Orbital-Symmetry Effects in Bimolecular Electron-Transfer Reactions: Back Electron Transfer

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Dedicated to Prof. *Nicholas J. Turro* on the occasion of his 60th birthday

Previous work has indicated orbital-symmetry effects upon forward electron transfer in *bi*molecular systems, with magnitude similar to that encountered in rigid *mono*molecular systems. The present work, which employs back electron transfer, supports and extends these earlier findings.

Introduction. – The importance of *bi*molecular electron-transfer reactions in many areas of chemistry, biology as well as industrial applications has led to considerable efforts towards an understanding of the factors which determine their efficiency [1]. It depends decisively on the back electron transfer (BET, with rate constant k_{bet}) within the incipient reactant pair formed after forward electron transfer (ET, with rate constant k_{et}). Several strategies have been proposed to reduce k_{bet}, among them the application of orbital symmetry (OS) restrictions. For a collection of pertinent references up to *ca.* 1995 we refer to [2], for later work to [3].

Most work cited above made use of *mono*molecular systems where the relative orientation of the donor (**D**) and the acceptor (**A**) moieties were fixed with the aid of a rigid spacer network. However, in [2] we could present evidence for the operation of OS effects also in *bi*molecular ET systems, *i.e.*, where **D** and **A** must first diffuse together before reaction can take place. We made use of two complementary vinylogous three-membered series of donors exhibiting about equal ET-driving force, but with frontier orbitals of alternating symmetry habitus. This led to the prediction of alternating forward ET-allowedness/forbiddenness which experimentally was borne out by an oscillatory or 'zig-zag' behavior of the rate constants k_{et}, if the two series were viewed in a complementary fashion.

We were guided in this strategy by the fact that the melting points of even- and odd-membered linear alkanes show an oscillatory behavior when plotted against chain length [4]. This alone brings to light a fundamental difference in the nature of the crystal packing between these two classes of compounds, regardless of its physical origin.

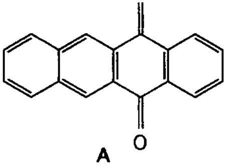
We now report evidence for OS effects in BET processes occurring in an ion pair ($\mathbf{D}^{+\cdot} \cdot \mathbf{A}^{-\cdot}$). It was formed upon diffusive encounter of **D** and excited **A*** to yield the complex ($\mathbf{D} \cdot \mathbf{A}$)* which then underwent primary forward ET. It is true that, kinetically viewed, BET is of *mono*molecular nature. In fact, it is exactly this feature which *ca.* ten years ago allowed to demonstrate unequivocally the '*Marcus* inverted region'. Only recently were appropriate conditions found to show it also in the case of *bi*molecular reactions [5]. Here, we apply the notion '*bi*molecular' rather in a structural sense as in our systems the reactants are not covalently linked and are, therefore, free to reach an optimal arrangement for BET.

Experimental. – The transient absorption (TA) and transient photocurrent (TP) apparatus have been described in [6]. They allow simultaneous observations of the optical and electrical events. Single-shot mode was used to prevent degradation of the solns. The energy of the laser pulses was monitored with an integrated photodiode which led to an assessment of the pulse variations and to the normalization of the peak currents.

These techniques allowed the measurement of the quantum yield of the primary forward ET (Φ_{et}) and of the subsequent free-ion formation process (Φ_{ion}). For the rate of separation of the ions, $k_{sep} = 5 \cdot 10^8 s^{-1}$ was taken from [7]. The presently decisive rate constant k_{bet} was obtained from the relationship $\Phi_{ion} = \Phi_{et} (k_{sep}/(k_{sep} + k_{bet}))$. The TP determination of Φ_{ion} was based on the calibration with the well-known system triplet benzophenone/DABCO in MeCN for which the mean value $\Phi_{ion} = 0.9$ was taken from the data in [8].

The acceptor 5,12-tetracenequinone (*Aldrich*) was recrystallized from Et_2O/tetrachloroethane. The donors (*Aldrich*, *Fluka* or *Lancaster*) were purified by standard procedures. The solvent MeCN (*Rathburn*) was dried by refluxing over P_2O_5, then distilled over a molecular sieve, and then redistilled. After every experiment, the H_2O content of the solns. was determined by *Karl-Fischer* titration; it did not exceed 50 ppm. The solns. were deoxygenated by Ar bubbling. Attention was paid to keep the concentrations of all reactants as low as possible in order not to change the dielectric properties of the solvent.

