Research Article

Electron transfer within 1,3-dinitrobenzene radical anions: electron hopping or superexchange?

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The intramolecular electron transfer on several 1,3-dinitrobenzene radical anions with different substituents on position 5 was studied by electron paramagnetic resonance and optical spectroscopies in MeCN. The radical anions are all charge-localized mixed valence species, as is common for *meta*-substituted dinitrobenzenes. Rate constants for the electron transfer reaction were obtained by the Marcus–Hush analysis of the intervalence optical bands assuming quartic-augmented energy surfaces and solvent-controlled dynamics. These calculated rate constants match quite well the experimental ones obtained by simulation of the electron paramagnetic resonance spectra, which rules out bridge-reduced states as intermediates in the reaction path and confirms the superexchange mechanism. Copyright © 2012 John Wiley & Sons, Ltd.
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Keywords: organic mixed valence; dinitroaromatic radical anions; Marcus–Hush theory; charge-transfer optical bands; intramolecular electron transfer; EPR spectroscopy

INTRODUCTION

Organic mixed valence (MV) compounds have been the subject of a considerable amount of research in recent years owing to their potential applications in molecular electronics.[1,2] Dinitroaromatic radical anions were among the first symmetrical organic MV compounds for which intramolecular electron transfer (IET) reactions were studied by electron paramagnetic resonance (EPR) spectroscopy.[3–7] More recently, accurate simulations of the EPR spectra of several dinitroaromatic radical anions generated by electrochemical reduction or by photolysis have shown that the rate of the IET reaction is extremely dependent on solvent. The reaction can be several orders of magnitude slower in alcohols than in aprotic solvents,[8–11] and optical spectroscopy in the NIR region showed that some of these radicals can change from being charge delocalized (or Class III in the Robin and Day terminology)[12] in solvents that induce a low reorganization energy (λ), to being charge-localized (or Class II) in high λ solvents.[13–16] Maybe owing to these unusual solvent effects, it has always been assumed that in symmetric dinitroaromatic radical anions, the negative charge would be instantaneously delocalized over the two nitro groups in the gas phase. Localization of charge in one of the nitro groups was only conceived by the stabilizing effect of solvation or a counter-ion in a contact ion-pair, although in these cases the symmetric structure was still considered an intermediate in the electron transfer reaction between nitro groups, in what is now known as an electron hopping mechanism. The energy profile of the reaction was then described as a three-minimum model, with the relative energies of the delocalized structure and the two nitro-localized ones depending on the degree of solvation, which would obviously stabilize preferentially the structures with the negative charge localized on the nitro groups.[17] The notion that localization of charge could occur spontaneously arose only within the theory of electron transfer

applied to MV coordination compounds in the late 1960s.[18–21] Lately, it has been shown that quantum mechanical calculations, in fact, obtain charge localization for 1,3-dinitrobenzene radical anion in the gas phase. Calculations using either UHF, MP2 or CASSCF methods showed that each structure with the charge localized on the nitros are absolute minima, with the symmetrical delocalized structure also optimizing as a minima but higher in energy.[22,23] However, reinvestigation of the reaction profile using the quadratic steepest descent reaction path calculation at the CASSCF level of theory showed that the delocalized structure of the 1,3-DNB radical anion corresponds to a transition state in the IET reaction profile.[24]

We have shown that applying the Marcus–Hush two-state model[18–21] to the intervalence charge-transfer band of 2,7-dinitronaphthalene radical anion predicts the IET rate obtained by EPR spectroscopy reasonably accurately, which shows that a symmetrical intermediate is not present on the ground-state surface.[22] In this case, the donor-to-bridge and bridge-to-acceptor electron transfer is simultaneous, and the bridge-reduced radical is a virtual state. This is known as the superexchange model. However, the rate of the IET reaction in 5-substituted 1,3-dinitrobenzene radical anions decreases with the electron-releasing power of the substituent on position 5.[25] The positive ρ value of the Hammett plot suggests an accumulation of negative charge on the ring in the transition state, which could be compatible

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with a bridge-centered intermediate. Alternatively, the substituent effect may result simply from the change in the reorganization energy λ and in the electronic coupling between the two nitro groups, H_{ab}, and the two-state model may still be applicable. In order to test this hypothesis, we prepared and studied the radical anions from 1,3-dinitrobenzenes derivatives **1–6** by EPR and optical spectroscopies. We used only symmetric substituents to avoid the existence of conformational isomers, which, on reduction to the radical anion, would give rise to a four-state MV system.

