(3)	1.37
13	TMT		1.50	28.9	5.9	6.6	2.109(3)	1.30
14	TMM		1.45	29.3	6.3	8.3	2.1^e	~1.5
15	DMT		1.43	20.8	6.0	7.1	2.1^e	~1.1

Table 1 (continued)

Aromatic donor			$E^0{}_{ox}{}^a$/V	$\nu_H{}^b/10^3$ cm^{-1}	$\Delta\nu_{1/2}{}^b/10^3$ cm^{-1}	$\varepsilon^c/10^3$ M^{-1} cm^{-1}	$r_{DA}{}^d$/Å	$\mathbf{H}_{MH}$/eV
16	OMN		1.34	21.6	5.9	6.2	2.16 (1)	0.99
17	EA		1.30	29.0	7.1	7.0	2.089(3)	1.46
18	MA		1.16	27.8	4.6	8.3	2.107(3)	1.26

[a] From ref. 15 and 18. [b] Estimated deviations are ±0.2 × 10^3 cm^{-1}. [c] Estimated deviations are ±0.3 × 10^3 M^{-1} cm^{-1}. [d] From ref. 15 and 17, estimated standard deviations are in parenthesis. [e] X-Ray crystallographic data for the 1:1 [ArH, NO]$^+$ complex are not available and r_{DA} is taken by analogy with that of similar arene complexes.

plexes. In the framework of the two-state (redox) system, the wave functions Ψ_G and Ψ_E of the ground and excited (adiabatic) states, respectively, are presented as a linear combination of the zero-order reactant and final diabatic states (ψ_r and ψ_f).[6,8,23]

$$\Psi_G = c_a\psi_r + c_b\psi_f \qquad (5)$$

$$\Psi_E = c_b\psi_r - c_a\psi_f \qquad (6)$$

The associated interaction diagram for the reactant $\{ArH + NO^+\}$ and final $\{ArH^{+\bullet} + NO^\bullet\}$ diabatic states is qualitatively depicted in Chart 1.[28]

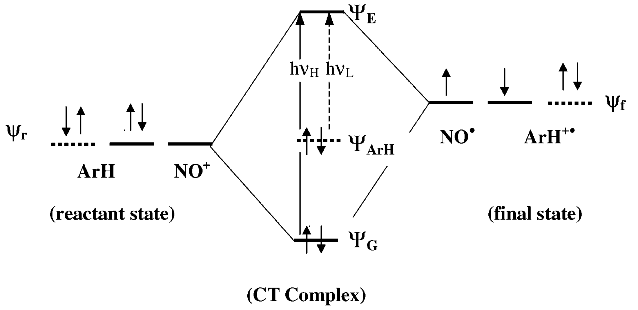


Chart 1

(A) Mulliken correlation of the charge-transfer absorption band. Within the framework of the two-state model (ψ_r and ψ_f), the energies of the lower (E_G) and upper (E_E) adiabatic states (obtained by the solution of the two-state secular determinant) are expressed as:[8,23]

$$E_G = (\varepsilon_r + \varepsilon_f)/2 - (\Delta_{rf}{}^2 + 4\mathbf{H}_{ab}{}^2)^{1/2}/2 \qquad (7)$$

$$E_E = (\varepsilon_r + \varepsilon_f)/2 + (\Delta_{rf}{}^2 + 4\mathbf{H}_{ab}{}^2)^{1/2}/2 \qquad (8)$$

where $\varepsilon_r = \int\psi_r H\,\psi_r$ and $\varepsilon_f = \int\psi_f H\,\psi_f$ are the energies of reactant and final diabatic states, H is the total Hamiltonian operator of the system, $\Delta_{rf} = \varepsilon_f - \varepsilon_r$ is the energy difference between reactant and final diabatic states, and $\mathbf{H}_{ab} = \int\psi_r H\,\psi_f$ is electronic coupling matrix element. Since the prominent (high-energy) absorption band $h\nu_H$ corresponds to the CT transition from the ground state of the precursor complex to the excited state (see Chart 1), it follows directly from eqn. (7) and (8) that:

$$h\nu_H = E_E - E_G = (\Delta_{rf}{}^2 + 4\mathbf{H}_{ab}{}^2)^{1/2} \qquad (9)$$

Eqn. (9) allows the energy difference Δ_{rf} to be evaluated from the spectral data ($h\nu_H$) and the electronic coupling elements ($\mathbf{H}_{MH}$ as $\mathbf{H}_{ab}$) listed in Table 1. The calculated values of Δ_{rf} are listed in Table 2.

The weak (symmetry-forbidden) low-energy band L in Table 2 was previously shown to correspond to the electronic transition from the filled (non-bonded) orbital on the arene donor to the unoccupied (antibonding) orbital of the precursor complex.[15] As such, the transition energy $h\nu_L$ is identified here as the difference between E_E of the excited state [eqn. (8)] and E_{ArH} of the diabatic (non-interacting) state:

$$h\nu_L = E_E - E_{ArH} = 1/2(\Delta_{rf}{}^2 + 4\mathbf{H}_{ab}{}^2)^{1/2} + \Delta_{rf}/2 \qquad (10)$$

The relationship of the experimental values of $h\nu_L$ in Table 2 and the calculated values based on eqn. (10) (Table 2) is illustrated in Fig. 2. Such a linear correlation indicates that the Mulliken–Hush coupling elements can reasonably describe the observed spectral dependence of the (low-energy) charge-transfer transition in the precursor complex with changes of the arene donor strength ($E^0{}_{ox}$), although the absolute values of the calculated $h\nu_L$ are consistently larger than the experimental ones (Table 2).[29]

(B) Charge distribution between donor and acceptor in the precursor complex. *1 Theoretical significance of the mixing coefficients.* According to Creutz, Newton, and Sutin's development of the Marcus–Hush formalism, the value of the electronic coupling element is related directly to the product of the normalized mixing coefficients and the energy gap between the ground and excited states:[6,23]

$$c_a c_b = \mathbf{H}_{ab}/(E_E - E_G) \qquad (11)$$

The energy difference ($E_E - E_G$) at the reactant minimum corresponds to the energy of the optical (charge-transfer) transition $h\nu_H$ listed in Table 1. Thus, the simultaneous solution of eqn. (11) and the normalization relationship $c_a{}^2 + c_b{}^2 = 1$ allows the square of the mixing coefficient to be calculated as:

$$c_b{}^2 = \tfrac{1}{2} - [1 - (2\mathbf{H}_{ab}/h\nu_H)^2]^{1/2}/2 \qquad (12)$$