Results and Discussion. – The common acceptor 5,12-tetracenequinone (**A**) was employed for the following reasons: *1*) It absorbs at longer wavelength than any of the employed diphenylpolyene donors **D** and can be excited with the frequency-doubled YAG-laser emission at 532 nm without coexciting any of the **D**'s. (Applying the frequency-tripled emission at 355 nm whenever **D** was not also coexcited led to results consistent with those obtained at 532 nm.) *2*) It is sufficiently soluble in MeCN (10^{-3} M) for obtaining an absorbance of 0.1 at 532 nm. *3*) It is a triplet quenchee whose long life time (see the data given in the *Table* based on [9]) allows efficient quenching by ET donors at such low concentrations as not to change the dielectric properties of the solvent. Note that its large phosphorescence life time $\tau_P = 420$ ms (*i.e.*, two orders of magnitude longer than that of triplet anthraquinone which emits from a state of n-π^* nature) is due to its emission from a state of π-π^* nature whose decay to the ground state is forbidden [9]. *4*) After forward ET it leads to triplet ion pairs $^3(\mathbf{D}^{+\cdot} \cdot \mathbf{A}^{-\cdot})$ whose BET to the ground state is slowed down by spin restrictions [10]. Therefore, slight differential effects due to OS can be expected to better express themselves. *5*) After ET, the unpaired electron occupies the LUMO in $\mathbf{A}^{-\cdot}$ which, considering only the quinone unit of the molecule in view of the predominant localization of the spin density in this moiety [11], behaves antisymmetric (*as*) with respect to the C_2 axis passing through its center. The present symmetry considerations for BET are based on this assumption.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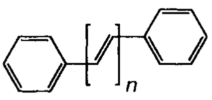
D(*n*); *n*=1–4

For the donors **D** the series of conjugated diphenylpolyenes **D**(*n*) with $n = 1-4$ was chosen where *n* denotes the number of C=C bonds in the conjugated polyene unit. This four-membered series of C_{2h} symmetry provides an improved testing ground for the expected 'zig-zag' behavior of a physico-chemical property with respect to the limited one employed in [2].

In view of what was said above about **A**, this choice finally allowed to consider for the intermediate ion pair a structure exhibiting a C_2 axis of symmetry, given that the decisive subunit of **A** and of all of the diphenylpolyene donors **D** possess this symmetry element. The values for k_{sep} (cited above) and k_{bet} (*cf. Table*) indicate that there is ample time for an internal rotational rearrangement of the two components from their relative orientation achieved after forward ET to the optimal one for decaying along BET.

Frontier-Orbital Symmetries in the Reactants. From elementary theory it follows that the frontier orbitals HOMO and LUMO of the series **D**(n) exhibit opposite symmetry habitus with respect to the C_2 axis (denoted below as *s* = symmetric and *as* = antisymmetric) which furthermore alternates along the series:

	D(1)	**D**(2)	**D**(3)	**D**(4)
HOMO	*s*	*as*	*s*	*as*
LUMO	*as*	*s*	*as*	*s*

Orbitals Involved in BET and Products Resulting Thereafter. The data in the *Table* show that the triplet energies of all diphenylpolyene donors are lower than that of **A**. Hence, BET within $^3(\mathbf{D}^{+\cdot} \cdot \mathbf{A}^{-\cdot})$ can either lead to ground state $^1\mathbf{D}$ and $^1\mathbf{A}$ by ET from the LUMO(**A**) to the HOMO(**D**) with concomitant spin flip (*Path 1*), or to $^3\mathbf{D}^*$ and ground state $^1\mathbf{A}$ involving the LUMO(**A**) and the LUMO(**D**) without spin flip (*Path 2*). Obviously, a resolution of this question is important as the OS predictions are opposite for the two cases: For *Path 1* the symmetries of the relevant orbitals coincide for **D**(2) and **D**(4), rendering BET allowed between the cations of these donors and $\mathbf{A}^{-\cdot}$, whereas for BET *Path 2* is favored for **D**(1) and **D**(3).