O_2N —⟨ring⟩— NO_2 with R below
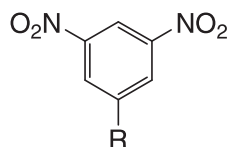
1: R=CF$_3$
2: R=F
3: R=H
4: R=C(CH$_3$)$_3$
5: R=COO$^-$
6: R=O$^-$

RESULTS AND DISCUSSION

Electron paramagnetic resonance spectra

Reduction of compounds **1–6** by sodium amalgam in acetonitrile (MeCN) results in EPR spectra that show alternating linewidth effects

caused by the IET reaction between nitro groups. An excess of Cryptand[2.2.2] was used to trap the sodium cation and avoid ion pairing, which would enhance charge localization by increasing the reorganization energy. As shown on Fig. 1, most EPR spectra are in a range where the relative intensity of the $\bar{m}=\pm 1$ lines of the nitrogen quintet is very sensitive to changes in rate values, leading to very accurate rate constant determinations. The exceptions are some spectra of **1**$^-$ and **2**$^-$ that reach the fast limit at temperatures around and above room temperature, and those of 1,3-dinitrobenzene (**3**) radical anion where line superposition strongly decrease the accuracy of the simulations. In this last case, we avoid the problem by using the perdeuterated compound **5**-*d4*.[26]

The rate constants for the IET reaction and the corresponding Eyring parameters are show in Table 1. The rate constants obtained here are three to five times faster than the ones obtained for the same radical anions in the same solvents, but prepared by electrolytic reduction in the presence of 0.02 M Bu$_4$N$^+$ClO$_4^-$.[25] Clearly, ion pairing with the electrolyte in polar solvents like MeCN is sufficient to affect the rate constant, as first found by Hosoi and Masuda.[27,28] Besides this difference, the behavior of the rate constant is the same: the reaction is faster for electron-withdrawing R groups and slower for electron-releasing groups, with a Hammett ρ value (versus σ_m) basically independent of the method of generation of the radicals.
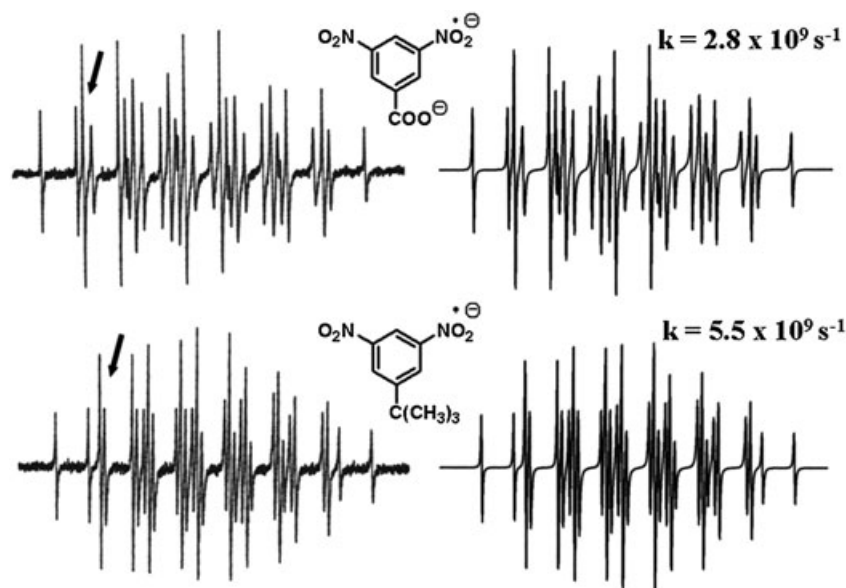

