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Hole Transfer Processes in *meta-* and *para-*Conjugated Mixed Valence Compounds: Unforeseen effects of bridge substituents and solvent dynamics

Julian Schäfer¹, Marco Holzapfel¹, Boryana Mladenova², Daniel Kattnig³, Ivo Krummenacher⁴, Holger Braunschweig⁴, Günter Grampp^{2*}, and Christoph Lambert^{1*}

¹Institut für Organische Chemie and Center for Nanosystems Chemistry, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany.

²Institute of Physical and Theoretical Chemistry, Graz University of Technology, Stremayrgasse 9, A-8010 Graz, Austria.

³Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, U.K.

⁴Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany.

Abstract

To address the question whether donor substituents can be utilized to accelerate the hole transfer (HT) between redox sites attached in para- or in meta-positions to a central benzene bridge we investigated three series of mixed valence compounds based on triarylamine redox centers that are connected to a benzene bridge via alkyne spacers at para- and metapositions. The electron density at the bridge was tuned by substituents with different electron donating or accepting character. By analyzing optical spectra and by DFT computations we show that the HT properties are independent of bridge substituents for one of the metaseries, while donor substituents can strongly decrease the intrinsic barrier in the case of the para-series. In stark contrast, temperature-dependent ESR measurements demonstrate a dramatic increase of both the apparent barrier and the rate of HT for strong donor substituents in the para-cases. This is caused by an unprecedented substituent-dependent change of the HT mechanism from that described by transition state theory to a regime controlled by solvent dynamics. For solvents with slow longitudinal relaxation (PhNO₂, oDCB), this adds an additional contribution to the intrinsic barrier via the dielectric relaxation process. Attaching the donor substituents to the bridge at positions where the molecular orbital coefficients are large accelerates the HT rate for meta-conjugated compounds just as for the para-series. This effect demonstrates that the para-meta paradigm no longer holds if appropriate substituents and substitution patterns are chosen, thereby considerably broadening the applicability of *meta*-topologies for optoelectronic applications.

Introduction

Meta- vs. para-conjugation is one of the key concepts used in organic chemistry to tune electronic communication along extended π -systems.¹ Meta-conjugation is generally believed to be weaker, because of destructive quantum interference of standing waves along the conjugation path, while there is constructive interference in the para-case.² The paradigm of strong para- and weak meta-conjugation has been a useful guideline for the design of conjugated materials for decades. In this article we address this basic theme by investigating thermally induced superexchange hole transfer (HT) processes in organic mixed valence (MV) radical cations by optical and ESR spectroscopy in solution. In these MV species two redox centers are connected via a bridging benzene ring with para- or meta-topology (Fig. 1).³ We varied the electron density of the benzene bridge by substituents, hereafter referred to as X, in order to probe electronic bridge effects for the two different substitution patterns. In the case of a superexchange HT mechanism, one expects that electron donors lower the energy of virtual bridge states and, thus, increase the electronic coupling between the redox centers thereby accelerating the HT. Electron acceptors are supposed to behave oppositely.⁴ We also expect that the solvent will exert a distinct influence on the HT dynamics by its polarity and also by solvent dynamic effects, which are related to the sluggish reorientation of the solvent dipoles on the timescale of the HT. With these aims in mind, we have studied three series of compounds as shown in Fig. 1 in several solvents. The electronic character of the substituents was varied from strongly electron donating (X = OMe) to strongly electron accepting (X = NO₂). In two series, **pX** and **mX**, the positions of the two substituents X at the central benzene ring are the same (positions 2 and 5; see Fig. 1, for the syntheses, see SI), while in the **mX46** series X is located at the 4- and 6-positions. This second *meta*-series was included to reveal the influence of the position of X. In all compounds we used triarylamines as redox centers because of their high radical cation stability and the important role they play in MV chemistry and optoelectronic devices.⁴⁻⁵

In order to delineate the energetic factors governing the HT in MV compounds, we use the standard two-state model with harmonic diabatic states, which are coupled to yield the adiabatic double-well ground state potential as shown in Fig. 1a.⁶ The splitting of the adiabatic potentials at the position of the avoided crossing, i.e. at the transition state, is twice the size of the electronic coupling *V* between the diabatic states. This coupling is a measure of the electronic communication between the redox centers. The optically induced HT from one minimum of the double well to the excited state potential surface is associated with an intervalence charge transfer (IV-CT) absorption band in the NIR spectral region. This optically induced HT moves a hole from the oxidized triarylamine redox center to the neutral one. The IV-CT energy corresponds to the total reorganization energy λ , which comprises an internal part λ_i and a solvent contribution, λ_o . An alternative HT pathway entails the thermally induced transfer between the two minima of the ground state adiabatic potentials via the transition state. In this process, a barrier with relative energy ΔG^* (see Fig. 1a) is to be surmounted. This thermally induced HT is the focus of the present study.

First we will analyze the steady-state optical spectra of the radical cations of **mOMe46** and the **pX** and **mX** compounds. This will provide information about reorganization energies and electronic couplings, which will be compared to DFT-computed properties. We will then present the HT rate constants and HT barriers as measured by temperature dependent ESR spectroscopy in diverse solvents with different dielectric responses. These measurements

will inform about the HT dynamics, which for some cases will be dominated by the solvent dynamic effect.



Figure 1. Mixed valence compounds, potential energy diagram and optical spectra. (a) Diabatic (red, dashed) and adiabatic (black) Gibbs energy potentials for a degenerate mixed valence radical cation. The charge distribution and the orientation of solvent dipoles (dark blue arrows) are sketched for three different situations: the hole located at the left triarylamine moiety, at the transition state, and at the right triarylamine moiety. (b) Reduced Vis-NIR spectra of all **pX** compounds and of **mOMe46** in PhNO₂. Gaussian fits to the IV-CT bands are given as dashed lines and magnified in the inset.

