

Electron Transfer from C₇₆ (C_{2v}') and C₇₈ (D₂) to Radical Cations of Various Arenes: Evidence for the Marcus Inverted Region

Dirk M. Guldi* and Klaus-Dieter Asmus

Radiation Laboratory and Department of
Chemistry and Biochemistry
University of Notre Dame, Notre Dame, Indiana 46556

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One of the most intriguing aspects of electron transfer theories is the characteristic parabolic dependence of the corresponding rate constants on the free energy changes.¹ The range in which the rate constants actually decrease with increasing the free energy toward the highly exothermic region is generally referred to as the Marcus inverted region. Experimental proof of it has been provided, for example, by some elegant pulse radiolysis studies by Miller *et al.* using donor–acceptor systems with rigid frameworks or matrices.^{2–11} Employing a constant distance between the two components eliminates diffusion processes and, consequently, converts the electron transfer to a truly unimolecular reaction controlled only by the activation energy of the electron transfer. Rate constants for bimolecular reactions, on the other hand, consist not only of an activation component (k_{act}) but also include a diffusion related term (k_{diff}), with the latter defining the upper limit of the observable rate. The bimolecular rate constant thus first increases with increasing driving force (i.e., when $k_{\text{diff}} > k_{\text{act}}$) before reaching the diffusional limit (at $k_{\text{diff}} \approx k_{\text{act}}$). However, in most cases, it does not decrease again at higher $-\Delta G$ but stays at this level. Reports on an inverted region for true bimolecular electron transfer have been scarce and practically limited to back electron transfer reactions within the charge-separated radical pair.^{12–18} The difficulty in determining the inverted region may have various reasons such as a low k_{diff} obscuring the decline of the overall rate and/or a high reorganization energy shifting the maximum of the Marcus relationship to higher $-\Delta G$.

One promising approach to encounter the difficulties is to elevate the diffusion-controlled limit by selecting a system of a large-sized electron donor and small-sized electron acceptor couple. This becomes evident by introducing the Stokes–Einstein relationship for the diffusion coefficient ($D_i = k_b T /$

$6\pi\eta r_i$) into the Smoluchowski equation which yields $\{k_{\text{diff}} = {}^{2/3}RT/\eta 10^3 [(r_1 + r_2)/r_1 + (r_1 + r_2)/r_2]\}$. The rate constant assumes its lowest value for equally sized reaction partners ($r_1 = r_2$) but increases with increasing difference between r_1 and r_2 . In combination with solvents of relatively low viscosity, a significantly large enough difference between k_{diff} and k_{act} at higher $-\Delta G$ is ensured. Another possibility is to look for systems with a small solvent reorganization energy, λ_s , because this facilitates reaching the maximum of the exothermic electron transfer process at lower $-\Delta G$ (and thus reaching the inverted region at lower energy). It appears that fullerenes are not only suited to improve on k_{diff} but also on λ_s . Concerning λ_s the pronounced possibility for charge and energy delocalization within the fullerene moiety may be expected to exert an effect in the desired direction as it minimizes vibrational differences between the reaction partners in the ground and transition state.

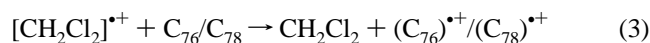
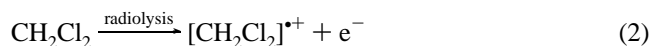
Fullerenes are also excellent candidates for the purpose of this investigation since they readily undergo redox reactions yielding easily detectable radical anions and cations. For the envisaged electron transfer reactions, we have chosen C₇₆ (C_{2v}') and C₇₈ (D₂), which exhibit particularly low ionization potentials of 7.10 and 7.05 eV, respectively,^{19,20} are available in sufficient quantities.

The reaction under investigation here is the electron transfer from the ground state of these C₇₆ and C₇₈ fullerenes to radical cations of various arenes, i.e.,



This reaction yields the radical cation of the fullerene and can conveniently be monitored through either the formation of the latter or the decay of the arene radical cations, since both species exhibit distinct optical absorptions.²¹ The technique chosen for experimental verification was pulse radiolysis, known to be one of the most powerful tools to investigate reactive intermediates.

