4484 J. Am. Chem. Soc. 1990, 112, 4484-4489

Electron-Transfer Reactions of Radical Anions: Do They Follow Outer- or Inner-Sphere Mechanisms?

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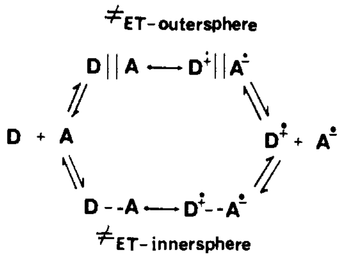
Abstract: From the valence bond curve crossing model, it is predicted that an electron-transfer (ET) reaction between an organic radical anion and an even-electron organic species should proceed by an inner-sphere ET mechanism. The resonance interaction in the transition state, B(inner-sphere), is estimated for two model reactions, (a) the self-exchange reaction between a radical anion and its parent compound and (b) the dissociative ET reduction of alkyl halides by radical anions. For reactions of type (a) B(inner-sphere) is estimated to be in the range of 2.3–7 kcal mol^{-1} (from transfer integrals in organic conductors), 5.7 kcal mol^{-1} (from an analysis by the Marcus theory of heterogeneous and homogeneous ET rate constants), 2.5 kcal mol^{-1} (from a comparison between experimental and calculated reorganization energies) and 4.1–5.5 kcal mol^{-1} (from a consideration of the distance dependence of intramolecular ET rate constants). For reactions of type (b), B(inner-sphere) comes out at 8.5 kcal mol^{-1} (from an analysis by the Marcus theory of heterogeneous and homogeneous ET rate constants) or 4.0 kcal mol^{-1} (from a comparison of experimental and calculated reorganization energies). The distinction between the inner-sphere ET mechanisms (a and b) and their corresponding bond-forming mechanisms is discussed and shown to emerge naturally from considerations of the inherent bonding properties of the configurations which participate in the curve crossing diagram. Accordingly, the transition state for the bond-forming mechanism is shown to be more distorted (relative to reactants), tighter, and with a larger B in comparison to the situation in the inner-sphere ET mechanism.

It is almost a convention nowadays to discuss slow organic electron-transfer (ET) reactions in terms of the outer-sphere mechanism,[1] in which the transition state is weakly bonded, with an electronic interaction between the reactants of ≤ 1 kcal mol^{-1}. This concept is both convenient and important since it allows us to pattern a great deal of experimental data in terms of the Marcus equation for outer-sphere ET processes.[2] This permits a simple and heuristically useful treatment on the basis of classical theory. To mention an example from organic chemistry, the outer-sphere assumption is very useful for devising experimental tests which distinguish between the S_N2 and ET mechanisms, in nucleophilic substitution reactions which yield only substitution products,[3-5] and for probing the structure of the transition state in S_N2 reactions by reference to an outer-sphere analogue.[6]

Transition-state structure is the foundation of mechanistic thinking in organic chemistry,[7] but the outer-sphere notion brings "structurelessness" into the thinking and conflicts thereby with traditional intuition about transition states. If bonding is so important in transition states of organic reactions, why then should ET reactions avoid this bonding and have nonbonded transition states?

Scheme I summarizes the ET mechanisms for a donor, D, and an acceptor, A. As can be seen, there exists an alternative for an outer-sphere ET step, and this is the inner-sphere mechanism,[8] where the donor and the acceptor moieties maintain a substantial interaction in the transition state. This has been amply demonstrated by Kochi and collaborators[9] who have emphasized the importance of charge-transfer complexes as precursors in ET reactions of alkenes and arenes. However, the inner-sphere interaction cannot be quantified in terms of the Marcus treatment and is therefore not a very convenient starting point for mechanistic studies of the type described above.[3-6] Despite this drawback, the inner-sphere mechanism is a viable alternative to the outer-sphere mechanism, certainly more in line with organic chemical thinking about transition-state structure and bonding. Yet, if we accept the inner-sphere case this leaves us with a new dilemma, namely to understand the difference between the inner-sphere ET mechanism and the polar, bond-forming mechanism which leads to substitution or addition products in a single step.[10] We thus have a double-headed problem: what is the nature of the ET transition state, and, if it has an inner-sphere structure, then what is its relationship to the transition state of a bond-forming polar mechanism?

Scheme I



The main purpose of this paper is to answer the above questions for bimolecular ET reactions in which one component involves

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(2) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265. (c) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: Heidelberg, 1987. This source gives a general review of the topic in organic chemistry and the use of the Marcus treatment as a means of organizing existing knowledge about organic ET reactions.

(3) (a) Lund, H.; Kristensen, L. H. *Acta Chem. Scand.* 1979, *B33*, 495. (b) Lund, T.; Lund, H. *Acta Chem. Scand.* **1986**, *B40*, 470. (c) Lund, H. *Tetrahedron Lett.* **1986**, *27*, 95.

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(5) Reference 2c, p 197.

(6) Lund, T.; Lund, H. *Acta Chem. Scand.* **1988**, *B42*, 269.

(7) "Transition-state structure" is an important branch of physical organic chemistry and related biochemical areas. See, e.g.: (a) Schowen, R. L. In *Transition States of Biochemical Processes*; Gandour, R. D., Schowen, R. L., Eds.; Plenum Press: New York, 1978. (b) Jencks, W. P. *Chem. Rev.* **1985**, *85*, 511. (c) Thornton, E. K.; Thornton, E. R. In *Transition States of Biochemical Processes*; Gandour, R. D., Schowen, R. L., Eds.; Plenum Press: New York, 1978. (d) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row, Publ.: New York, 1987; pp 203–247.