Results

Optical spectroscopy. Reduced⁷ absorption spectra of oxidized **mOMe46** and the **pX** and **mX** radical cation MV compounds were obtained after oxidation of neutral precursor compounds in PhNO₂ with SbCl₅ (see Experimental and the SI for additional spectra and their deconvolution in Figs. S1-S14).

These spectra display a Gaussian-shaped IV-CT band in the NIR with a maximum at ca. 7000-9000 cm⁻¹ (see Fig. 1b). Depending on the nature of the bridging unit between the triarylamines, a second band, associated with the HT from the oxidized triarylamine to the bridge, is also visible at somewhat higher energy than the IV-CT band (ca. 10000 cm⁻¹). This "bridge band" strongly overlaps with the IV-CT band and the nearby π - π * band of the triarylamine.^{4,5b} For the *para*-series the IV-CT bands are pronounced and shift slightly to lower energies as the electron donating character of X is increased. By contrast, the IV-CT bands for the *meta*-series are very weak and are hard to discern from the baseline, indicating a much smaller electronic coupling (for spectra of **mX** see SI, Fig. S2). An exception is

mOMe46, which also displays a sizable IV-CT band (Fig. 1b). For the *para*-series and **mOMe46**, Mulliken-Hush theory was used to calculate the electronic coupling V_{12} from analysis of the IV-CT band using DFT computed dipole moment differences.⁸

In the framework of Marcus-Hush theory the electronic coupling V_{12} is given by $V_{12} = \frac{\mu_{ab} \tilde{V}_{max}}{\Delta \mu_{c2}}$. Here, \tilde{V}_{max} is the energy of the IV-CT band. The transition dipole moment μ_{ab}

 $V_{12} = \frac{\gamma_{ab}}{\Delta \mu_{12}}$. Here, \tilde{v}_{max} is the energy of the IV-CT band. The transition dipole moment μ_{ab} is the projection of the adiabatic transition dipole moment of the IV-CT band on the diabatic

dipole moment difference $\Delta \mu_{12} = \sqrt{\Delta \mu_{ab}^2 + 4\mu_{ab}^2}$ of the fully localized (noninteracting) diabatic states. While μ_{ab} is obtained by integrating the IV-CT band, we used DFT-computed adiabatic dipole moment difference for $\Delta \mu_{ab}$ (see section below).

The so evaluated couplings are given in Table 1. We also recorded the absorption spectra of the *para*-series and **mOMe46** in *ortho*-dichlorobenzene (*o*DCB), which is significantly less polar than PhNO₂ and gives rise to much smaller solvent reorganization energies. Consequently, the IV-CT band shifts to lower energies, e.g. for **pOMe** from 7280 cm⁻¹ to 4670 cm⁻¹, for **pCN** from 9310 cm⁻¹ to 6680 cm⁻¹ and for **mOMe46** from 6980 cm⁻¹ to 5700 cm⁻¹ (for the corresponding spectra see SI, Figs. S13). In the latter case, this shift leads to a more distinct IV-CT band, well separated from the bridge band. The IV-CT bands of the *para*-series in DCM, which is a solvent of intermediate polarity, display maxima between those found for PhNO₂ and *o*DCB (see Fig. S14 in the SI).

TD-DFT computations. Due to the low intensity of the IV-CT band of the meta-series cations, the Mulliken-Hush analysis could not be reliably employed to extract reorganization and coupling parameters. Thus, we performed UDFT optimizations and TD-DFT computations for all three series of MV compounds in PhNO₂ (see Experimental).⁹ The computed dipole moment differences $\Delta \mu_{ab}$ between ground and IV-CT state, transition moments μ_{ab} and transition energies E_{ab} are summarized in Table 2. As can be seen from the large dipole moment differences $\Delta \mu_{ab}$, all compounds possess a strongly asymmetric and thus localized charge distribution where one triarylamine is positively charged while the other is neutral. Within the **mX** series, the dipole moment difference $\Delta \mu_{ab}$ remains constant, whereas, for the pX series it decreases as the electron donating character of the substituent X increases. Similarly, the **mX46** series shows a very moderate increase in the charge delocalization on going from X = CN to OMe. The IV-CT transition energy E_{ab} , and thus the reorganization energy, decreases with increasing electron-donating strengths of X. This trend excellently agrees with the experimental observation in the para-series, for which data are available. The transition moments μ_{ab} in the *para*-series are much larger than those in the **mX** series, reflecting a more efficient electronic coupling V_{12} in the former. The **mX46** series of MV compounds displays intermediate behavior; the transition moments are small for X =CN and CI, just as for **mX**, but rise dramatically to values approaching those of the paraseries for mOMe46.

Using the above calculated data ($\Delta \mu_{ab}$, μ_{ab} and E_{ab}) we estimated the electronic coupling V_{12} by the Mulliken-Hush formalism as introduced above. With V_{12} values between 60 and 180 cm⁻¹ for the **mX** series these couplings are much smaller than for the **pX** series , for which V_{12} is ca. 900 cm⁻¹ for X = NO₂ to Cl, but rises for **pMe** (1140 cm⁻¹) and **pOMe** (1320 cm⁻¹). As expected on the basis of the transition dipole moments, the couplings in the **mX46** series

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lie between those of the **mX** and **pX** series. The magnitude of these couplings places the thermal HT of all compounds in the so-called adiabatic regime, for which the limiting factor is the motion over the transition state (possibly subject to solvent dynamics). As discussed in detail below, this observation dictates the choice of the adequate rate theory for describing the dynamic HT processes.

