

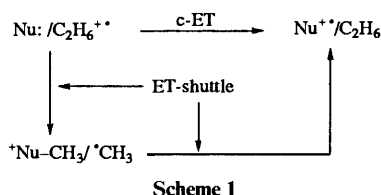
Electron transfer mechanisms: a mechanistic changeover induced by an intramolecular spacer in a model reaction of the $\text{NH}_3/\text{C}_2\text{H}_4^{+\cdot}$ pair

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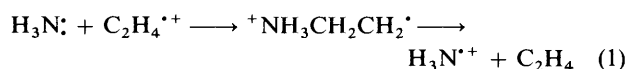
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Computational evidence is reported for a reversal in the type of an electron transfer (ET) mechanism, induced by an intramolecular linkage of the donor (amine) and acceptor (cation radical) moieties *via* a single $-\text{CH}_2-$ spacer. An isotope effect probe is suggested to detect this mechanistic changeover.

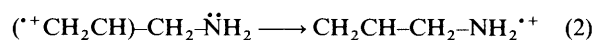
Recently^{1a} we have reported theoretical results showing that ethane cation radical ($\text{C}_2\text{H}_6^{+\cdot}$) undergoes ET reactions with nucleophiles (Nu^\cdot) *via* a mechanistic manifold involving two distinct archetypes which are exemplified in Scheme 1. The first is the concerted ET (c-ET) mechanism that proceeds directly *via* structured (inner-sphere)^{1b-d} or non-bonded (outer-sphere) transition state. The second is an indirect shuttle-ET mechanism in which a group transfers to-and-fro as a redox-pair and relays thereby a single electron from the nucleophile to the substrate,^{1a} as exemplified in Scheme 1 by the sequence of bond-making followed by oxidative cleavage. As has been noted the transition states (TSs) of the c-ET and shuttle-ET mechanisms share similar electronic features, and as such constitute a mechanistic family with variable transition state character.^{1a}



The shuttle-ET has been found since then in a variety of $\text{Nu}^\cdot/\text{RH}^{+\cdot}$ combinations.² This ubiquity of the ET-shuttle along with its relation to c-ET raises two fundamental questions: what are the limiting conditions for the shuttle-ET and when will it revert to the traditional c-ET mechanism? This communication addresses these questions and demonstrates by means of *ab initio* calculations on model systems how a prevailing shuttle-ET between ethene cation radical and ammonia [eqn. (1)] can be converted into a direct ET



mechanism [eqn. (2)] by an intramolecular linkage of the



amine/ethene cation radical pair with a $-\text{CH}_2-$ spacer. Being very simple these systems serve merely to illustrate a clear strategy for controlling the mechanism of an ET process.

The various species in eqns. (1) and (2) were computed with the GAUSSIAN 92 package^{3,4} using the 6-31G* basis set⁵ with standard techniques of geometry characterisation and path-

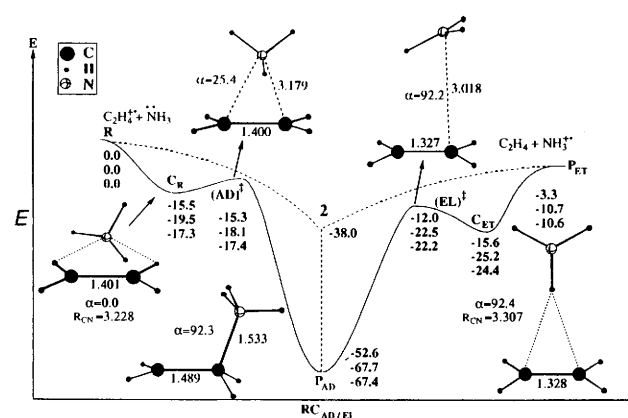
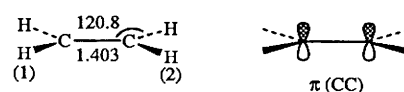