(8) (a) Reference 2c, p 14. (b) Reference 1, p 185.

(9) (a) For recent reviews, see: Kochi, J. K. *Angew Chem., Int. Ed. Engl.* **1988**, *27*, 1227; *Acta Chem. Scand.* **1990**, *44*, xxxx. (b) See, also: Schlesener, K.; Amatore, C.; Kochi, J. K. *J. Phys. Chem.* **1985**, *89*, 3747.

(10) For a discussion of the ET-polar dichotomy, see: Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212.

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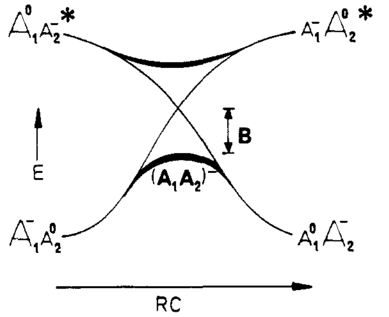

Figure 1. An avoided crossing diagram for the ET between two identical molecules (except for the charge). The large A indicates the geometry of the radical anion, while the small A indicates the geometry of the neutral molecule. At the crossing point the geometry is intermediate and represented by boldface, identical letters.

an *odd electron species*, i.e., radical anions or radical cations. Thus we will analyze cases of ET reactions of *radical anions* ($A^{\bullet-}$) in nondissociative and dissociative processes (eq 1 and 2), and we shall project the differences between the inner-sphere ET and the alternative bond-forming processes, i.e., addition and substitution, respectively. The analysis will involve theoretical considerations and examination of experimental data. As will be seen, available

$$A_1^{\bullet-} + A_2 \rightleftharpoons A_1 + A_2^{\bullet-} \qquad (1)$$

$$A^{\bullet-} + R\text{-}X \rightarrow A + R^{\bullet} + X^- \qquad (2)$$

evidence has a heavier weight in favor of the inner-sphere ET mechanism in cases of odd-electron reactants. This leaves the outer-sphere model as a rare phenomenon, at least in organic *ET reactions of odd-electron reagents*,[11] confined to situations where judicious choice of structural features of the reagents make the outer-sphere step a default option.[12]

Discussion

A. A Theoretical Analysis. Aromatic and other flat conjugated molecules constitute the typical reactants of eq 1.[2c,13] Let us consider then *two identical molecules* (A) undergoing electron transfer, for example, naphthalenide anion and naphthalene. The radical anion and the neutral molecule possess slightly different equilibrium geometries.[14] For simplicity we may indicate the geometry of the radical anion by a larger letter than that of the neutral molecule, as shown in Figure 1.

In the ground state of Figure 1, the anion and the molecule are in their relaxed equilibrium geometries, and the solvent molecules also occupy equilibrium positions which match the charges of the two molecular species. In the excited states the geometries and the charges are in mismatch. The star in the excited states indicates that the solvent molecules now occupy nonequilibrium positions, in mismatch with the charges of the molecular species.[2a,14a]

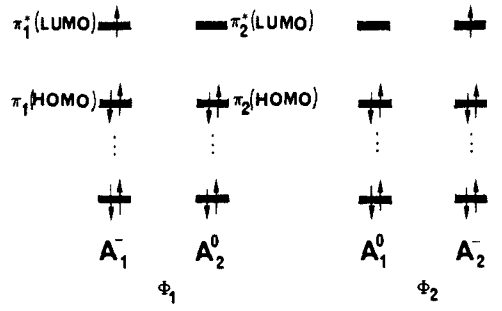

Figure 2. MO representations of the $A_1^-A_2^0$ and $A_1^0A_2^-$ configurations at the crossing point of Figure 1. The resonance interaction is proportional to the overlap of the orbitals which participate in the electron shift, i.e., $B \propto$ overlap(π^*_1 and π^*_2).

The reaction coordinate in Figure 1 refers to the interchanges in the geometries of the molecular species and in the orientations of the solvent molecules, at any given distance $d(A_1A_2)$ between the species. At the crossing point the geometries of the molecules and the solvent orientations around them are identical, and there exists a resonance between the two configurations, **1**. This

$$A_1^-A_2^0 \longleftrightarrow A_1^0A_2^-$$

1

resonance is the cause of the avoided crossing and the resonance energy lowering, *B*.[14]

We emphasize that the individual configurations in Figure 1 and later in Figures 2 and 3 are by themselves nonbonded, and bonding is acquired only by the quantum mechanical resonance mixing at the transition state. Thus, in addition to bond and solvent reorganization, the reaction coordinate will involve an initial approach of A_1 to A_2 to the transition-state distance and then their recoil past the transition state.

A lucid conceptualization of the resonance interaction is achieved if the configurations in **1** are represented in MO terms as in Figure 2. By using simple rules of configuration interaction,[14,15] the reasonance interaction *B* can be shown to be proportional to the overlap between the π^*-LUMO's of the two molecules A_1 and A_2.[14,15]

The degree of avoided crossing in Figure 1 will therefore depend on the LUMO–LUMO overlap which in turn depends on $d(A_1A_2)$. This distance will be determined by a *compromise between the tendency to maximize the avoided crossing interaction and the opposite tendency to minimize the short range repulsive* A_1^0/A_2^- (A_1^-/A_2^0) *interactions* within each configuration. The two opposing effects will reach an optimum at some intermediate $d(A_1A_2)$. We should therefore expect *one or a few distinct transition states with defined structures and $d(A_1A_2)$ which maintain resonance interactions proportional to the LUMO–LUMO overlap of the two species*.

