

Review Article

Problems and Prospects of the Concerted Dissociative Electron Transfer Mechanism

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Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

Ebersson, L., 1999. Problems and Prospects of the Concerted Dissociative Electron Transfer Mechanism. – Acta Chem. Scand. 53: 751–764. © Acta Chemica Scandinavica 1999.

The concepts of consecutive and concerted dissociative electron transfer have been examined, with particular emphasis on the reduction of organic halides. The possible presence and role of intermediate radical anions are discussed, as well as the application of the Marcus theory of outer-sphere electron transfer to halide reduction. Results of advanced quantum chemical calculations are briefly presented. The problems of the concerted mechanism with respect to the principle of microscopic reversibility are outlined, and the future importance of femto-second spectroscopy to the firm establishment of the concerted mechanism is stressed.

A tribute to Henning Lund

It is a great pleasure for me to acknowledge the important role which Henning Lund has played in my scientific life. When I embarked on a study of anodic acetoxylation in 1963 I had great inspiration from his pioneering study on anodic oxidation processes where the direct oxidation mechanism was suggested for the first time.¹ He was instrumental in getting us under way by running the first voltammetric curves of anisole in acetic acid/acetate solutions, showing that indeed the discharge of anisole took place before that of the solvent-supporting electrolyte. Eventually we were able to purchase a polarimeter and have a potentiostat built at the Electronics Service Department of Lund University. The latter was a magnificent device, the like of which has probably been seen neither before nor after its period of active duty. For some unknown reason, it had an ordinary 60 W light bulb as one of the resistors, which under operation blinked majestically with a frequency of 0.2–0.5 Hz and thus gave visitors a vivid impression of the mysteries of organic electrochemistry.

Later, it was greatly rewarding to follow the work of the Aarhus group in the area of electron transfer reactions, especially the reduction of organic halides. My interest in this area, and presumably that of many others, was provoked by an excellent early review by Elving and Pullman² which contained many imaginative suggestions

about mechanistic problems. Unfortunately, my preoccupation with anodic reactions prevented me from doing much on halide reduction, except for thinking about the problem. However, one result was the notion of concerted dissociative electron transfer to alkyl halides and its possible connection with the Marcus theory. On the occasion of Henning's formal retirement, I thought it would be appropriate to review a few features of this mechanism since he has been so deeply involved with it. Probably he will not agree on everything I am going to say, but that's the way of science!

Introduction

Electron attachment in the gas phase. Gas phase electron attachment to a molecule with a potentially cleavable bond is classified into two categories, namely (i) consecutive dissociative [eqn. (1), followed by eqn. (2)] and (ii) concerted dissociative reactions [eqn. (3)]. As a general rule, endothermic reactions proceed by the consecutive electron attachment mechanism while exothermic reactions proceed by the concerted route. Only rarely will both mechanisms apply to a single compound.³



Electron attachment in the condensed phase. Similar mechanisms for electron attachment to RX^- or electron removal from RX^- have been formulated for reactions in solution, but the distinction between them has not been as clear-cut as in the gas phase. In particular, the term 'dissociative electron transfer' has often been taken to denote only the concerted mechanism, and much work has been performed to delineate its scope and limitations.⁴ The fact that RX^- most often is identical with an organic halide, perhaps the single most important compound class in organic chemistry, explains the predominance of the work on concerted electron transfer (ET) mechanisms.

Historical development. The formulation of the concerted dissociative ET mechanism can be traced to at least two lines of study, involving the calculation of standard potentials by thermochemical cycles. One came from a mechanistic analysis of the Kolbe anodic oxidation of carboxylates $RCOO^-$ by theoretical estimates of standard potentials.⁵ In addition to the straight $1e^-$ oxidation of the carboxylate to the unstable acyloxyl radical [eqn. (4)], a mechanism involving simultaneous electron transfer to the anode and cleavage of the carbon-carbon bond [eqn. (5)] was considered.



$$E^\circ = 2.17 \text{ V vs. SCE for } R = \text{CH}_3$$



$$E^\circ = 1.31 \text{ V vs. SCE for } R = \text{CH}_3$$

The latter mechanism was included for no other reason than the prevailing preference for concerted mechanisms in physical organic chemistry,⁶ believed to offer more favourable energetics than stepwise mechanisms. The consequences of this suggestion were understandably not analysed in terms of ET theory; Marcus published his first paper on homogeneous ET in 1956⁷ and on electrode reactions in 1963–1965.⁸

Thermochemical data were available for all species involved in eqns. (4) and (5), also acyloxyl radicals,⁹ in spite of their low stability (the rate constant for decarboxylation of the acetoxyl radical was ca. 10^9 s^{-1}). It was concluded that the concerted mechanism was in best agreement with the experimental fact that the Kolbe reaction is irreversible in the electrochemical sense, proceeding at a considerable overpotential. Some heat, but little illumination, was generated by the ensuing discussion of the role of adsorbed intermediates¹⁰ and of the test of the concerted mechanism involving competition experiments, carried out by Skell *et al.*¹¹ The concerted mechanism was later¹² ruled out by the application of no less formidable a tool than Occam's razor,¹³ although in retrospect it is not clear why this principle cannot equally well be applied to eqn. (4) as the potential-determining step in the Kolbe reaction. At least from the viewpoint of product formation, the acyloxyl radical has practically no role in the chemical mechanism. More

seriously, the lifetimes of many types of acyloxyl radical (Table 1) were found to be finite,¹⁴ and therefore eqn. (4) is feasible from this point of view. Recently, exceptionally fast cases have been found,¹⁵ and it may be that even faster decarboxylations might still be found.

The second line of study originated from Hush¹⁶ who probably was first to estimate standard potentials from thermochemical data, and dealt with the methyl halides. His overall electrode reaction involved concerted dissociative ET [eqn. (6)], presumably for the reason that thermochemical data for $RX^{\cdot-}$ were not available. The inclusion of $RX^{\cdot-}$ as a species adsorbed in the reaction pathway was explicitly discussed. The electrochemical rate constants k_0 at the standard potential were 7×10^{-9} , 3×10^{-5} and $1 \times 10^{-4} \text{ cm s}^{-1}$ for $X = \text{Cl, Br and I}$, respectively, characterizing the electrode processes as electrochemically irreversible.



$$E^\circ = -0.91, -0.98, -0.94 \text{ V (X = Cl, Br, I) vs. SCE}$$

The same approach was used later to calculate redox potentials for the $1e^-$ reduction of an extensive series of alkyl halides in non-aqueous media.¹⁷ The purpose was to analyse experimental rate constants of halide reductions by ET reagents ranging from the solvated electron to transition metal complexes in terms of the Marcus theory (see below). The use of the concerted dissociative model was again motivated by the lack of thermochemical data on alkyl halide radical anions. As discussed below, the Marcus theory can be applied to alkyl halide reduction, provided a transition state model with an almost completely broken C–X bond is postulated. It has repeatedly been pointed out that the Marcus theory was not intended for such a situation – but neither was its application to hydrogen or group transfer reactions.

Thus we see that the introduction of the concerted dissociative ET step in carboxylate oxidation or halide reduction was largely dictated by considerations with little basis in ET theory. Mechanistic trends or calculational expediency, respectively, were the fathers of this invention.