Table 2 Comparison of the experimental and calculated values of the low-energy band in arene/nitrosonium complexes

Aromatic donors	$h\nu_L$(exp)/eV	$\Delta_{rf}{}^a$/eV	$h\nu_L$(calcd)^b/eV
BEN	2.92	3.46	3.58
TOL	2.79	3.08	3.37
o-XY	2.66	3.14	3.42
p-XY	2.55	3.02	3.38
MES	2.57	2.72	3.19
TBB	2.44	2.95	3.30
DUR	2.45	2.59	3.18
TPB	2.34	2.50	3.08
PMB	2.42	2.29	3.01
HMB	2.45	2.32	3.03
HEB	2.32	2.45	3.05
TMT	2.24	2.48	3.04
TET	2.24	2.3	2.94
MA	2.16	2.36	2.90
EA	2.23	2.09	2.84
OMN	2.13	1.81	2.25
DMT	2.03	1.51	2.05
TMM	2.23	2.03	2.84

[a] Calculated from eqn. (9) and the data in Table 1. [b] Calculated from eqn. (10) and the values of electronic coupling element from Table 1.

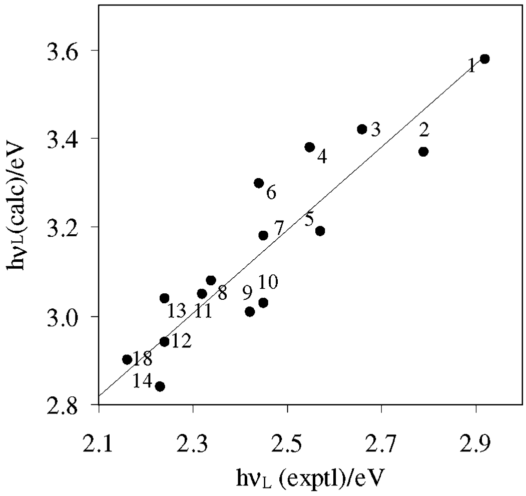


Fig. 2 Correlation of the experimental and calculated energies of the low-energy band in [ArH, NO$^+$] complexes. Numbers identify the aromatic donors in Table 1.

Since the mixing coefficients c_a and c_b transform the initial and final diabatic states into the ground and excited-state wave functions according to eqn. (5) and (6); their squares $c_a{}^2$ and $c_b{}^2$ represent the fraction of the electronic charge residing on the donor andthe acceptor, respectively. As such, the values of $c_b{}^2$ will reflect the progress of electron transfer when the reaction coordinate is presented in terms of changes in the electronic configuration.[9]

2 Experimental measure of the degree of charge transfer. The progress of electron transfer is represented by the electronic charge distribution between the donor and acceptor in the intermediate (charge-transfer) complex. This measurement in the case of [ArH,NO$^+$] complexes is facilitated by the diatomic character of the acceptor, together with the relatively large change in the simple N–O (IR) stretching frequencies attendant upon the reduction of nitrosonium (ν_{NO} = 2272 cm^{-1}, r_{NO} = 1.06 Å) to nitric oxide (ν_{NO} = 1876 cm^{-1}, r_{NO} = 1.15 Å).[30] Thus, the variation of the charge transferred from the arene donor to NO$^+$ (in the CT complex) is hereinafter designated as Z, and it is directly expressed as:[17]

$$Z = (\nu_{NO^+}{}^2 - \nu_{CT}{}^2)/(\nu_{NO^+}{}^2 - \nu_{NO}{}^2) \qquad (13)$$

where the subscripts NO$^+$ and NO represent the uncomplexed nitrosonium cation and nitric oxide, respectively, and ν_{CT} is the frequency of the partially reduced NO moiety in the series of precursor (CT) complexes.

By definition, the value of Z = 1.0 is attained when one electron overall has been transferred from the donor to the acceptor so that the intermediate complex can be formally depicted as [ArH$^{+\bullet}$, NO$^\bullet$]. The experimentally determined values of Z listed in Table 3[17] indicate that this redox situation is obtained in the isergonic region where $\Delta G^0 \approx 0$ for hexamethylbenzene and related hexaalkylsubstituted benzenes with oxidation potentials $E^0{}_{ox} \approx 1.5 - 1.6$ V *vs.* SCE[18] to match the reduction potential of $E^0{}_{red}$ = 1.48 V for the nitrosonium acceptor.[31]

3 Correlation of the theoretical and experimental measures. The degree of charge transfer measured experimentally as Z [eqn. (13)] should coincide with that predicted theoretically as $c_b{}^2$ in eqn. (12). Since the latter requires reliable $\mathbf{H}_{ab}$ values,

Table 3 Electronic coupling elements for nearly isergonic Class III complexes (as derived from the energy of the optical electron transfer $h\nu_H$) and recalculated donor/acceptor separations

Aromatic donor	$h\nu_H/10^3$ cm^{-1}	Z^a	$\mathbf{H}_{ab}{}^b$/eV	$R_{DA}{}^c$/Å
HMB	30.1	0.97	1.87	1.65
HEB	29.5	0.93	1.83	1.56
TMT	28.9	0.93	1.79	1.52
TET	28.9	0.97	1.79	1.64
TMM	29.3	–	1.82	1.74

[a] From Kim *et al.* in ref 17. [b] From eqn. (14). [c] Corrected separation based on eqn. (4).

we note that the electronic coupling element can be evaluated directly from the experimental charge-transfer transition energies:

$$h\nu_{\mathrm{H}} = 2\mathbf{H}_{\mathrm{ab}} \tag{14}$$

according to the Mulliken, Hush and Sutin treatment[20,21,23] of the Robin–Day Class III complexes like [ArH, NO$^+$], which exist in the isergonic region of the driving force. For such precursor complexes, the combination of eqn. (12) and (14) predicts the mixing coefficient to be $c_b{}^2 = 0.5$. Since a pair of electrons are redistributed in [ArH, NO$^+$] complexes (see Chart 1), the theoretical value of $2c_b{}^2 = 1.0$ pertains, which is in exact harmony with the experimental $Z = 1.0$. Table 3 lists the values of $\mathbf{H}_{\mathrm{ab}}$ evaluated from eqn. (14) using the optical (CT) transition energies $h\nu_{\mathrm{H}}$ listed in Table 1.