The TD-DFT method was also used to estimate the electronic coupling from half of the lowest excitation energy $E_{ab}(TS)/2 = V_{12,TS}$ calculated at the geometry of the HT transition state, which directly corresponds to half the splitting of adiabatic potentials at the avoided crossing (see Fig. 1a). The values so obtained are summarized in Table 2; the subscript TS is used to label the transition state-based approach. These couplings are in good agreement with V_{12} for the *meta*-series, but exaggerate the influence of the substituents for the *para*-series.

The reorganization energy (= IV-CT energy E_{ab}) and the electronic coupling can be used to calculate the barrier (see Fig. 1) for the thermally activated HT process via equation (1)

$$\Delta G^* = \lambda / 4 \cdot V + V^2 / \lambda, \tag{1}$$

where λ comprises a solvent (λ_0) and an inner-sphere (λ_i) part. For the **pX** series, we observe a reduction of the Marcus-Hush barrier on going from pNO₂ to pOMe. This is a direct consequence of the increasing electronic coupling, which not only reduces the barrier at the avoided crossing, but also increases the charge delocalization. This charge delocalization leads to a smaller adiabatic charge transfer distance $r_{ab} = \Delta \mu_{ab}/e$ and thereby reduces the reorganization energy $\lambda = E_{ab}$ by up to 20% (see Table 2) via its solvent part, which directly depends on r_{ab} (cf. the classical Marcus expression of the outer-sphere reorganization energy)^{3c}. The latter aspect is usually disregarded in standard electron transfer (ET) theories, which suggest that the reorganization energy is independent of the electronic coupling. The **mX46** series behaves similarly; in the **mX** systems these effects are less pronounced. For the latter, the DFT calculations show small and weakly varying electronic couplings V_{12} and E_{ab} decreases by only ca. 900 cm⁻¹ on going from **mNO**₂ to **mOMe**, compared to the 1900 cm⁻¹ reduction in the *para*-series. The impact of this behavior on the HT barrier becomes obvious when looking at Fig. 2a, where we have plotted the HT barrier ΔG^*_{MH} , the electronic coupling V_{12} , and the hypothetical barrier in the absence of electronic coupling (= $E_{ab}/4$, cf equation 1). For the **mX** series $E_{ab}/4$ and ΔG^*_{MH} agree very well and are almost independent of the substituent. However, in the para-series, ΔG^*_{MH} decreases strongly for **pMe** and **pOMe**, because V_{12} rises by almost the same amount while $E_{ab}/4$ decreases to a lesser extent. The same effects as for **pX** are observed for **mX46** in an even more pronounced way. For the para-series, analysis of the IV-CT bands and the DFT computations reveal the same general trend for the electronic coupling V_{12} and the HT barrier $\Delta G^*_{\rm MH}$.

An alternative way to estimate the HT barrier is to use the energy difference ΔG^*_{TS} between the optimized ground state structure and the symmetric transition state structure which is readily available from the optimization of the respective structures. The close agreement of ΔG^*_{TS} and ΔG^*_{MH} for the *para*-series (see Table 2) demonstrates the correctness of the underlying assumption of adiabatic Gibbs energy surfaces constructed from harmonic potentials, i.e. Marcus Hush theory, and the applicability of Mulliken-Hush theory to estimate the electronic coupling. However, a closer inspection of Fig. 2b shows that, while ΔG^*_{TS} is slightly higher than ΔG^*_{MH} for X = NO₂ to Me, this order is reversed for X = OMe. While this

could be fortuitous, it might also point towards a more complex hypersurface structure at the transition state. In previous works^{4,5b} we found evidence that, in the case of **pOMe**, low lying bridge states distort the ground state hypersurface in a way that leads to the appearance of a third minimum on the ground state hypersurface (besides the two MV states), for which the hole is localized at the bridge moiety. This leads to an additional decrease of the TS energy. One could easily conceive a situation in which this TS becomes one of higher order, a suggestion that might be indicated by the two imaginary frequencies of the "transition state" of **pOMe** (see Table 2).

The influence of the solvent dielectric properties on the reorganization energy is one of the decisive aspects in Marcus ET theory, We thus set out to test the performance of the DFT computations in this regard. We chose **pCN** as an exemplary MV compound and recomputed all pertinent quantities from Table 2 in *o*DCB and in the intermediately polar dichloromethane (DCM), see Table 3. While the general red-shift of the IV-CT band energy on going from PhNO₂ to *o*DCB is well reflected in these computations, its magnitude is underestimated. The (transition) dipole moments and the electronic coupling appear to be solvent dependent to a much lesser extent. Accordingly, the HT barrier drops from PhNO₂ to *o*DCB because of the smaller IV-CT band energy, i.e. reorganization energy.



Figure 2. Energy parameters depending on substituents for PhNO₂ solvent. (a) DFT computed potential energy parameters $E_{ab}/4$ (black symbols), ΔG^*_{MH} (blue symbols) and V_{12} (red symbols) of **pX** (dashed lines), **mX** (solid lines), and **mX46** (dash-dotted lines) compounds. The data points for $E_{ab}/4$ of **pX** and **mX46** are almost superimposed. (b) Hole transfer barriers of **pX** in PhNO₂ determined by analysis of the IV-CT band, ESR spectra or DFT calculations using the Marcus-Hush (MH) formalism or explicit calculations at the transition state (TS). (c) The same parameters as in b), in DCM, where available. (d) The same parameters as in b), in oDCB, where available.