Cleavage of intermediate halide radical anions

The role of intermediates in mechanisms. The idea that a concerted mechanism has an energetic advantage over a

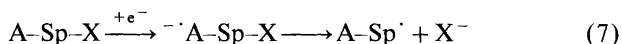
Table 1. Rate constants k for the decarboxylation of acyloxyl radicals, $RCOO^\cdot$, at ambient temperature.^{14,15,62}

R	k/s^{-1}
Substituted vinyl	10^6 – 10^7
Substituted ethynyl	$(2\text{--}5) \times 10^5$
Ph	2×10^6
Substituted Ph	$(2\text{--}200) \times 10^4$
Alkyl	$(1\text{--}11) \times 10^9$
$\text{Ar}_2\text{C}(\text{OH})$	$(1\text{--}8) \times 10^{11}$
$\text{Ar}(\text{R})\text{NCH}(\text{R}^1)$	10^6 – 10^7

stepwise mechanism has been replaced by a different notion, namely *that reaction mechanisms are determined by the lifetime of possible intermediates*.¹⁸ If an intermediate has a lifetime which is longer than the time of a bond vibration, $\approx 10^{-13}$ s = 100 fs, the reaction follows a stepwise mechanism. The concerted mechanism is followed when the intermediate does not exist by the criterion given above. This definition provides a clear distinction between the two types of mechanism. It also allows for straightforward refutation of the concerted mechanism: once an intermediate has been shown to possess some lifetime, a stepwise mechanism must prevail. Thus the feasibility of the concerted dissociative electron transfer mechanism, introduced largely for its calculational expediency, can be decided by an examination of the intermediates involved and their lifetimes.

Consecutive dissociative ET. Before we continue with the discussion of the concerted mechanism, a few words about the consecutive mechanism is in order. Table 2 shows dehalogenation rate constants of representative cases of halogenated radical anions, as determined by pulse radiolysis¹⁹ or electrochemical methods.²⁰ The stability of a halogenated radical anion is conferred by the presence of an electron-accepting group, or in its absence, of a strong C–X bond, as in simple haloarenes. The order of leaving group ability is as expected, $F < Cl < Br < I$. The effect of solvent is pronounced, the cleavage rates being generally higher in dipolar aprotic solvents than in water. In the latter type of solvent, cleavage of individual radical anions followed either the Gutmann acceptor or donor number.^{20c} In some cases, the solvent change from water to DMF appears to induce a transition from the consecutive to the concerted mechanism (3- and 4-cyanobenzyl bromide).^{20c}

The consecutive cleavage mechanism can be considered²¹ as a sequence of two ET steps: (i) formation of the radical anion in which the electron is located in the π^* orbital of the aromatic system, followed by (ii) an intramolecular ET reaction which locates the electron in the C–Br σ^* orbital. This step may or may not be of the concerted dissociative type. Thus we can formally view an organic halide as composed of an acceptor (A), a spacer group (Sp) and a halogen atom (X). The reaction sequence describing most cases in Table 2 thus can be written as in eqn. (7). Studies of halides with structures modelled after this approach have recently²² been reported [eqn. (8)].

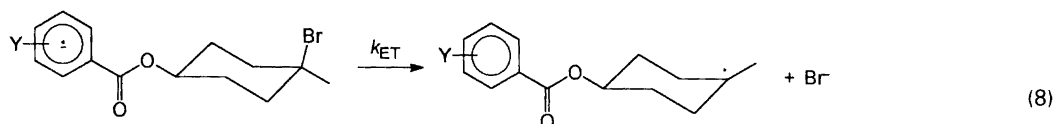


Structural evidence for radical anions of organic halides. A large number of radical anions of organic halides have been generated by γ irradiation in low-temperature matrices of inert solvents and subjected to EPR spectroscopic study. Table 3 lists representative cases of simple aromatic, vinylic, acetylenic, polyhalo and alkyl halides.^{23–25} The most important feature is the characterization of

Table 2. Rate constants k of halide ion cleavage, from various types of radical anion [eqn. (2)] at ambient temperature.^{19,20}

R	X	Solvent	k/s^{-1} for loss of X^-
4-Nitrobenzyl	Cl	Water	4×10^3
4-Nitrobenzyl	Cl	DMF	4×10^6
4-Nitrobenzyl	Cl	CH ₃ CN	2×10^4
4-Nitrobenzyl	Br	Water	1.7×10^5
4-Nitrobenzyl	Br	DMF	Too fast to be measurable
4-Nitrobenzyl	Br	CH ₃ CN	6×10^8
3-Nitrobenzyl	Cl	Water	<5
3-Nitrobenzyl	Cl	DMF	8×10^1 ; 8×10^1
3-Nitrobenzyl	Cl	CH ₂ Cl ₂	4
3-Nitrobenzyl	Cl	HMPA	1.7×10^2
3-Nitrobenzyl	Cl	THF	2.5×10^1
3-Nitrobenzyl	Br	Water	6×10^1
3-Nitrobenzyl	Br	CH ₃ CN	3.5×10^1
2-(4-Nitrophenyl)ethyl	Br	Water	$\approx 2 \times 10^1$
4-Nitrophenyl	Cl	DMF	1×10^{-2}
4-Nitrophenyl	Br	DMF	4×10^{-3}
4-Cyanobenzyl	F	DMF	7×10^6
4-Cyanobenzyl	Cl, Br	Water	$> 3 \times 10^7$ (estd. 10^9 , 10^{10})
4-Cyanobenzyl	Br	DMF	Concerted dissociative
3-Cyanobenzyl	Br	Water	1.3×10^7
3-Cyanobenzyl	Br	DMF	Concerted dissociative
4-Cyanophenyl	F	Water	6.5×10^5
4-Cyanophenyl	Cl	Water	5×10^6
4-Cyanophenyl	Cl	DMF	1.6×10^8
4-Cyanophenyl	Br	Water	$> 3 \times 10^7$
4-Acetylphenyl	Cl	Water	$\approx 1 \times 10^2$
4-Acetylphenyl	Cl	DMF	3×10^5
4-Acetylphenyl	Br	Water	5×10^3
4-Acetylphenyl	Br	DMF	3×10^7
4-Acetylphenyl	I	Water	1.4×10^5
3-Acetylphenyl	Cl	DMF	1.9
3-Acetylphenyl	Cl	CH ₃ CN	1.3
3-Acetylphenyl	Cl	THF	0.6
3-Acetylphenyl	Br	Water	$\approx 1 \times 10^2$
3-Acetylphenyl	Br	DMF	2×10^5
4-Carboxylatophenyl	F	Water	6×10^5
4-Carboxylatophenyl	Cl	Water	4×10^7
1-Naphthyl	Cl	DMF	1.6×10^7
1-Naphthyl	Br	DMF	6×10^7
9-Anthryl	Cl	DMF	1.6×10^2 ; 6.2×10^1 ; 1.3×10^2
9-Anthryl	Cl	CH ₃ CN	1.6×10^2 ; 1.3×10^2 ; 1.7×10^2
9-Anthryl	Cl	CH ₂ Cl ₂	1.7×10^2
9-Anthryl	Cl	THF	2.4×10^1
9-Anthryl	Br	DMF	2.5×10^6

most unstable halide radical anions as being of σ^* type, i.e., the attached electron resides in the C–X orbital and not in the π^* orbital. Apparently a σ^* radical anion represents an energy minimum on the way to the products of cleavage. Nitroaryl-containing radical anions, which are much more persistent, have been characterized by their EPR spectral properties as having the attached electron in a mixed π^* – σ^* orbital. Only one radical anion should exist, the pure π^* nitroaryl and the C–X σ^* orbitals representing valence bond forms of the actual resonance hybrid.^{23g}



Y	$\log(k_{ET}/s^{-1})$
H	5.5
3-PhO	4.7
3-F	3.8
2,3-Benzo	2.4
4-SO ₂ Me	0.3
4-CN	-0.2

Table 3. Observations of paramagnetic species formed upon electron attachment to organic halides and their characterization.²³⁻²⁵

