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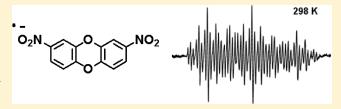
# Dynamics of Intramolecular Electron Transfer in Dinitrodibenzodioxin Radical Anions

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Supporting Information

**ABSTRACT:** The activation energy for intramolecular electron transfer in radical anions of 2,7-dinitrodibenzodioxin and 2,8-dinitrodibenzodioxin, obtained by simulation of their temperature-dependent EPR spectra, are well predicted by the values calculated by the two-state Marcus—Hush model from the optical charge-transfer bands using quartic-adjusted energy surfaces. The electronic coupling is higher in the 2,8-dinitrodibenzodioxin ( $H_{ab} = 485 \text{ cm}^{-1}$ ) than in the 2,7-dinitrodibenzo-



dioxin radical anion ( $H_{ab} = 250 \,\mathrm{cm}^{-1}$ ), but for each solvent the reorganization energy, taken as the maximum of the optical band, is only slightly higher in the latter. These values are consistent with the fact that the reaction is faster in the 2,8-dinitrodibenzodioxin radical anion isomer, as determined by EPR spectroscopy. The pre-exponential factors obtained combining the EPR-derived rate constants and the activation energies calculated from the optical bands fit well the theoretical (modified) nonadiabatic values in the less viscous solvents. However, for the more viscous solvents, the trend of the pre-exponential values with solvent can only be explained if dynamical solvent effects increasingly influence their value. The influence of solvent dynamics in the 2,8-dinitrodibenzodioxin radical anion starts in the less viscous solvents DMF and DMSO, but in the 2,7-dinitrodibenzodioxin isomer this is only fully evident for the more viscous PhCN and HMPA. The influence of solvent dynamics is higher in the radical with the lowest activation barrier.

#### **■ INTRODUCTION**

Dinitroaromatic radical anions are useful compounds in the study of mixed-valence chemistry not only due to its facile synthesis but also mostly because their optical spectra allow a clear distinction between the charge-localized and chargedelocalized mixed-valence state. Charge-delocalized mixed valence anions may be described as  $\mathbf{M}^{-1/2} - \mathbf{B} - \mathbf{M}^{-1/2}$ , where the two charge-bearing units M symmetrically attached to the bridge B have instantaneously the same fractional charge. Delocalized mixed-valence compounds, also referred as class III in the Robin-Day terminology,<sup>2</sup> show narrow low-energy optical bands, often with vibrational structure. A significant number of dinitroaromatic radical anions that have the two nitro groups in a conjugated substitution pattern that leads to a large electronic interaction between them are charge-delocalized and show in fact narrow low energy optical bands with vibrational structure. On the contrary, class II compounds are described as two charge-localized structures in equilibrium,  $\mathbf{M}^{-1} - \mathbf{B} - \mathbf{M}^0 \leftrightarrows \mathbf{M}^0 - \mathbf{B} - \mathbf{M}^{-1}$ , and show wide and featureless Gaussian-shaped low-energy optical bands. Hush theory was developed specifically for localized class II compounds and uses two diabatic parabolic energy surfaces to describe the reactants and products (i.e., the two localized structures in equilibrium) that are allowed to interact through an electronic coupling  $H_{ab}$ . This produces two adiabatic surfaces, a ground-state surface and an excited-state surface.

In Marcus—Hush theory the system is described by only two parameters: the reorganization energy  $\lambda$  and the electronic coupling  $H_{ab}$ . For Gaussian-shaped charge-transfer bands both parameters can be extracted from the experimental band. The energy maximum of the band occurs at  $\lambda$ , and the electronic coupling  $H_{ab}$  is given by the Hush eq 1

$$H_{ab} = 0.0206.N(\varepsilon_{\text{max}}\Delta\nu_{1/2}\lambda)/d_{ab}$$
 (1)

where  $\varepsilon_{\rm max}$  is the maximum intensity,  $\Delta \nu_{1/2}$  is the width at halfheight,  $\lambda$  is the energy maximum of the band, and  $d_{ab}$  is the diabatic electron-transfer distance. We added to the Hush equation the Chacko refractive index (n) correction  $N=3n^{1/2}/(n^2+2)$ , used for the same purpose by Gould and co-workers. We have shown previously that the values of  $\lambda$  and  $H_{ab}$  obtained from the charge-transfer band predict the intramolecular electron-transfer rate constant of the 2,7-dinitronaphthalene radical anion, obtained by simulation of the EPR spectra, at least as accurately as the electron-transfer distance can be determined. Another important question in electron transfer is the role of solvent on the rate of the reaction. The solvent affects the activation energy through the reorganization energy  $\lambda$ , in what

