Review Article

The Variety of Molecular Schemes at the Border between Polar and ET Mechanisms*

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Experiments exploring the mechanisms operating at the border between polar and ET mechanisms are described. Starting from a given donor–acceptor (D–A) couple the following mechanistic possibilities are examined on appropriate systems: in-cage versus out-of-cage reactivity, hidden ambident reactivity, pre-equilibria (ion pairing, clustering etc.) where one type of subspecies reacts by ET and another type by polar mechanisms, observations hinting deceptively at the coexistence of ET and a polar pathway, for a given D–A couple, transitions states of varying looseness.

The proposed coexistence of ET and polar pathways in a given D–A system is therefore far more often a starting point for further mechanistic investigation than a mechanistic conclusion.

I. Introduction

Progress in mechanistic chemistry has often been associated with the end of a given dogma. Thus, for a while it was thought that the high improbability of the existence of a triple bond in a six-membered ring was sufficient to discard any mechanism involving a benzyne intermediate. This certainty was then shaken by Roberts *et al.*[1] and this challenge led to a whole field of new experiments increasing both the general understanding of molecular mechanisms and the range of synthetic tools available to the chemist.[2] Similarly, the realization that the fate of a couple comprising an electrophilic substrate and a nucleophilic reagent could be much more varied than the traditional pattern S_N1, S_N2, E1, E2, opened up a completely new branch of mechanistic and synthetic theory.[3] Looking at an electrophile–nucleophile couple simultaneously from the traditional angle and from the point of view of a redox couple was indeed another breakthrough in the mechanistic way of thinking.[4] A characteristic of such breakthroughs is that we often reject them when they appear, but after some years, we become so comfortable with them that they, in turn, become established dogma which slow down the pace of understanding chemistry.

In this report, we intend to deal with those molecular schemes that can be examined when, in a given mixture of substrate and reagents leading to diamagnetic products, some experimental data (kinetics, spectroscopic evidence, final products) indicate the coexistence of several mechanistic pathways. More specifically, some of these involve

exclusively *diamagnetic* intermediates or transition states, whereas some involve also *paramagnetic* intermediates and transition states. We will explore this question with a view biased by the experiments that we have performed for over the last 10 years and attempt answer the apparently simple question 'when an electrophile–nucleophile couple reacts and provides evidence for the participation of both diamagnetic and paramagnetic pathways at which step does the discrimination occur?'
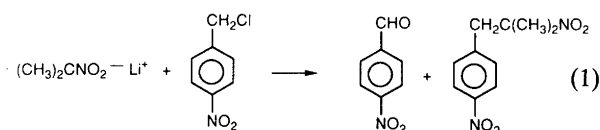
The driving force in this venture was a proposition that we made in 1982. 'If the S_N2 mechanism is viewed as an inner-sphere electron transfer mechanism (the carbon being the bridge), it appears ... .' This proposition was an attempt to bridge the S_N2 concepts and the field of electron transfer mechanisms.[5a] Combined with a quotation made in this same 1982 paper 'J. K. Kochi[6] indeed proposed "According to this formulation, outer-sphere and inner-sphere processes are largely distinguished by the magnitude of the intermolecular separation between the alkyl metal (donor) and the oxidant (acceptor) in the transition states for electron transfer. As such, there should be a continuum of activated complexes differing principally in geometrical constraints, which are manifested in the context of Marcus theory in the work term as well as the reorganization energy",' the preceding proposition obviously entails the experimental challenge: could we find S_N2-type situations where such a continuum occurs and study the patterns of reactivity associated with such a continuum? This question is more ambitious than the one formulated in the preceding paragraph. It often is so: one starts with a glamorous aim, then the pressure of experimental difficulties recalls that several successive less glamorous questions must be settled before addressing the main one.

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Before giving this partial view of a very general problem I would like to encourage the rereading of reviews devoted to this problem viewed from different angles: molecular assisted homolysis,[7] role of charge-transfer complexes in reactivity,[8] the borderline between electron transfer and polar processes[9] and exciplexes reacting through their polar or through their ion radical form.[10]
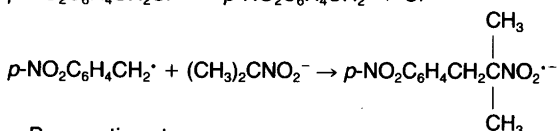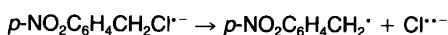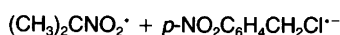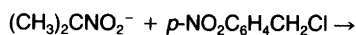
II. In-cage, out-of-cage schemes

The reaction which has triggered the interest in electron transfer mechanisms amongst organic chemists involves the reaction of p-nitrobenzyl halides with lithium nitronate anion, eqn. (1).
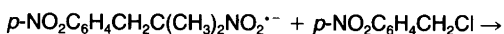
$$(CH_3)_2CNO_2^- \ Li^+ \ + \ \overset{CH_2Cl}{\underset{NO_2}{\bigcirc}} \ \longrightarrow \ \overset{CHO}{\underset{NO_2}{\bigcirc}} \ + \ \overset{CH_2C(CH_3)_2NO_2}{\underset{NO_2}{\bigcirc}} \quad (1)$$

In 1964, Kornblum proposed that the aldehyde was the outcome of a 'classical' S_N2 mechanism whereas the product involving the formation of a C–C bond was the result of an electron transfer from the nitronate anion to the p-nitrobenzyl halide.[3a] At this time, however, the chain nature of this electron transfer initiated pathway was missed and one had to wait until 1966 when Russell and Kornblum proposed what is now the generally accepted mechanism[3b,c] (Scheme 1).