Halide	Solvent ^a	T/K	Radical anion	Type of radical
4-NO ₂ C ₆ H ₄ CH ₂ Cl	CD ₃ OD or MeTHF	77-160	4-NO ₂ C ₆ H ₄ CH ₂ Cl ^{•-}	$\pi^*-\sigma^*$
4-NO ₂ C ₆ H ₄ CH ₂ Br	CD ₃ OD or MeTHF	77-160	4-NO ₂ C ₆ H ₄ CH ₂ Br ^{•-}	$\pi^*-\sigma^*$
3-NO ₂ C ₆ H ₄ CH ₂ Cl	Ethanol	298	3-NO ₂ C ₆ H ₄ CH ₂ Cl ^{•-}	$\pi^*-\sigma^*$
4-NO ₂ C ₆ H ₄ Cl	DME or THF	293	4-NO ₂ C ₆ H ₄ Cl ^{•-}	π^*
PhBr	Toluene-MeTHF	77	PhBr ^{•-}	σ^*
PhI	MeTHF	77	PhI ^{•-}	σ^*
1,4-I ₂ C ₆ H ₄	MeTHF	77	4-IC ₆ H ₄ I ^{•-}	σ^*
C ₆ F ₅ Cl	TMS, CD ₃ OD or MeTHF	77	C ₆ F ₅ Cl ^{•-}	σ^*
C ₆ F ₅ Br	MeTHF	77	C ₆ F ₅ Br ^{•-}	σ^*
C ₆ F ₅ I	TMS, CD ₃ OD or MeTHF	77	C ₆ F ₅ I ^{•-}	σ^*
PhC≡Cl	CD ₃ OD	77	PhC≡Cl ^{•-}	σ^*
F ₂ C=C(F)F	(² H ₁₂)TMS	120	F ₂ C=C(F)F ^{•-}	σ^*
F ₂ C=C(F)Cl	(² H ₁₂)TMS	98	F ₂ C=C(F)Cl ^{•-}	σ^*
F ₂ C=C(F)Br	(² H ₁₂)TMS	98	F ₂ C=C(F)Br ^{•-}	σ^*
CF ₃ Cl	TMS, Me ₄ C, MeTHF	101	CF ₃ Cl ^{•-}	σ^*
CF ₃ Br	TMS, Me ₄ C, MeTHF	121	CF ₃ Br ^{•-}	σ^*
CF ₃ I	TMS, Me ₄ C, MeTHF	98	CF ₃ I ^{•-}	σ^*
CFCl ₃	Neat	77	CFCl ₃ ^{•-}	σ^*
CBr ₄	CD ₃ OD	77	CBr ₄ ^{•-}	Distorted tetrahedral
CH ₃ Cl	CD ₃ CN	77	[•] CH ₃ ...Cl ⁻	CT complex
CH ₃ Br	CD ₃ CN	77	[•] CH ₃ ...Br ⁻	CT complex
CH ₃ I	CD ₃ CN	77	[•] CH ₃ ...I ⁻	CT complex
(CF ₃) ₃ CCl	MeTHF	87	(CF ₃) ₃ CCl ^{•-}	σ^*

^aMeTHF = 2-methyltetrahydrofuran, DME = 1,2-dimethoxyethane.

The third type of paramagnetic product was obtained from simple alkyl halides R-X and is best described as a charge transfer complex between R[•] and X⁻, held together in the rigid matrix.^{23d,f} The extent of charge transfer deduced from the EPR spectral parameters was 4, 10 and 17% for complexes between R[•] and Cl⁻, Br⁻ and I⁻, respectively. The CH₃...Br⁻ complex could be generated from CH₃[•] and Br⁻ in a CH₃CN matrix at 77 K and its decay rate constant measured, showing that such a complex is a kinetically definable species²⁶ and must have a finite lifetime.

Application of the Marcus theory to alkyl halide reduction

The first attempt to apply the Marcus theory to alkyl halide reduction encompassed a rather heterogeneous collection of reactions, such as reduction by solvated electrons, by aromatic radical anions and transition metal

complexes.¹⁷ Since the Marcus approach to ET in organic systems had just only begun to be more generally appreciated,²⁷ there was need for further extension into new groups of reactions, and an exploration of the limits of the theory.

At the time the Marcus treatment was limited to *outer-sphere* electron transfer between donors D and acceptors A, assuming that the DA and D^{•+}A^{•-} states could be described by parabolic functions and the ET transition state as the avoided crossing between them (Fig. 1). The outer-sphere concept had been borrowed from the chemistry of transition metal complexes – it meant that the exchange of an electron between two complexes took place with only solvent reorganisation and minor bond reorganization within the complexes. Explicitly, no bond formation between or cleavage within their inner coordination spheres was allowed. Evidently, this had to be replaced by a different usage and terminology in the case of D and A being organic species. Thus it was suggested

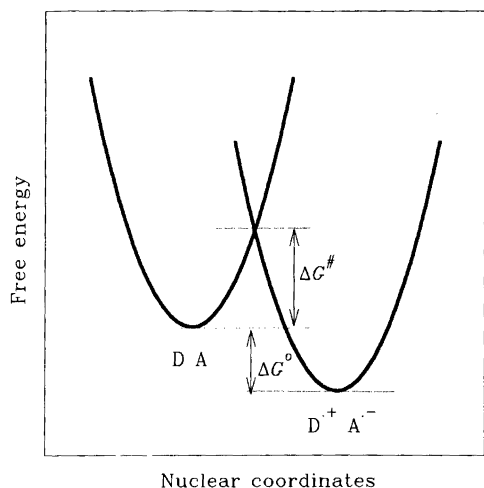


Fig. 1. Free energy diagram for the outer-sphere electron transfer between a donor D and an acceptor A.

that the *electronic* interaction between D and A in the ET transition state should be less than a specified, small energy quantity, and 1 kcal mol⁻¹ was suggested to be a suitable higher limit.²⁸ It was once suggested²⁹ that such a transition state should be denoted 'non-bonded' and correspond to 'non-bonded ET' instead of 'outer-sphere ET', but this nomenclature was never generally accepted.

The borderline of 1 kcal mol⁻¹ is so small that no serious error is introduced by the neglect of the electronic term, yet large enough not to introduce problems with

non-adiabaticity. Naturally, this borderline is an arbitrary one and must be regarded as a convention. It is clear that situations must exist where the electronic interaction term is larger but still ET occurs directly to the D⁺A⁻ products.³⁰ This problem has been dealt with by detailed quantum chemical calculations,^{30a-d} and it has been established that fairly strongly bonded D A transition states can exist which collapse directly to D⁺A⁻ products. This is hardly surprising in view of the propensity of organic molecules to participate in reactions involving strongly bonded transition states. As emphasized by Pross,³¹ electron transfer to or from organic molecules appears to take place by default.

Figure 2 shows some detail of the calculations performed on the gas phase reaction between cyanoformaldehyde radical anion and the series of alkyl chlorides RCl with R = Me, Et, iPr and *t*-Bu.^{30d} The initial state C_R is an ion-dipole cluster with a long O-C² bond and an almost unperturbed C²-Cl bond. Two types of transition state can be reached from this cluster, one being of the normal S_N2(O) type, where the O-C² and C²-Cl bonds are extended in the way expected for an S_N2 transition state. This transition state leads to the products [CH₃OCH[•](CN) + Cl⁻] in the normal way.