Comparison of the $\mathbf{H}_{\mathrm{ab}}$ values in Table 3 with those in Table 1 ($\mathbf{H}_{\mathrm{MH}}$) obtained from the Mulliken–Hush eqn. (4) indicates the value of $\mathbf{H}_{\mathrm{MH}}$ to be consistently smaller by 0.3–0.4 eV. We believe that part of the discrepancy lies in the proper evaluation of the separation parameter r_{AD} in eqn. (4). Since the latter derives from eqn. (11) by a consideration of the transition dipole in the CT excitation, the assignment of the separation parameter can be somewhat arbitrary for a redox dyad as structurally diverse as the arene donor and the nitrosonium acceptor are.[26] As such, our preliminary choice of r_{DA} based on the molecular structure determined by X-ray crystallography (*vide supra*) could be in serious error. Accordingly, let us treat r_{DA} in the Mulliken–Hush eqn. (4) as a disposable parameter, by constraining the value of $\mathbf{H}_{\mathrm{MH}}$ to abide by the more reliable value of $\mathbf{H}_{\mathrm{ab}}$ based on eqn. (14). The result leads to "corrected" values of the separation parameter R_{DA} in Table 3, which are generally 0.5 Å smaller than those based on X-ray crystallographic analyses. Indeed, such a shortening of the interaction distance between the donor/acceptor dyad accords with our qualitative expectations based on the integrated orbital overlap.[32]

In the absence of reliable experimental values of r_{DA},[26] the electronic coupling elements for the other [ArH, NO$^+$] complexes can be calculated from the identity $2c_b{}^2 = Z$ according to eqn. (12) (Table 4).[33] The values of $\mathbf{H}_{\mathrm{ab}}$ obtained in such a way are very close to the values obtained directly from the CT band energy [eqn. (14)] for the complexes near the isergonic point (Table 3). The linear relationship between $\mathbf{H}_{\mathrm{ab}}$ based on IR changes and $\mathbf{H}_{\mathrm{MH}}$ based on the oscillator strength of the CT bands is presented in Fig. 3.[33] Indeed, such a linear correlation provides additional experimental support for the electronic description of the precursor complex in terms of the diabatic-state formulation in eqn. (5) and (6) and Chart 1.

Discussion

I Electron transfer *via* the strongly coupled (precursor) complex

The redox dyads consisting of various arene donors (ArH) and the nitrosonium acceptor (NO$^+$) in eqn. (1) present an unusual opportunity to examine intermolecular electron-transfer processes proceeding *via* strongly coupled (precursor) complexes with diagnostic charge-transfer absorptions. In the context of Sutin's development of the Marcus–Hush formulation,[8] this redox system can be described as a two-step transformation of the reactant diabatic state $\{\mathrm{ArH} + \mathrm{NO}^+\}$ to the final state $\{\mathrm{ArH}^{+\bullet} + \mathrm{NO}^\bullet\}$ *via* the strongly coupled (charge-transfer) complex [ArH, NO]$^+$ that resides in a single (potential energy) well.[34] The intersecting potential-energy surfaces that represent the two diabatic states for such an electron transfer are pictorially illustrated by the dashed lines in Fig. 4. For clarity, the diabatic reactant and final curves r and f, respectively, in Fig. 4 are drawn for the ArH/NO$^+$ pair in the isergonic region of the driving force ($\Delta G^0 = 0$) and for a reorganization energy of $\lambda_{\mathrm{CR}} = 2.5$ eV.[27] The potential-energy surface of the precursor complex (PC) is presented at $\mathbf{H}_{\mathrm{ab}} = 1.8$ eV, as determined from the spectral data according to eqn. (14).[8]

II Molecular and electronic structures of the precursor complex

The unmistakable coincidence of theory with experiment is established by the experimental values of Z [eqn. (13)] that are equal to twice the theoretical (mixing) coefficient $c_b{}^2$ [eqn. (12)] for the complexes in Table 3, which lie near the isergonic point.[33b] This, together with the measured values of $\mathbf{H}_{\mathrm{ab}} = 1.7 \pm 0.1$ eV, indicates that the lowest potential-energy surface in Fig. 4 represents the [ArH, NO]$^+$ precursor complex. Finally, X-ray crystallographic analyses of isolated (crystalline) complexes confirm the structures of the aromatic moiety to be coincident with that of the cation radical (ArH$^{+\bullet}$), and the structure of the nitrogen oxide moiety to be that of nitric oxide (NO$^\bullet$).[35,36] In other words, when the precursor complex is viewed from the point of view of its nuclear coordinates, its position along this coordinate is very close to that of the diabatic final state, in which $X_{\min}$ is unity, as described by Sutin.[8] From the standpoint of the mixing coefficients, this takes place at $c_b{}^2 = 0.5$, but the minimum is located at $2c_b{}^2 = 1.0$ when *two* electrons are redistributed (see Chart 1). Thus, for these diamagnetic donor/acceptor dyads, the value of the mixing coefficient (*i.e.*, $c_b{}^2$) at the complex minimum is one-half the value of the charge transferred. Because the equilibrium (nuclear) coordinates are determined by the electron-density distribution, the position of the precursor complex along the reaction coordinates (in terms of nuclear configuration) should correspond to the final (product) diabatic state ($X_{\min} = 1.0$).[37]

The fact that a complete redistribution of the electron density between ArH and NO$^+$ is observed at the precursor stage may be even more surprising if the microscopic reverse process (involving nitric oxide oxidation by the arene cation radical) is considered. In such a case, the diffusive interaction of ArH$^{+\bullet}$ and NO$^\bullet$ will not involve any nuclear (intramolecular) reorganization or charge transfer, since the formation of the precursor complex will require no change in nuclear and electronic coordinates ($X_{\min} = 0$), although these nearly symmetric Class III systems would otherwise correspond to $X_{\min} = 0.5$.[8, 37]

III Electron-transfer mechanism for strongly coupled donor/acceptor dyads

The molecular and electronic characterization of the precursor (charge-transfer) complex as the critical intermediate allows us to draw some unexpected conclusions regarding the electron-transfer mechanism. Thus, the *single* electron transfer reaction [eqn. (1)] between the arene donor and the nitrosonium acceptor is a two-stage process that occurs first *via* the redistribution of a *pair* of electrons (see Chart 1) at the stage of complex formation, and then the homolytic dissociation of the intermediate complex to the free aromatic cation radical and free nitric oxide. Since the nuclear configuration and charge distribution between the donor and acceptor in the strongly coupled complex correspond to those extant in the products, no additional electron transfer is needed in the second (follow-up) stage. Furthermore, with some modification the shift of the electron pair is satisfactorily described within the framework of the model developed for single-electron motion, that is: (i) the values of electronic coupling elements ($\mathbf{H}_{\mathrm{ab}}$) and the mixing coefficients ($c_b{}^2$) are reasonably determined from a (one-electron) optical transition, and (ii) the use of one-electron mixing coefficients in eqn. (5) and (6) allows the electron-density distribution and the molecular geometry of the intermediate complex (multiplying by two) to be anticipated.