A logical experiment to examine this question was to search for the rise of the T-T absorption of $^3\mathbf{D}^*$ after BET. Unfortunately, these absorptions lie in the 400-nm region [12] where **A**, being regenerated upon BET, absorbs strongly.

A less direct approach is to compare the results for the diphenylpolyenes **D**(*n*) with those for donors whose triplet energy is higher than that of **A**, rendering population of their triplet states after BET energetically unfeasible. Hence, decay of the triplet ion pair is only feasible along *Path 1*. The *Table* lists some test donors of benzene and biphenyl type, as well as DABCO (= 1,4-diazabicyclo[2.2.2]octane). The resulting $^3(\mathbf{D}^{+\cdot} \cdot \mathbf{A}^{-\cdot})$ all show significantly higher values for Φ_{ion} and lower values for k_{bet}. The former values indicate increased ionic dissociation, the latter are typical for the rate of spin inversion in triplet ion pairs [13]. Note that a dominant effect due to driving force differences can be excluded as the oxidation potentials of the diphenylpolyenes lie well within the range of those spanned by the test donors.

We conclude that this outcome for the test donors expresses the spin restrictions operating in the BET decay of their triplet ion pairs to $^1\mathbf{D}$ and $^1\mathbf{A}$ along *Path 1*. Accordingly, we conclude for the diphenylpolyenes **D**(*n*) that BET produces $^3\mathbf{D}^*$ and $^1\mathbf{A}$ along *Path 2*, as here no spin inversion and less conversion of potential energy into heat is involved. It follows that the relevant orbital interactions and ensuing OS predictions apply as summarized in the *Table* and visualized in *Fig. 1*.

Table. *Physical Properties of the Donors* **D**(n), *Orbital-Symmetry Predictions for Back Electron Transfer* (BET) *within the Complex* $^3(\mathbf{D}^{+\cdot} \cdot \mathbf{A}^{-\cdot})$ *Yielding* $^3\mathbf{D}^* + {}^1\mathbf{A}$ (*i.e.*, *Path 2*, see text), *Free Ion Yields* Φ_{ion}, *Rate Constants log* k_{bet} (in MeCN), *and Free Energies* ΔG_{bet} (neglecting the C term in the solvent MeCN). Data for substituted benzenes, substituted biphenyls, and for DABCO are given for comparison. The acceptor **A** is 5,12-tetracenequinone with the physical constants: $E_T = 2.53$ eV, $E_{red} = -1.0$ V in DMF *vs.* SCE, $\tau_p = 420$ ms, $\Phi_P = 0.14$ in EPA at 77 K (data from [9]). The LUMO of **A** is antisymmetric (*as*) with respect to the C_2 axis.

Donors **D**(*n*)	IP_a/eV	Ref.	E_{ox}/V in MeCN, *vs.* SCE	Ref.	E_T/eV	Ref.	Symmetry of LUMO of **D** with respect to C_2 axis	BET is	Φ_{ion}	log k_{bet}	ΔG_{bet}/eV
D(1)	7.48	[15]	1.48	[21]	2.17	[12]	*as*	allowed	0.01	10.62	−0.31
D(2)	7.27	[15]	1.23	[22]	1.82	[12]	*s*	forbidden	0.03	9.82	−0.41
D(3)	7.05	[15]	1.07	[22]	1.47	[12]	*as*	allowed	0.03	10.22	−0.60
D(4)	6.82	[15]	0.96	[22]	1.24	[12]	*s*	forbidden	0.14	9.49	−0.72
1,4-Dimethylbenzene	8.44	[16]	1.84	[23]	3.49	[27]			0.32	9.02	
1,4-Dimethoxybenzene	7.53	[17]	1.34	[23]	3.40	[a]			0.77	8.17	
1,1′-Biphenyl	8.05	[18]	1.78	[23]	2.85	[27]			0.44	8.80	
4,4′-Dimethyl-1,1′-biphenyl	7.35	[18]	1.46	[24]	2.75	[28]			0.37	8.93	
4,4′-Dimethoxy-1,1′-biphenyl	7.48	[19]	1.30	[25]	2.70	[a]			0.44	8.80	
DABCO	7.10	[20]	0.57	[26]	>3.90	[29]			0.77	8.17	

[a] Estimated value.