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Table 1. Cyclic Voltammetry Data (V, vs Fc/Fc<sup>+</sup>) for Dinitroaromatic Compounds in 0.1 M TBAP/MeCN at 298 K

Compound Structure	$E^{o}_{I}$	$E^{o}_{2}$	$\Delta E^o = E^o{}_1 - E^o{}_2$	$K_{\rm comp}$
O <sub>2</sub> N O NO <sub>2</sub>	-1.44	-1.54	0.10	49
O <sub>2</sub> N	-1.47	-1.55	0.08	22
2,6-dinitroanthracene <sup>a</sup>	-1.26	-1.40	0.14	232
o <sub>2</sub> N No <sub>2</sub> 2,7-dinitroanthracene <sup>a</sup>	-1.34	-1.58	0.24	11400
2,6-dinitrobiphenylene	-1.34	-1.54	0.20	2400
2,7-dinitrobiphenylene	-1.28	-	< 0.02	< 2

<sup>&</sup>lt;sup>a</sup> From ref 9.

is often called a static solvent effect. However, for fast reactions and/or viscous solvents the solvent dynamic has to be taken into account explicitly in the reaction rate constant. We detected solvent dynamic effects on the rate of intramolecular electron transfer in 2,2'-dimethyl-4,4'-dinitrobiphenyl and 4,4'-dinitrotolane radical anions, increasing in that order. Solvent effects were only detected for 2,7-dinitronaphthalene radical anion in the more viscous solvent benzonitrile. This difference in the role of solvent dynamics on these three radicals reflects the order of how close these compounds lie to the class II/class III borderline, which is also the reverse order of their activation barriers. Unfortunately, the 2,7-dinitronaphthalene radical anion is not very stable in HMPA, and the other two radicals are chargedelocalized in this highly viscous solvent. In this work we report on optical and thermal intramolecular electron transfer in the radical anions of 2,7-dinitrodibenzodioxin (27DNDD) and 2,8dinitrodibenzodioxin (28DNDD), which are localized mixedvalence species on all solvents studied, and compare the rate constants obtained by simulation of the EPR spectra with the ones calculated from the optical band parameters in a broader range of solvent.

$$O_2N \xrightarrow{1} O_2 O_2N \xrightarrow{O_2N} O_2 NO_2$$
27DNDD 28DNDD

#### EXPERIMENTAL SECTION

**27DNDD** and **28DNDD** were prepared according to literature procedures and purified by elution from silica with hexane/toluene.<sup>8</sup>

**2,7-Dinitrodibenzodioxin (27DNDD).** Mp: 271-273 °C (*N*-methypyrrolidinone, lit. 267-269 °C). UV (DMF):  $\lambda_{\rm max} = 342$  nm, log  $\varepsilon = 4.00$ . <sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>):  $\delta$  7.93 (dd,

2H, J = 8.9 Hz and J = 2.6 Hz), 7.82 (d, 2H, J = 2.6 Hz), 7.03 (d, 2H, J = 8.9 Hz). <sup>13</sup>C NMR:  $\delta$  146.0, 143.7, 140.7, 121.2, 116.9, 112.8 **2,8-Dinitrodibenzodioxin (28DNDD).** Mp: 218–220 °C (ethanol, lit. 212–215 °C). UV (DMF):  $\lambda_{\text{max}} = 370$  nm, log  $\varepsilon = 3.97$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.91 (dd, 2H, J = 8.9 Hz and J = 2.6 Hz), 7.81 (d, 2H, J = 2.6 Hz), 7.03 (d, 2H, J = 8.9 Hz).

**Preparation of Samples.** Radical anions were prepared in vacuum sealed glass cells equipped with an ESR tube and a quartz optical cell. The concentration of the samples was determined spectrophotometrically before reduction using the UV data above. A large excess of Cryptand [2.2.2] was used. Reduction was achieved by contact with 0.2% Na—Hg amalgam.