Some preliminary estimates of these resonance interactions can be provided from the studies of the "transfer integrals" in organic conductors.[16,17] In the case of anion radical based conductors (with mixed valence stacks) the transfer integral is identical with the avoided crossing in Figure 1. Experimentally determined transfer integrals for flat π-system stacks are in the range of ≥ 0.1–0.25 eV,[16] and this may be taken as an estimate of *B*. Another source is derived from gas-phase studies of $(A)_2^-$ and $(A)_2^+$ dimers where the resonance interactions range between 0.13 and 0.3 eV.[15,18,19]

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[11] We point out that for even-electron cases as in S_N2 reagents the outer-sphere ET may be the only possible ET process, and our conclusions here do not pertain to such cases. See analysis in Shaik, S. S. *Acta Chem. Scand.* **1990**, *44*, 205. Furthermore, in such (even-electron) systems the bond-forming process is synonymous with the inner-sphere mechanism. For such a definition of the S_N2 mechanism, see: Chanon, M. *Bull. Soc. Chim. Fr.* **1982**, Part II, 197.

[12] Well documented cases of outer-sphere ET involving organic species are rare and in most cases involve reactions between an organic and an inorganic reagent, such as the reaction between tetraalkylstannanes and iron(III)phenanthrolines (see: Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593. Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928) or 12-tungstocobalt(III)ate and 4-methoxytoluene (see Eberson, L. *J. Am. Chem. Soc.* **1983**, *105*, 3192).

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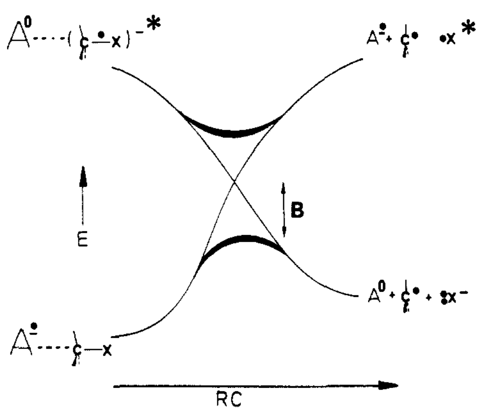


Figure 3. An avoided crossing diagram for a dissociative ET between a radical anion and alkyl–X. The small and large A's have the same meaning as in Figure 1.

The highest estimated gas-phase value is 0.9 eV for quinones.[20] We may therefore bracket the typical B value of inner-sphere ET reactions of the type shown in eq 1 (or an ET reaction between a neutral molecule and a radical cation) in the following range:

$$2.3 \text{ kcal mol}^{-1} \leq B(\text{inner-sphere}) \leq 7 \text{ kcal mol}^{-1} \quad (3)$$

Furthermore, if we accept that the inner-sphere transition state of eq 1 can be modelled by the state of a dimer, $(A_1A_2)^-$ in an organic conductor, we can also estimate the transition-state distance, $d(A_1A_2)$, using crystallographic data.[17] Following this rationale we can sketch an approximate picture of the TS for an inner-sphere mechanism of eq 1, as shown in **2** along with the corresponding B value. In a later section we present an extended and more detailed analysis of experimental data related to the problem of defining B(inner-sphere).

$$A_1 \leftarrow 3.0\text{–}3.5\ \text{Å} \rightarrow A_2$$

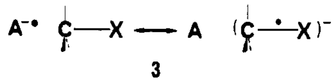
$$B \sim 2.3\text{–}7 \text{ kcal/mol}$$

2

A dissociative ET between a radical anion and an alkyl–X (eq 2) follows a similar rationale. There is one difference now, in that the reaction coordinate also involves stretching of the C–X bond to the point of breaking and movement along the umbrella mode of the valence angles around the carbon, as shown in Figure 3. Past the transition state, the reactants will recoil until virtually full separation of A, R•, and X:⁻ occurs.

As before, the curve crossing will occur at *any* distance d(A--RX), and an optimum distance will be achieved as a result of the tendency to maximize the avoided crossing interaction, on the one hand, and minimize the short-range $A^{\bullet-}$/RX repulsion on the other hand.

In complete analogy to the previous case (eq 1), also here the resonance interactions in the transition state **3** will be proportional



3

to the overlap between the π^*-LUMO of A and the σ^*-LUMO of the stretched C–X bond in the transition state. Since in this case one of the orbitals is more localized (the σ^*-LUMO), it is very likely that the LUMO–LUMO overlap will be larger than that which exists between the two delocalized π^*-LUMO's in the preceding case. Our initial preference is therefore to bracket B(inner-sphere) in the upper half of the range given in eq 3, i.e., $5 \leq B \leq 7$ kcal mol^{-1}, and accordingly the d(A--RX) at the transition state is expected to be approximately 3 Å.

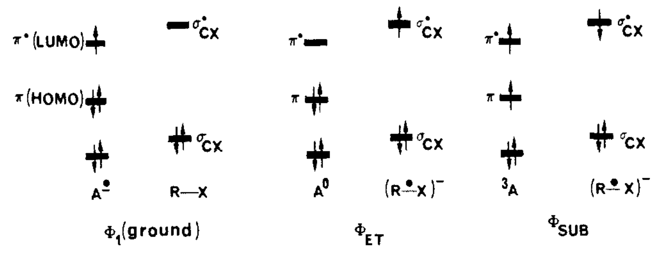
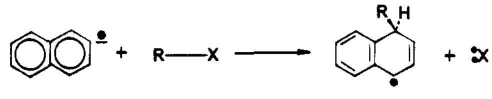


Figure 4. MO representations of the ground state for $A^{\bullet-}$ + R–X and the excited states which participate in avoided crossings of the ET and substitution processes, respectively. Following the caption of Figure 2 the resonance interaction for the substitution process is proportional to the π-HOMO/σ^*_{CX} overlap since these are the orbitals which participate in the electron shift between Φ_I and Φ_{SUB}.