Initiation step

$(CH_3)_2CNO_2^- + p\text{-}NO_2C_6H_4CH_2Cl \rightarrow$

$(CH_3)_2CNO_2^\bullet + p\text{-}NO_2C_6H_4CH_2Cl^{\bullet-}$

$p\text{-}NO_2C_6H_4CH_2Cl^{\bullet-} \rightarrow p\text{-}NO_2C_6H_4CH_2^\bullet + Cl^{\bullet-}$

$$p\text{-}NO_2C_6H_4CH_2^\bullet + (CH_3)_2CNO_2^- \rightarrow p\text{-}NO_2C_6H_4CH_2\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}NO_2^{\bullet-}$$

Propagation step

$p\text{-}NO_2C_6H_4CH_2C(CH_3)_2NO_2^{\bullet-} + p\text{-}NO_2C_6H_4CH_2Cl \rightarrow$

$p\text{-}NO_2C_6H_4CH_2C(CH_3)_2NO_2 + p\text{-}NO_2C_6H_4CH_2Cl^{\bullet-}$

Scheme 1.

They described the mechanism as an electron transfer initiated chain reaction and Bunnett, after extending the scope of the mechanism to the field of halogeno aromatic substrates, christened it $S_{RN}1$; this label is presently the most used acronym to describe this type of reaction.[4c] Paradoxically, however, the most important step of the picture, the chain initiating electron transfer step was very poorly understood although generally accepted as such. This is not a total surprise; the early studies on chain reactions had shown that one of the biggest difficulties in disentangling the successive steps of a chain reaction is the establishment

of the actual nature of the initiating step.[11] Incidentally, the earliest researchers in the field of chain reactions already knew that a good way to trigger a chain reaction between Cl_2 and H_2 is to add small amounts of sodium to the starting reaction mixture.[12]

When Eberson performed a critical evaluation of the various electron transfer mechanisms which had been proposed in the literature through the scrutinity of Marcus theory, he reached the conclusion that the simple examination of the e° and λ of the partners in this reaction did not lead to a straightforward conclusion concerning the feasibility of an electron transfer.[13] This author was supposing an electron transfer between the partners in their ground state.

Before tackling the question 'where does the mechanistic discrimination between polar and ET take place?,' one must first clarify the problem. The first experiments and reviews[4] describing the results in this field were not specific enough. It was often not specified whether the reaction had been performed under irradiation, in sunlight or in complete darkness. In the first two cases, the mechanistic discrimination between polar and ET pathways is obvious. The ET pathway is mainly the result of the reactivity of excited state species (either free or engaged in a charge transfer complex) whereas the polar one results from the reactivity of species in their ground state. The conditions of complete darkness are those in which we are interested. The first thing to do was to check the feasibility of reaction (1) in the dark.

The results gathered in Table 1 show that the reaction is indeed feasible. In itself, this is not a complete proof of a thermal electron transfer as the initiating step. Indeed any paramagnetic impurity [including $(CH_3)_2CNO_2^\bullet$ [15] possibly obtained by the reaction of nitronate with its conjugated acid or with O_2] able to abstract an halogen from $p\text{-}NO_2C_6H_4CH_2Cl$ would trigger the chain as efficiently as an electron transfer. Such a situation would place the $S_{RN}1$-type processes in the classical class of S_H2-initiated chain reactions.[11] The precautions that we took to avoid such a possibility were to work with carefully purified substrates, reagents and solvents, to free the reacting system as much as possible from O_2 and to perform the reaction under N_2. These precautions do not totally guarantee that the reported results are completely safe. Anyone who has consid-
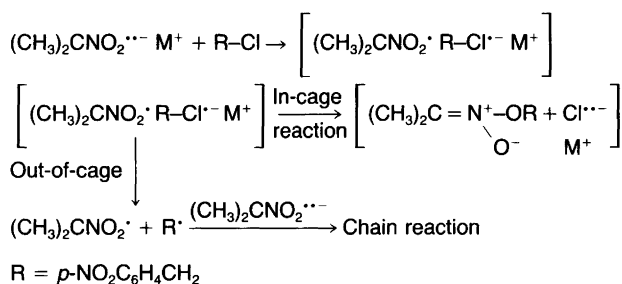
Table 1. Reaction of $p\text{-}NO_2C_6H_4CH_2Cl$ with nitronate anion in the dark, in different solvents[a] at 20 °C.

Solvent[b]	% Substrate transformed[c]	C/O ratio[d]
THF	5	10
DMF	97	6.9
EtOH	18	0.75
THF/HMPA (4/1)	95	0.15

[a]Under N_2. [b]Reagent concentrations. [c]After 8 h reaction at 20 °C. [d]Determined by GLC. [e]Ref. 14.

ered the experimental precautions which should be taken to elucidate the initiation step of a long chain reaction will understand why it is difficult to be categorical about discarding the possibility of an S_H2-initiated chain reaction.[16]

Let us suppose that the precautions taken to avoid the pitfalls mentioned above have been sufficient; we can now address the question of ET-polar molecular discrimination. The first scheme used to rationalize such a discrimination was the in-cage, out-of-cage hypothesis.[17] Applied to the initiation step described in Scheme 1, it would give Scheme 2.

$$(CH_3)_2CNO_2^{\cdot\cdot-} \; M^+ + R\text{--}Cl \rightarrow \left[(CH_3)_2CNO_2^\cdot \; R\text{--}Cl^{\cdot-} \; M^+ \right]$$

$$\left[(CH_3)_2CNO_2^\cdot \; R\text{--}Cl^{\cdot-} \; M^+ \right] \xrightarrow[\text{reaction}]{\text{In-cage}} \left[(CH_3)_2C = N^+\text{--}OR + Cl^{\cdot\cdot-} \atop \quad\quad\quad \setminus O^- \quad M^+ \right]$$

Out-of-cage $\downarrow$

$$(CH_3)_2CNO_2^\cdot + R^\cdot \xrightarrow{\;(CH_3)_2CNO_2^{\cdot\cdot-}\;} \text{Chain reaction}$$

$$R = p\text{-}NO_2C_6H_4CH_2$$

Scheme 2.