Table 4 Corrected values of the electronic coupling elements $\mathbf{H}_{ab}$ based on the comparison of c_b^2 and Z

Aromatic donor	$c_b^{2\,a}$	Z^b	$\mathbf{H}_{ab}{}^c$/eV
BEN	0.03	0.52	1.62
TOL	0.08	0.61	1.69
o-XY	0.07	0.69	1.76
p-XY	0.10	0.70	1.78
MES	0.13	0.75	1.77
TBB	0.10	0.80	1.79
DUR	0.15	0.86	1.86
PMB	0.19	0.92	1.86
HMB	0.19	0.97	1.87
HEB	0.17	0.93	1.83
TMT	0.16	0.93	1.79
TET	0.18	0.97	1.79

[a] Based on eqn. (12) with $\mathbf{H}_{ab}$ from eqn. (4) [b] Based on eqn. (13). [c] Recomputed from eqn. (12) based on $2\,c_b^2 = Z$ from column 3.

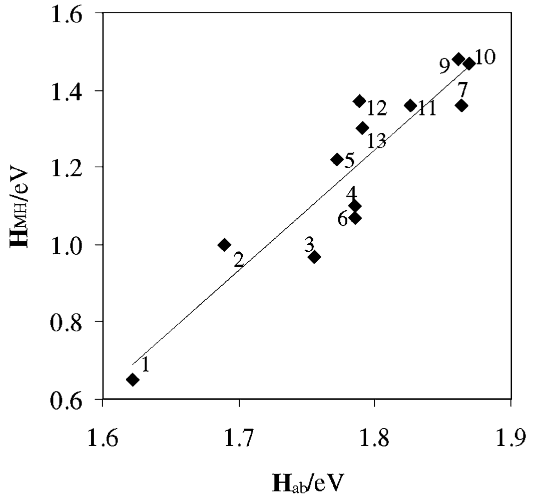


Fig. 3 Direct comparison of the electronic coupling elements $\mathbf{H}_{MH}$ based on the UV-Vis data and $\mathbf{H}_{ab}$ based on the IR data. Numbers identify aromatic donors in Table 1.

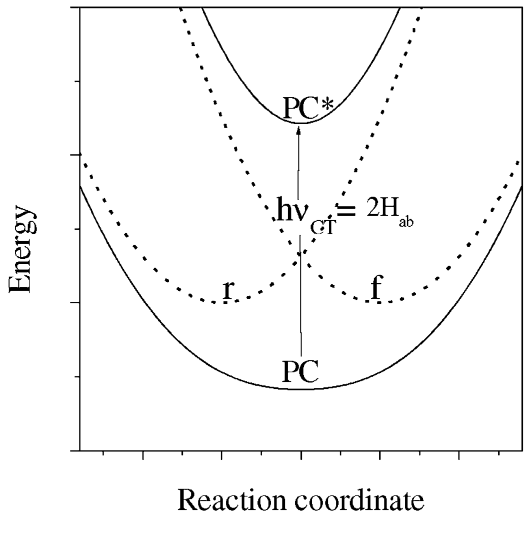


Fig. 4 Potential-energy surface of the precursor complex (PC) relative to the reactant (r) and final (f) diabatic states (dashed lines) for electron transfer in Class III with $\lambda = 2.5$ eV and $\mathbf{H}_{ab} = 1.8$ eV.[45]

Owing to the absence of an activation barrier,[38] the rate of product formation in these Class III systems will be limited by the homolytic dissociation step—the increasing strength of the donor/acceptor interaction leading to *lower* equilibrium concentrations of the electron-transfer products {$\text{ArH}^{+\bullet}$ and $\text{NO}^\bullet$}, which in turn will lead to diminished rates of any subsequent reaction leading to stable (diamagnetic) products.[39,40] Thus, in contrast to weakly and moderately coupled charge-transfer complexes (like those in Robin–Day Class II), the strongly coupled counterparts such as those examined in this study lead to slower rates of formation of ion radicals and their (follow-up) products.[41]

IV Optical electron transfer *via* strongly coupled arene/nitrosonium complexes

Photoinduced electron transfer within intermolecular electron donor/acceptor or EDA complexes is effected *via* the direct irradiation of their charge-transfer absorption bands.[42] In the general context of Mulliken theory[21] for weak complexes, in which the electronic coupling is limited (*e.g.*, $\mathbf{H}_{ab} < 500$ cm^{-1}), the ground state of the precursor complex is primarily expressed as:[1]

$$\Psi_G = a\psi_{D,A} + b\psi_{D^+,A^-} \tag{15}$$

where $\psi_{D,A}$ and ψ_{D^+,A^-} represent the "no-bond" and the dative wavefunctions, respectively, with the mixing coefficients $a \gg b$.[43] Therefore, the optical transition from the ground state of the weak EDA complex (with $X_{min} \approx 0$) to the charge-transfer excited state:

$$\Psi_E = b\psi_{D,A} - a\psi_{D^+,A^-} \tag{16}$$

is accompanied by a large dipole change. As such, the energy of the Franck–Condon state usually differs from that of the thermally equilibrated pair of the ion radicals ($D^{+\bullet}$, $A^{-\bullet}$) by an amount roughly corresponding to a reorganization penalty. Such a fast vibrational relaxation, we believe, basically distinguishes the ion-radical pair formed *via* charge-transfer excitation of Class II complexes from that derived from photoexcitation of Class III complexes.[44] In the case of the arene/nitrosonium dyad of interest here, the strong electronic coupling with $\mathbf{H}_{ab} \gg \Delta G_{ET}{}^0$ (as in Fig. 4) leads to mixing coefficients in eqn. (5) that are comparable (*i.e.*, $c_a \approx c_b$) and thus no appreciable electron transfer occurs from the aromatic donor to NO^+ (in the precursor complex) upon the optical transition—the electron-density distribution between the donor and acceptor moieties being roughly comparable in both the ground and excited states. As such, the optical transition is more appropriately designated as a bonding-to-antibonding rather than a charge-transfer transition (as it is in weak EDA complexes).[45]