<sup>13</sup>C NMR: δ 145.9, 144.5, 141.0, 120.8, 117.0, 112.7.

**Instrumentation.** Cyclic voltammetry (CV) and controlled potential electrolysis (CPE) were performed in Bu<sub>4</sub>NClO<sub>4</sub>/MeCN (0.1 M) using a Pt wire (CV) or a Pt-gauze (CPE) as working electrodes. Potentials were measured versus  $[Fe(\eta^5-C_5H_5)_2]^{0/4}$  (internal reference) at 200 mV/s. A potentiostat/galvanostat radiometer analytical voltammetry PST050 VoltaLab equipment was used for VC and CPE studies. EPR spectra were measured in a Bruker esp300e spectrometer equipped with a variable temperature unit and simulated by a computer program that solves the Bloch equations for a two-state model. UV/vis/NIR spectra were obtained with a Shimadzu UV-3101PC spectrometer.

#### **■ RESULTS AND DISCUSSION**

Cyclic Voltametry. Cyclic voltametry of 27DNDD and 28DNDD in acetonitrile shows two partially superimposed reversible waves separated by 0.10 and 0.08 V, respectively. This corresponds to a relatively high degree of disproportionation of the radical anions into the neutral and dianion species when compared with other dinitroaromatic systems with identical distances between nitro groups. As can be seen in Table 1, the separation between the two reduction waves in either of the two dinitroanthracene isomers is larger than in 27DNDD or 28DNDD. Moreover, 2,6-dinitroanthracene and 2,7-dinitroanthracene show distinct values of  $\Delta E^{\circ} = E^{\circ}_{1} - E^{\circ}_{2}$  according to the substitution pattern. In the former compound the two nitro groups are conjugated (in what is often called a kekule substitution pattern), thus stabilizing the dianion and decreasing  $E_1^{\circ}$  –  $E_{2}^{\circ}$ . The same effect occurs for the two dinitrobiphenylene isomers: the nonconjugated 2,6-dinitrobiphenylene shows two reduction waves separated by 0.20 V, but 2,7-dinitrobiphenylene, where the two nitro groups are conjugated, shows an unresolved single reduction wave corresponding to a two-electron reduction, as determined by controlled-potential electrolysis. In the case of the two dinitrodibenzodioxins, there is no direct resonance between the two nitro groups across the central dioxin ring neither in 27DNDD nor in 28DNDD and the two compounds have similar  $\Delta E^{\circ}$  values.

The comproportionation equilibrium constant is given by eq 2

$$K_{\text{comp}} = [\bullet -]^2 / ([2 -][0]) = \exp[\Delta E^{\circ}(F/RT)]$$
 (2)

At 298 K and with the potentials in volts eq 2 corresponds to

$$K_{\text{comp}} = \exp(\Delta E^{\circ}/0.0257) \tag{3}$$

The values of  $K_{\rm comp}$  vary from several orders of magnitude in strongly coupled class III compounds to the statistical minimum of 4 in weakly coupled class II systems, although cases of potential compression ( $K_{\rm comp} < 4$ ) or even potential inversion

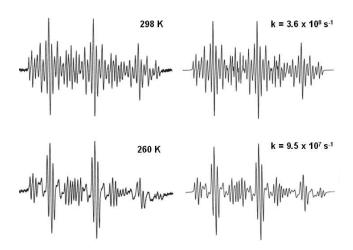


Figure 1. Experimental EPR spectra in PhCN (left-hand side) and computer simulations (right-hand side) of the 27DNDD radical anion.

 $(K_{\rm comp} < 1)$  are known. <sup>10</sup> The reduction potentials of 2,7-dinitrobiphenylene (Table 1) show that some structural feature must be responsible for the potential compression. The comproportionation equilibrium constants calculated from eq 2 are  $K_{\rm comp} = 49$  for **27DNDD** and  $K_{\rm comp} = 22$  for **28DNDD**. The relatively small value for both isomers suggests a small electronic interaction between the two nitrobenzene units.