Figure 1. Experimental (left-hand side) and simulated (right-hand side) EPR spectra of radicals **4**$^-$ (below) and **5**$^-$ (above) in MeCN at 250 K. The arrows show the $\bar{m}=+1$ line of the first nitrogen quintet, whose intensity is very sensitive to the rate of intramolecular electron transfer

Table 1. Rate constants at 298 K and Eyring parameters extracted from EPR spectra in MeCN

Radical anion	$k_{298 K}$[b] $(10^8 s^{-1})$	T range (K)	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (eu)	$\Delta G^{\neq}_{298 K}$ (kcal/mol)
1 (R = CF$_3$)	288	230–280	2.24	−3.15	3.18
2 (R = F)	283	225–280	2.43	−2.54	3.19
3 (R = H)[a]	164	226–285	2.86	−2.20	3.52
4 (R = t-Bu)	161	230–280	2.89	−2.10	3.53
5 (R = COO$^-$)	75	228–290	3.27	−1.91	3.84
6 (R = O$^-$)	42	250–340	3.80	−1.76	4.32

[a]From reference[26]
[b]Obtained by interpolation of the Eyring plot.

Optical spectra and Marcus–Hush calculations

Optical spectra were recorded at several stages of compounds **1–6** reduction, and the maximum of the radical anion was selected. Figure 2 shows the low-energy portion of these spectra. All the radicals show the wide and Gaussian-shaped charge-transfer band typical of localized Class II MV compounds. There is no evidence of the radical dianion spectrum at this stage of reduction: the difference of the two reduction potentials in **3**, for example, is 0.443 V,[29] which corresponds to a very high comproportionation constant of 3×10^7. The band maximum energy and molar absorptivity, as well as the width at half-height shown in Table 2 were obtained by fitting the shape of the bands with Gaussian functions.

For Gaussian bands, the electronic coupling H_{ab} is given by the Hush Eqn (1)

$$H_{ab} = 0.0206 N \left(\varepsilon_{max}\ \Delta n_{1/2} \lambda \right)^{1/2} / d_{ab} \qquad (1)$$

where ε_{max} is the maximum intensity (in $M^{-1} cm^{-1}$), $\Delta \nu_{1/2}$ is the width at half-height (cm^{-1}), λ is the energy maximum of the band (cm^{-1}), and d_{ab} is the diabatic electron-transfer distance (in Å). We use here the Chacko refractive index (n) correction $N = 3n^{1/2}/(n^2 + 2)$.[30] This parameter has a value of 0.914 for acetonitrile. To calculate H_{ab} by the preceding equation, one
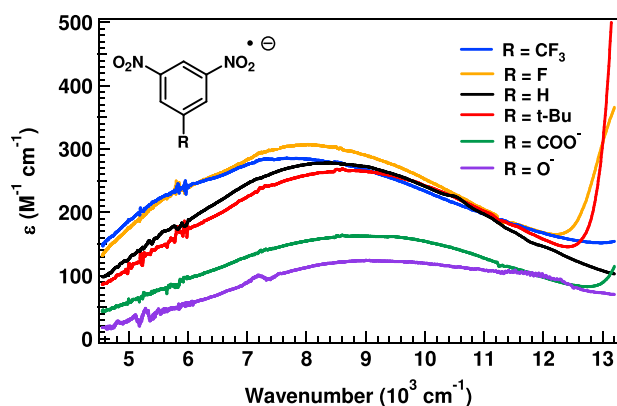
needs to estimate the electron transfer distance on the diabatic surfaces, d_{ab}. In this work, the adiabatic reaction distance d_{12} was calculated from the change of the transition dipole moment of the reaction, using $d_{12} = \Delta \mu_{12}/e$, where e stands for the elementary charge. The $\Delta \mu_{12}$ vector is collinear with the N-N axis owing to the symmetry of the radicals. The reaction transition dipole moment μ_{12} was obtained by theoretical calculations of the charge-localized radicals $\mathbf{1}^-$-$\mathbf{6}^-$ using UHF/6-31 + G* with the Tomasi's polarized continuum solvation model and a dielectric constant of 36, and $\Delta \mu_{12}$ obtained using simple trigonometry. The *ter*-butyl substituted radical $\mathbf{4}^-$ calculation failed to converge for some reason, and we used the dipole moment of the methyl-substituted radical anion instead. The distance on the adiabatic surface d_{12} was converted to the diabatic d_{ab} using the published equation.[31] The results obtained (Table 1) are nearly independent of the substituent and around 8% smaller than the N-N distances. This ratio is close to the d_{ab}/d_{NN} ratio found for other dinitroaromatic radical anions.[14,15,37] However, this ratio is very dependent on the nature of the CBU, because strong electron withdrawing CBU like the nitro group tend to pull negative charge and increase the effective d_{ab} in radical anions. The nature of the bridge also influences d_{ab}, with long bridges allowing a higher accumulation of charge and decreasing d_{ab}. Barlow and co-workers found effective electron transfer distances 28 to 46% smaller than d_{NN} in a series of bis(triarylamine) radical cations with 11 to 29 bonds between nitrogens.[32]