In conclusion of this section, we may say that the inner-sphere mechanism appears to be an optimum choice between the tendency of transition states to minimize intermolecular repulsion and maximize bonding. The outer-sphere alternative constitutes an extreme and mostly idealized situation where intermolecular repulsion is minimized at the expense of nearly zero bonding. This latter kind of mechanism will be reserved for situations where little or no bonding may be achieved by intermolecular approach. Such cases are typical for certain metal complexes in cases where the LUMO is localized on an atom which is highly encumbered sterically,[12] or when one LUMO is extremely delocalized and due to a size mismatch the molecules can maintain only very small LUMO–LUMO overlap due to a small area of contact.

B. The Difference between Inner-Sphere ET and Polar Bond-Forming Mechanisms. A question which emerges from the above analysis is as follows: what is the difference between inner-sphere ET and substitution or addition reactions, as exemplified in eqs 4 and 5, if the B value for the inner-sphere ET reaction is as significant as we think it is?



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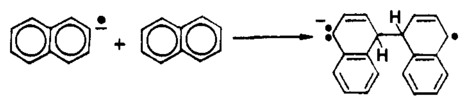

(5)

As has been shown recently,[21] the excited state which participates in the avoided crossing diagram for the substitution process (eq 4) involves a higher degree of excitation relative to the ET process. Figure 4 exemplifies configurations for the reaction between a π-radical anion ($A^{\bullet-}$) and an R–X molecule, and the additional excitation is seen to be a $\pi \rightarrow \pi^*$ singlet → triplet excitation in the neutral A molecule.

The crossing mechanism between the ground (Φ_I) and the Φ_{SUB} excited state cannot occur now at any d(A--RX). Instead the crossing will be promoted mainly due to the coupling of one of the ^{3}A odd electrons with the odd electron of $(R\text{–}X)^{-\bullet}$ in Φ_{SUB} into an intermolecular bond. This coupling will require a short d(A--RX), an extensive cleavage of the R–X bond, and a loss of the planarity of the aromatic molecule. Put differently, because the diagram energy gap for the substitution process is larger than that of the ET process, the crossing will be achieved only if the reactants are closer together in order to enjoy maximum bond coupling in Φ_{SUB}, and if both R–X and A undergo more extensive bond breaking.[22] Typical C–C bond distances in transition states of bond-forming reactions are[23] ≈ 2–2.3 Å and hence much shorter

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than the distances of ≥3 Å in the inner-sphere ET transition state in **2**. This means in turn that B for substitution is going to be larger than the same quantity for the inner-sphere ET step. We except a jump in the magnitude of B(SUB) relative to B(inner-sphere), much the same as the respective diagram gaps differ by a quantum of excitation (Figure 4). For large changes in the gap, the relationships between the corresponding B values will depend on the relative gap sizes,[24] and if we assume for simplicity a linear relation between B and the gaps we may write eq 6:

$$B(\text{SUB}) \approx B(\text{inner-sphere})^*[(\Delta E_{\text{CT}} + \Delta E_{\text{ST}})/\Delta E_{\text{CT}}] \quad (6)$$

Here ΔE_{CT} is the vertical charge-transfer energy gap for the ET process (see Φ_1 and Φ_{ET} in Figure 4), while ΔE_{ST} is the additional singlet → triplet excitation in Φ_{SUB} for the substitution process.

There are two fundamental differences between the inner-sphere ET and the bond-forming mechanism. The first one refers to the orientation of the reactants in the transition state, due to the different orbitals which are responsible for the avoided crossing interaction in the two mechanisms. Thus, following the rules of configuration mixing,[14,22b] B(SUB) will be proportional to the overlap between the σ^*_{CX}-LUMO and the π-HOMO orbitals of the two reactants. In comparison, B(inner-sphere) for the respective ET processes is proportional to the π^*-LUMO/σ^*_{CX} overlap (see discussion above). This difference will be expressed in the structure of the respective transition states; the substitution process will orient the reactants in a manner which optimizes the π-HOMO/σ^*_{CX} overlap, whereas the inner-sphere ET process will orient the reactants so as to optimize the π^*-LUMO/σ^*_{CX} overlap. To generalize also for the reaction in eq 4, we simply replace σ^*_{CX} by the corresponding π^*.