EPR Spectra. The EPR spectra of the 27DNDD and 28DNDD radical anions show temperature dependent alternating line broadening effects in all solvents studied due to intramolecular electron transfer. Figures 1 and 2 show representative spectra in benzonitrile (PhCN) and their computer simulations. Alternating broadening occurs in all pairs of pseudoequivalent coupling constants, as is evident in the spectra at low temperature. Computer simulation of the spectra afforded the rate constants for the reaction at different temperatures, as plotted in Figure S3, Supporting Information. The rate constant values at 298 K and the Eyring parameter are shown in Table 1. Details on the spectra and simulations can be found in the Supporting Information.

The solvent dependence of the rate constants roughly reflect the solvent dependence of the reorganization energy  $\lambda$  (see below), as found before for other dinitroaromatic radical anions.<sup>11</sup> The reaction is consistently faster in the **28DNDD** radical anion than in its isomer.

**Optical Spectra.** Reduction of **27DNDD** and **28DNDD** in five aprotic solvents with 0.2% Na/Hg using an excess of [2.2.2] cryptand to sequester the sodium ion results in the radical anion optical spectra shown in Figures 3 and 4.

Both radical anions show broad and low-intense intervalence charge-transfer bands in the near-infrared, typical of localized (class II) mixed valence compounds. The bands are partially superimposed with higher energy bands, and the spectra were simulated by adding calculated Gaussians curves, thus providing the parameters for the intervalence band shown in Table 2. The simulations of the 28DNDD radical anion spectra yield parameters for the intervalence band very close to the first estimate obtained directly from the experimental spectra, but simulations of the 27DNDD isomer's bands were a necessity due to a higher degree of superposition. Examples of simulated spectra are presented in the Supporting Information. According to the Marcus—Hush two-state model the maximum of the intervalence band for class II compounds equals the reorganization energy λ. The values

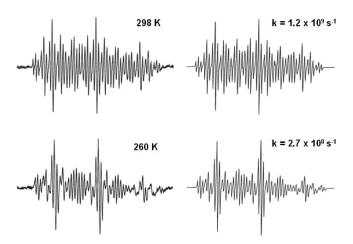
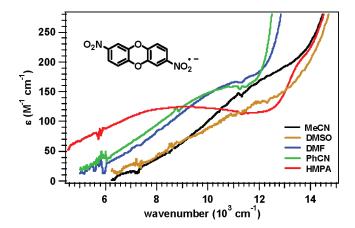


Figure 2. Experimental EPR spectra in PhCN (left-hand side) and computer simulations (right-hand side) of the 28DNDD radical anion.



**Figure 3.** Optical spectra of the **27DNDD** radical anion in five aprotic solvents.

of  $\lambda = h v_{\rm max}$  in Table 1 change with solvent according to the pattern obtained for other dinitroaromatic radical anions, and the values on the same solvent seem to be slightly higher for the **27DNDD** radical anion, which is consistent with the reaction being slower in this isomer.

According to the  $K_{\text{comp}}$  calculated by eq 2, the maximum fraction of radical anion obtained under the electrochemical conditions is 0.78 for the 27DNDD isomer and 0.70 for the 28DNDD isomer. However, ion-pairing with the 0.1 M electrolyte stabilizes the dianion preferentially to the radical anion or the neutral, compressing  $\Delta E^{\circ} = E^{\circ}_{1} - E^{\circ}_{2}$  and favoring disproportionation. Under the conditions used for the optical spectra, reduction produces only one sodium ion per radical anion and the presence of the cryptand strongly disfavor ion pairing, thus decreasing the degree of disproportionation. Nevertheless, we should expect that the extinction coefficients of Figures 1 and 2 do not represent 100% of radical anion not only due to disproportionation but also possibly due to some degree of decomposition of these unstable radicals, and so the extinction coefficients of Table 2 were corrected using the above values of  $K_{\text{comp}}$  (uncorrected values shown under brackets in Table 2).