Fig. 1 Stepwise ET-shuttle mechanism for the $\text{NH}_3/\text{C}_2\text{H}_4^{+\cdot}$ pair. Geometries correspond to the ROHF/6-31G* level. The three energies (kcal mol^{-1}) given below each species correspond to the ROHF/6-31G*, UMP2/6-31G* and ROMP2/6-31G*//ROHF/6-31G* levels, respectively. α Is the angle between the C_2H_4 plane and the N atom. R = reactants, C_R = reactant cluster, $(\text{AD})^\ddagger$ = addition transition state, P_AD = addition product, $(\text{EL})^\ddagger$ = elimination transition state, C_ET = electron transferred cluster, P_ET = electron transferred products. The dashed energy profile corresponds to the π approach (see the text). The H-bonds in C_R and C_ET are shown by dotted lines. The energy for 2 is a UMP2/6-31G* datum.

following.⁶ The ROHF, UHF, UMP2 and ROMP2/ROHF levels of theory, which are employed here, are the highest common levels, and were chosen after verifying that all the critical points of the reaction profile in the Fig. 1 remain intact up to UQCISD(T) and UCCSD(T) levels. The common levels employed here give virtually identical mechanistic information, even though the UMP2 level exaggerates spin contamination⁷ for one of the transition states of eqn. (2) (see later AD^\ddagger in Fig. 2).



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The long C-C bond isomer of $\text{C}_2\text{H}_4^{+\cdot}$ arises from the ionization of the $\pi(\text{C}-\text{C})$ orbital as shown in 1 for the ROHF level. It is noted that at the UHF and ROHF levels the $\text{C}_2\text{H}_4^{+\cdot}$ cation radical is planar, but slightly twisted at the UMP2 level ($\tau \cong 5^\circ$). This twisting feature is well known from the studies

of Cederbaum *et al.*,^{8a} Buenker and Peyerimhoff^{8b} and Bellville and Bauld.^{8c} A twist angle of 3.5° is also obtained at the UMP2 level for the reactant cation radical of eqn. (2). This difference between the HF and MP2 levels does not affect the qualitative essence of the ET mechanisms which are virtually identical at the three computational levels.

The electron transfer mechanisms found in this study are schematized by the reaction profiles in Figs. 1 and 2. Fig. 1 shows the addition–elimination stepwise mechanism for the intermolecular $C_2H_4^{*+}/NH_3$ combination, eqn. (1), in general accord with the previous results of Yates and Radom.⁹ Here an initial reactant cluster (C_R)† undergoes first a nucleophilic addition process leading to an addition product (P_{AD}).‡ This addition product undergoes in turn an elimination of an NH_3^{*+} species and thereby the process results in a net electron transfer from the nucleophile to the cation radical.† The dashed lines in Fig. 1 show the potential energy curves in a π -trajectory in which the two reactants maintain overlap between the nitrogen's lone pair and the π -type orbitals of the ethylene cation-radical (see 2 below). The addition–elimination mechanism is retained even though the trajectory now by-passes the clusters and saddle points. In contrast with this shuttle-ET mechanism, the intramolecular $-CH_2-$ spacer [eqn. (2)] induces a dramatic change and the reactant§ undergoes two distinct direct mechanisms for the ET and addition processes (Fig. 2), *via* two transition states (AD^\ddagger and ET^\ddagger). Two questions follow: what is the origin of this mechanistic changeover? Is there a characteristic probe that can distinguish between the two mechanisms?