Experimentally, time-resolved (laser-flash) experiments with $[\text{ArH,NO}]^+$ complexes show high quantum efficiencies for the co-production of transient aromatic cation radicals $\text{ArH}^{+\bullet}$ (and nitric oxide).[46] Three types of spectral transients are observed. Initially (on the subpicosecond timescale), the thermally equilibrated ion-radical pair and the σ-adduct are derived more or less simultaneously [eqn. (18)] from the first-formed Franck–Condon state (asterisk) with an experimental quantum efficiency of unity:[47]

$$[\mathrm{ArH,NO}]^{+} \xrightarrow{h\nu_{\mathrm{CT}}} [\mathrm{ArH,NO}]^{+}* \qquad (17)$$

$$[\mathrm{ArH,NO}]^{+*} \xrightarrow{(<\mathrm{ps})} \{\mathrm{ArH}^{+\bullet},\mathrm{NO}\}_{\mathrm{solv}} + \mathrm{ArH(NO)}^{+} \qquad (18)$$

where the subscript (solv) identifies the thermally equilibrated pair of ion radicals.[48,49] The rapid (electronic) decoupling of the (non-bonded) excited state in eqn. (17) involves an essentially barrierless transformation (on the vibrational timescale of 10^{-13}–10^{-14} s), since no additional electron redistribution is required from the donor to the acceptor—the electron density distribution (and nuclear configuration) in the ground state already being that of the arene cation radical and nitric oxide, that is $X_{\min}$ is unity. As a result, only fast solvent reorganization is needed for its relaxation in eqn. (18). In the subsequent step, the thermally equilibrated (solvent-caged) radical pair suffers a first-order separation to the free ion radical and nitric oxide:

$$\{\mathrm{ArH}^{+\cdot},\mathrm{NO}^{\cdot}\}_{\mathrm{solv}} \xrightarrow{(\mathrm{ps})} \mathrm{ArH}^{+\cdot} + \mathrm{NO}^{\cdot} \qquad (19)$$

on the diffusional timescale of $\tau \sim 10^{-11}$ s with decreasing quantum efficiency for the hexamethylbenzene, pentamethylbenzene, durene and *o*-xylene complexes of: $\Phi = 0.70$, 0.60, 0.4 and 0.1, respectively.

Finally, on the microsecond timescale, the second-order (thermal) recombination of the freely diffusing aromatic cation radical and nitric oxide regenerates the initial (precursor) complex:

$$\mathrm{ArH}^{+\cdot} + \mathrm{NO}^{\cdot} \xrightarrow{(\mu\mathrm{s})} [\mathrm{ArH,NO}]^{+} \qquad (20)$$

the overall rate of which is rather constant and nearly independent of the donor strength (E^{0}_{ox}) of the arene. As such, the latter is the mirror image of complex formation and thus bereft of an activation barrier.[50]

Most importantly, the temporal behavior of all these spectral transients is quite independent of the excitation energy—the first-order rates and quantum yields being the same for both the 350 nm and 540 nm irradiations (corresponding to the second and third harmonics of the output from the Nd^{3+}-YAG laser).[47] Such experimental observations thus provide unambiguous confirmation for the spectral assignment in Chart 1, in which the identical excited state is populated by photoexcitation of either the high ($h\nu_{\mathrm{H}}$) or the low ($h\nu_{\mathrm{L}}$) energy absorption bands.

Taken all together, the facile kinetic processes in eqn. (17)–(20) point to the $\mathrm{ArH/NO^{+}}$ dyad as a highly reversible redox system. Continuous irradiation of the $[\mathrm{ArH, NO}]^{+}$ complexes by and large leads to a quasi-photostationary state for the concentrations of ion-radical species, and it generally leads to no permanent photochemical transformation—the arene donor generally being recovered intact. However, there are several exceptional situations. First, there is the extent to which the aromatic cation radical is unstable and can readily undergo a fast first-order transformation, such as a unimolecular mesolytic cleavage, as in the case of bicumene, or rapid rearrangement as in hexamethyl(Dewar)benzene, *etc.*[49] Second, there is the extent to which the (paramagnetic) nitric oxide is instantly scavenged (irreversibly) by dioxygen and other radical traps.[51] Third, there is the extent to which the σ-adduct in eqn. (18) can be transformed prior to homolytic reversion to the ion-radical pair and the precursor complex.[47,51] The alternative loss of the α-proton from the σ-adduct or Wheland intermediate [eqn. (18)] does not appear to be a viable pathway since there is little evidence for a CT-photoactivated pathway to aromatic nitrosation.[39]

Conclusions

Electron transfer in the organic redox system consisting of various arene donors (ArH) and the nitrosonium acceptor (NO^{+}), can be quantitatively accommodated within the theoretical formulation of a two-state model[8] in which the reactant diabatic state $\mathrm{r} = \{\mathrm{ArH} + \mathrm{NO}^{+}\}$ and the final diabatic state $\mathrm{f} = \{\mathrm{ArH}^{+\bullet} + \mathrm{NO}^{\bullet}\}$ are based on the Mulliken (charge-transfer) formulation.[21] Thus, the formation of $\mathrm{ArH/NO^{+}}$ complexes is theoretically described as the redistribution of an electron pair (from the arene donor) according to the interaction diagram depicted in Chart 1. The experimental values of the charge-transfer transition agree with the Mulliken–Hush predictions (based as they are on the one-electron optical transition), provided the electron-density distribution is obtained by doubling the mixing coefficients c_{b}^{2} in eqn. (12). In other words, the electron distribution between the donor and the acceptor in (diamagnetic) charge-transfer complexes (with an even number of electrons) is twice that in (paramagnetic) precursor complexes usually treated by electron-transfer theories. Therefore, the position of the charge-transfer complex along the nuclear (configuration) coordinate also corresponds to the doubled values of the quadratic (final-state) mixing coefficient, that is $2c_{\mathrm{b}}^{2}$, this conclusion being especially relevant to strongly coupled complexes for which the mixing coefficient c_{b} closely approaches c_{a}. The equilibrium structure (*i.e.*, nuclear configuration) of the charge-transfer complex is determined by the corresponding electron-density distribution, and its position along the reaction coordinate corresponds to the product state ($X_{\min} = 1.0$) for Class III complexes ($c_{\mathrm{a}}^{2} \approx c_{\mathrm{b}}^{2}$) that lie close to the isergonic potential. As such, thermal electron transfer in strongly interacting (Class III) systems is adequately described as an initial heterolytic (two-electron) bond formation of the precursor complex: (PC) = $[\mathrm{ArH,NO}]^{+}$ *via* the redistribution of an electron pair, followed by the homolytic dissociation of PC to the non-interacting radical-ion pair $\{\mathrm{ArH}^{+\bullet} + \mathrm{NO}^{\bullet}\}$, without substantial redistribution of the electron density between the donor and the acceptor.[52] Optical electron transfer induced by direct irradiation of the charge-transfer absorption band converts the same precursor complex to the first excited state, which is energetically related to the thermally equilibrated pair of ion radicals $\{\mathrm{ArH}^{+\bullet} + \mathrm{NO}^{\bullet}\}$ by an amount roughly corresponding to the reorganization penalty. The same excited state is populated in the $\mathrm{ArH/NO^{+}}$ redox system by the deliberate irradiation of either the high-energy ($h\nu_{\mathrm{H}}$)or the low-energy ($h\nu_{\mathrm{L}}$) absorption bands of the precursor complex.