The adiabatic electron-transfer distance was calculated from the change in dipole moment of the radicals upon the reaction, and transformed into diabatic distances according to the published procedure. <sup>12</sup> The diabatic distances used were  $d_{ab} = 8.76 \text{ Å}$ for **27DNDD** and  $d_{ab} = 8.51$  Å for **28DNDD**, obtained from the change of the dipole moment of the UHF/6-31G\* localized structure, calculated using a polarized continuum model to simulate solvation with a dilectric constant of  $\varepsilon = 38$ . These distances are 11% smaller than the calculated N-N distances in both radicals,

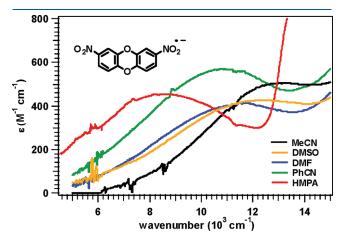


Figure 4. Optical spectra of the 28DNDD radical anion in five aprotic solvents.

showing that the charge is somewhat delocalized into the aromatic rings. The electronic couplings  $H_{ab}$  calculated through eq 1 are shown in Table 3 for both isomers. Although the values diverge in different solvents, they are within experimental error from being the same. An average value of  $H_{ab} = 250 \text{ cm}^{-1}$  is obtained for **27DNDD** and  $H_{ab} = 485 \text{ cm}^{-1}$  for **28DNDD**.

Marcus-Hush theory uses parabolas to describe the two interacting energy surfaces, but this predicts intervalence bands that are often narrower than the experimental ones. The right bandwidth can be predicted with a quartic correction to the shape of the energy surfaces. Adding a quartic term makes the two diabatic surfaces intersect at energies lower than  $\lambda/4$ , resulting in activation energies that are smaller than the ones predicted with parabolic surfaces, as can be seen in Table 3.14

Comparison of Optical and EPR Results. Figure 5 compares the activation free energies obtained by EPR spectroscopy (Table 2) with the ones calculated from the optical spectra parameters (Table 3). The results obtained using quartic-fitted energy surfaces are in general more close to the  $\Delta G^*_{
m opt}$  =  $\Delta G^{\dagger}_{
m EPR}$ line than the ones that use classical parabolic surfaces, the only exceptions being the results in HMPA. The changes with solvent are well predicted in each series, but the  $\Delta G^*_{
m opt}$  calculations underestimate the experimental  $\Delta G^{\dagger}_{\mathrm{EPR}}$  values in MeCN and overestimate them in HMPA, which makes the trend line (not shown in Figure 5) in each series having a slope higher than 1. This might be an evidence of the contribution of solvent

Table 2. Rate Constants and Eyring Parameters Extracted from EPR Spectra

		27DNDD				28DNDD				
	MeCN	DMSO <sup>a</sup>	DMF	PhCN	HMPA	MeCN	DMSO <sup>a</sup>	DMF	PhCN	HMPA
$k$ (298 K), $10^8 \mathrm{s}^{-1}$	0.48	2.1	3.4	3.9	15	2.8	7.2	13	11	32
$\Delta H^{\dagger}$ (kcal/mol)	8.5		4.6	5.3	3.4	6.5		4.5	4.7	2.9
$\Delta S^{\dagger}$ (eu)	1.2		-4.2	-1.4	-5.1	2.0		-2.2	-1.4	-5.3
$\Delta G^{\dagger}_{(298 \text{ K})} \text{ (kcal/mol)}$	7.0		5.8	5.7	4.9	5.9		5.0	5.1	4.5
a Spectra in a yeary short range of temperatures due to the high melting point of the selvent										

Spectra in a very short range of temperatures due to the high melting point of the solvent.

Table 3. Parameters of the Class II Charge-Transfer Bands<sup>a</sup>

Table 5. I drameters of the Cause II Charge Transfer Datas										
	27DNDD									
solvent	$hv_{\text{max}} (\text{cm}^{-1})$	$\varepsilon_{ m max}~({ m M}^{-1}~{ m cm}^{-1})$	$\Delta v_{1/2} \left( \mathrm{cm}^{-1} \right)$	$H_{ab}^{b} (\mathrm{cm}^{-1})$	$\Delta G^*_{\mathrm{par}}^{c}$ (kcal/mol)	quartic C	$\Delta G^*_{ ext{quart}}^d  ext{(kcal/mol)}$			
MeCN	13300	230 (180)	6800	310	8.66	0.161	7.67			
DMSO	12400	155 (120)	7450	245	8.20	0.290	6.70			
DMF	11700	154 (120)	7070	235	7.72	0.264	6.41			
PhCN	11000	200 (155)	7070	250	7.18	0.297	5.83			
HMPA	8950	160 (125)	8330	230	5.77	0.684	3.82			
	28DNDD									
solvent	$h\nu_{\rm max}~({\rm cm}^{-1})$	$\varepsilon_{\rm max}~({ m M}^{-1}~{ m cm}^{-1})$	$\Delta\nu_{1/2}~(\text{cm}^{-1})$	$H_{ab}^{e} (\mathrm{cm}^{-1})$	$\Delta G^*_{\mathrm{par}}^{c}\left(\mathrm{kcal/mol}\right)$	quartic C	$\Delta G^*_{ m quart}^{d} \left( m kcal/mol ight)$			
MeCN	13000	720 (505)	6230	535	7.84	0.096	7.23			
DMSO	12300	610 (427)	7980	515	7.40	0.377	5.59			
DMF	11300	579 (405)	6870	455	6.84	0.252	5.62			
PhCN	10600	800 (560)	6660	490	6.26	0.252	5.11			
HMPA	8650	650 (455)	7260	430	5.02	0.487	3.50			