An outstanding difference between Figs. 1 and 2 is the extremely exothermic addition process in the intermolecular case (Fig. 1). This however is insufficient by itself to account for the striking difference in Figs. 1 *vs.* 2 because the addition reaction is the thermodynamically favourable step in both systems. The reason appears to originate in the interplay of the thermodynamic and the transition state (TS) resonance energy factors. According to the valence bond configuration mixing (VBCM)¹⁰ analysis, the ET-TS requires the optimization of the overlap between the π -orbital of $C_2H_4^{*+}$ and the lone-pair orbital of NH_3 , $n(NH_3)$, while the addition TS requires the optimization of the overlap between $\pi^*(C_2H_4^{*+})$ and the lone pair of NH_3 . It is apparent that both conditions require approach of the nucleophile in the π -plane of the cation radical. In the intermolecular process (Fig. 1), the π -plane approach leads to strong $n(NH_3)-\pi$ and possibly $n(NH_3)-\pi^*$ overlaps. These strong overlaps combined with the favourable thermodynamics for the N–C bond making stabilize all the points along the π -plane trajectory, shown in the dashed lines in Fig. 1. So much so that this trajectory leads in a barrierless manner to the addition product (P_{AD} , Fig. 1), *via* structure 2 which lies $38.0 \text{ kcal mol}^{-1}$ (UMP2//UMP2) below the entrance channel of the $C_2H_4^{*+}/NH_3$ reactants and acts as a transition state for the rearrangement process^{9,11} of the addition product to its mirror image ($^+H_3N-CH_2-CH_2^+$ and $^+H_2C-CH_2-NH_3^+$). As a

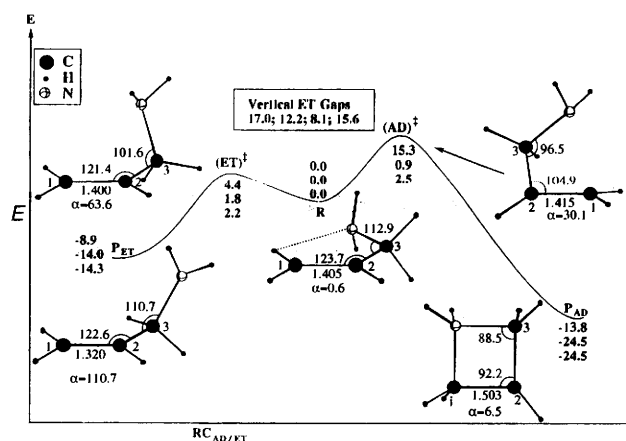
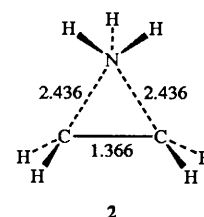


Fig. 2 Concerted ET (c-ET) and addition mechanisms for (^+H_2CCH)– CH_2 – NH_2 . ROHF/6-31G* geometries are indicated. The three energies (kcal mol^{-1}) given below each species correspond to the ROHF/6-31G*, UMP2/6-31G* and ROMP2/6-31G*/ROHF/6-31G* levels, respectively. $\alpha = C1-C2-C3-N$ dihedral angle. The labels of the species can be read from the caption to Fig. 1. The values in the box are vertical ET energy gaps in kcal mol^{-1} (ROHF//ROHF; UMP2//UMP2; ROMP2//ROHF; and UHF//UHF from left to right in respective order). The H-bond in C_R is shown by a dotted line.

consequence of this strong overlap, the only TSs observable for the intermolecular process in Fig. 1 are conformational TSs along non-overlapping trajectories between the $n(NH_3)$ orbital and the π -plane orbitals of $C_2H_4^{*+}$. Thus, the entire bonded trajectory in Fig. 1 is occupied by the addition–elimination pathway, such that the ET process occurs if at all by shuttle-ET.



The strong overlap as well as the thermodynamic sink of the addition product are both mitigated by the $-CH_2-$ spacer. Indeed, the intramolecular system (Fig. 2) requires either a four- or three-membered ring structure in order to orient the nucleophile moiety ($-NH_2$) in the π -plane of the cation radical. This creates, in turn, a strain-induced barrier for the addition process, as well as a competitive c-ET pathway with a well defined TS (ET^\ddagger , Fig. 2).