The second fundamental difference between the two mechanisms is the nature of the intermolecular covalent bonding along the reaction coordinate, by appeal to Figure 4. In the ET(inner-sphere) process both configurations, Φ_1 and Φ_{ET}, are nonbonded by themselves and whatever covalent bonding between A and RX is achieved *only* due to the configuration mixing, i.e., the avoided crossing. This in turn means that intermolecular bonding is *maximal* at the transition state, where the avoided crossing occurs, but *bonding diminishes beyond the transition state* toward the reactant and product extremes, where configuration mixing is minimal. Thus, any stereochemical information that builds up in the structure of the ET(inner-sphere) transition state will fade out past the transition state as the two reactants [e.g., A and $(R^\bullet + X{:}^-)$] will separate due to the decreasing configuration mixing. On the other hand, in the substitution mechanism, the Φ_{SUB} configuration is intrinsicially bonded due to pairing up of the odd electrons of the two reactants. This bonding[25] is independent of the configuration mixing and increases with the decrease of the intermolecular distance between A and RX. Thus, past the transition state of the substitution reaction, the reaction profile will be dominated by Φ_{SUB}, and intermolecular bonding $(^3A^*\text{--}R^\bullet)$ will increase gradually all the way to formation of a full bond. Consequently, the sterochemical information (backside attack on RX in accord with the role of the LUMO/σ^*_{CX}) that typifies the substitution transition state continues to build up all along the reaction coordinate, until fully established at the product stage. An analogous discussion is appropriate for the dichotomy of ET(inner-sphere) and addition mechanisms of reactions 1 and 5, respectively.

Table I. Comparison between Calculated and Experimental k_{hom} for A/$A^{\bullet-}$ Reactions in DMF at the Hg Electrode[a]

	k_{het}/	log k_{hom}, $M^{-1}\ s^{-1}$		
compound	cm s^{-1} [b]	calc[c]	exptl	difference[d]
benzonitrile	4.9	4.38	8.78	4.4
4-cyanopyridine	2.0	3.60	8.94	5.3
o-tolunitrile	4.3	4.27	9.00	4.7
m-tolunitrile	4.2	4.25	8.79	4.5
p-tolunitrile	6.6	4.64	9.95	5.3
phthalonitrile	7.4	4.74	9.18	4.4
terephthalonitrile	2.8	3.89	9.30	5.4
nitrobenzene	10	5.00	7.48	2.5
1,3-dinitrobenzene	6.5	4.63	8.78	4.3
1,4-dinitrobenzene	2.2	3.68	8.86	5.2
m-nitrobenzonitrile	5.8	4.53	8.23	3.7
dibenzofuran	21	5.64	9.38	3.7
dibenzothiophene	12	5.16	9.23	4.1
1,4-naphthoquinone	4.6	4.32	8.66	4.3
anthracene	27	5.86	9.52	3.7
perylene	20	5.60	9.68	4.1
naphthalene	23	5.72	8.83	3.1
trans-stilbene	27	5.86	9.11	3.3
α-methyl-*trans*-stilbene	5	4.40	8.15	3.8
hexamethyl-*trans*-stilbene	2.8	3.89	7.78	3.9
tetracene	22	5.68	9.41	3.7
cyclooctatetraene	0.014	−0.70	4.00	4.7

[a] Data were taken from the following: Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317. Huebert, B. J.; Smith, D. E. *J. Electroanal. Chem.* **1971**, *31*, 333. Dietz, R.; Peover, M. E. *Discuss. Faraday Soc.* **1968**, *45*, 155. [b] Corrected for the double layer effect. [c] Calculated from eq 7 with $Z_{\text{hom}} = 10^{11}\ M^{-1}\ s^{-1}$ and $Z_{\text{het}} = 10^4$ cm s^{-1}. [d] The average difference comes out at 4.2 log units.

To summarize, the inner-sphere ET transition state has an isomeric relationship to that of the bond-forming process. The individual reactants in the ET process are significantly less distorted, and their intermolecular distance is *longer*. Owing to the longer intermolecular distance, the sensitivity of ET(inner-sphere) to steric effects is expected to be insignificant in comparison with the bond-forming mechanisms. Moreover, owing to the decrease of intermolecular bonding past the transition state of an ET(inner-sphere) reaction, the stereochemical information (e.g., optical activity) is expected to undergo randomization. These features are observed in the experimental ET data[2c-4] of reactions between radical anions and alkyl halides. We wish to emphasize that these features are expected for an inner-sphere ET mechanism and cannot constitute compelling evidence for an outer-sphere ET mechanism. In fact, the resonance interaction, B(inner-sphere), is a significant quantity ranging between the values in eq 3. If there is provision for intermolecular overlap, the inner-sphere ET transition state will be energetically more favored than the corresponding outer-sphere transition state by approximately the resonance energy quantity, B(inner-sphere). There is no obvious reason to expect formation of the nonbonded and structureless outer-sphere transition state to be the dominant mechanism in ET reactions of radical ions[11] (anions and cations).

C. Analysis of Experimental Data. There are a few experimental results which point to the possibility that ET reactions of radical anions are indeed of the inner-sphere rather than the outer-sphere variety. As an anchor point, we use the assumption that electrochemical ET steps at inert electrodes are of the outer-sphere type, requiring only very weak coupling between substrate and metal orbitals in the transition state of the heterogeneous ET process.[26] We then use the relationship of eq 7, developed by Marcus, between the homogeneous ET rate constant, k_{hom}, of a self-exchange reaction and the corresponding heterogeneous ET

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(23) See, e.g., the C–C distance (a) in S_N2 transition states: Mitchell, D. J.; Schlegel, H. B.; Shaik, S. S.; Wolfe, S. *Can. J. Chem.* **1985**, *63*, 1642. Houk, K. N.; Paddon-Row, M. N. *J. Am. Chem. Soc.* **1986**, *108*, 2659. (b) In radical additions to olefins: Canadell, E.; Eisenstein, O.; Ohanessian, G.; Poblet, J. M. *J. Phys. Chem.* **1985**, *89*, 4856. Arnaud, R.; Elliger, Y.; Subra, R.; Douady, J. *Theochem.* **1984**, *110*, 203. Arnaud, R.; Barone, V.; Olivella, S.; Russo, N.; Solé, A. *J. Chem. Soc., Chem. Commun.* **1985**, 1331. (c) In cycloaddition reactions: Bernardi, F.; Olivucci, M.; McDogall, J. J. W.; Robb, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 544. Bernardi, F.; Bottoni, A.; Robb, M. A.; Field, M. J.; Hillier, I. H.; Guest, M. F. *J. Chem. Soc., Chem. Commun.* **1985**, *1051*. (d) A somewhat shorter C–C distance (1.75 Å) has been computed for the exchange reaction $CH_3^+ + CH_3CH_3 \rightarrow CH_3CH_3 + CH_3^+$, in the following: Lipkowitz, K. B.; Larter, R. M., Boyd, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 85.