Thus, the polar product would be the result of an in-cage reaction for the intermediates (formed by a common ET step from the substrate and reagent) whereas the ET product would be the result of an out-of-cage reaction for the same intermediates. The in-cage, out-of-cage scheme has been often proposed to rationalize the molecular discrimination between polar and ET pathways.[17] In the present example, one experimental observation agrees with such a hypothesis: $p\text{-}O_2NC_6H_4CH_2Cl^-$ is longer lived than $p\text{-}O_2NC_6H_4CH_2Br^-$ and should therefore have more time to escape from the cage.[18] $p\text{-}O_2NC_6H_4CH_2Cl$ yields more product with C–C bond formation than does $p\text{-}O_2NC_6H_4CH_2Br$ in agreement with its longer lifetime.[4b]

The in-cage, out-of-cage scheme as the situation where ET–polar discrimination could occur calls for further sets of experimental checks. The first is to induce cage escape events by application of a magnetic field to the reaction mixture.[19] We have performed reaction (1) in the presence of fields of various intensities and the results listed in Table 2 show no effect of the magnetic field on the C/O-alkylation ratio. The second set of experimental checks

Table 2. Magnetic field effects on the selectivity of eqn. (1).[a]

	$p\text{-}O_2NC_6H_4CHO$ Product **A** (in-cage)	$p\text{-}O_2NC_6H_4CH_2(CH_3)_2NO_2$ Product **B** (out-of-cage)
Earth B	29	38
2.1 Tesla	28	34
17 Tesla	28	35

[a]Solvent, ethanol; concentration; 5×10^{-2} mol^{-1}; temperature; 60 °C: starting material: $p\text{-}O_2NC_6H_4CH_2Br$. From Ref. 22.

involve making the solvent cage more resistant to cage escape processes[20] (Table 3).

Table 3 shows that when the viscosity of the solvent increases the quantity of C-alkylation increases. These results, again, strongly contrast with the expectations that the in-cage, out-of-cage scheme would have favoured.

The results of the preceding experiments added to the illuminating experiments performed by Neta's group[18a] and some frontier orbital considerations[22] led us to formulate an alternative to the in-cage, out-of-cage scheme.

III. Hidden ambident reactivity

The λ values associated with $p\text{-}NO_2C_6H_4CH_2Cl$ in Eberson's treatment of the $S_{RN}1$ reactivity of this substrate reflected the view prevailing at this time for ET–polar molecular discrimination.[13] Indeed, the value was taken to be the same ($\lambda=65$ kcal mol^{-1}) as that taken for a simple benzyl halide. In other words, the discrimination of ET and polar processes was mainly localized on the C–halogen bond. The first suggestion that this might be an oversimplification originated from pulse radiolysis studies performed in Neta's group.[18a] These studies showed that when an electron is added to a p-nitrobenzyl halide, it is first localized on the nitro part of the substrate; only after a given time does it migrate intramolecularly to the antibonding part of the C–halogen bond leading to immediate cleavage of the bond. Symons and Bowman later confirmed and amplified these studies.[18b] These results converged with the molecular orbital treatment of p-nitrobenzyl halides (Table 4) to suggest that these substrates are hidden ambident electrophiles.
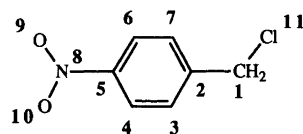
This terminology describes a situation where an electro-

Table 3. Effect of solvent viscosity on the selectivity of eqn. (1).[a]

	$p\text{-}O_2NC_6H_4CHO$ Product **A** (in-cage) (%)	$p\text{-}O_2NC_6H_4CH_2C(CH_3)_2NO_2$ Product **B** (out-of-cage) (%)	O/C
EtOH ($\eta=1.2$ cP)	65	5	13
DEG[b] ($\eta=20$ cP)	5	65	0.08

[a]Concentration of the substrate–reagent: 5×10^{-2} mol l^{-1}; $T = 20\,°C$. [b]DEG = diethyleneglycol. From Ref. 14.

Table 4. Localization of frontier orbitals (MNDO) in *p*-nitrobenzyl chloride, with C–Cl perpendicular to the plane defined by the σ-skeleton of C_6H_4.[a]

MO N[b]	Energy[c]	Atomic orbital coefficients on main atoms[d]										
		1	2	3	4	5	6	7	8	9	10	11
28	−10.74	0	−0.55	−0.31	0.21	0.56	0.21	−0.3	0	−0.13	−0.13	−0.15
30[e] (LUMO)	−1.64	−0.12	−0.48	0.22	0.33	−0.44	0.33	0.22	−0.28	0.26	0.26	−0.16
32	0	−0.23	−0.28	0.26	0	−0.18	0	0.26	0.56	−0.39	−0.39	−0.22
33	0.92	−0.21 0.19 0 −0.55[f]	0.12	0	−0.23[f]	−0.32[f]	−0.23[f]	0	−0.25[f]	−0.15[f]	0.15[f]	0 0.16 −0.47 −0.47[f]

[a]Calculations were performed on Cl rather than on Br in order to save computing time: this should not affect the conclusions extracted from these data. [b]The atomic orbital basis is made of 50 orbitals and, therefore, 50 molecular orbitals (MO) represent this molecule in eV. [c]When π-type MO, the figure stands for the coefficient of p_z; when σ-type MO, the coefficients are given in the order: s, p_x, p_y, p_z. [e]Only the MO where the conformation of C–Cl plays a role are indicated; the other ones remain unchanged in their localization. [f]p_z.

phile possesses an obvious electrophilic center which leads to some of the observed products; the rest of the observed products are better rationalized if one supposes that the electrophilic substrate has a second, hidden, electrophilic center (electrophoric might possibly be a more appropriate term). This center is a LUMO largely localized elsewhere in the molecule; the electron transfer takes place to this LUMO and a subsequent intramolecular electron transfer leads the electron to a place where it plays its role of activation (here dissociative activator).[21] This activation leads to a structural modification in the part of the molecule undergoing the structural change (here substitution). The simple consideration of the final product is, however, mechanistically misleading because the initial event has taken place elsewhere in the molecule. The scope of hidden ambident reactivity is revealed if one considers all the combinations diplayed in Table 5.