In the second transition state the cyanoformaldehyde radical anion approaches the halide via its carbon atom, and it has the characteristics of an S_N2(C) transition state for sterically less hindered situations (R = Me, Et), leading to R-C(O[•])(H)CN and Cl⁻. For R = iPr and

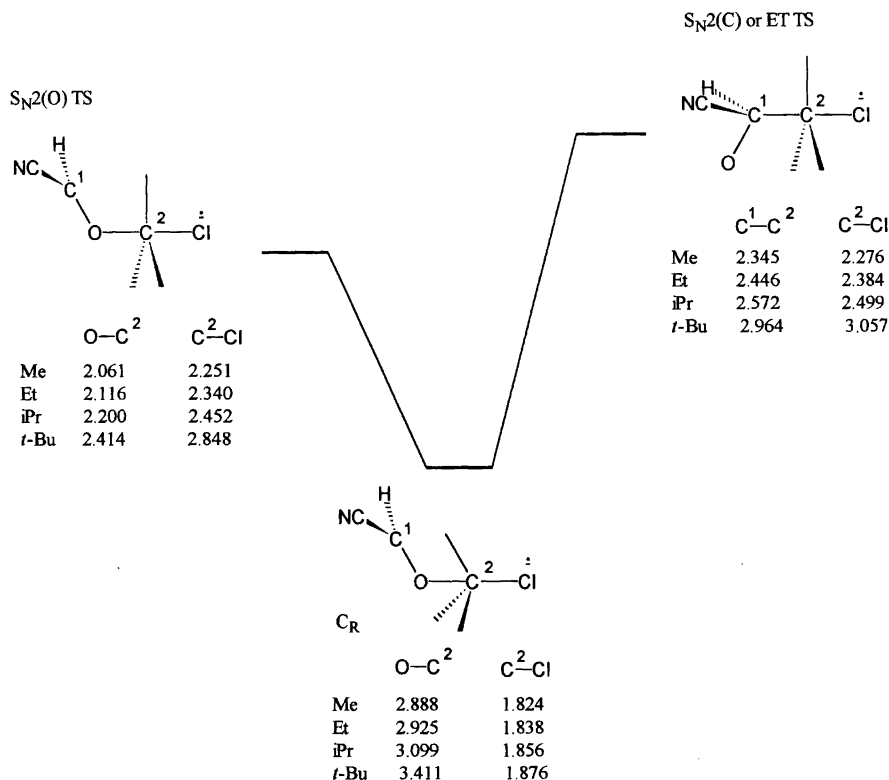
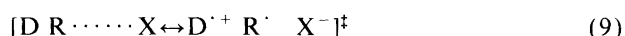


Fig. 2. Some critical bond lengths calculated for the ion-dipole cluster C_R between cyanoformaldehyde radical anion and R-Cl (R = Me, Et, i-Pr and *t*-Bu) and the transition states leading to O-alkylation, C-alkylation or electron transfer [Ref. 30(c)].

t-Bu, the transition state has more loosened bonds and is the one leading to products of electron transfer, $\text{NC(H)C=O, R}^\cdot + \text{Cl}^-$. The bonding in the ET transition state is significant, 6 kcal mol⁻¹ for *t*-BuCl and 14 kcal mol⁻¹ for *i*PrCl. The changeover from an S_N2(C) to an ET transition state takes place over a rather narrow range of C¹-C² distances, between 2.4 and 2.5 Å. To emphasize the relationship between the two mechanisms they were denoted 'entangled' hybrid mechanisms. In the transition region between the two, the ridge separating the ET and S_N2(C) presumably is broad and shallow, thus making bifurcations possible for systems of this type. Thus new experimental tests were suggested, for example studies of the stereochemistry of dissociative ET as a function of temperature [ET at low temperature, incursion of S_N2(C) at higher temperature], determination of kinetic isotope effects of dissociative ET reactions, and studies on conformationally locked systems.^{30d}

The application of the Marcus theory to alkyl halide reduction had to overcome the problem of getting access to standard potentials of the $\text{RX} + \text{e}^- \rightarrow \text{RX}^{\cdot-}$ reaction. As already mentioned above, the Hush method of calculating the potentials of the $\text{RX} + \text{e}^- \rightarrow \text{R}^\cdot + \text{X}^-$ reaction was adopted (Table 4), since no easy way to estimate thermochemical data for alkyl halide radical anions existed. Thus it was implied that the transition state for ET between D and RX should be formulated as the

resonance hybrid of eqn. (9). The left-hand resonance form has the C-X bond lengthened to the point of breaking, and the bond is broken in the right-hand resonance form.



This is a situation not compatible with the original area of validity of the Marcus theory, as defined above, and it has been popular to emphasize this rather obvious point. Yet the first application clearly showed that alkyl halide reduction by a wide range of ET reductants, some of them now known to be of inner-sphere type, broadly followed a parabolic relationship of the Marcus type. It was possible to distinguish between different halogen types, in that reorganization energies decreased in the order Cl > Br > I, thus indicating that the transition state model of a significantly lengthened C-X bond was not too wide of the mark. Moreover, the model very clearly singled out archetypal S_N2 reactions as not having even a remote possibility of being of ET type (Fig. 3).

Further applications of the Marcus theory to the electrochemical reduction of alkyl halides followed the same lines, but used a revised set of thermochemical data for radicals to calculate standard potentials (Table 4).³² The reorganization energies λ_{RX} of alkyl halides were found to be very large. Later, the non-validity of the Marcus theory to concerted ET-bond cleavage was

Table 4. Standard potentials E_{RX}° and reorganization energies λ_{RX} obtained either from $k_{\text{ET}}/E_{\text{AA}}^\circ$ data ('unbiased') or by thermochemical calculations.^{33,35,36}

Compound	$E_{\text{RX}}^\circ/\text{V}$ vs. SCE, ^a unbiased	λ _{RX} /kcal mol ⁻¹ , ^b unbiased	$E_{\text{RX}}^\circ/\text{V}$ vs. SCE, ^c calcd.	λ _{RX} /kcal mol ⁻¹ , ^d	$E_{\text{RX}}^\circ/\text{V}$ vs. SCE, ^e calcd.	λ _{RX} /kcal mol ⁻¹ , ^f
Ethyl bromide	-1.65; -1.73	106; 98	-1.14	74		
Butyl chloride	-1.95; —; —*	120; —; —*	-1.29	80	-1.37	152
Butyl bromide	—*; -1.70; -2.03	—*; 100; 62	-1.14	74	-1.23	122
Butyl iodide	-1.48; —; -1.82	96; —; 46	-1.22	58	-1.21	96
Isobutyl iodide*	-1.21	124				
2-Butyl chloride	-1.94; —; —*	116; —; —*	-1.37	80	-1.41	154
2-Butyl bromide	-1.74; -1.57; -1.60	94; 106; 96	-1.21	74	-1.25	124
2-Butyl iodide	-1.50; —; -1.56	88; 66	-0.93	58	-0.97	116
<i>tert</i> -Butyl chloride	—*; —; -1.42	—*; 148	-1.31	80	-1.28	158
<i>tert</i> -Butyl bromide	-1.49; —; -1.25	110; 120	-1.06	74	-1.04	138
<i>tert</i> -Butyl iodide	—; —; -0.62	—; —; 128	-1.01	58	-0.91	106
Neopentyl chloride	-1.54	168				
Neopentyl bromide	-2.05; -1.83	90; 108				
Neopentyl iodide	-1.91	70				
1-Bromoadamantane	-1.85	108				
1-Iodoadamantane	—; -1.98	—; 50				
<i>exo</i> -Norbornyl bromide	-2.12	66				
Isobornyl bromide	-2.03	72				
Bornyl bromide	-1.87	100				
Benzyl chloride	-1.04; -0.84	128; 144	-0.70		-0.76	
Benzyl bromide	—; -0.19	—; 166				
1-Phenylethyl chloride	-1.24	112				
Carbon tetrachloride	-1.08	72	-0.72			

^aThe first value is taken from Ref. 35, the second one from Ref. 36 and the third one from Ref. 33; an asterisk * indicates that a value has been omitted because of large errors. ^bAssuming a constant value of λ_{AA}^{•-} = 20 kcal mol⁻¹. ^cFrom thermochemical calculations on $\text{RX} + \text{e}^- \rightarrow \text{R}^\cdot + \text{X}^-$ (Ref. 17). ^dObtained by application of the Marcus theory to rate data, using standard potentials from column 4. ^eFrom thermochemical calculations on $\text{RX} + \text{e}^- \rightarrow \text{R}^\cdot + \text{X}^-$ (Ref. 32). ^fObtained by application of the Marcus theory to rate data, using standard potentials from column 6.