Table 1. Experimental	data	evaluated	from	the	IV-CT	band	analysis	and	from
temperature dependent ESR spectra in PhNO ₂ and in oDCB at 295 K									

			IV-CT band					ESR		
			${ ilde{ u}}_{\max}^{IVCT}/{ extsf{cm}^{-1}}^{d}$	$\mu_{ m ab}$ /D $_{e}$	V ₁₂ /cm ⁻¹ _{b,e}	$\Delta G^*_{\text{IV-CT}}$ / cm ⁻¹	ΔG^*_{ESR} / cm ^{-1 a}	T range / K	<i>k</i> _{ESR} (295 K) /	
		mOMe46	6980	3.0	320	1430	1070 + 150	290-315	40	
	mX46	mMe46	8410	1 1	140	1970	1370 ± 130 1360 + 110	280-300	48	
		mOMe	0110	1.1	110	1070	1640 ± 30	280-345	1.0	
		mMe					1740 ± 20	280-360	2.5	
	mΧ	mCl					1600 ± 20	280-335	1.3	
õ		mCN					1630 ± 20	285-350	1.5	
۲ ۲		mNO₂					1790 ± 140	280-320	1.0	
ш		рОМе	7280	5.0	550	1310	1700 ± 90	280-320	57	
		рМе	8310	4.7	540	1570	1380 ± 60	295-345	35	
	рХ	рСІ	8980	4.1	480	1790	1420 ± 50	280-325	11	
		pCN	9310	3.5	420	1930	1430 ± 50	280-320	9.9	
		pNO₂	9100	3.7	450	1850	1410 ± 80	280-310	11	
	m¥46	mOMe46	5700	3.6	330 ^c	1120	$\textbf{970} \pm \textbf{50}$	260-300	87	
B	111740	mMe46	7020	1.8	180	1580	1080 ± 30	255-275 ^f	14 ^a	
		рОМе	4670	7.4	510 <i>°</i>	710	1250 ± 40	260-305 ^g	201	
ğ		рМе	5860	5.9	470 ^c	1030	-		-	
0	рΧ	pCl	6480	4.4	370 <i>°</i>	1270	900 ± 40	260-280′	16 ^a	
		pCN	6680	4.3	370	1320	840 ± 60	260-285'	14 ^a	
		pNO ₂	6760	3.9	340 °	1370	970 ± 20	260-275'	<u>16</u> ^a	
	mX46	mOMe46	6110	3.4	330	1220	1008 ± 40	235-260	160°	
		mMe46	7970	1.7	200	1800	1210 ± 20 [/]	240-280'	<u>11°</u>	
_		рОМе	6010	7.4	650	920	660 ± 50	200-230 ⁹	322ª	
Σ		рме	7110	6.2	600	1230	970 ± 20	250-310	114	
ă	рΧ	pCI	//10	4.6	470	1490	$1020 \pm 20''$	220-250'	29°	
			8030	4.1	420	1610	$1050 \pm 20'$	220-260	21"	
		ρΝΟ ₂	8010	3.9	410	1620	-	-	-	

^aExtrapolated to 295 K. ^bCalculated by Mulliken-Hush theory using experimental data and the DFT computed dipole moment difference $\Delta \mu_{ab}$, see Table 2. ^cUsing DFT computed dipole moment differences in DCM, which hardly differ from those in *o*DCM, see Table 3. ^d±5%. ^e±20%. ^fRate constants at higher temperatures than the indicated range deviate from the linear trend in the ln($k_{ESR}/T^{1/2}$) vs. 1/T plot towards lower rates. ^gRate constants at higher temperatures than the ln($k_{ESR}/T^{1/2}$) vs. 1/T plot towards lower rates. ^gRate constants at higher temperatures than the indicated range deviate from linearity in the ln($k_{ESR}/T^{1/2}$) vs. 1/T plot towards higher rates.

Table 2. TD-DFT computed data in PhNO2 E_{ab} μ_{ab} /D^a $\Delta \mu_{ab}$ V_{12} /cm⁻¹ $E_{ab}(TS)/2 = \Delta G^*_{MH}$ ΔG^*_{TS} $/cm^{-1}$ /D V_{12} /cm⁻¹ $/cm^{-1}$ $/cm^{-1}$ $/cm^{-1}$

		-au	μ_{ab}	$\Delta \mu_{ab}$	12,011			AO 15
		/cm⁻¹		/D		V _{12,TS} /cm ⁻¹	/cm⁻¹	/cm ⁻¹
	mOMe46	7256	7.57	62.83	850	1137	1063	1005 ^b
mV46	mMe46	8216	2.39	70.23	279	183	1784	1837
111740	mCl46	8800	1.09	72.55	133	166	2069	2089 ^b
	mCN46	9442	1.29	72.70	167	221	2196	2151
	mOMe	8496	0.55	72.83	64		2061	
	mMe	8480	1.55	73.76	178	209	1946	2273 ^c
mΧ	mCl	8904	0.84	74.61	100	156	2127	2142
	mCN	9271	1.33	73.83	167	192	2153	2165 ^b
	mNO ₂	9382	1.30	74.55	163		2185	
	рОМе	7414	12.48	65.57	1319	1825	769	628°
	рМе	8106	10.47	71.51	1139	1094	1048	1119
рΧ	рСІ	8829	8.29	76.38	937	581	1370	1482
	pCN	9237	7.57	77.24	888	415	1506	1622
	pNO₂	9267	7.85	75.01	950	426	1464	1579

^{*a*}Projection of transition moment onto the dipole moment difference vector $\Delta \mu_{ab}$. ^{*b*}Minimum according to frequency calculation. ^{*c*}Two imaginary frequencies.

Table 3. TD-DFT computed data for pCN in PhNO₂, DCM and oDCB

		E _{ab} /cm ⁻¹	$\mu_{ m ab}$ /D a	$\Delta \mu_{ m ab}$ /D	V ₁₂ /cm ⁻¹	$E_{ab}(TS)/2$ = $V_{12,TS}$ /cm ⁻¹	$\Delta G^*_{\rm MH}$ /cm ⁻¹	ΔG^*_{TS} /cm ⁻¹
	PhNO ₂	9237	7.57	77.24	888	415	1506	1622
pCN	DCM	8026	8.12	77.78	820	760	1270	1321 ^{<i>b</i>}
	<i>o</i> DCB	8033	8.10	77.94	817	429	1274	1366 ^b

^{*a*}Projection of transition moment on the dipole moment difference vector $\Delta \mu_{ab}$. ^{*b*}Minimum according to frequency calculation.