It could be applied to many examples of published results taking into account the structural electrophores and holephores recognized in chemistry. Crozet and Vanelle recently extended the synthetic scope of $S_{RN}1$ (long-distance induced $S_{RN}1$) using such an approach.[26] Norris,[27,28] Shaik,[29] Lund,[30] Welvart,[31] Eberson[32] and Savéant[33] have explored the possibility of an initial electron transfer in a part of the substrate or in an orientation different from that involved in a polar competing mechanism.

In this scheme, molecular discrimination between ET and polar pathways occurs early in the sequence of events. The discrimination would occur depending upon the relative orientations of the donor and of the acceptor in the solvent cage preceding the transition state. The orientation leading to a polar product would correspond to a spatial disposition leading to a good overlap between the oxygen

lone pairs in the nitronate anion and the C side of the C–X antibonding orbital. As weak overlap characterizes outer-sphere electron transfer a far wider range of relative orientations could lead to electron transfer. The range of orientations is tempered by the reports showing that some electron transfers are definitely dependent upon the relative spatial disposition of the donor and acceptor.[34]

For the present case, the best disposition of the partners would correspond to a situation in which the plane defined by C, N and O nuclei in the nitronate anion and the plane defined by the carbon atoms of the aromatic ring are paral-

Table 5. Scope of hidden ambident reactivity taking into account the various types of activation[21] induced by electron transfer.

	Type of transformation[b]	Possible examples
Reductive activation[a]		
Dissociative	El–X $\xrightarrow{\text{NU}}$ El–Nu	Eqn. (1)
Associative	El–C = Y $\xrightarrow{e}$ El–C–C–El (Y, Y)	Ref. 23
Oxidative activation[c]		
Dissociative	Hl–Z $\longrightarrow$ Hl· + Z⁺	Ref. 24
Associative	2 Hl–C = Y $\longrightarrow$ C–C (Y, Y; Hl, Hl)	Ref. 25

[a]El stands for electrophore (structural entity with low-lying LUMO). [b]X stands for potential leaving group; Y = sp^2 C, N, O; Z = Sn, Hg, Pb, Tl or even CR_2.[24] [c]Hl stands for holephore (structural entity with high-lying HOMO).

lel. Thus, the electron transfer would be between two π systems, and the value of the reorganisation energy λ would be smaller than the 65 kcal mol^{-1} associated with an electron transfer in the C–X antibonding orbital.[13] Taking λ as 34.5 kcal mol^{-1} and applying it to the Marcus equation describing reaction (1), one obtains a value for k of 8×10^{-7} M^{-1} s^{-1} in place of the value of 3×10^{-11} obtained with $\lambda = 65$ kcal mol^{-1}.

Thus, consideration of hidden ambient reactivity increases the calculated rate of electron transfer by four orders of magnitude.

This increase is not sufficient to reach the range of observed rate constants ($k \approx 2 \times 10^{-2}$ M^{-1} s^{-1}) but is a step in the right direction. Another step had to be taken to understand why an electron transfer could explain the initiation of the chain reaction for the nitronate–p-nitrobenzyl halide reaction occurring in the dark. This will be the object of Section IV.

Another point of general interest involves pushing the hidden ambient reactivity concept to an extreme. This extreme is to consider that, in the reactivity of alkyl halides, there are two reaction centers: the C end (prone to innersphere electron transfers) and the halogen end (more prone to outer-electron transfer). Kochi was the first to consider this possibility[35a] and we have discussed it with respect to the reactivity of various transition-metal centered organometallics towards alkyl halide.[35b] It could also rationalize the observations reported for the reactivity of radical anions towards alkyl halides.[29,33] It is however impossible, at this point, to discriminate experimentally between the model where a donor would perceive methyl iodide as a sphere with no spatial anisotropy with respect to electron transfer and the model where such spatial anisotropy (e.g. preference on the X side) would prevail.

At the presentation of this report in Göteborg, Hoz made an interesting comment about the concept of hidden ambient reactivity. This concept would not be consistent with the Curtin–Hammett principle. This principle, mainly used in conformationally mobile systems, states that 'if two or more isomeric forms of a compound which are in rapid equilibrium undergo a reaction in which each isomeric form gives rise to its own characteristic product, the ratio of the products so formed is independent of the relative energy levels of the various starting forms and depends only on the relative energy levels of the transition states by which the products are formed – provided that the activation energy for product formation is large compared with the activation

energy for the interconversion of the isomeric starting material'.[36] This principle has seen numerous applications and the main exceptions follow from the last part of the preceding proposition not being fulfilled. For hidden ambient reactivity one would have to replace the term 'isomeric forms' by 'relative spatial orientations of the two reactive partners'. The application of this principle to p-nitrobenzyl halide substrates indicates that the leading parameter would be the relative $\Delta G^{\neq}$ for the S_N2-type transition state and for the electron transfer transition states. The S_N2-type transition state with its orbital overlap requirements clearly leads to a greater loss of freedom than the transition states associated with electron transfer. One therefore expects a more negative $\Delta S^{\neq}$ for the polar pathway in agreement with the observed facts.[37] The preceding discussion therefore suggests that the Curtin–Hammett principle and hidden ambient reactivity are not contradictory as long as transition states rather than relative ground-state orientations are referred to.