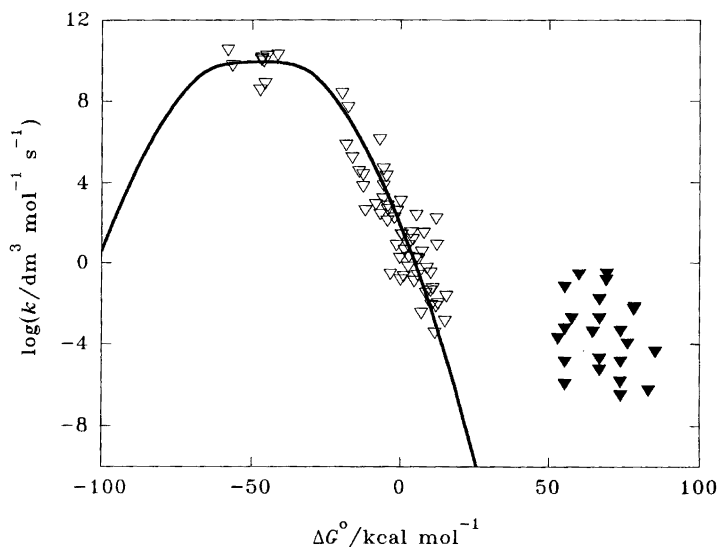


Fig. 3. Marcus plot of electron transfer reductions of alkyl halides (empty symbols), as contrasted with archetypal S_N2 reactions (Finkelstein reactions; filled symbols) treated as ET processes (Ref. 17).

emphasized, and a model based on intersecting Morse type curves was developed.³³ This approach led to the same quadratic equation for ΔG_{ET}^\ddagger as that developed by Marcus [eqn. (10)], but λ_{RX} was now obtained as the sum of the solvent reorganization term λ_0 and the dissociation energy of the RX bond, D_{RX} [eqn. (11)]. Further developments have emerged.³⁴

$$\Delta G_{ET}^\ddagger = 0.25 \times \lambda_{RX} / [1 + \Delta G^\circ / \lambda_{RX}]^2 \quad (10)$$

$$\lambda_{RX} = \lambda_0 + D_{RX} \quad (11)$$

A number of studies included electrochemical experiments involving redox catalysis of the reduction of alkyl halides by electrogenerated radical anions $A^{\cdot-}$.^{32,33,35,36} For each halide a number of radical anions with a range of known potentials was employed, resulting in a set of $\log k_{ET} - E_{A/A^{\cdot-}}^\circ$ pairs. Unbiased values of E_{RX}° and λ_{RX} can be extracted from such data, and are shown in Table 4, 'unbiased' taken to mean that these values are not dependent on any assumption about the mechanism being of the concerted dissociative type. This is the case for the calculated E_{RX}° given in columns 4 and 6 of Table 4. The unbiased potentials are subject to relatively large errors, as is expected from consideration of the relatively narrow experimental region in relation to the Marcus parabola, and a few values were discarded for that reason.

As seen in Fig. 4, in all cases but one (*tert*-butyl iodide) the unbiased standard potentials are significantly more negative than the ones calculated for the $RX/R^{\cdot-} + X^-$ couple. This is expected if the actual electrode reaction involves an intermediate with the characteristics of the radical anion. The calculated potentials have, built into themselves, the full energetic advantage of the cleaved C-X bond, whereas the intermediacy of a radical anion would move the standard potential to a more negative value.

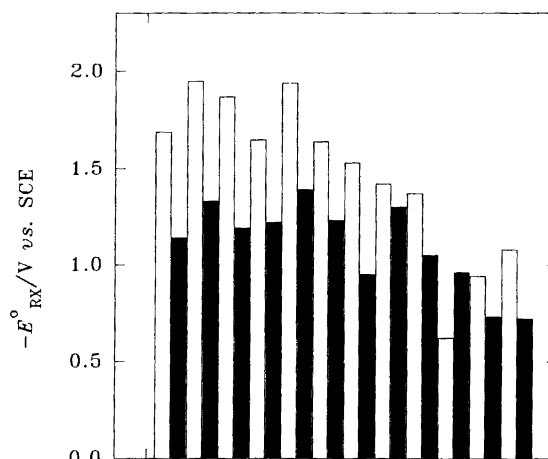


Fig. 4. Unbiased E_{RX}° (empty bars; mean values in the appropriate cases) and calculated E_{RX}° (filled bars; mean values in the appropriate cases) shown pairwise for the halides listed in Table 4; from left to right ethyl bromide, butyl chloride, butyl bromide, butyl iodide, 2-butyl chloride, 2-butyl bromide, 2-butyl iodide, *tert*-butyl chloride, *tert*-butyl bromide, *tert*-butyl iodide, benzyl chloride and carbon tetrachloride.

An interesting deviation from Marcusian behaviour was noted³⁷⁻³⁹ in the case of the reaction between *tert*-butyl bromide and radical anions $A^{\cdot-}$, in that $\log k_{ET}$ varied linearly with $E_{A/A^{\cdot-}}^\circ$ over a reactivity range of more than 13 powers of ten (Fig. 5). Explanations based on faulty experimentation⁴⁰ could be rejected,³⁸ and it was instead suggested that a decreasing degree of the inner-sphere contribution to the TS with increasing exergonicity might cause this effect. Another explanation might be based on the assumption that the reorganization energies of the radical anions, $\lambda_{A/A^{\cdot-}}$, might vary in a regular fashion with the corresponding standard potentials, $E_{A/A^{\cdot-}}^\circ$, for example according to a linear function. The structural factors influencing $\lambda(0)$ and E° appear to

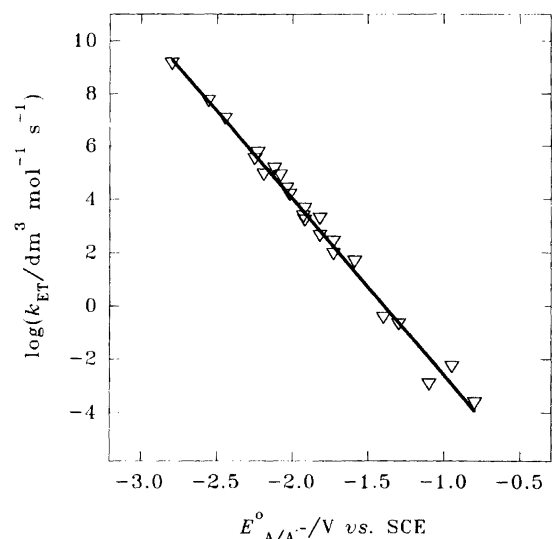


Fig. 5. Plot of $\log(k_{\text{ET}}/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$ vs. $E_{\text{A/A}^-}^0/\text{V}$ vs. SCE for reactions between *tert*-butyl bromide and radical anions. The equation of the regression line is $\log k_{\text{ET}} = -9.2 - 6.6 \times E_{\text{A/A}^-}^0$.

run in parallel,²⁷ and any linear dependency should be amenable to experimental testing. The reasoning is as follows.