(24) A relationship between the gap size and B is discussed in the following: Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J. M. *J. Phys. Chem.* **1988**, *92*, 5086.

(25) This bonding is due to the spin-pairing energy of two electrons (in Φ_{SUB}), much the same as in the Heitler-London wave function. See ref 22b for details.

(26) Hale, J. M. In *Reactions of Molecules at Electrodes*; Hush, N. S., Ed.; Wiley: London, 1971; Chapter 4.

Table II. Comparison between Calculated and Experimental Free Energies of Activation for Alkyl Halide Self-Exchange at the Electrode and in Homogeneous Solution (DMF)[a]

compound	$\Delta G^{\ast}_{het}$, eV	$\Delta G^{\ast}_{hom}$, eV calc[b]	$\Delta G^{\ast}_{hom}$, eV exptl	difference, eV (kcal mol^{-1})[c]
BuI	0.80	1.60	1.18	0.42 (9.7)
BuBr	0.98	1.96	1.38	0.58 (13.4)
sec-BuI	0.79	1.58	1.31	0.27 (6.2)
sec-BuBr	0.90	1.80	1.40	0.40 (9.2)
t-BuI	0.74	1.48	1.21	0.27 (6.2)
t-BuBr	0.93	1.86	1.56	0.30 (6.9)

[a] Data were taken from the following: Andrieux, C. P.; Gallardo, I.; Saveant, J.-M.; Su, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 638. [b] Calculated from eq 8. [c] Average value of difference = 0.37 eV.

Table III. Comparison between Calculated and Experimental Reorganization Energies for A/A$^{\bullet-}$ Couples in DMF Using the Born Equation (the Marcus Spherical Model)[a]

compound	λ, kcal mol^{-1} calc	λ, kcal mol^{-1} exptl	difference, kcal mol^{-1}
naphthalene	17.0	8.2	8.8
anthracene	18.4	8.8	9.6
trans-stilbene	18.2	10.5	7.7
dibenzofuran	19.2	9.3	9.9
benzonitrile	22.5	12.1	10.4
o-tolunitrile	21.3	11.3	10.0
m-tolunitrile	21.3	12.1	9.2
p-tolunitrile	21.3	11.3	10.0
m-nitrobenzonitrile	21.5	15.1	6.4
phthalonitrile	21.7	10.2	11.5
terephthalonitrile	21.7	9.7	12
pyromellitonitrile	21.6	10.9	10.7
pyridine-2-carbonitrile	23.1	11.6	11.5
nitrobenzene	22.1	19.1	2.9
m-chloronitrobenzene	16.7	21.5	4.8
p-chloronitrobenzene	16.9	21.5	4.6
3,5-dichloronitrobenzene	20.9	15.2	5.7
m-dinitrobenzene	21.4	12.2	9.2
p-dinitrobenzene	21.4	11.7	9.7
benzoquinone	22.9	13.1	9.8
1,4-naphthoquinone	20.1	12.8	7.3

[a] Taken from a compilation in ref 28, assuming that λ_i is negligible.

rate constant, k_{het}. Assuming that the collision factors Z_{hom} and Z_{het} are 10^{11} M^{-1} s^{-1} and 10^4 cm s^{-1}, respectively, we calculate

$$0.5 \log(k_{hom}/Z_{hom}) = \log(k_{het}/Z_{het}) \quad (7)$$

by eq 7 the expected values of k_{hom} from known experimental k_{het}, and we then compare k_{hom}(calc) to the experimentally measured rate constants. Table I shows that k_{hom}(calc) are much smaller than the experimentally determined k_{hom}, on the average by a factor of $10^{4.2}$. This corresponds to a B value of 5.7 kcal mol^{-1}, which compares well with the values in eq 3.

Similar data have been given for the dissociative ET reduction of alkyl halides, R–X, except that the data are expressed as free energies of activation for the heterogeneous and homogeneous self-exchange reactions [R–X/(R--X)$^{\bullet-}$], respectively, in which case eq 7 can be transformed into eq 8. Again we use the

$$\Delta G^{\ast}_{hom} = 2\Delta G^{\ast}_{het} \quad (8)$$

electrode kinetics data to calculate a $\Delta G^{\ast}$ for the homogeneous process and compare it with the experimentally determined value (see Table II), and again we find that the calculated rate is much smaller than the experimental one, yielding an average B for the alkyl halides of Table II equal to 0.37 eV or 8.5 kcal mol^{-1}, again in satisfactory agreement with our preceding theoretical analysis.