IV. Electrophilic assistance to electron transfer and the role of pre-equilibria in making the electron transfer step feasible

We remained satisfied with the hidden ambient reactivity explanation of the initiation step of the reaction for a number of years. However, last year in our molecular modeling center, while preparing new slides showing the possible spatial dispositions associated with electron transfer we saw the arrangement shown in Scheme 3. This picture was an eye opener. Could it be that, in this position,
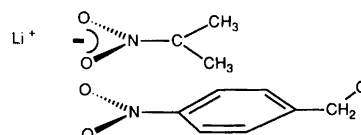
Scheme 3.

the lithium counter-ion acts as a bridge between the two nitro groups holding the substrate and the reagent together?
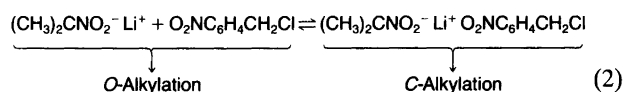
The experiments described in Table 6 did not actually provide an answer to this question but suggested the possibility of electrophilic assistance to electron transfer. Within such a scheme, ET–polar discrimination corresponds to the reactivity of two different electrophilic species. The ET

Table 6. Li$^+$ electrophilic assistance in the selectivity of the substitution reaction of p-nitrobenzyl chloride with the lithium salt of 2-nitropropane.[a]

Nitronate cation	12-Crown-4 (1,4,7,10-tetraoxacyclododecane)	C-Alk. (4)	O-Alk. (%)	[C-Alk.]/[O-Alk.]
Li$^+$	No	69	10	6.9
Li$^+$	Yes	6	85	0.07

[a] Solvent DMF.

takes place on the p-nitrobenzyl halide complexed by Li^+ and the polar mechanism on the free p-nitrobenzyl halide [eqn. (2)].

$$(CH_3)_2CNO_2^- \, Li^+ + O_2NC_6H_4CH_2Cl \rightleftharpoons (CH_3)_2CNO_2^- \, Li^+ O_2NC_6H_4CH_2Cl$$

$$\underbrace{}_{\textit{O}\text{-Alkylation}} \qquad \underbrace{}_{\textit{C}\text{-Alkylation}} \qquad (2)$$

Such a scheme is not without precedent: electrophilic assistance to electron transfer has been repeatedly reported.[38] The results given in Table 6 could also be rationalized by proposing that, in the 'naked anion', the S_N2 reactivity is enhanced relative to the reductive reactivity. More precise kinetic measurements are needed to settle this point.

The experiments described in Table 6 highlight the risk in proposing elaborate explanations in terms of transition-state geometries when simpler pre-equilibria schemes have not been discarded. The pre-equilibrium which leads to ET–polar discrimination may be the above-mentioned electrophilic assistance but it may also be the existence of different degrees of ion pairing[10b,39] or of clustering.[40] In particular, Farid's photochemical experiments have shown the different reactivities of the same substrate according to which molecular assembly surrounds it[41a] and this effect is general in photochemistry.[41b,c] In the ion pairing scheme of ET–polar discrimination, the solvent-separated ion pair of the nitronate (SSIP) would lead to the S_N2 pathway, whereas the ET process would occur for contact ion pairs (CIP). The crown-ether experiments therefore suggest that, rather than a continuum of TS between ET and polar pathways, both mechanisms occur independently and simultaneously in the mechanistic borderline region (cf. the S_N1–S_N2 borderline[42]).

The theoretical treatment of ion-pairing processes suggests that shallow potential-energy surfaces correspond to the transformations between the various active species.[39f] Thus, the relative participation of ET and polar pathways, when both are available (i.e. when the rate of the outer-sphere ET between the electrophile and the nucleophile under a CIP state which is ruled by Marcus equation is of the same order of magnitude as the rate of the inner-spere ET taking place between the nucleophile in an SSIP state and the electrophile), would be ruled by the relative populations of the CIP and SSIP an by the intrinsic microscopic rates associated with the specific environment. The temperature dependence of ET vs. polar products which has been attributed to different $\Delta S^{\ne}$ contributions[33] for the respective transition states could also be due to temperature effects on the pre-equilibrium term.

We have not measured the change of E° of p-nitrobenzyl halide when a Li counter-ion is attached on the NO_2 part. Other data on electrophilic assistance to electron transfer suggest that this change may reach values as high as 1 V.[43] Taking the value of 0.8 V and keeping the λ value of 34.5 kcal mol^{-1}, one may obtain a new value for k (so that E° p-$O_2NC_6H_4Cl^-Li^+$ is 0.69 V vs. NHE) for electron transfer

between nitronate anion and Li^+ p-nitrobenzyl chloride: $k_{calc} = 2.85 \times 10^{-2}$ M^{-1} s^{-1}. This value is not very different from the experimental value ($\sim 10^{-2}$ M^{-1} s^{-1}). We are presently performing experiments to check whether electrophilic assistance is a requirement for this reaction performed in the dark or whether other conditions give rise to the ET polar discrimination (CTC? clustering?).
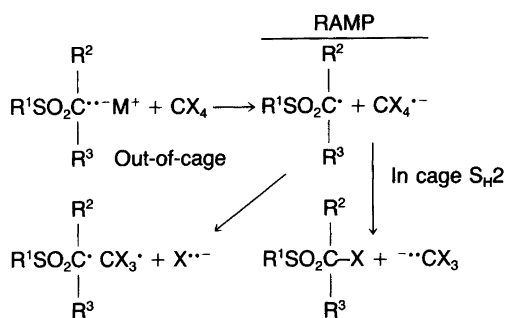
The preceding section illustrates the difficulties associated with the search for the molecular origin of ET–polar discrimination when the initial electron transfer triggers a chain reaction. One of these difficulties, not discussed but which is also present, is the use of selectivity experiments (C/O alkylation) to gain insight into the initiation step of a chain reaction. Indeed, product selectivity analysis in a chain reaction may depend also on the competition between the propagation step and the non-chain step in the overall transformation (i.e. propagation step, Scheme 1, vs. S_N2). kinetic simulation experiments are presently in progress to study the leading parameters for such selectivity with a variety of kinetic rate constants for the elementary steps of the complete mechanism.