The Marcus expression for ΔG^\ddagger in the particular case under study can be simplified to a linear expression [eqn. (12)], since $[\lambda_{\text{RX}} + \lambda_{\text{A/A}^-}]/2$ is sufficiently larger than $23.06 \times \Delta G^\circ = 23.06 \times [E_{\text{A/A}^-}^\circ - E_{\text{RX}}^\circ]$ to allow for neglecting the quadratic term [typically $(115 + 20)/2 = 67.5$ vs. $23.06 \times (-2 + 1.4) = 15 \text{ kcal mol}^{-1}$].

$$\begin{aligned} \Delta G^\ddagger &= 0.125 \times (\lambda_{\text{RX}} + \lambda_{\text{A/A}^-}) \\ &\times [1 + 2 \times 23.06 \times (E_{\text{A/A}^-}^\circ - E_{\text{RX}}^\circ)/(\lambda_{\text{RX}} + \lambda_{\text{A/A}^-})]^2 \\ &\approx 0.125 \times (\lambda_{\text{RX}} + \lambda_{\text{A/A}^-}) \\ &\times [1 + 2 \times 2 \times 23.06 \times (E_{\text{A/A}^-}^\circ - E_{\text{RX}}^\circ)(\lambda_{\text{RX}} + \lambda_{\text{A/A}^-})] \\ &= 0.125 \times [(\lambda_{\text{RX}} + \lambda_{\text{A/A}^-}) + 92.2 \times (E_{\text{A/A}^-}^\circ - E_{\text{RX}}^\circ)] \end{aligned} \quad (12)$$

Combining the simplified expression with the Eyring equation, $\log k_{\text{ET}} = 11 - \Delta G^\ddagger/2.303RT$, and putting $\lambda_{\text{A/A}^-} = C \times E_{\text{A/A}^-}^\circ$ gives the following expression:

$$\begin{aligned} \log k_{\text{ET}} &= [11 - 0.125 \times (\lambda_{\text{RX}} - 92.2 \times E_{\text{RX}}^\circ)/1.364] \\ &\quad - E_{\text{A/A}^-}^\circ \times 0.125 \times (C + 92.2)/1.364 \end{aligned} \quad (13)$$

With λ_{RX} and E_{RX}° obtained from Table 4 (unbiased $115 \text{ kcal mol}^{-1}$, -1.37 V ; calculated $106 \text{ kcal mol}^{-1}$, -1.05 V), the intercept of eqn. (13) becomes -11 or -7.6 , average -9.3 , and the slope, assuming that $C = -20$, -6.6 . These values compare well with those of the equation of the regression line in Fig. 5, $\log k_{\text{ET}} = -9.2 - 6.6 \times E_{\text{A/A}^-}^\circ$.

Ab initio calculations of alkyl halide radical anions

Table 5 summarizes relevant *ab initio* calculations on the stability of alkyl halide radical anions, including a few perhalogenated ones.⁴¹⁻⁴⁵ Looking at one key species, $\text{CH}_3\text{Cl}^{\cdot-}$, we see that the results vary between methods and investigators, from indicating stability of the radical anion both in the gas and solution phase to indicating non-existence in the solution phase. The difference between the various methods has been ascribed to the use of basis sets with diffuse functions; if the potential surface of the negative ion is energetically above that of the neutral system, the extra electron will be placed into the most diffuse orbital available in the basis set, essentially simulating the neutral system plus a free electron.⁴⁴ One set of calculations differed qualitatively in the outcome,⁴³ in that $\text{CH}_3\text{Cl}^{\cdot-}$ of C_{3v} symmetry was found to be less stable; the species of C_{2v} symmetry was lower in energy and had a barrier for cleavage of about 3 kcal mol^{-1} .

Thus the knowledge regarding the stability of $\text{R-X}^{\cdot-}$ obtained from quantum chemical calculations is somewhat uncertain. It seems that $\text{R-X}^{\cdot-}$ are predicted to have some lifetime in the gas phase, whereas their solution behaviour cannot easily be judged. This is not surprising, since the role of solvation cannot yet be satisfactorily accounted for in such calculations. Clearly, more work is required before the final word can be said on this difficult problem.

Estimates of the activation energy E_a for dissociative ET of halides in the gas phase from data on electron-molecule collisions

A classical approach to the calculation of activation energies E_a for dissociative electron attachment [eqn. (3)] to halides has recently been developed by Marcus.⁴⁶ The potential energy curve $V(x)$ for RX as a function of the RX bond length x was assumed to be of the Morse type [eqn. (14)], whereas for the radical anion a repulsive Morse curve was first assumed [eqn. (15)]. Here D and D^- are bond dissociation energies, E_x is the electron affinity of X^\cdot , and x_0 is the equilibrium value of x . From these expressions, the vertical attachment energy E_v can be used to obtain information on D^- [eqn. (16)].

$$V(x) = D(1 - e^{-a(x-x_0)})^2 - D \quad (14)$$

$$V^-(x) = D^- e^{-2a(x-x_0)} - E_x \quad (15)$$

$$E_v = V^-(x_0) - V(x_0) = D^- + D - E_x \quad (16)$$

Table 6 shows D^- calculated from experimental values of E_v , D and E_x for a few halides of interest. The third column shows the experimentally determined activation energies E_a^{obs} for the dissociative attachment reaction of eqn. (3). An attempt to calculate E_a from eqns. (14) and (15) however gave values that were too large and it was therefore found necessary to include an attractive term

Table 5. *Ab initio* calculations of barriers to C–X bond cleavage of alkyl halide radical anions in the gas or solution phase.

RX ^{•-} (Ref.)	Method	Gas phase barrier/kcal mol ⁻¹	$r_{C-X}^\ddagger/\text{Å}$ in gas phase	Solution barrier/kcal mol ⁻¹	$r_{C-X}^\ddagger/\text{Å}$ in solution phase	Remarks
CH ₃ Cl ^{•-} (41)	SCF/6-31+G*	19	2.28	None		Solvation simulated by restricting the basis set
CH ₃ F ^{•-} (42)	CASSCF	55	2.0	33	2.0	Solvation estimated by the Born model
CH ₃ Cl ^{•-} (42)	CASSCF	31	2.5	17	2.2	Solvation estimated by the Born model
CH ₃ Cl ^{•-} (43)	UMP2/6-31+G*	Very low	3.9			C _{3v} symmetry
CH ₃ Cl ^{•-} (43)	UMP2/6-31+G*	≈3	3.8			C _{2v} symmetry
CH ₃ F ^{•-}	MP3/4-31G	49	1.97	None		Solvation estimated by the ellipsoidal cavity method
CH ₃ Cl ^{•-} (44)	MP3/4-31G	24 ^a	2.20 ^a	None		Solvation estimated by the ellipsoidal cavity method
CH ₃ Br ^{•-} (44)	MP3/4-31G	16	2.30	None		Solvation estimated by the ellipsoidal cavity method
CH ₃ I ^{•-} (44)	MP3/4-31G	10	2.47	None		Solvation estimated by the ellipsoidal cavity method
CF ₃ Cl ^{•-} (44)	MP2/4-31G	15 ^{b,c}	2.2 ^{b,c}	None		Solvation estimated by the ellipsoidal cavity method
CF ₃ Cl ^{•-} (45)	CBS-MP2	21		—		
CF ₃ Br ^{•-} (45)	CBS-MP2	9		—		

^aA shallow minimum of -0.8 kcal mol⁻¹ at $r_{C-Cl}=4.1$ Å was also calculated. ^bRead off a graph. ^cA minimum of -9.8 kcal mol⁻¹ at $r_{C-Cl}=3.1$ Å was also calculated.

Table 6. Calculated values of D^- [eqn. (16)] and experimental and calculated E_a values [eqns. (15) and (17), using $c=0.6$] for some halides in the gas phase.⁴⁶

R–X	D^-/eV	$E_a^{\text{obs}}/\text{eV}$	$E_a^{\text{calc}}/\text{eV}$
CH ₃ –Cl	3.53	0.54	0.64
<i>t</i> -C ₄ H ₉ –Cl	1.84	0.47	0.46
ClCH ₂ –Cl	1.41	0.33	0.32
Cl ₂ CH–Cl	0.67	0.14	0.09
CH ₃ –Br	2.75	0.25	0.39
C ₃ H ₇ –Br	1.43	0.34	0.30
C ₂ H ₅ –I	1.17	0.05	0.06

into $V^-(x)$, as shown in eqn. (17),

$$V^-(x) \approx D^- [-c e^{-b(x-x_0)} + (1+c) e^{-2d(x-x_0)}] - E_x \quad (17)$$

where c is a positive constant which vanishes for a purely repulsive curve. Putting $b=d=a$ in eqns. (15) and (17) it was possible to show that a value of $c=0.6$ gave E_a^{calc} in good agreement with the experimental values (Table 6).

The revised eqn. (17) for $V^-(x)$ displays a small potential energy minimum which is $0.056D^-$ for $c=0.6$.