Figure 3. ESR spectra and rate constant analysis. (a) Linear fit of experimental $\ln(k_{ESR}/T^{1/2})$ vs 1/T for four exemplarily chosen MV species in PhNO₂. The dashed line is at 295 K. (b) ESR spectra of **pOMe** and **mOMe** at selected temperatures in PhNO₂ and their calculated best fitting lineshapes.

Temperature-dependent ESR measurements of the MV radical cations were used to determine the HT rate constants k_{ESR} in PhNO₂ by digital line shape analysis and the HT barriers from the slope of $\ln(k_{ESR}/T^{1/2})$ vs 1/T plots (see Experimental and Fig. 3 for selected examples and Table 1).¹⁰ From the experimental ESR data in Table 1 some preliminary conclusions can be drawn. 1) At 295 K, the HT rate constants of all **mX** compounds are an order of magnitude smaller than those of the **pX** compounds. This qualitatively agrees with general observations made before for other MV compounds in a similar context.¹¹ 2) The rate constants are almost independent of the substituents within the **mX** series. 3) Within the **pX** series the rate constants are constant for acceptor substituents (X = NO₂, CN, Cl) but increase on going from **pCI** to compounds with donor substituents (X = Me, OMe). This demonstrates that strong donor substituents, which increase the electron density at the bridge, can be used to accelerate the HT rates. 4) Within the **mX** series the ET barriers are almost independent of the substituents (average ΔG^* : 1680 ± 80 cm⁻¹). 5) Within the **pX** series the barriers are constant for the substituents NO₂, CN and Cl and significantly lower than those of the **mX** series. However, for X = OMe, the barrier is much larger and approaches those of the **mX** series. The latter effect is surprising, as, at first sight, it appears to contradict the concomitant increase in HT rate. The same holds true for **mOMe46**.

In order to elucidate the solvent dependence of this unforeseen effect we also measured the rate constants and barriers for the **pX** series and selected **mX46** species in the significantly less polar solvents *o*DCB and DCM. These results are included in Table 1 and show the analogous effect concerning the HT rate constants, that is, k_{ESR} is almost independent of

substituent for X = NO₂ to CI and similar in all three solvents but rises dramatically for X = OMe in *o*DCB and particularly in DCM. Compared to the results in PhNO₂, the barriers are significantly lower in *o*DCB, because the less polar solvent exerts smaller solvent reorganization energy in line with the observations made above for the IV-CT band. However, for X = OMe, the barrier is significantly higher than that for all other bridge substituents in PhNO₂ and in *o*DCB, while in DCM it is lower. At this point we note that most compounds in *o*DCB and in DCM display either positive or negative deviations of the ln($k_{ESR}/T^{1/2}$) vs 1/*T* plot in the higher temperature regime which we assign to decomposition processes. In these cases only the data at low temperatures were used for the analysis of the barriers and the rate constants were extrapolated to room temperature.

Discussion

HT dynamics. In order to explain the observations above concerning the HT dynamics we tried to calculate the HT barrier and rate constants using established electron transfer theories.¹² In general, rate constants of electron transfer processes are given by equation (2)

$$k = A \cdot \exp\left(-\frac{\Delta G^*}{k_{\rm B}T}\right),\tag{2}$$

where ΔG^* is the HT barrier, given by equation (1). In principle four different scenarios could apply to the HT process in the present setting, which, depending on the coupling matrix element and the dielectric relaxation properties of the solvent, give rise to different preexponential factors in equation (2):¹³ I) strongly diabatic limit, II) strongly adiabatic solvent dynamic controlled situation with cusped barrier, III) the same as II) but with parabolic barrier and, IV) adiabatic transition state theory. Only cases III) and IV) apply to the present work, for reasons given in the SI.

In case III) solvent friction controls the dynamics by the longitudinal solvent relaxation time τ_{L} . For larger couplings a parabolic free energy surface (PAR) at the TS results and A is given by:

$$A_{\rm PAR} = \frac{1}{\tau_{\rm L}} \sqrt{\frac{\lambda_{\rm o}}{8\pi^2 V_{12}} - 1} \,. \tag{3}$$

In case IV), with uniform motion to the transition state, the pre-exponential factor, which can be interpreted as a well frequency, is:¹³⁻¹⁴

$$A_{\rm TST} = \frac{1}{2\pi} \sqrt{\zeta \frac{2k_{\rm B}T}{I}} \qquad \text{with } \zeta = \frac{2\varepsilon_{\rm s} + \varepsilon_{\infty}}{3\varepsilon_{\rm s}g}, \qquad (4)$$

where ε_s and ε_{∞} are respectively the static and optical dielectric constants of the solvent, *g* is the Kirkwood correlation factor and *I* is the average moment of inertia of the solvent molecule, as given in the SI.¹⁵

Rips and Jortner¹⁶ have suggested inequalities based on the adiabaticity parameter $\kappa_{A} = \frac{4\pi V^{2} \tau_{L}}{\hbar \lambda_{o}}$ to decide upon the electron transfer regime and, thus, which prefactor applies. If κ_{A} lies in the interval given by

$$\frac{1}{\pi} \left(\frac{k_{\rm B}T}{V_{\rm 12}}\right)^2 2\zeta \omega_{\rm rot} \tau_{\rm L} \ll \kappa_{\rm A} \leq \frac{4\pi}{2\zeta \omega_{\rm rot} \tau_{\rm L}},\tag{5}$$

where $\omega_{rot} = \frac{\hbar}{l}$ is the rotation frequency of the solvent molecules, transition state theory (TST) applies. If κ_A is smaller than the left-hand term the HT is diabatic, if it is significantly larger than the right-hand term, the reaction is adiabatic and controlled by solvent dynamics.