V. Possibly deceptive electron transfers and the use of free radical clocks

In view of the ambiguities associated with $S_{RN}1$ processes for the study of the molecular discrimination between ET and polar mechanisms we searched for possibly better candidates.

Polyhalogenomethanes presented attractive features. First, compounds such as CCl_4 and CBr_4 offered no possibility for a hidden ambident pattern of reactivity: all four halogens are the same and the central carbon atom is too sterically hindered to possess any direct reactivity. Secondly, their LUMO lies lower in energy than in most alkyl monohalides; therefore, they are better electron acceptors than most of their alkyl halide counterparts, as shown by their electron affinities[44] and reduction potentials.[44] Thirdly, their radical anions display longer lifetimes than those derived from alkyl halides.[45] Fourthly, Pross, using the mixed configuration model, proposed that CCl_4 should be more prone to react according to an electron transfer pathway than CH_3X.[46] Fifthly, the mechanistic propositions found in the literature to rationalize the thermal reactivity of polyhalogenoalkanes cover the following schemes: straightforward ionic displacement on positive halogen,[47] electron transfer induced chain[48] or non-chain radical[49] reactions, ionic chain reactions,[50] coexistence of several mechanisms[51] and RARP (radical anion radical pair).[52] Thus, one may hope to find situations where ET and polar mechanisms could coexist.

The RARP hypothesis, put forward by Meyers to rationalize a large set of experimental observations, already encompassed the possibility of such a coexistence.[52] Indeed, this author had proposed that the reactivity of α-sulfo carbanions and α-keto carbanions correspond to the situation shown in Scheme 4.

RAMP

R^2 R^2

$R^1SO_2C^{\cdots-}M^+ + CX_4 \longrightarrow R^1SO_2C^{\cdot} + CX_4^{\cdot-}$

R^3 Out-of-cage R^3 In cage S_H2

R^2 R^2

$R^1SO_2C^{\cdot} CX_3^{\cdot} + X^{\cdots-}$ $R^1SO_2C-X + {}^{\cdots}CX_3$

R^3 R^3

Scheme 4.

The acronym RARP stands for radical anion radical pair; it stresses that the radicals involved in this reaction are not 'free' radicals but caged radicals. Indeed, free radicals would lead to racemization of the carbon bearing the negative charge whereas Meyers observed retention of configuration when an optically active α-sulfo carbanion was halogenated during reaction with CCl_4.[52] In one way, this RARP scheme resembles the in-cage, out-of-cage mechanism described in Section II. The difference is that, here, the step leading to the final halogenated product is an S_H2 (bimolecular homolytic substitution) on a radical anion. Such a step cannot be proposed for alkyl halides because of the short lifetime of their radical anions.[53]

Because the experiments with an optically active carbanion include the possibility of small amounts (3–5 %) of racemized products resulting from 'a leak of the cage', we decided to explore the mechanism using free-radical clocks.[54] The first free-radical clock that we designed is shown in Scheme 5.

no traces of cyclized products
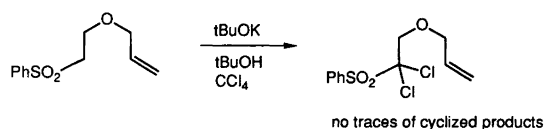
Scheme 5.

The absence even of traces of cyclized halogenated compounds in the presence or in the absence of magnetic field pleaded against a RARP representation in which some of the intermediate species would have leaked out of the solvent cage.

We could have stopped the investigation here and decided that the RARP hypothesis was not supported by free-radical clock studies. But the situation was not that simple. First, Meyers had been able to trap $CCl_3^{\cdot}$ in the medium. Secondly, the free-radical clock that we had used was not a very fast one and there were precedents in the literature where too slow a radical clock had led to erroneous conclusions later corrected by using faster free-radical clocks.[55,56]

The third reason deserves a special paragraph because it deals with a rather widespread general argument in the

literature. This general argument is that one can prove the intervention of radical intermediates by indirect observations (rates of reaction, selectivities, sensitivity to steric hindrance) even if these radicals are not spectroscopically seen or chemically trapped.[56] This is a very challenging situation: apparently everything goes as if the radicals were present in a solvent cage and displayed such a reactivity towards their partner in this cage that this reactive act would be faster than anything else including intramolecular trapping of the radical. In the specific reaction of α-sulfo carbanions towards CCl_4 Scheme 6 describes the situation.


$k = 10^8 - 10^9\,s^{-1}$ $k > 10^{10}\,s^{-1}$?
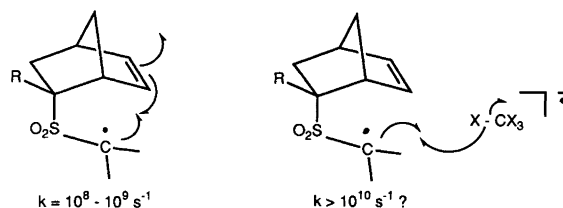
Scheme 6.