<sup>&</sup>lt;sup>a</sup> The values of  $\varepsilon_{\max}$  were corrected by taking into account the disproportionation of the radical anion (uncorrected values under brackets). <sup>b</sup> From eq 1. Average value of  $H_{ab} = 250 \text{ cm}^{-1}$ .  $^c\Delta G^*_{par} = \lambda/4 - H_{ab} + H_{ab}^2/\lambda$ , using  $h\nu_{max} = \lambda$ .  $^d\Delta G^*_{quart} = (\lambda/4)(1 + C/4)/(1 + C) - H_{ab} + H_{ab}^2/\lambda$ , using  $h\nu_{max} = \lambda$ .  $^e\Delta G^*_{quart} = (\lambda/4)(1 + C/4)/(1 + C) - H_{ab} + H_{ab}^2/\lambda$ , using  $h\nu_{max} = \lambda$ .  $^e\Delta G^*_{quart} = (\lambda/4)(1 + C/4)/(1 + C) - H_{ab} + H_{ab}^2/\lambda$ , using  $h\nu_{max} = \lambda$ .  $^e\Delta G^*_{quart} = (\lambda/4)(1 + C/4)/(1 + C) - H_{ab} + H_{ab}^2/\lambda$ , using  $h\nu_{max} = \lambda$ .  $^e\Delta G^*_{quart} = (\lambda/4)(1 + C/4)/(1 + C) - H_{ab} + H_{ab}^2/\lambda$ , using  $h\nu_{max} = \lambda$ .  $^e\Delta G^*_{quart} = (\lambda/4)(1 + C/4)/(1 + C) - H_{ab} + H_{ab}^2/\lambda$ , using  $h\nu_{max} = \lambda$ .  $^e\Delta G^*_{quart} = (\lambda/4)(1 + C/4)/(1 + C) - H_{ab} + H_{ab}^2/\lambda$ , using  $h\nu_{max} = \lambda$ .  $^e\Delta G^*_{quart} = (\lambda/4)(1 + C/4)/(1 + C) - H_{ab} + H_{ab}^2/\lambda$ , using  $h\nu_{max} = \lambda$ .  $^e\Delta G^*_{quart} = (\lambda/4)(1 + C/4)/(1 + C) - H_{ab} + H_{ab}^2/\lambda$ , using  $h\nu_{max} = \lambda$ .

dynamics to the rate of the reaction. The solvent-controlled rate equation (see eq 6 below) is proportional to the reverse of the solvent relaxation time,  $\tau_{\rm solv}$ . This parameter roughly correlates with the solvent viscosity and has an exponential dependence on temperature of the form  $\tau_{\rm solv} = b \exp(H/RT)$ .

The parameter H has dimensions of energy and, in case the system follows solvent-controlled dynamics, adds to the Marcus activation energy, increasing its apparent value. This would make the experimental values of  $\Delta G^{\dagger}_{\text{EPR}}$  exceed the Marcus—Hush value of  $\Delta G^{\ast}_{\text{opt}}$  particularly in the most viscous solvents like HMPA.