The electron transfer studies were carried out in deoxygenated CH₂Cl₂ which, upon radiolysis, leads to the generation of the solvent radical cation ($[\text{CH}_2\text{Cl}_2]^{\bullet+}$). This species is a strong oxidant capable of oxidizing many organic compounds, including arenes and fullerenes.^{22–24} Direct oxidation of C₇₆ and C₇₈ (4.0×10^{-5} M) by $[\text{CH}_2\text{Cl}_2]^{\bullet+}$, conducted in deoxygenated solutions via the sequence of reactions shown in eqs 2 and 3, has been carried out to characterize the radical cations of the fullerenes.^{21,25–27} Differential absorption spectra recorded upon



pulse radiolysis for the C₇₆-containing solutions exhibited the

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- (27) The electron, after solvation, will react with the solvent to yield Cl⁻ and •CH₂Cl with the latter possibly adding to the fullerenes. Spectroscopically, these processes are clearly distinguishable from the radical cation formation.

Table 1. Rate Constant for Electron Transfer from C₇₆ (C_{2v}⁺) and C₇₈ (D₂) to Various (Arene)⁺ in Dichloromethane at Room Temperature

compound	IP [eV] ^a	<i>k</i> _{obs} [M ⁻¹ s ⁻¹]		monitored wavelength [nm] ^b
		C ₇₆	C ₇₈	
durene	8.2	6.6 × 10 ⁹	6.9 × 10 ⁹	330
naphthalene	8.15	8.9 × 10 ⁹	9.3 × 10 ⁹	400
<i>m</i> -terphenyl	8.01	1.1 × 10 ¹⁰	1.5 × 10 ¹⁰	410
biphenyl	7.95	2.0 × 10 ¹⁰	2.5 × 10 ¹⁰	400
hexamethylbenzene	7.9	2.1 × 10 ¹⁰	2.0 × 10 ¹⁰	340
triphenylene	7.86	2.9 × 10 ¹⁰	2.3 × 10 ¹⁰	400
phenanthrene	7.85	3.0 × 10 ¹⁰	2.5 × 10 ¹⁰	380
fluorene	7.78	3.2 × 10 ¹⁰	2.9 × 10 ¹⁰	400
9-anthraldehyde	7.69	2.9 × 10 ¹⁰	3.0 × 10 ¹⁰	480
chrysene	7.59	4.5 × 10 ¹⁰	4.2 × 10 ¹⁰	400
9,10-dibromoanthracene	7.58	2.8 × 10 ¹⁰	2.7 × 10 ¹⁰	460
anthracene	7.45	1.5 × 10 ¹⁰	1.7 × 10 ¹⁰	430
pyrene	7.41	1.0 × 10 ¹⁰	1.1 × 10 ¹⁰	440
coronene	7.29	3.6 × 10 ⁹	<i>c</i>	400
9-anthracenemethanol	7.21	7.8 × 10 ⁸	2.0 × 10 ⁹	460

^a Taken from ref 29. ^b Arene radical cation absorption. ^c Not measured.

formation of a transient with a distinct maximum at 960 nm, accompanied by additional absorptions at 550 and 770 and a shoulder at 1050 nm. In analogy to those of C₆₀ and C₇₀, these absorption bands are attributed to the π-radical cations of the fullerenes, formed with a rate constant *k*₃ (C₇₆) > 2.0 × 10¹⁰ M⁻¹ s⁻¹. The spectral assignment is further substantiated by similar absorption features recently reported for a synthetic [(C₇₆)⁺][CB₁₁H₆Br₆⁻] salt (hexabromocarborane).²⁸ Corresponding near IR features for C₇₈⁺ were much weaker showing, however, also a distinct band around 980 nm. The assignment of the infrared bands to the radical cations of the fullerenes is further corroborated by the decay kinetics of the latter.

In analogy to eq 3, arene radical cations were generated via eq 4, e.g., with deoxygenated CH₂Cl₂ solutions containing 2 × 10⁻² M of the respective arenes. The formation and lifetime



of the various (arene)⁺ radical cations were monitored via their respective absorptions in the UV-vis region (see Table 1). Addition of variable amounts of C₇₆ and C₇₈ in the 10⁻⁵ M concentration range resulted in an accelerated decay of the respective radical cation absorption of the arenes with rates linearly depending on the fullerene concentration. At the same time, formation of the fullerene radical cations was observed in the near IR, suggesting the underlying process to be an intermolecular electron transfer according to eq 1. The bimolecular rate constants *k*₁ obtained for a large number of arenes with ionization potentials ranging from 7.21 eV (9-anthracenemethanol)²⁹ to 8.2 eV (durene)²⁹ are listed in Table 1.