Here, an S_H2 step on a CX_4 radical anion (in which C–X bonds are expected to be very weak) would be faster than the intramolecular reaction of the radical on the double bond. It would even be fast enough to compete with the flipping of the intermediate carbon centered α-sulfonyl radical which leads to racemization.[52] The recent studies on the oxygen rebound mechanism in the microsomal cytochrome P-450 hydroxylation of hydrocarbons provides an example of such an extremely fast S_H2-type reaction.[57] Pushed to an extreme this picture becomes fuzzy. When this S_H2 step becomes sufficiently fast one cannot distinguish experimentally between a RARP hypothesis and a displacement reaction on a positive halogen whose transition-state valence-bond representation would contain contributions from paramagnetic resonance structures reminiscent of Linnett's benzene representation.[58]

Therefore, we decided to design and synthetise faster free-radical clocks[59] (Scheme 7). The clock that we first
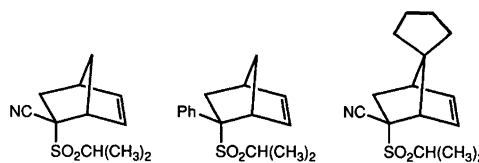
Scheme 7.

designed was substituted at C-5 by a CN group to avoid the possibility of a Ramberg–Bäcklund rearrangement. It is a rather fast clock [eqn. (3)]:[60] even when reaction (3) is


(3)
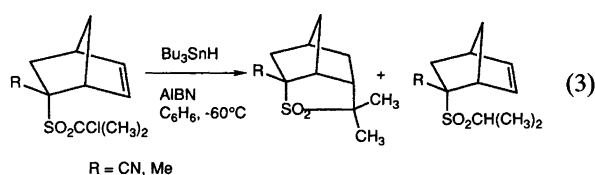
R = CN, Me

performed in the presence of a fiftyfold excess of Bu_3SnH only 35 % of the uncyclized product is found at the end of the reduction ($R = CN$). Supposing that the SO_2 group exerts a negligible effect on the adjacent carbon-centered radical for the S_H2 reaction of this radical on Bu_3SnH (i.e. $k_{S_H2} = 6.3 \times 10^6 \, M^{-1} \, s^{-1}$) and using the competition method designed by Ingold et al.,[61] one finds that the rate of cyclization of this α-sulfonyl radical is about 2×10^8 ($R = CN$) or $10^9 \, M^{-1} \, s^{-1}$ ($R = Ph$).

The stabilizing effect of SO_2 on an α-carbon-centered radical has recently been calculated by Clark as being equal to 0.5 kcal mol^{-1}.[62] Thus, its effect on reactivity should be rather small; even if one takes a tenfold deactivation effect of this group on S_H2 toward Bu_3SnH, the rate of cyclization of the norbornenyl clock with $R = Ph$ stays in the range of $10^8 \, M^{-1} \, s^{-1}$ which ranks among the fastest clocks presently reported for an intramolecular addition to a double bond.[63,64]

An X-ray crystallographic determination provides some clues as to the reasons why these free-radical clocks are so fast.[60] The information provided by an X-ray determination of these radical precursors is shown in Scheme 8.

α1 = 107.7°
α2 = 117.5°
α3 = 108.5°
α4 = 106.0°

α1 = 108.4°
α2 = 108.6°
α3 = 107.5°
α4 = 104.0°
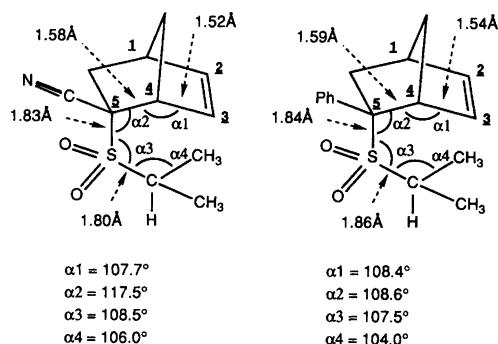
Scheme 8.

These structures show the reasons for the high reactivity of these intramolecular traps. First is the restricted rotations around the bonds 3–4 and 4–5. The only degrees of freedom left to the radical for escaping the spatial situation where it is the closest to the double bond is rotation around the C5–S bond. Secondly, the structural characteristics of SO_2 (C–S bond lengths and C–S–C angle) bring the carbon-centered radical into closer spatial proximity to the double bond than does a CH_2 (Ashby's clock).[65] Thirdly, the phenyl group, which pushes the whole SO_2R group into closer spatial proximity to the double bond than does the CN, leads to a compound whose radical cyclization rate is about ten times that measured for the CN compound. We are presently combining these trends with the use of molecular mechanics to design even faster free-radical clocks.[66]

When the halogenation reaction of α-sulfo carbanions with polyhalogenomethanes (CCl_4, CBr_4) was performed with the two abovementioned rapid free-radical clocks, no cyclized products were found in the final mixture (Scheme 9). Performing the reaction in magnetic fields of low (2.1 T) or high (17 T) intensity did not change this result.
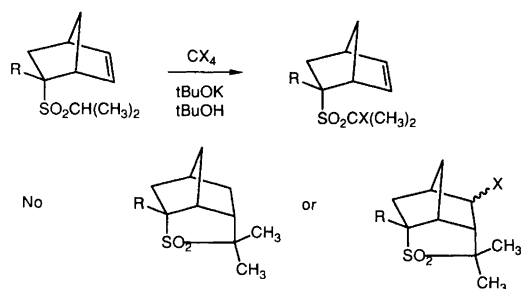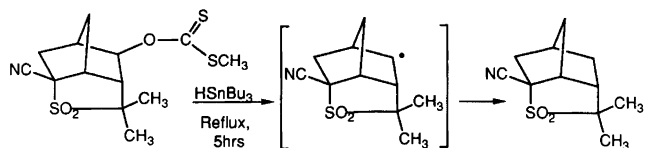

Scheme 9.

The absence of cyclized products could be a misleading observation in the absence of a number of complementary experiments. The first is to check that if the halogenated cyclized compound were formed in the medium (tBuOH, KOH), it would tolerate the conditions and would not react further to give another product. This halogenated, cyclized product was independently prepared and remained unchanged when placed in the reaction mixture at 25 °C for 5 h. The second experiment is to ascertain that the role of
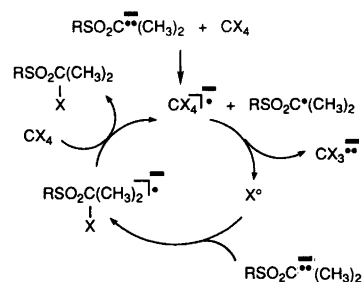
Scheme 10.

the α-sulfo carbanion is not one shown in Scheme 10 or any other carbanion-initiated chain reaction.