Experimental

Materials

Nitrosonium hexachloroantimonate was prepared from $\mathrm{SbCl_5}$ and NOCl according to the literature procedure.[17] The alkylbenzenes (Aldrich) were purified by repeated recrystallization from ethanol or fractional distillation. The syntheses of triethanododecahydrotriphenylene (TET), trimethanododecahydrotriphenylene (TMT), dimetoxydurene (TMM), triphenylene, 1,1,4,4,7,7,10,10,13,13,16,16-dodecamethyl-1,2,3,4,7,8,9,10,13,14,15,16-dodecahydrodinaphtoanthracene (DMT), cycloannulated naphthalene 1,1,4,4,7,7,10,10-octamethyl-1,2,3,4,7,8,9,10-octahydronaphthacene (OMN), 9,10-diethoxy-1,4,5,8-diethano-1,2,3,4,5,6,7,8-octahydroanthracene (EA), and 9,10-dimethoxy-1,4:5,8-dimethano-1,2,3,4,5,6,7,8-octahydroanthracene (MA) were described previously.[18*c*,35,53] All of the compounds were characterized by their melting points, IR, ^{1}H NMR, ^{13}C NMR, MS and elemental analysis. Dichloromethane (Merck) was purified according to standard laboratory procedures and was stored in Schlenk flasks under an argon atmosphere.[54]

Instrumentation

The UV-Vis absorption spectra were recorded on a HP 8453 diode-array spectrometer. The ^{1}H and ^{13}C NMR spectra were obtained on a General Electric QE-300 FT NMR spectrometer. Infrared (IR) spectra were recorded on a Nicolet 10D FT spectrometer. The electrochemical apparatus and the procedure for the determination of the oxidation potentials have been described elsewhere.[18,31] Procedures for the X-ray crystallographic analysis and crystal data of the aromatic donors, their nitrosonium complexes, and the cation radicals salts were described previously.[15,17,35] (Note that the X-ray structure details of various compounds mentioned here are on deposit and can be obtained from the Cambridge Crystallographic Data Center, U.K.)

Measurement of the charge-transfer spectra of CT complexes with nitrosonium

The spectral data in Table 1 were typically measured at $[NOSbCl_6]_0 = 0.2–1.0$ mM and $[ArH] = 0.2–20$ mM in 0.1–1.0 cm quartz cuvette at 22 °C under an agron atmosphere. The UV-vis spectra were deconvoluted into Gaussian components in order to obtain the CT transition energy and the widths of the H and L bands. Extinction coefficients for the nitrosonium complexes with relatively weak donors (BEN to MES) were determined from the absorption of solutions at a constant nitrosonium concentration and different concentrations of donor by the graphical methods of Drago (involving the dependence of $K_{CT}{}^{-1}$ against ε_{CT}) and by the Benesi–Hildebrand procedure (based on the dependence of $[NO^+]/A_{CT}$ *versus* $[ArH]^{-1}$).[55] For electron-rich donors, the extinction coefficients were calculated from absorbance of the solutions measured with a large excess of either nitrosonium or arene [since under these conditions the concentration of the complexes (due to high formation constants) were practically equal to the concentration of the reagent at lower concentration]. All operations were performed in Teflon-capped cuvettes equipped with a side arm in an inert atmosphere box.

Acknowledgements

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References and notes

1 (*a*) R. Foster, *Organic Charge-Transfer Complexes*, Academic, New York, 1969; (*b*) *Molecular Complexes*, ed. R. Foster, Crane, Russak and Co., New York, 1971 and 1973, vol. 1 and 2.

2 D. Astruc, *Electron-Transfer and Radical Processes in Transition-Metal Chemistry*, VCH, New York, 1995.

3 T. M. Bockman and J. K. Kochi, in *Photosensitization and Photocatalysis Using Inorganic and Organometallic Compounds*, ed. K. Kalyanasumdaraman and M. Grätzel, Kluwer, Dordrecht, 1993.

4 A. P. deSilva, in *Electron Transfer in Chemistry*, ed. V. Balzani, Wiley, New York, 2001, vol. 5.

5 (*a*) R. A. Marcus *Discuss. Faraday Soc.*, 1960, **29**, 21; (*b*) R. A. Marcus *J. Phys. Chem.*, 1963, **67**, 853; (*c*) R. A. Marcus *J. Chem. Phys.*, 1965, **43**, 679; (*d*) R. A. Marcus and N. Sutin, *Biochim. Biophys. Acta*, 1985, **811**, 265.

6 M. D. Newton, in *Electron Transfer in Chemistry*, ed. V. Balzani, Wiley, New York, 2001, vol. 1, p. 3.

7 R. A. Marcus *J. Phys. Chem.*, 1992, **96**, 1753.

8 (*a*) B. S. Brunschwig and N. Sutin, in *Electron Transfer in Chemistry*, ed. V. Balzani, Wiley, New York, 2001, vol. 2, p. 583; (*b*) See also: N. Sutin *Prog. Inorg. Chem.*, 1983, **30**, 441; (*c*) B. S. Brunschwig and N. Sutin, *Coord. Chem. Rev.*, 1999, **187**, 233; (*d*) N. Sutin *Adv. Chem. Phys.*, 1999, **106**, 7.

9 The reaction coordinate for electron transfer can be represented in different nuclear, electronic, and free-energy terms. The generalized nuclear coordinate (or nuclear configuration) is most frequently used as the abscissa and $X_{min} = 0$ corresponds to the nuclear coordinate characteristic of the non-interacting reactants, while $X_{min} = 1$ is that of the products. Alternatively, the abscissa can be determined either as the fraction of electron transferred from the donor to the acceptor (in which case $X_{min} = 0$ and $X_{min} = 1$ correspond to the non-interacting donor/acceptor system with the electron on the donor and the acceptor, respectively) or as the free-energy difference between the initial and final states (in which case $X_{min} = 0$ corresponds to the transition state).[6,8]

10 For the expression of the ground and excited adiabatic states *via* the zero-order initial (reactant) and final (product) states wavefunctions see eqn. (5) and (6).