As a consequence of the irreversible character of most of the oxidation processes of the arenes in electrochemical experiments, it is probably not feasible to correlate any measured half-wave potentials with -Δ*G*. The driving forces of eq 1 were, therefore, related to the difference in the respective ionization potentials of the arenes and the fullerenes (-Δ*G* = ΔIP = IP_{arene} - IP_{fullerene}). The corresponding relationship of the measured rate constants for the electron transfer reactions, *k*₁, versus these -Δ*G* values are shown in Figure 1a,b for C₇₆ and C₇₈, respectively. In both cases, a pronounced parabolic dependence is observed as it is expected for a Marcus-type behavior. Both maxima appear around 0.6 eV, corresponding to a total reorganization energy of 13.8 kcal mol⁻¹. This value is in

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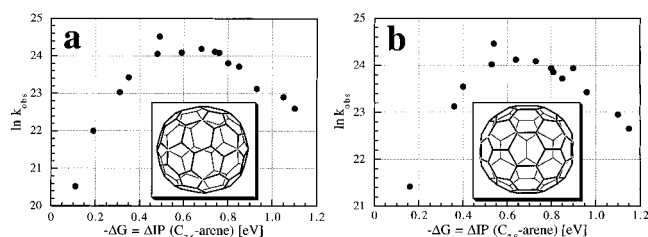


Figure 1. Plot of ln *k*_{obs} for electron transfer from (a) C₇₆ (C_{2v}⁺) and (b) C₇₈ (D₂) to (arene)⁺ in dichloromethane at room temperature as a function of the free energy changes for the reactions.

excellent agreement with those calculated from the classical dielectric continuum model (eq 5) for the different arenes (*λ*_s = 11.14–16.33 kcal mol⁻¹) with the radii of the reactant (*r*₁ and *r*₂), refraction index (*n* = 1.424) of the solvent, and dielectric constant (*ε* = 9.08) of the solvent. Furthermore, it is noted that the total reorganization energy is relatively small. A similar conclusion has recently been forwarded by Imahori *et al.* for C₆₀-related electron transfer reactions.³⁰

$$\lambda_s = \left\{ \frac{1}{2r_1} + \frac{1}{2r_2} + \frac{1}{r_{12}} \right\} \left\{ \frac{1}{n^2} - \frac{1}{\epsilon} \right\} (\Delta z e)^2 \quad (5)$$

Since the total reorganization energy consists of two major contributions, namely, the solvent-related term (*λ*_s) and a parameter (*λ*_v) reflecting the changes in internal vibrational modes it appears that the latter are of lesser importance in our systems. Minor vibrational differences in the oxidized state of the fullerene relative to its ground state can be rationalized in terms of the large degree of electron and energy delocalization within the resonance structure of the π-system of the fullerene. This is also manifested in small Raman and Stokes shifts, as verified, for example, upon reduction and photoexcitation of fullerenes.^{31,32}

The relatively low reorganization energy is clearly beneficial for the possibility of establishing a Marcus-inverted region. Equally favorable is undoubtedly the selection of relatively large-sized donor molecules (C₇₆ lattice constant of 15.3 ± 0.1 Å), small-sized acceptor molecules, and a solvent of relatively low viscosity (*η* = 0.414 at 25 °C) which elevate the diffusion-controlled barrier and separate it sufficiently from the actual electron transfer rates. For C₇₆ and naphthalene, for example, a value of *k*_{diff} = 3.0 × 10¹⁰ M⁻¹ s⁻¹ can be computed from Smoluchowski's theory of diffusion-controlled reactions. This is clearly higher than the observed rate constants identifying the latter as a true measure of *k*_{act}. The decline in rate constants at higher -Δ*G* is thus considered to reflect a true Marcus-inverted behavior. The ratio between the maximum rate and the rate at the high exothermic end (durene) in our set of experiments is 7. This is only somewhat smaller than the factor of 30 reported for intramolecular electron transfer reactions in rigid spaced donor-bridge-acceptor dyads.

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