For the majority of scenarios relevant here (e.g. with $V_{12} = 200 \text{ cm}^{-1}$, $\lambda_0 = 6000 \text{ cm}^{-1}$, $\tau_L = 4.3 \times 10^{-12} \text{ s}^{-1}$, $I = 742 \times 10^{-47} \text{ kg m}^2$, $\varepsilon_8 = 35.90$, $\varepsilon_{\infty} = 3.48$, g = 1), the adiabaticity parameter κ_A is much larger than unity (e.g. $\kappa_A = 67.8$) and larger than the left-hand term in equation (5) (e.g. 0.029) but smaller than the right-hand term (e.g. 147), indicating uniform adiabatic behavior as described by TST. However, for larger couplings, e.g. $V_{12} = 1000 \text{ cm}^{-1}$, the adiabaticity parameter $\kappa_A = 1697$ is much larger than the right-hand limit, indicating that solvent controlled dynamics dominate, which is covered by case III (and II).

In case III) the temperature dependence of π_{-}

$$\frac{1}{\tau_{\rm L}} = \frac{1}{\tau_{\rm L0}} \exp(-H_{\rm L}/k_{\rm B}T)$$
(6)

induces an effective increase of the HT barrier.¹⁷ The barrier H_L amounts to 1439 cm⁻¹ ($\tau_{L0} = 3.55 \times 10^{-15}$ s) for nitrobenzene in the investigated temperature range¹⁸ and, thus, cannot be disregarded. However, this value contradicts the experimental activation barriers as, following this model, H_L would constitute the major part of the barrier, while the intrinsic Marcus barrier $E_{ab}/4$ (and hence the reorganization energy) would be predicted as unreasonably small.

On the other hand, IV) appears to be reasonable for electronic couplings on the order of 100-600 cm⁻¹ and given the high moment of inertia of nitrobenzene. Therefore, we used equation (2) with the A_{TST} prefactor to estimate the electronic coupling and the reorganization energy from the experimental barriers and rate constants at 295 K. The applicability of the TST also justifies the estimation of the HT barrier by plotting $\ln(k_{\text{ESR}}/T^{1/2})$ vs. 1/*T* (see Fig. 3). For the **mX** series with $V_{12} = 200 \text{ cm}^{-1}$ ¹⁹ and $\lambda_0 = 6000 \text{ cm}^{-1}$ ($\lambda_v = 2000 \text{ cm}^{-1}$) reasonable rate constants ($k_{\text{TST}} = 1.5 \times 10^7 \text{ s}^{-1}$) and barriers ($\Delta G^* = 1805 \text{ cm}^{-1}$) were obtained in comparison with the experimental data (see Table 1). For the *para*-series with X = NO₂ to Me plausible rate constants ($k_{\text{TST}} = 8.6 \times 10^7 \text{ s}^{-1}$) and barriers ($\Delta G^* = 1445 \text{ cm}^{-1}$) could be estimated by increasing V_{12} to 600 cm⁻¹. However, the markedly high rate and barrier of both **pOMe** and **mOMe46** could not be modelled by equations (3) and (4).²⁰

Using large coupling coefficients (in agreement with the results from the optical data) increases κ_A beyond the upper limit in equation (5). This again hints at a regime controlled by

solvent dynamics. In agreement with this finding, we used an interpolation between the TST and the PAR regime, which is given by equation (7):

$$k = \frac{k_{\text{PAR}} \cdot k_{\text{TST}}}{k_{\text{PAR}} + k_{\text{TST}}}.$$
(7)

With this interpolation, a larger coupling $V_{12} = 1200 \text{ cm}^{-1}$ together with a somewhat smaller solvent reorganization energy ($\lambda_0 = 5000 \text{ cm}^{-1}$) gives $k = 74 \times 10^7 \text{ s}^{-1}$ and $\Delta G^* = 1700 \text{ cm}^{-1}$. These values are in much better agreement with the experimental values for **pOMe** ($k_{\text{ESR}} = 57 \times 10^7 \text{ s}^{-1}$ and $\Delta G^*_{\text{ESR}} = 1700 \text{ cm}^{-1}$) and **mOMe46** ($k_{\text{ESR}} = 40 \times 10^7 \text{ s}^{-1}$ and $\Delta G^*_{\text{ESR}} = 1970 \text{ cm}^{-1}$). Thus, it appears that the higher electronic coupling in **pOMe** and **mOMe46** shifts the system towards the solvent dynamically controlled regime with the consequence that both the barrier (via the additional activation energy H_L in the pre-exponential term) and the rate constant increase compared with the respective values for **pMe**.

In order to support this interpretation we also analyzed the results for the **pX** series in two other solvents that differ significantly from PhNO₂ with respect to their dielectric properties, that is, in *o*DCB, a distinctly less polar solvent compared to PhNO₂ that nonetheless shows a very similar longitudinal solvent relaxation time τ_{L} (6.0 ps for *o*DCB and 4.3 ps for PhNO₂ at 295 K, see SI), and in DCM, which is somewhat more polar than *o*DCB but exhibits a much shorter relaxation time (0.49 ps, see SI).