11 (*a*) Strong electronic interactions are to be considered relative to the Marcus reorganization energy, that is $\mathbf{H}_{ab}/\lambda$ as shown in Fig. 1; (*b*) The donor/acceptor interaction can be (equivalently) considered in terms of either: (i) reactant and final (diabatic) states ψ_r and ψ_f, respectively, or (ii) the donor and acceptor (molecular) orbitals, ψ_D and ψ_A, respectively. The corresponding electronic coupling elements, $\mathbf{H}_{rf}$ or $\mathbf{H}_{DA}$, are then essentially the same; (*c*) The electronic coupling element is also included (as $\mathbf{H}_{ab}{}^2$) in the pre-exponential factor for the electron-transfer rate[2,6,8].

12 The contribution of the electronic coupling element to (i) the free energy of activation is given by: $\Delta G^* = \lambda\ (1 - 2\mathbf{H}_{ab}/\lambda)^2/4$ and (ii) the reaction minimum is determined by: $X_{min}{}^r = 1/2[1 - (1 - 4\mathbf{H}_{ab}{}^2/\lambda^2)^{1/2}]$, as defined by Sutin *et al.*[8].

13 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.

14 This is owing largely to the fact that one-electron oxidations of organic donors yield paramagnetic cation radicals that for the most part are highly transient (*i.e.*, reactive).[36].

15 S. V. Rosokha and J. K. Kochi, *J. Am. Chem. Soc.*, 2001, **123**, 8985.

16 For this intermolecular redox process, there is full electron delocalization between the donor and acceptor, and no energetic barrier exists between the precursor and successor complexes.[15].

17 E. K. Kim and J. K. Kochi, *J. Am. Chem. Soc.*, 1991, **113**, 4962. See also ref. 15.

18 (*a*) J. O. Howell, J. M. Goncalves, C. Amatore, L. Klasinc, R. M. Wightman and J. K. Kochi, *J. Am. Chem. Soc.*, 1984, **106**, 3968; (*b*) For the definition of donor strength in the context of $E^0{}_{ox}$, see: J. K. Kochi, in *Comprehensive Organic Synthesis*, ed. B. Trost and I. Fleming, Elsevier, New York, 1991, vol. 1; (*c*) R. Rathore, S. V. Lindeman and J. K. Kochi, *J. Am. Chem. Soc.*, 1997, **119**, 9393.

19 The pertinent arene cation radicals are persistent on the time scale required for the equilibrium measurements. At long times (hours and days), eqn. (2) is not a true equilibrium, since $ArH^{+\bullet}$ (especially those derived from arenes with higher values of $E^0{}_{ox}$) can lead irreversibly to more stable (diamagnetic) products.

20 (*a*) N. S. Hush *Z. Electrochem.*, 1957, **61**, 734; (*b*) N. S. Hush *Trans. Faraday Soc.*, 1961, **57**, 557; (*c*) N. S. Hush *Prog. Inorg. Chem.*, 1967, **8**, 391; (*d*) N. S. Hush *Electrochim. Acta.*, 1968, **13**, 1005.

21 R. S. Mulliken and W. B. Person, *Molecular Complexes*, Wiley, New York, 1969.

22 (*a*) W. D. Reents, Jr. and B. S. Freiser, *J. Am. Chem. Soc.*, 1980, **102**, 271; (*b*) S. Brownstein, E. Gabe, F. Lee and L. Tan, *J. Chem. Soc., Chem. Commun.*, 1984, 1566.

23 C. Creutz, M. D. Newton and N. Sutin, *J. Photochem. Photobiol. A: Chem.*, 1994, **82**, 47.

24 It should be noted that in strongly adiabatic cases, some of the parameters (especially r_{DA} and $\Delta\nu_{1/2}$) used in eqn. (4) (valid for Gaussian CT bands) are difficult to measure. In addition, optical transitions in Class III system are bonding/antibonding, rather than charge transfer. See ref. 6.

25 (*a*) In accord with common usage, the electronic coupling element (**H**) will referred to as $\mathbf{H}_{ab}$, except when specific reference is made to that ($\mathbf{H}_{MH}$) based on the Mulliken–Hush eqn. (4); (*b*) Note that (similar to calculations in the MO LCAO framework[15]) $\mathbf{H}_{MH}$ values for the complexes of hindered donors are lower than for unhindered ones (compare $\mathbf{H}_{MH}$ values for HMB and PMB with those for TET, TMT, and HEB in Table 1).

26 The operationally corrected values (R_{DA}) are listed in Table 3. For the discussion of r_{DA} in strongly interacting systems, see ref. 6.

27 (*a*) In cross exchange $\lambda_{CR} = (\lambda_{NO} + \lambda_{ArH})/2$, where $\lambda_{ArH} \approx 2$ eV and $\lambda_{NO} \approx 3$ eV; see: L. Eberson, R. Gonzalez-Luque, J. Lorentzon, M. Merchan and B. O. Roos, *J. Am. Chem. Soc.*, 1993, **115**, 2898; (*b*) T. Lund and L. Eberson, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1435; (*c*) L. Eberson, *Electron Transfer Reactions in Organic Chemistry*, Springer-Verlag, New York, 1987.

28 The reactant and final states in Chart 1 include the non-interacting (degenerate) arene HOMO, which is presented as a dotted line.

29 (*a*) The discrepancy probably arises from the overestimation of (i) Δ_{rf} in eqn. (10) as the difference between $h\nu_H$ and $\mathbf{H}_{MH}$ in eqn. (9) and (ii) r_{DA} in eqn. (4); (*b*) For the invariance of the high-energy band ($h\nu_H$) with changes in E^0_{ox}, see discussion in ref. 15.

30 See Kim *et al.* in ref. 17.

31 K. Y. Lee, D. J. Kuchynka and J. K. Kochi, *Inorg. Chem.*, 1990, **29**, 4196.

32 In the zero-order approximation, Δr_{DA} is simply taken at the intersection of ψ_r and ψ_f.[26].

33 The comparison of r_{DA} and R_{DA} in Tables 1 and 3 shows that similar (≈0.5 Å) shortenings of the effective separation parameters are observed for $[ArH, NO]^+$ complexes near the isergonic point. The same correction of the effective separation can be applied to all the other complexes, and the electronic coupling elements $\mathbf{H}_{ab}$ were recomputed with the revised $R_{DA} = 1.6$ Å. Based on these corrected values of $\mathbf{H}_{ab}$ (which are about 30% higher than the corresponding $\mathbf{H}_{MH}$ values), the values of $c_b{}^2$ can also be corrected according to eqn. (12).