The electronic couplings H_{ab} calculated through Eqn (1) are shown on Table 2. The coupling is higher for electron-withdrawing R groups and decreases for electron-releasing substituents. Decreasing the reduction potential of the bridge in anionic MV compounds lowers the energy gap between the SOMO of the donor (the reduced nitro group in this case) and the LUMO of the bridge. The enhancement of electronic coupling by lowering the energy gap to the bridge is a well-known effect in MV chemistry.[14,3–13,15–35]

The parabolic diabatic surfaces used in the classical Marcus–Hush two-state model produce charge-transfer bands having a width at half-height of $\Delta \bar{\nu}_{1/2}^{Hush} = [16RT(\ln 2)E_{op}]^{1/2}$.[20,21] Most mixed-valence compounds show experimental bands much broader than this value. For example, $\Delta \bar{\nu}_{1/2}^{Hush} = 4260\ cm^{-1}$ for radical $\mathbf{1}^-$, which is substantially smaller than the experimental value of $\Delta \bar{\nu}_{1/2} = 7900\ cm^{-1}$. To account for this discrepancy, Nelsen used a quartic correction to the shape of the energy

Figure 2. Low-energy portion of the optical spectra of the charge-localized radicals $\mathbf{1}^-$-$\mathbf{6}^-$, showing the wide and Gaussian-shaped charge-transfer band

Table 2. Parameters obtained from the Class II charge transfer bands of radical anions $\mathbf{1}^-$ to $\mathbf{6}^-$ in MeCN

Radical anion	$h\nu_{max}$ (cm^{-1})	ε_{max} ($M^{-1} cm^{-1}$)	$\Delta\nu_{1/2}$ (cm^{-1})	d_{ab}	H_{ab} (cm^{-1})	ΔG^*_{par}[b] (kcal/mol)	quartic C	ΔG^*_{quart}[c] (kcal/mol)	k_{opt}[d] ($10^8 s^{-1}$, 298 k)
1 (R = CF$_3$)	7900	290	7260	4.32	562	4.17	0.555	2.65	334
2 (R = F)	8000	305	7145	4.47	556	4.25	0.521	2.78	272
3 (R = H)[a]	8400	280	6760	4.38	542	4.57	0.407	3.26	124
4 (R = t-Bu)	8700	260	6960	4.45	531	4.80	0.424	3.41	98.4
5 (R = COO$^-$)	8870	165	6710	4.44	419	5.21	0.363	3.94	40.8
6 (R = O$^-$)	9010	125	5770	4.50	336	5.53	0.189	4.76	10.4