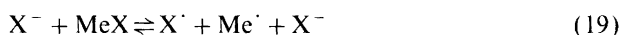
With D^- in the range 1–2 eV, this minimum energy comes out at 1.3–2.6 kcal mol⁻¹.

The principle of microscopic reversibility and dissociative electron transfer

The principle of microscopic reversibility⁴⁷ offers a powerful method of analysing reaction mechanisms and discarding less suitable ones. For our purpose it is best expressed in the following form: 'the mechanism of a reversible reaction in the rearward direction is identical with the mechanism in the forward direction run backward.' The analysis of a composite mechanism can be performed on the individual elementary steps.

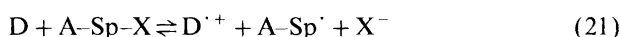
Some years ago, Lewis⁴⁸ examined the sometimes suggested notion of the S_N2 mechanism being of ET type⁴⁹ by applying the principle of microscopic reversibility to some of the critical steps involved. In one version, the S_N2 identity reaction [eqn. (18) = the Finkelstein reaction for X⁻ equal to halide ion] is formulated as an ET step followed by a recombination step [eqns. (19) and (20)]. Each step must be reversible and the forward and reverse rates must be equal.





The reverse of eqn. (20) is a homolysis step, an unrealistic step for any X of interest in the S_N2 reaction because of the high barriers involved. The principle of microscopic reversibility moreover requires that this reaction has the same rate as the forward reaction of eqn. (18). Finally, the reverse of eqn. (19) is a termolecular step, a kinetically very unfavourable situation. A similar analysis of four other seemingly plausible versions of the ET mechanism ruled them out because of the inclusion of unlikely intermediates, steps with no analogy in ordinary chemistry, energetically unfavourable decomposition modes of radical anions, intermediacy of hypervalent anions of type $XMeX^-$ and/or termolecular steps.

To exemplify the use of the principle of microscopic reversibility on dissociative ET, let us consider first the consecutive dissociative ET reaction for a halide of type $A-Sp-X$, using a donor D as reductant, and written as the equilibrium of eqn. (21). Clearly, this reaction is not an elementary step (defined as a reaction with one transition state only), but it can be written as a series of elementary steps, as for example in eqns. (22)–(24). A step involving a π^* to σ^* radical interconversion [eqn. (23)] is included to account for this possible feature of consecutive dissociative ET.



From the viewpoint of the principle of microscopic reversibility, eqn. (22) presents no problem. It is a reversible reaction with bimolecular reactions on each side. As written here, eqn. (23) is an equilibrium between two electron isomers, a π^* and a σ^* radical. The existence of such equilibria was a topic of lively discussion some 25 years ago,⁵⁰ and the reaction is included here for the sake of completeness. It is really not necessary to include it; as seen from Table 3, most radical anions of interest here have the σ^* structure, either because they are formed in this state or have undergone the π^* to σ^* interconversion rapidly after attachment of the electron.

Equation (24) constitutes the crucial C–halogen bond cleavage step, written as a reversible one. Evidence for the reversibility of this step comes from the rich experimental material available for the $S_{RN}1$ reaction which has both the dissociative and associative part of the reaction $R-Nu \rightleftharpoons R^\cdot + Nu^-$ as critical elementary steps.⁵¹ Truly, Nu⁻ is different in the dissociative and associative processes (examples, see Table 7), but there is no reason why the reversibility of eqn. (24) should not prevail for most nucleophiles, including halogen groups which are used as leaving groups in the forward reaction. Theoretical calculations⁵² of the homolytic bond dissociation energies of benzylic halide radical anions in

Table 7. Rate constants k and standard free energy changes ΔG° for the association between phenyl radical and various nucleophiles.⁵³

Nu ⁻	$k/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$, for $\text{Ph}^\cdot + \text{Nu}^-$	$\Delta G^\circ/\text{kcal mol}^{-1}$
CN ⁻	$< 10^6$	-34
PhO ⁻	No reaction	5
Fluorenyl ⁻	9×10^8	-21
PhCOCH ₂ ⁻	7×10^8	-43
PhS ⁻	8×10^7	-4
NH ₂ ⁻	4×10^8	-36
NO ₂ ⁻	2×10^8	-23
Br ⁻	No reaction	13

the sense $R-X \rightarrow R^\cdot + X^-$ show these to vary between the extremes of 17 (4-nitrobenzyl bromide) and $-6.5 \text{ kcal mol}^{-1}$ (benzyl chloride), most values being centred in the range $2-3 \text{ kcal mol}^{-1}$. Such energy quantities are fully compatible with reversibility. For aryl halide radical anions, it was recently⁵³ pointed out that no experimental sign of the associative reaction ever has been detected, in line with the calculated endergonicity, 13 kcal mol^{-1} , of the $\text{Ph}^\cdot + \text{Br}^-$ step. It is however not clear that any deliberately planned attempts to study this problem by for example using isotopically labelled halide ion have ever been made.

Thus for a consecutive dissociative ET reaction of general type [eqns. (21)–(24)] the principle of microscopic reversibility, together with the fact that the mechanism in the forward direction is well established, immediately tells us the the reverse process has identical transition states, although appearing in the reverse order (Fig. 6).

The extension of the principle of microscopic reversibility to a concerted dissociative step immediately raises some interesting problems. By definition, the reaction must be an elementary process, proceeding via a single transition state. Matching the redox properties of D and

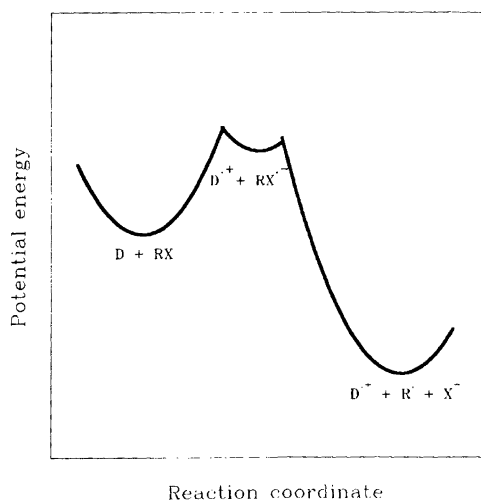
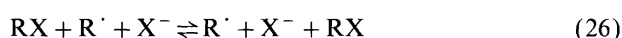


Fig. 6. Energy diagram for a consecutive dissociative electron transfer between D and RX.

R–X to design an approximately thermoneutral process presents no difficulty, and thus eqn. (25) represents concerted dissociative electron transfer.

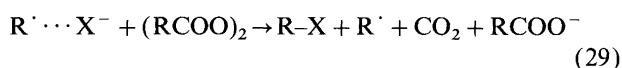
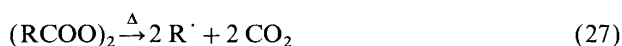


The main difficulty with eqn. (25) is that the reverse reaction must proceed via a termolecular encounter of $D^{\cdot+}$, R^{\cdot} , and X^- , in principle a very unlikely event. Therefore, we are faced with the paradox that a thermoneutral reaction appears as being irreversible: the forward reaction can be made to go reasonably fast, but the reverse reaction must be very slow due to its termolecular nature. These statements cannot be simultaneously correct, and hence the concerted dissociative ET step is ruled out by the principle of microscopic reversibility. Looking at the identity reaction of $RX/R^{\cdot} + X^-$ [eqn. (26)] we are faced with similar difficulties.



We can try to beat trimolecularity in eqn. (25), and for example allow for a weak associative force between R^{\cdot} and X^- to produce weak CT complexes $R^{\cdot} \cdots X^-$ which can be oxidized back to R–X by $D^{\cdot+}$. This amounts to representing the reverse reaction by two elementary steps, but this is prohibited by the principle of microscopic reversibility since the mechanisms of the forward and reverse reaction now do not proceed by exactly the same pathway in either direction. Any assumed complex $R^{\cdot} \cdots X^-$ must appear symmetrically in the mechanism.