We compare below the pre-exponential factors A of the rate constant (eq 4)

$$k = A \exp(-\Delta G^*/RT) \tag{4}$$

obtained from the EPR rate constants at 298 K and using either the parabolic or the quartic activations energies (first two rows of Table 4) with theoretical calculated ones using three different methods. In the nonadiabatic regime, the transmission factor depends on the electronic coupling  $H_{ab}$ . Levich and Dogonadze<sup>15</sup> deduced the rate equation by using Fermi's "golden rule" with the pre-exponential factor given in eq 5. In the nonadiabatic regime the electronic coupling is much smaller than RT, so originally the activation energy used was simply  $\lambda/4$ . We have expanded the range of use of eq 5 to a "less nonadiabatic" region by using the Marcus  $\Delta G^*$  value in the exponential term, as shown in eq 4.

$$A_{\rm na} = 2\pi/(N_{\rm A}\hbar)H_{\rm ab}^{2}(4\pi\lambda RT)^{-1/2}$$
 (5)

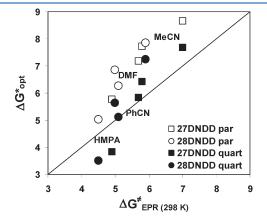


Figure 5. Comparison of the activation energies of the IET reaction calculated from the optical band parameters  $(\Delta G^*_{\mathrm{opt}})$  and obtained from EPR spectra simulation  $(\Delta G^{\dagger}_{\mathrm{EPR}})$ .

We also used an adiabatic equation where an electronic transmission factor  $\kappa$  was added to the pre-exponential term, so that it could be used in a "less than adiabatic" region (eq 6).<sup>16</sup>

$$A_{\rm ad} = \kappa \nu_{\rm v} (\lambda_{\rm v}/\lambda)^{1/2} \tag{6}$$

Equation 6 has the disadvantage of being dependent on the separation of  $\lambda$  into its vibrational and solvent components, which introduces additional uncertainty. The vibrational component  $\lambda_{\rm v}$  was calculated by the 4-point method described earlier. DFT calculations (UB3LYP/6-31G\*) using 4-nitrocathecol as a model compound yield  $\lambda_{\rm v}=15.1$  kcal/mol (5280 cm $^{-1}$ ). An estimated value of  $\nu_{\rm v}=4.5\times10^{13}$  s $^{-1}$  was used, corresponding to  $h\nu_{\rm v}=1500$  cm $^{-1}$ , the value commonly used for aromatic compounds. The transmission factor  $\kappa$  was calculated as described before. <sup>16</sup>

In cases of fast reactions and/or viscous solvents the kinetics of the reaction may be controlled by the dynamics of the solvent. The pre-exponential factor in this solvent-controlled regime was developed by Zusman and is given by 18

$$A_{\text{solv}} = \tau_{\text{solv}}^{-1} (\lambda_{\text{s}} / 16RT)^{1/2} \tag{7}$$

where  $\lambda_s$  is the solvent component of the reorganization energy and  $\tau_{\rm solv}$  the solvent longitudinal relaxation time. The term  $(\lambda_s/16RT)^{1/2}$  is often close to unity (from 1.02 to 1.55 in this work), so eq 7 sets a higher limit of  $1/\tau_{\rm solv}$  for the rate of solvent-controlled reactions. We used literature experimental solvent relaxation times from emission relaxation of Coumarin 153. Table 4 compares the values of the three calculated pre-exponential factors with the ones obtained experimentally from the EPR spectra by using either the parabolic or the quartic activation energies obtained from the optical spectra parameters.

As found before, the values obtained using quartic-fitted energy surfaces are in general more close to the calculated ones. The values of  $A_{\rm EPR}$  obtained by using the quartic activation energies for 27DNDD in the less viscous solvents and for 28DNDD in MeCN are very close to the nonadiabatic calculated values, although they are also within experimental error from A<sub>ad</sub>. The calculated values of  $A_{na}$  or  $A_{ad}$  fail to predict the solvent dependence of the preexponential factor.  $A_{na}$  and  $A_{ad}$  do not change much from MeCN to HMPA, but the values of  $A_{EPR}$  decrease in the same sequence. We suggest that both radicals follow  $A_{na}$  (or  $A_{ad}$ ) for the less viscous solvents. However, the dynamics of the solvent start to influence the rate constant as the solvent relaxation time increases, but the system never seems to reach a full solvent-controlled regime. In **28DNDD** the influence of solvent starts in the less viscous solvents DMF and DMSO, but in the 27DNDD isomer this is only fully evident for the more viscous PhCN and HMPA. This can be better seen in Figure 6, where the values of  $\ln(A_{EPR}/A_{ad})$  are plotted