[a]From reference[26]
[b]$\Delta G^*_{par} = \lambda/4 - H_{ab} + H_{ab}^2/\lambda$, using $h\nu_{max} = \lambda$.
[c]$\Delta G^*_{quart} = (\lambda/4).(1 + C/4)/(1 + C) - H_{ab} + H_{ab}^2/\lambda$, using $h\nu_{max} = \lambda$.
[d]Calculated using Eqn (2) and ΔG^*_{quart}.

surfaces.[36] The quartic parameter C of Table 2 was fit to produce charge-transfer bands with the experimental width at half-height shown in the same table. Adding a quartic term makes the two diabatic surfaces intersect at energies lower than λ/4, resulting in activation energies that are smaller than the ones predicted with parabolic surfaces.[36] Both parabolic and quartic activation energies are shown in Table 2. Figure 3 compares the activation free energies at 298 K obtained from the EPR spectra simulations with the parabolic and quartic activation free energies obtained from the charge-transfer optical bands. At this point, one should note that the free energies of Fig. 3 have very different origins. The Eyring equation used to fit the temperature-dependence of the EPR-derived rate constant assumes that the system obeys transition-state theory. This is normally not accepted for ET reactions, which are believed to occur by tunneling. Other temperature-dependence rate equations would yield slightly different activation energy values. Having this in mind, we find remarkable that the change of the activation energy with the substituent is reasonably well predicted in both series, although it is clear that the values calculated using quartic-augmented parabolic surfaces fit much better the $\Delta G^{\neq}_{epr}$ values. However, the trend line in each series has a slope higher than one, an effect found before in plots of this type.[37,38]

Alternatively, one can compare the rate constants directly. This avoids the use of Eyring equation to transform the rate constants obtained from EPR spectra into energies, but involves the transformation of the activation energies obtained from the optical bands into rate constants. We have found before that the kinetics of the IET reaction in dinitroaromatic radical anions with low activation barriers is controlled by the solvent dynamics. The rate equation for this solvent-controlled kinetic regime is given by[39]

$$k_{solv} = \tau_{solv}^{-1}(\lambda_s/16RT)^{1/2}\exp(-DG^*/RT) \tag{2}$$

where τ_{solv} is the solvent relaxation time. We used $\tau_{solv} = 0.26$ ps for MeCN, obtained experimentally from emission relaxation of Coumarin 153 in this solvent.[40] Equation (2) has the disadvantage of requiring the separation of the reorganization energy into its internal and solvent components. We used the value of the
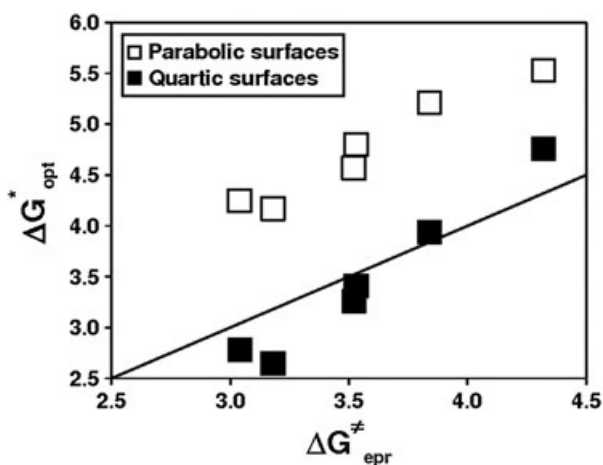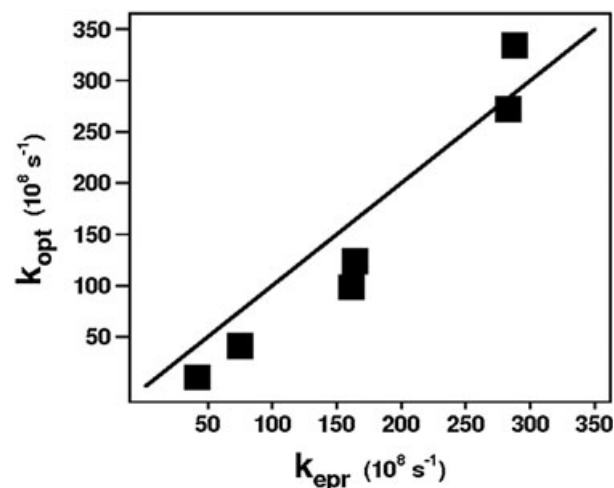