The conclusion from this exercise is that a concerted dissociative ET step appears to be excluded by the principle of microscopic reversibility. Thus, there must exist somewhere on the reaction pathway an energy minimum with the composition $R^{\cdot} \cdots X^-$. If one can demonstrate convincing cases of the reverse reaction experimentally, the problem would be solved. A perhaps not too conclusive test is described above, namely that the $CH_3^{\cdot} \cdots Br^-$ complex could be formed from CH_3^{\cdot} and Br^- and identified as a kinetically separate entity via its decay behaviour. With mild ET oxidants, like diacyl peroxides,⁵⁴ as $D^{\cdot+}$, it may be possible to demonstrate the reverse reaction [eqns. (27)–(29)].



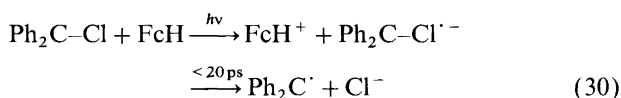
Other putative concerted dissociative ET reactions

Table 8 lists some examples of other reactions which have been discussed in the context of a concerted dissociative ET mechanism. These reactions comprise homogeneous and/or electrochemical transformations of carboxylates, peroxide derivatives, sulfides, disulfides,

sulfonium ions, borates, *N*-halo sultams and *N*-halo imides. In relation to alkyl halide reductions, relatively little work has been performed on these reactions, and therefore they will not be further discussed here.

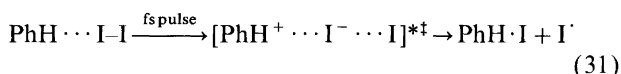
Direct observation of the transition state of dissociative ET

With the advent of femtosecond spectroscopy,^{55,56} the possibility of direct observation of the reaction pathway of dissociative ET steps is available, and thus many of the problems touched upon above will be accessible for critical experiments. An early forerunner in halide chemistry was the demonstration⁵⁷ by picosecond spectroscopy that the radical anion of diphenylmethyl chloride, possibly formed as an intermediate by photochemically induced ET between ferrocene and diphenylmethyl chloride, must have a lifetime < 20 ps [eqn. (30)].



The application of fs techniques to study the cleavage of alkyl halogenide radical anions has, to my knowledge, not been attempted so far, presumably because of the difficulty in finding systems amenable for study. CT complexes are needed for such studies, and even if CT complexes between polyhalides and electron donors are known,⁵⁸ it is not clear that simple alkyl monohalides engage in CT complex formation.

A similar problem is however posed by the photoexcitation of the classical benzene-iodine CT complex [eqn. (31)].

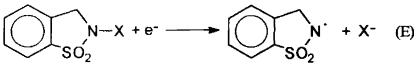
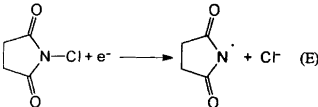
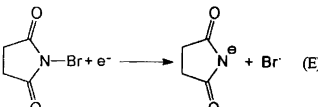


The transition state is created by an fs pulse, and after the ET the $PhH^{\cdot+} I^-$ intermediate has a transient existence of ≈ 750 fs in the gas phase.⁵⁹ Two pathways then lead to products: (i) the I–I bond breaks to give an I^{\cdot} and I^- , the latter combining with $PhH^{\cdot+}$ to give $PhH \cdot I$ which dissociates into PhH and I^{\cdot} , and (ii) fast back ET (≈ 200 fs) to give PhH and iodine on a dissociative potential which produces two I^{\cdot} . In the condensed phase (hydrocarbon) the reaction proceeds on a timescale of less than 25 ps, suggesting a significant role of solvation in promoting a new reaction path, not accessible in the gas phase.⁶⁰

The excitation of the tetranitromethane–naphthalene CT complex in acetonitrile by a 100 fs pulse gave trinitromethanide ion and naphthalene radical cation, no evidence for the intermediacy of $(NO_2)_4C^{\cdot-}$ being obtained. Presumably, this radical anion cleaved to NO_2 and trinitromethanide within the risetime of the initial pulse.⁶¹

Acknowledgements. I thank Gunnar Karlström and Björn Roos for valuable comments on the quantum-chemical calculations cited. Financial support from the Swedish

Table 8. Putative concerted dissociative ET reactions and some of their characteristics.

Reaction, written in its concerted version ^a	Comments	Reference
$\text{RCOO}^- \rightarrow \text{R}^\cdot + \text{CO}_2 + \text{e}^-$ (E)	Kolbe anodic reaction; see the text ^b	5, 12
$(\text{RCOO})_2 + \text{e}^- \rightarrow \text{RCOO}^\cdot + \text{RCOO}^-$ (C)	Obeys the Marcus theory with large λ ; application to hydroquinones suggests inner-sphere mechanism	
$4\text{-NCC}_6\text{H}_4\text{COO-OBu}^t + \text{e}^- \rightarrow 4\text{-NCC}_6\text{H}_4\text{COO}^- + t\text{-BuO}^\cdot$ (E)	Switch from concerted to stepwise mechanism on decreasing the potential	65
$\text{RO-OR} + \text{e}^- \rightarrow \text{RO}^\cdot + \text{RO}^-$ (E)	Marcus theory applies	66
$t\text{-BuO-OBu-t} + \text{e}^- \rightarrow t\text{-BuO}^\cdot + t\text{-BuO}^-$ (C)	Rate constants $\approx 10^4$ times slower than those predicted by the modified Marcus theory; non-adiabatic dissociative ET?	67
$\text{Ph}_3\text{C-S-Ph} + \text{e}^- \rightarrow \text{Ph}_3\text{CS}^\cdot + \text{PhS}^-$ (E and C)	Switch from concerted to stepwise mechanism with change of driving force? k_{cleavage} of radical anion $8 \times 10^{11} \text{ s}^{-1}$	68
$\text{Ph}_3\text{C-S-C}_6\text{H}_4(4\text{-CN}) + \text{e}^- \rightarrow \text{Ph}_3\text{CS}^\cdot + 4\text{-CNC}_6\text{H}_4\text{S}^-$ (E and C)	Consecutive mechanism k_{cleavage} of radical anion $1.2 \times 10^8 \text{ s}^{-1}$	69
$\text{ArS}^+(\text{R})\text{R}' + \text{e}^- \rightarrow \text{Ar}^\cdot + \text{S}(\text{R})\text{R}'$ (E)	Switch from concerted to stepwise mechanism with increase of voltammetric scan rate	70
$\text{PhS-SPh} + \text{e}^- \rightarrow \text{PhS}^\cdot + \text{PhS}^-$ (C)	Radical anion is rapidly cleaved	71
$\text{Ar}_4\text{B}^- \rightarrow \text{Ar}^\cdot + \text{Ar}_3\text{B}^- + \text{e}^-$ (C)	Marcus theory applies; lifetime of $\text{Ar}_4\text{B}^\cdot > 40 \text{ ps}$	72
 $\text{N-X} + \text{e}^- \rightarrow \text{N}^\cdot + \text{X}^-$ (E)	Concerted dissociative ET for X=F, Cl, Br	73
 $\text{N-Cl} + \text{e}^- \rightarrow \text{N}^\cdot + \text{Cl}^-$ (E)	Stepwise mechanism; radical anion cleaves with $k = 8 \times 10^5 \text{ s}^{-1}$	74
 $\text{N-Br} + \text{e}^- \rightarrow \text{N}^\cdot + \text{Br}^-$ (E)	Stepwise mechanism; radical anion cleaves with $2 \times 10^7 < k < 2 \times 10^9 \text{ s}^{-1}$	74

^aE = electrochemical reaction; C = homogeneous reaction. ^bA concurrent electrochemical study⁷⁵ of the oxalate dianion, $^-\text{O}_2\text{C-CO}_2^-$, has demonstrated a stepwise dissociative ET mechanism.

Natural Science Research Council is gratefully acknowledged.

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Received November 30, 1998.