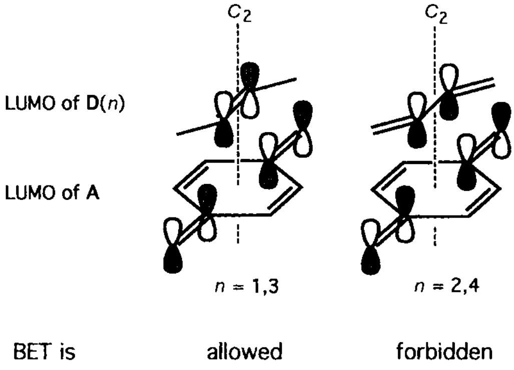

Fig. 1. *Relevant atomic interactions between the frontier orbitals involved in the BET process according to* Path 2. Overlap situations corresponding to 'allowed BET' and to 'forbidden BET' are depicted (see text).

These conclusions are supported by the proper oscillatory or 'zig-zag' behavior of the rate constants k_{bet} as given in the *Table* and visualized in *Fig. 2*, those for **D**(1) and **D**(3) being clearly larger than those for **D**(2) and **D**(4).

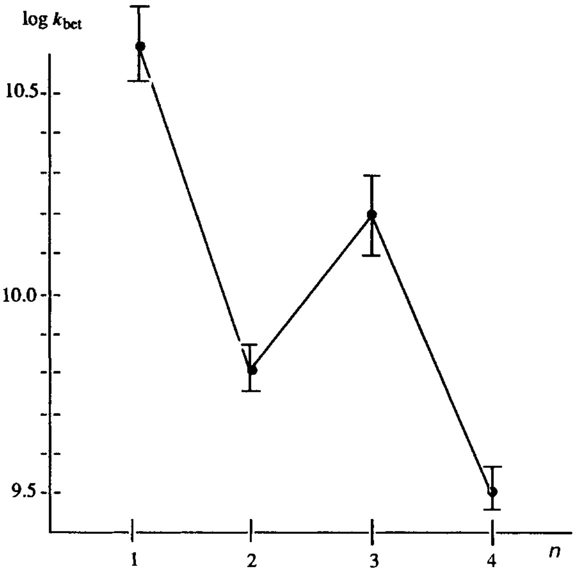

Fig. 2. *Evidence for the operation of orbital-symmetry factors: 'zig-zag' behavior of the rate constants for BET as a function of the number of double bonds* n *in the systems* **D**(n), n = 1–4 (see text)

Conclusions. – In our previous work on forward ET in *bi*molecular systems [2], we concluded that the OS effect manifests itself, its magnitude being similar to that observed in rigid *mono*molecular systems [14] where the ratio of the rate constants between allowed and forbidden situations did not exceed one order of magnitude. The present work on BET is in line with these earlier findings.

Although the observed OS effect is relatively small, it nevertheless may be partly responsible for the scatter of points in many published *Rehm-Weller* plots where it was generally not taken into account. It may also be employed in the fine tuning of BET rate constants.

Two final remarks are appropriate: *1*) Contrary to the situation encountered in [2], the driving force for the present systems is not constant but increases with increasing number n of C=C bonds of **D**(n) as shown in the *Table*. Theory predicts that ET rate constants correlate smoothly with the associated driving force. Hence, the presently observed 'zig-zag' behavior of k_{bet} cannot be due to a nonconstant driving force along the series. *2*) It is at first sight remarkable to find this OS effect at all in our non-rigid systems. From the orbital interaction diagram above it follows that the prediction of 'forbiddenness' (*i.e.*, zero-overlap situations) is independent from the relative rotational angle of the partners. But this is not so for the 'allowed' case where overlap depends critically upon this angle. Importantly, any departure of the complex from idealized axial symmetry will weaken the presently employed selection rule. The actual observations result from a superposition of BET events in individual $^3(\mathbf{D}^{+\cdot} \cdot \mathbf{A}^{-\cdot})$ geometries. It appears that in the 'allowed' cases of **D**(1) and **D**(3) those geometries of the complexes are preferentially populated which result in optimal overlap for fast BET.

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