Although not as satisfactory as in PhNO₂, transition state theory again gives the best agreement with the experimental data in *o*DCB for **pNO₂**, **pCN**, and **pCI**. e.g. with $V_{12} = 300$ cm⁻¹, $\lambda_0 = 3500$ cm⁻¹, $\lambda_i = 2000$ cm⁻¹, $I = 736 \times 10^{-47}$ kg m², $\varepsilon_s = 9.93$, $\varepsilon_{\infty} = 2.03$, and g = 1 we obtain $k = 50 \times 10^7$ s⁻¹ and $\Delta G^* = 1091$ cm⁻¹. Within TS theory no reasonable combination of parameters could be found which for **pOMe** reproduced the observed increase of both the rate constant and the HT barrier. However, as above, using eq. 7 as the interpolation to the solvent dynamic regime together with eqs. 3, 4 and 6 with $\lambda_0 = 3000$ cm⁻¹, $V_{12} = 1000$ cm⁻¹ and assuming a temperature dependence of the longitudinal solvent relaxation with a somewhat lower barrier ($H_L = 1080$ cm⁻¹) for *o*DCB as PhNO₂ (see SI) we obtain $k = 176 \times 10^7$ s⁻¹ and $\Delta G^* = 1278$ cm⁻¹ in good agreement with the experimental data.

Assuming similar HT parameters for the *para*-series in DCM ($V_{12} = 200 \text{ cm}^{-1}$, $\lambda_0 = 4000 \text{ cm}^{-1}$, $\lambda_v = 2000 \text{ cm}^{-1}$, $I = 48 \times 10^{-47} \text{ kg m}^2$, $\varepsilon_s = 8.83$, $\varepsilon_\infty = 1.98$, g = 1) TS theory yields $k = 68 \times 10^7 \text{ s}^{-1}$ and $\Delta G^* = 1307 \text{ cm}^{-1}$. Both values are slightly larger than those observed for X = CN and Cl. Increasing the electronic coupling to $V_{12} = 1200 \text{ cm}^{-1}$ and applying eq. 7 gives a barrier of 721 cm⁻¹ with $k_{\text{TST}} = 1133 \times 10^7 \text{ s}^{-1}$. Both values are in good agreement with experiment. Thus, in contrast to PhNO₂ and *o*DCB, in DCM the barrier in the **pX** compounds becomes smaller with rising rate constant. This is due to the fact that the DCM relaxation constant causes only a small barrier $H_L = 401 \text{ cm}^{-1}$ [see SI]. This finding proves that the rise of the HT barrier for **pOMe** in PhNO₂ and in *o*DCB is indeed caused by the additional barrier exerted by the solvent dynamics.

It is important to note that what we measured by ESR spectroscopy is an "apparent" barrier, calculated as the derivative of $\ln(k_{\rm ESR}/T^{1/2})$ vs. 1/*T*. The intrinsic Marcus barrier as defined by eq. 1 decreases for both **pOMe** and **mOMe46** as a result of the deformation of the hypersurface in the TS region. This can be seen from both the analysis of the IV-CT band and the DFT computations. This relationship is most obvious when looking at Fig. 2b where

 the barriers of the **pX** compounds obtained by the three different methods are plotted. Here, the most interesting aspect is the deviating behavior of the ESR-determined apparent barriers. While there is a very good agreement with the DFT computed values for $X = NO_2$ to CI, the transition of the HT mechanism towards the solvent dynamic regime leads to an increase of the apparent barrier for **pMe** and, in particular, **pOMe**. The same holds true for the barriers in *o*DCB (Fig. 2d) but not for DCM (Fig. 2c), for which solvent dynamics do not add much to the apparent HT barrier.

Electronic coupling. The manifold influences of bridge substituents on the electronic coupling in the para- and the meta-series of MV compounds is the central point of this work. Comparing the rate constants of **mOMe46** and **mMe46** with all the other compounds in the studied solvents shows that the HT rate of **mOMe46** is similar to **pOMe** or **pMe** while the rate of **mMe46** is similar to **pX** with X = CN to NO₂. This demonstrates that placing strong donor substituents in 4- and 6-position at the central benzene bridge in the meta-series can accelerate the HT to enter the regime observed for the para-series. This is most likely caused by a surprisingly large electronic coupling in the **mOMe46** as can be seen from the data in Table 1 and 2. As we have shown above, the IV-CT energy at the TS corresponds to twice the electronic coupling V_{12} . This excitation is caused by the promotion of an electron from the β -HOMO to the β -LUMO orbital (see Fig. 4 for selected examples with X = Me)²¹ in an unrestricted UDFT computation where the α -orbitals contain n and the β -orbitals n-1 electrons in different spin orbitals. In general, electron donating substituents (Me and in particular OMe) exert a destabilizing effect on the MOs when attached to positions where there is a significant orbital coefficient at the benzene bridge. Consequently the β -LUMOs of mMe46 and of pMe are destabilized. This also applies to mMe, but to a much lesser extent, because only one of the methyl substituents is attached to a benzene position with significant orbital coefficient. In this way, the symmetry of the involved MOs and the position of the substituents play a decisive role in determining the electronic coupling.



Figure 4. Selected β -HOMO and β -LUMO plots of transition states. The UDFT computed MOs of **mMe46**, **mMe** and **pMe** that are responsible for the lowest energy excitation at the geometry of the transition state.



Figure 5. ESR determined (= apparent) HT barriers ΔG^*_{ESR} and HT rate constants k_{ESR} for the **mX46** (dashed dotted line), **pX** (solid line) and **mX** (dashed line) series of MV compounds in PhNO₂.