The cases discussed above both can be said to capitalize on a "failure" of the Marcus theory, embodied in eqs 7 and 8, to correlate kinetic data of heterogeneous and homogeneous ET processes. Our diagnosis is that we should indeed consider the Marcus theory to be correct for outer-sphere ET and instead view the experimental data for homogeneous self-exchange rate constants with some skepticism; maybe they pertain to processes with inner-sphere character? With the latter assumption, a B value can be defined for the inner-sphere process, and in addition we can define a set of new reorganization energies of self-exchange, stripped from the inner-sphere component (see below).

We can go one step further and maintain that the Born equation provides an adequate tool for calculating λ_o, the solvent reorganization energy,[27] which in addition to the bond reorganization energy, λ_i, constitutes the reorganization energy λ of the Marcus treatment (eq 9).[2] For flat aromatic molecules with good possibilities of delocalization it has been estimated that $\lambda_o \gg \lambda_i$ in

$$\lambda = \lambda_o + \lambda_i \quad (9)$$

non-hydrogen-bonding solvents, so that as a first approximation λ can be set equal to λ_o for such molecules, although it should be noted that this has not been established from calculations based on experimentally determined geometries. It is a common conclusion that the Born equation overestimates λ (see Table III),[28] in most cases by ca. 10 kcal mol^{-1}. But does it? It might as well be probable that the calculated λ values are correct for an outer-sphere step and the measured ones tainted by inner-sphere behavior. From this viewpoint we again can estimate a B value (=λ/4), this time of ≈2.5 kcal mol^{-1}. This is a lower limit of B(inner-sphere) which would be larger if the assumption that λ_i is negligible does not hold.

A similar estimate of λ for the dissociative ET reduction of alkyl halides by radical anions can be made. Here λ_i is dominated by the energy required to cleave the C–X bond (the bond energy D_o), whereas λ_o is the mean value of the solvent reorganization energies of the self-exchange reactions A/A$^{\bullet-}$ and R–X/(R--X)$^{\bullet-}$ (eq 10).[29]

$$\lambda(RX/A^{\bullet-}) = D_o + \lambda(A/A^{\bullet-})/2 + \lambda(RX/R\text{--}X^{\bullet-})/2 \quad (10)$$

Table IV shows how $\lambda(RX/A^{\bullet-})$, calculated from eq 10, compares with experimentally derived values. As before, we note that experimental values are smaller than the calculated ones, on the average by 15.8 kcal mol^{-1}, corresponding to B = 4.0 kcal mol^{-1}.

The same conclusion can be reached from a different direction, by appeal to the work of Miller, Closs, and collaborators[13] who have studied intra- and intermolecular ET processes between (biphenyl)$^{\bullet-}$ and a variety of flat conjugated π-systems. The studies involved both intra- and intermolecular processes in ways which allowed control over or estimation of the intermolecular distances. The unequivocal conclusion from these studies is that the ET rate constant falls off exponentially with an increase of the intermolecular distance.[13a,b] This necessarily means that an inner-sphere ET is faster than the outer-sphere alternative. A value of B(inner-sphere) can be estimated from the equation for B which was used by Miller et al. in their rigid matrix study.[13b] By using Miller's experimentally fitted B_o, d^0 and a parameters, and our proposed $d(A_1A_2)$ of ≈3–3.5 Å in the inner-sphere transition state (see **2**) we can extrapolate from eq 11 a B(inner-sphere) in the range of 4.1–5.5 kcal mol^{-1}.

$$B = B_o \exp[-(d - d^0)/2a] \quad (11)$$

$$B_0 = 0.9 \text{ kcal mol}^{-1};\ d^0 = 6 \text{ Å};\ a = 0.83 \text{ Å}$$

It appears then that the inner-sphere mechanism possesses an inherent preference over the outer-sphere mechanism. This preference derives from preferred bonding in the transition state, and this in turn means a well-structured transition state with a defined distance and stereochemistry, albeit this stereochemical information is lost past the transition state.

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[27] For recent analyses of the validity and success of the Born equation, see: (a) Jayaram, B.; Fine, R.; Sharp, K.; Honig, B. *J. Phys. Chem.* **1989**, *93*, 4320. (b) Rashin, A. A.; Honig, B. *J. Phys. Chem.* **1985**, *89*, 5588.

[28] Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79.

[29] Equation 10 follows from the rules given by Marcus for the calculation of reorganization energy in the parabolic approximation. The same expression has been derived by using Morse expressions for describing the potential energy curves, see: Saveant, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 6788.

Table IV. Comparison of Calculated (eq 10) and Experimental Reorganization Energies for Dissociative ET between Alkyl Halides and Radical Anions[a]

compound class	D_0, kcal mol^{-1}	$\lambda(A/A^{\bullet -})$, kcal mol^{-1}	$\lambda(RX/RX^{\bullet -})$, kcal mol^{-1}	$\lambda(RX/A^{\bullet -})$, kcal mol^{-1} calc	$\lambda(RX/A^{\bullet -})$, kcal mol^{-1} exptl	difference, kcal mol^{-1}
RCl	79.8[b]	21[c]	26.2[d]	103.4	87.6[b]	15.8
RBr	67.7[b]	21[c]	25.8[d]	91.1	73.7[b]	17.4
RI	53.7[b]	21[c]	25.5[d]	77.0	62.7[b]	14.3

[a] Experimental data were taken from the following: Saveant, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 6788. [b] Average value for primary, secondary, and tertiary butyl halide. [c] Taken from Table III. [d] Calculated for the spherical Marcus model from the Born equation (see ref 28).