34 These strongly coupled (CT) complexes will hereinafter be designated as $[ArH, NO]^+$ with the positive charge placed outside the brackets to indicate the presence of a single (potential energy) well.

35 For the structure of arene cation radicals, see: R. Rathore, A. S. Kumar, S. Lindeman and J. K. Kochi, *J. Org. Chem.*, 1998, **63**, 5847.

36 R. Rathore and J. K. Kochi, *J. Org. Chem.*, 1995, **60**, 4399.

37 (*a*) By comparison, the minimum in Class III complexes lies at $X_{min} = 0.5$ for odd-electron ($D^{+\bullet}$) systems such as the (intramolecular) mixed-valence complexes $D\text{-br-}D^{+\bullet}$ (br = bridge) and the intermolecular ion-radical dimers $D_2{}^{+\bullet}$ in which only *one electron* is redistributed (unambiguously) between the donor/acceptor moieties; (*b*) The distinction between $X_{min} = 0.5$ or 1.0 does not even arise in weakly coupled redox pairs since $c_b{}^2 \ll c_a{}^2$. The critical distinction in diamagnetic (even-electron) systems is for electron redistribution in complex formation to occur at $X_{min} = 1.0$ for strongly interacting systems with $c_b{}^2 = c_a{}^2 = 0.5$; (*c*) See: S. V. Lindeman, S. V. Rosokha, D. Sun and J. K. Kochi, *J. Am. Chem. Soc.*, 2002, **124**, 843; (*d*) J. K. Kochi, R. Rathore and P. Le Magueres, *J. Org. Chem.*, 2000, **65**, 6826; (*e*) P. Le Magueres, S. V. Lindeman and J. K. Kochi, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1180.

38 See: S. Skokov and R. A. Wheeler, *J. Phys. Chem. A.*, 1999, **103**, 4261.

39 E. Bosch and J. K. Kochi, *J. Org. Chem.*, 1994, **59**, 5573.

40 For the rapid follow-up reactions resulting from the homolytic coupling of such ion-radical pairs, see: R. Rathore and J. K. Kochi, *Adv. Phys. Org. Chem.*, 2000, **35**, 193.

41 In the limit of very strong interactions, irreversible binding of nitric oxide occurs and the usual redox products are not obtained. Such effects are observed in the nitrosonium interaction with tethered diarenes such as calixarenes, see: R. Rathore, S. V. Lindeman, S. S. P. Rao and J. K. Kochi, *Angew. Chem., Int. Ed.*, 2000, **112**, 2123. These are also characteristic of the interaction of nitrosonium with transition-metal complexes (see, *e.g.*, D. Astruc, in *Electron Transfer in Chemistry*, ed. V. Balzani, Wiley, New York, 2001, vol. 2, p. 714).

42 See ref. 40 and references therein.

43 (*a*) Eqn. (15) and (16) in the two-state model correspond to the reactant (r) and final (f) state wavefunctions ψ_r and ψ_f in eqn. (5) and (6); (*b*) The mixing coefficients in eqn. (15) and (16) are normalized, so that $a^2 + b^2 = 1$.

44 Strictly speaking, this is true only for redox systems in the isergonic region of the driving force. The deviation of the Franck–Condon state from the thermally equilibrated ion-radical pair increases with increasing endergonicity, but not as rapidly as that resulting from the charge-transfer excitation of Class II complexes.

45 The free-energy diagram for the bonding/antibonding transition (*i.e.*, PC → PC*), is shown in Fig. 4, and the charge-transfer transition is shown in Fig. 1.

46 Generally speaking, the irradiation of diamagnetic (CT) complexes (with even numbers of electrons) results in radical-pair formation as the primary photoproducts. In weakly interacting and/or highly endergonic systems, the ground state is characterized by mixing coefficients $a \gg b$ and (charge-transfer) irradiation generates excited states that are close to the (non-bonded) radical pair.

47 (*a*) T. M. Bockman, Z. J. Karpinski, S. Sankararaman and J. K. Kochi, *J. Am. Chem. Soc.*, 1992, **114**, 1920; (*b*) S. M. Hubig and J. K. Kochi, *J. Am. Chem. Soc.*, 2000, **122**, 8279.

48 The experimental time resolution of ~1 ps is insufficient to resolve the branching in eqn. (18) to the thermally equilibrated ion-radical pair and to the σ-adduct. In the case of the latter, related studies[49] established the radical coupling of $ArH^{+\bullet}$ and $NO_2{}^{\bullet}$ to proceed to the σ-adduct with no (measurable) activation energy.

49 (*a*) E. K. Kim, T. M. Bockman and J. K. Kochi, *J. Am. Chem. Soc.*, 1993, **115**, 3091; (*b*) S. M. Hubig and J. K. Kochi, *J. Org. Chem.*, 2000, **65**, 6534.

50 As a radical-pair combination, a statistical factor must be taken into account for this microscopic reverse process.

51 (*a*) E. K. Kim and J. K. Kochi, *J. Org. Chem.*, 1993, **58**, 786; (*b*) E. K. Kim, M. Christl and J. K. Kochi, *Chem. Ber.*, 1990, **123**, 1209; (*c*) Y. Takahashi and J. K. Kochi, *Chem. Ber.*, 1988, **121**, 253

52 A similar mechanism was proposed earlier by Steenken *et al.* for redox processes of radicals. See: (*a*) S. Steenken *Top. Curr. Chem.*, 1996, **177**, 125; (*b*) M. Bietti and S. Steenken, in *Electron Transfer in Chemistry*, ed. V. Balzani, Wiley, New York, 2001, vol. 2, p. 494.

53 (*a*) R. Rathore, S. Lindeman, A. S. Kumar and J. K. Kochi, *J. Am. Chem. Soc.*, 1998, **120**, 6931; (*b*) R. Rathore and J. K. Kochi, *J. Org. Chem.*, 1995, **60**, 4399.

54 (*a*) D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon, New York, 2nd edn., 1980; (*b*) D. F. Shriver and M. A. Drezdzon, *The Manipulation of Air-sensitive Compounds*, Wiley, New York, 2nd edn., 1986.

55 (*a*) R. S. Drago, *Physical Methods in Chemistry*, W. B. Saunders Company, Philadelphia, 1977; (*b*) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703.