If such a situation were to prevail and if a long chain were to follow the initiation step, then the reaction would be of the ET type; however, the radcal clock would give rise only to very small amounts of cyclized products. This second possible pitfall has been discarded by Meyers's group who showed that the halogenation of sulfones in the absence of Cu^{++} is not a chain reaction.[52] The third precaution to be taken when using a new free-radical clock is to check that the intramolecular reaction of the radical does not correspond to a reversible reaction.[67] This eventuality was

Scheme 11.

checked by performing the Barton's reaction shown in Scheme 11.[68] No norbornenyl products were detected in this reduction; the intermediate radical is therefore less prone to β-scission than to H atom abstraction. Given these

experiments, we are led to the conclusion that the α-sulfo-carbon-centered radical reacts with the CX_4^- anion at a rate greater than 10^{10} M^{-1} s^{-1} or that the halogenation reaction occurs by a straightforward nucleophilic attack on the positive halogen. The retention of configuration in halogenations reported by Meyers is a further important argument in favor of a straightforward nucleophilic attack on a positive halogen. For more compelling evidence, this experiment using chiral α-sulfonyl substrates should be repeated to check whether the retention is actually 100 % or reaches only 95 % or more.

VI. Variable transition-state structure

When all the possibilities described in sections II–V have been experimentally rejected, the mixed configurations model provides an attractive rationalization of reactions where an ET and a polar mechanism coexist. In this model it is considered that the structural variations caused in a transition state by structural or medium effects may suffice to go from a polar to an ET pathway in a given reaction.[73a,b] It is therefore in line with Kochi's proposition (see the introduction) of the existence of a continuum between outer-sphere and inner-sphere mechanisms.

This model deserves careful experimental verification. First of all, one must be sure, for a reaction where polar and ET pathways coexist, that the place where molecular discrimination takes place is actually a common transition state rather than a series of equilibria (ion pairing, clustering, electrophilic assistance) where some sets of species of the equilibrium follow a polar pathway and others follow an ET pathway. In one way, the variable transition-state structure model could be reconciled with the pre-equilibrium model (section IV). If one sees the overall selectivity as the result of a competition of nucleophilic species involved in an SSIP against the reductant species involved in a CIP, one would have to suggest that the transition state associated with the first case is tighter than the transition state associated with the second.

Among the difficulties which make a serious experimental check of the mixed configuration model difficult, one must cite the high uncertainty presently prevailing in the structural representation of S_N2 transition states. For some authors, the structural variations (lengths of the bonds to be formed, angles etc.) associated with a given substitution reaction are non-existent: this is the conclusion reached independently by Arnett[69] and by Bordwell.[70] Our work in this field using steric effects to monitor structural transition-state variations when one changes the leaving group from tosylate to triflate in the Menschutkin reaction[71] indicates that tiny variations consistent with More O'Ferrall diagrams[72] could occur. At the other end of the range, the mixed configuration model advocates a considerable structural variability of the S_N2 transition state for a given S_N2 reaction.[73] These propositions are not necessarily contradictory: Lund's results suggest that if a continuum of situations exists in the S_N2 mechanism, the borderline is clos-

er to the ET extreme.[74] It could therefore be that in the classical S_N2 representation, small structural variability prevails, whereas, at the other extreme, larger structural variabilities characterize transition states.

VII. The need for further experimental studies

Arguably the most influential report of the decade on the ET/polar problem is Pross' review.[9a] This report is invariably cited in papers describing situations where ET and polar pathways coexist. Furthermore, this report provided examples which suggested the existence of a continuum between ET and polar pathways. One approach, when studying a mechanistic problem, is first to gather all the formal possibilities, then to find experiments able to discriminate between them. A drawback of Pross' report is that the main formal mechanistic possibility that it offers is that of a continuum of transition states when polar and ET mechanisms are apparently present (section VI). Therefore, when this review is cited because some experimental observations indicate the coexistence of ET and polar pathways, this citation seems directly to support the continuum ET–polar scheme.

We have illustrated in this paper that several other molecular schemes are actually available when experiments demonstrate the coexistence of polar and ET pathways for a D–A couple. There could quite possibly be others not described in this report. Particularly important is that ET–polar discrimination, rather than being settled in a transition state, could simply arise from pre-equilibria (various degrees of ion pairing, clustering, electrophilic assistance, etc.). The role of such pre-equilibria has clearly been identified in pure ET processes,[75] photochemistry,[41,42] electrochemistry[76] and organometallic chemistry.[77] There is no reason why this should be neglected when the border between ET–polar processes is under scrutiny.

To summarize, we initiated these experimental studies in 1982 in a kind of one-track minded spirit 'search for experimental proof that there could be a continuum between ET and polar pathways'. We have not found any. This does not mean that there is none. However, the material described in this present article reminds us that the general methodology of mechanistic determinations applies to this problem too. This methodology is summarized in Fig. 1.
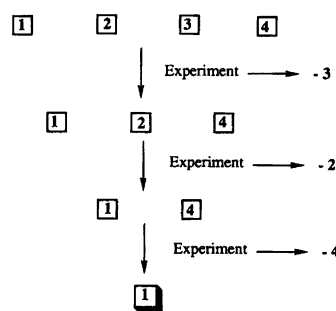

Fig. 1. Determination of a mechanism.

When the behavior of an electrophile–nucleophile couple suggests that diamagnetic and paramagnetic pathways coexist, the first important step is to make an inventory of all mechanisms which could account for the experimental observation. Only then can we begin to design experiments able to select from the various possibilities. If only one possibility is forgotten at the inventory step, then the sword of Damocles hangs over the conclusions.

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