D. Can *B*(inner-sphere) Be Quantified? Clearly, additional experimental verification of the above conclusion is needed for acceptance of the inner-sphere ET mechanism, despite the weight of evidence that already points in this direction. A possible strategy is to emulate the method of Miller and Closs[13] and separate the radical anion ($A^{\bullet -}$) from the acceptor moiety, as illustrated in 4

4

for the dissociative electron transfer. This approach, coupled with studies of the corresponding intermolecular processes will provide an approximative *B* value for the inner-sphere mechanism in the bimolecular case.[30] Alternatively, the size of the spacer in **4** can be varied to study the dependence of the intramolecular rate constant on distance, in much the same way as in the Miller–Closs studies. Finally, variations of A and X in **4** and its bimolecular counterpart will allow for studies of the dependence of *B*(inner-sphere) on the structure and nature of the reactants.

E. The Effect of Our Conclusions on Mechanistic Studies in Organic Chemistry. The conclusion that inner-sphere ET may be the preferred ET mechanism for reactions between pairs of odd- and even-electron reactants has some implications for mechanistic studies. In order to define the outer-sphere behavior of a particular ET reaction, experimentally determined λ values of the relevant self-exchange reactions [λ(0)] are often used to calculate "outer-sphere" ET rate constants which are then compared with actually measured ET rate constants. If the experimental λ(0) values reflect inner-sphere behavior in the way discussed above, they do not represent the true outer-sphere values, and thus mechanistic conclusions might be less reliable. Figure 5 shows an example, the reduction of alkyl bromides by radical anions,[3b] where the regression curve a corresponds to a λ of 67 kcal mol^{-1}. As shown above, this would be an inner-sphere mechanism with a sizable *B*(innersphere), above estimated to be 8.5 and 4.0 kcal mol^{-1}, respectively, by analyzing two sets of data by the Marcus treatment. Conservatively, we assume a *B*(innersphere) in the lower end of the interval, 5 kcal mol^{-1}, and thus obtain a λ of 67 + 4*5 = 87 kcal mol^{-1} for the ideal outer-sphere process. Curve *b* shows the Marcus parabola for this λ value. The difference between the two curves is significant and corresponds to a rate ratio of ca. 10^3. Note also that an inner-sphere process can adhere almost perfectly to the Marcus equation. This strongly contrasts to the behavior of archetype S_N2 reactions, typified by the Finkelstein reaction, cases of which have been treated as dissociative ET processes and plotted in Figure 5.[31]

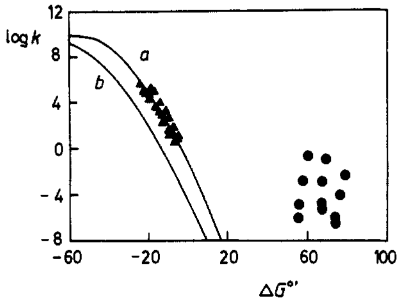

Figure 5. Plot of log *k*, M^{-1} s^{-1} vs $\Delta G^{\circ\prime}$, kcal mol^{-1} for the reduction of alkyl bromides by radical anions.[3b] Curve a is the best fit of the experimental data to the Marcus equation and corresponds to a λ of 67 kcal mol^{-1}. Curve b corresponds to λ = 87 kcal mol^{-1} and represents "ideal" outer-sphere behavior. The data points to the right correspond to Finkelstein S_N2 reactions of alkyl bromides, treated as dissociative ET steps.[31]

As indicated in Figure 5 an inner-sphere ET mechanism adhers perfectly well to the Marcus equation provided that *B*(inner-sphere) is a constant. While an approximate constancy of *B*(inner-sphere) seems likely, this still may or may not be valid. This will have to be ascertained in order to realize the full potential of the Marcus equation in mechanistic studies of organic reactions.[3-6]

Summary

This paper presents a theoretical and experimental analysis of organic ET reactions of radical anions. It is concluded that the inner-sphere mechanism should have an inherent preference over the outer-sphere case unless intermolecular overlap is impossible for steric or other reasons. The conclusion can be generalized to radical cations as well. We then propose that organic ET reactions of radical ions should possess relatively compact transition states with definite structures and significant intermolecular bonding (*B*). A similar conclusion has been reached by Kochi and collaborators[9] who have shown that many ET reactions are initiated from charge-transfer complexes, by our definition already a relatively compact structure. Our conclusions do not necessarily pertain to ET reactions between even-electron reactants.[11]

A possible method is outlined for the determination of the resonance interaction, *B*, in the inner-sphere ET transition state. The ability to determine *B*(inner-sphere) will provide the means to determine the corresponding quantity in the S_N2 mechanism, as suggested by Lund and Lund.[3,6]

Acknowledgment. S.S.S. is grateful to C. Amatore, J. K. Kochi, H. Lund, and T. Lund for enlightening comments. The research at BGU was supported by the Basic Research Foundation administered by the Israel Academy of Sciences and Humanities and at UL by the Swedish Natural Science Research Council.

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(30) If the intermolecular ET process is slow, which is always true for the dissociative ET, then

$$k_{\text{inter}} = Kk_{\text{ET}}$$

where *K* is the equilibrium constant for the complex formation ($A^{\bullet -}$ + RX $A^{\bullet -}$/RX), while k_{ET} is the ET rate constant within the complex. Since the dissociative process is expected to be slow, the process is adiabatic and following transition state theory we can obtain

$$B(\text{inner-sphere}) = 2.303RT \log [k_{\text{ET}}/k_{\text{intra}}] - 2.303RT \log K$$

assuming $B_{\text{intra}} \approx 0$.

(31) Eberson, L. *Acta Chem. Scand.* **1982**, *B36*, 533.