Conclusions

The main conclusions of this work are summarized in Fig. 5: The schizophrenic observation that the HT rate constants and the apparent (ESR measured) HT barriers increase simultaneously for **pMe** and **pOMe** in PhNO₂ and oDCB can be explained by an increasingly important solvent dynamic effect and an additional, effective barrier that is associated with the longitudinal solvent relaxation time. To our knowledge, this is the first time that such a transition of mechanism from the regime where TST applies to the regime where for a parabolically (PAR) shaped transition state solvent dynamics control the charge transfer has been clearly observed. While this aspect pertains to solution reactions only, the influence of bridge substituents has to be considered for any bridge moiety and, thus, is of crucial importance for, for example, organic electronic devices, be it on the molecular level or in the bulk. Here we have shown that both rate constants and HT barriers are almost independent of substituents for the **mX** series, while in the **pX** series there are dramatic changes for donor-substituted derivatives. Thus, HT rate constants can easily be tuned in paraconjugated systems by attaching substituents to the bridge units. This is a result of orbital symmetry in the transition state. Due to vanishing orbital coefficients at the bridge, these influences are much weaker in the **mX** conjugated systems. The **mX46** series bridges the gap between the **mX** and **pX** compounds. That is, for electron-withdrawing substituents these compounds behave like the **mX** compounds, but for electron-donating substituents they are rather similar to the **pX** compounds. Our findings complement a recent study by Grozema et al.¹, which discusses the differences of constructive and destructive quantum interference in cross-conjugated vs. linearly conjugated pathways in donor-bridge-acceptor and analogous metal-bridge-metal junctions. In this study it became clear that hole-, electron- and mixed electron/hole-transfer pathways may experience different quantum interference effects depending on the involved bridge orbitals and their symmetry. However, in our study we could show that the mere topology of the conjugation pathway is no longer the decisive factor but can be overruled by substituent effects. Thereby, the long-standing para-meta paradigm can be overcome, which broadens the use of conjugative topologies for new applications such as organic field effect transistors or photovoltaic devices where e.g. charge transport in ring- or helix-like structures based on meta-connected tolan units could provide interesting novel applications.

Experimental

MH Analysis. For all MV compounds we measured the Vis/NIR optical spectra of the monoradical cations by oxidative titration of solutions in nitrobenzene (PhNO₂) orthodichlorobenze (oDCB) and dichloromethane (DCM) with solutions of SbCl₅ in the respective solvent. Although comproportionation during the oxidation step inevitably leads to a mixture of neutral, monocation and dication species,^{5a} only the monocation is mixed valent and displays a IV-CT band. This band was evaluated by fitting the reduced spectra with Gaussian functions (see SI). IV-CT band integration then yields the adiabatic transition moment μ_{ab} .

DFT Computations. Structure optimizations of the ground states and TD-DFT computations of the excited states were performed for all three series of MV compounds using a specially adjusted hybrid functional with 35% exact-exchange admixture, a SVP basis set and the

COSMO polarizable continuum model accounting for solvent effects^{9a,9b} using Gaussian09.²² The time-dependent (TD-DFT) calculations were done at the same level of theory. ΔG^*_{MH} in Table 2 was evaluated from equation (1) and the computed data. The transition state was optimized at constrained geometries, imposing either C_i or C_s symmetry where possible. The nature of the stationary states was characterized by frequency calculations, which gave one imaginary frequency in most cases. In some cases we obtained zero or two imaginary frequencies. The hypersurface is so shallow in this region that we nonetheless assume that these structures correspond closely to the true transition state.

ESR Spectroscopy. We measured temperature-dependent ESR spectra of the radical cations in fluid PhNO₂ and oDCB between 280 and 360 K and in DCM between 220 and 300 K in order to determine the HT barriers. For some compounds in oDCB and in DCM we experienced instability approaching rt and above. Therefore, only measurements at lower temperature were used for the analysis and the reported rate constant at 295 K (see Table 1) was estimated by extrapolation. The radical cations were generated at a concentration of ca. 1×10⁻⁴ M by oxidation with tris(bromophenyl)ammonium hexachloroantimonate (Aldrich). ESR measurements were performed on a Bruker ELEXSYS E-500 X-band ESR spectrometer or on a Bruker ELEXSYS E-580 CW/FT spectrometer equipped with a digital Bruker-temperature control unit. Variable temperatures were kept constant at \pm 0.5 K. Experimental details concerning the sample preparation and handling, the ESRspectroscopic measurements, and the evaluation of the rate constants from line-broadening effects are all explained in detail in our previous paper.^{10b} HT rate constants k_{ESR} were determined from lineshape analysis using hyperfine coupling constants determined from model compounds with only one triarylamine as given in references.¹⁰ In particular, we used the hfc of two triarylamine ortho-protons of the two anisyl groups (4 x $a_{\rm H,1}$ = 0.188 mT) and the two ortho-protons of the phenylene ring, which is joined to the bridge (2 x $a_{\rm H,2}$ = 0.159

mT). The nitrogen hfc (ca. 0.9 mT) was freely fitted for each spectrum at each temperature as it is slightly temperature dependent. All other hfcs are very small and were neglected. Activation barriers were then obtained by linear fits of $\ln(k_{ESR} / \sqrt{T})$ vs. 1/*T*.

Associated Content

Supplementary information

Experimental and computational details. This material is available free of charge via internet at http://pubs.acs.org.

Author Information

Corresponding Author

christoph.lambert@uni-wuerzburg.de

Notes

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(20) For example, further increasing the coupling to $V_{12} = 1000 \text{ cm}^{-1}$ gave $k_{\text{TST}} = 41 \times 10^7 \text{ s}^{-1}$ but a much too low barrier ($\Delta G^* = 1125 \text{ cm}^{-1}$). On the other hand, increasing the reorganization energy by 3000 cm⁻¹ ($\lambda_0 = 9000 \text{ cm}^{-1}$) yielded a reasonable barrier ($\Delta G^* = 1841 \text{ cm}^{-1}$) but a much too small rate constant ($k_{\text{TST}} = 1.2 \times 10^7 \text{ s}^{-1}$)

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