Figure 4. Comparison of the rate constants for the IET reaction on the radical anions **1**⁻ to **6**⁻ calculated from the optical band through Eqn (2) and using quartic-augmented energy surfaces (k_{opt}) and the ones obtained from EPR spectra at 298 K

internal reorganization energy calculated before for radical **3**⁻, $\lambda_i = 2000$ cm⁻¹,[22] and calculated λ_s by difference using the energy maximum of the charge-transfer optical bands as λ. Although this introduces additional uncertainty on the calculated rate constants, using alternatively $\lambda_i = 3000$ cm⁻¹ results in rate constants 7 to 10 per cent smaller, which is certainly within the order of experimental error. For simplicity, the rate constants were calculated using only the quartic activation energies, for which the agreement with k_{epr} is better. The results are shown on the last column of Table 2 and compared with the rate constants obtained from the EPR spectra (Table 1) in Fig. 4. The rate constants calculated by the Marcus–Hush analysis from the charge-transfer bands using quartic energy surfaces reproduce quite well the change of the experimental rate constants with the substituent, especially considering the uncertainties on the calculation of the charge-transfer diabatic distance, d_{12}, and on the internal relaxation energy, λ_i. This confirms that bridge-reduced radicals are not effective intermediates in the reaction profile, that is, the IET occurs by superexchange and not by electron hopping. In case of a hopping mechanism, one would expect the reaction to be much faster than what the Marcus–Hush theory predicts, and that this difference should increase for electron-withdrawing R groups, because these substituents would stabilize preferentially the bridge-reduced intermediate and increase the rate of the reaction.[41]

Figure 3. Comparison of the activation free energies (in kcal/mol) of the IET reaction calculated from the optical band parameters (ΔG^*_{opt}) and obtained from EPR spectra ($\Delta G^{\neq}_{epr}$) for the radical anions **1**⁻ to **6**⁻ at 298 K in MeCN. The line represents $\Delta G^*_{opt} = \Delta G^{\neq}_{epr}$

CONCLUSIONS

The rate constants for IET in radicals **1**⁻ to **6**⁻ calculated by the Marcus–Hush two-state model analysis of the charge-transfer bands using quartic energy surfaces reproduce quite well the experimental rate constants obtained by simulation of the dynamic effects on the EPR spectra. This excludes the presence of a bridge-centered intermediate in the electron transfer between nitro groups and confirms that the reaction occurs by a superexchange mechanism.

EXPERIMENTAL

Commercial compounds **1** (Aldrich), **3** (BDH), and 3,5-dinitrobenzoic acid (Fluka) were recrystallized before use. The remaining compounds were prepared and purified as published before.[25] The anions **5** and **6** were prepared by adding alcoholic KOH to a solution of the parent neutral compounds in ethanol until no further precipitation occurred. The potassium salts were filtered, washed with ethanol, and dried under vacuum.

The radical anions (or radical dianions in the case of **5** and **6**) were prepared in vacuum-sealed glass cells equipped with an EPR tube and a quartz optical cell. Reduction was achieved by contact with 0.2% Na-Hg amalgam. The nitro compound, an excess of commercial cryptand[2.2.2] to sequester the cation, and the Na-Hg amalgam were introduced in different chambers of the cell under nitrogen.

The rate constants for the IET reaction were obtained by simulating the experimental EPR spectra. The simulation program solves the Bloch equations for a two-state model. Asymmetric line broadening was included in the simulations by making the intrinsic line width Γ of each line dependent on its nitrogen quantum number $\bar{m}$, according to the empirical equation $\Gamma(\bar{m}) = A + B\bar{m} + C\bar{m}^2$.[42]

Theoretical calculations were done using Gaussian 03.[43]

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