Table 4. Comparison of Pre-exponential Factor Obtained from the EPR Rate Constants at 298 K and the Parabolic or the Quartic Activations Energies in Table 3 with the Ones Calculated from eqs 5-7 (Units:  $10^{12}$  s<sup>-1</sup>)

		27DNDD					28DNDD				
solvent	MeCN	DMSO	DMF	PhCN	HMPA	MeCN	DMSO	DMF	PhCN	НМРА	
$A_{\rm EPR}^{a}$ (parabolic)	109	220	157	72	26	159	194	136	43	9.0	
$A_{\mathrm{EPR}}^{a}$ (quartic)	21	17	17	7.4	0.95	57	9.1	17	6.2	0.69	
$A_{\mathrm{na}}^{}b}$	20	13	12	14	13	59	56	45	54	46	
$A_{ m ad}^{c}$	9.2	6.8	6.7	7.8	8.2	19	19	17	20	26	
$A_{\mathrm{solv}}^{d}$	3.4	0.41	0.86	0.15	0.065	3.3	0.41	0.84	0.14	0.057	

<sup>&</sup>lt;sup>a</sup> Apparent pre-exponential factor calculated from the experimental  $k_{\rm EPR}$  at 298 K and the parabolic and quartic activation energies  $\Delta G^*_{\rm opt}$  obtained from the optical spectrum. <sup>b</sup> From eq 5 at 298 K. <sup>c</sup> From eq 6 at 298 K. <sup>d</sup> From eq 7 at 298 K.

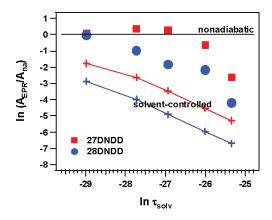


Figure 6. Plots of  $\ln(A_{\rm EPR}/A_{\rm na})$  vs  $\ln(\tau_{\rm solv})$  for 27DNDD and 28DNDD using quartic energy surfaces. The horizontal line at 0 corresponds to the nonadiabatic equation (5), and the lines connecting the crosses correspond to the pure solvent-controlled regime  $(\ln(A_{\rm solv}/A_{\rm na}))$ .

versus  $\ln(\tau_{\rm solv})$ . If a full solvent-controlled regime were attained, the graphic would show plots with slopes close to -1 due to the dependence of the pre-exponential factor on the reverse of the solvent relaxation time, as shown by the blue and red lines.

The experimental values of  $A_{\rm EPR}$  (quartic) are well fitted by the nonadiabatic pre-exponential factors from eq 5 in the low viscous solvents, but the rates calculated in the solvents of higher viscosity increasingly deviate from the experimental ones due to the transition of the system dynamics to a solvent-controlled regime. This deviation is stronger in the **28DNDD** isomer, which, as found before for other dinitroaromatic radical anions, has a smaller activation barrier. A similar plot using  $A_{\rm ad}$  instead of  $A_{\rm na}$ , although more scattered, leads to the same conclusions and is shown in the Supporting Information.

#### CONCLUSIONS

The kinetics of the intramolecular electron-transfer reaction in 27DNDD and 28DNDD radical anions in MeCN are well fitted by the Marcus—Hush two-state classical model analysis of the optical charge-transfer band and by using a modified non-adiabatic pre-exponential factor. However, as the viscosity of the solvent increases, the inclusion of solvent dynamics on the pre-exponential factor is necessary to explain the experimental data. The influence of solvent dynamics in the 28DNDD radical anion can be detected in DMF and DMSO, but in the 27DNDD isomer this is only fully evident for the more viscous solvents PhCN and HMPA. The influence of solvent dynamics is higher in the radical with the lowest activation barrier (27DNDD), as found before for other dinitroaromatic radical anions.

#### ASSOCIATED CONTENT

**Supporting Information.** Complete ref 13; rate constants, hyperfine splittings, and intrinsic line width parameters of EPR spectra; Eyring plots and examples of optical spectra simulations for **27DNDD** and **28DNDD** radical anions; plots of  $\ln(A_{\rm EPR}/A_{\rm ad})$  vs  $\ln(\tau_{\rm solv})$  for **27DNDD** and **28DNDD**. This material is available free of charge via the Internet at http://pubs.acs.org.

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