The structured nature of ET^\ddagger can be seen by looking at the various geometrical parameters involved in the ET process in Fig. 2. In addition to the C–C distance that shortens, the major change that occurs is in the C1–C2–C3–N dihedral angle (α) which starts as 0.6° in the reactant and increases to 63.6° in the ET^\ddagger . This angular variation enables the requisite overlap to be achieved between the lone pair orbital on the nitrogen atom and the C–C π orbital. The parameter C2–C3–N angle exhibits an interesting trend. This angle is 111 – 113° in both the reactant and the ET product but goes to as low as 101.6° in ET^\ddagger though this angle shrinking involves significant strain. This indicates the propensity for specific bonding in the ET-TS even against adverse structural strain. The C1–C2–C3 angle which is roughly the same (123 – 124°) in both the reactant and ET^\ddagger , and relatively small (104.9°) in the addition TS (AD^\ddagger) indicates that ET^\ddagger achieves the maximum bonding when the lone pair orbital points towards the centre of the C–C bond while the addition

† The reactant cluster (C_R) in Fig. 1 is stabilized by hydrogen bonding between the positively charged hydrogens of the cation-radical and the negatively charged nitrogen. Similarly, the ET cluster (C_{ET}) is stabilized by an inverse hydrogen bond.

‡ P_{AD} in Fig. 1 was recently identified by means of neutralization–reionization mass spectrometry.¹⁷ A proton abstraction pathway also exists which is exothermic by $20.8 \text{ kcal mol}^{-1}$ relative to the reactants. This proton abstraction path starts a shuttle-ET *via* H^+ transfer to NH_3 followed by back transfer of H^+ from NH_4^+ to $H_2C=CH^+$.

§ The reactant's conformation in Fig. 2 is locked by a hydrogen bond between the positive hydrogen of the olefinic cation radical moiety and the negatively charged nitrogen, with a rotation barrier of 8.5 – $11.4 \text{ kcal mol}^{-1}$ about the CH_2NH_2 bond. The $CH-CH_2$ rotational barrier is also significant ($7.1 \text{ kcal mol}^{-1}$).

TS optimizes its bonding when the lone pair points specifically towards the site of attack, the C1 carbon. Furthermore, the negative, albeit small, entropy of activation computed for both ET and addition processes, -3.5 and -6.0 eu, respectively, indicates the two TSs are both bonded and possess definite structures.

To identify a potential mechanistic probe we calculated possible kinetic isotope effects for the two processes of Fig. 2. Our results show that the NH_2/ND_2 isotope effect, which is inverse (0.987) for the addition process and normal (1.123) for the ET process, is a potential differentiation between the two mechanisms. For comparison, the equilibrium isotope effect for the addition step of the shuttle-ET mechanism in Fig. 1 is 0.233, while for the overall ET process the equilibrium isotope effect is 2.932.

There exist plenty of experimental data on ET and addition reactions of nucleophiles with π -cation radicals. A few of these cases involve ET-shuttle analogues of Fig. 1. Thus, Ebersson *et al.*¹² have reported ET-shuttles in the reaction between aromatic cation radicals and nucleophiles. Davis and Gilbert¹³ have reported an ET-shuttle in the reaction of oxidants with olefins—precisely the reverse process of Fig. 1 (starting from the right-hand side). A similar mechanism has been proposed by Steenken¹⁴ for the radiation-induced damage of DNA bases. Grützmacher¹⁵ *et al.* have reported ET reactions between the dichloroethene cation radicals and the $\text{NH}(\text{CH}_3)_2$. These later reactions were implied to proceed *via* direct c-ET mechanism, but the lack of mechanistic studies may not necessarily warrant this assignment. The shuttle-ET mechanism may still be the leading mechanism. In any event, to the best of our knowledge, mechanistic changeovers have not been studied before in organic ET reactivity. Based on our isotope effect calculations the NH_2/ND_2 kinetic isotope effect can serve to distinguish the shuttle-ET and c-ET alternatives. This could be a test of our proposal that ET reactions of cation radicals proceed *via* a mechanistic manifold.¹⁴ Should the test verify, the use of spacers[¶] would then be a general strategy for mechanistic reversal of an ET process in cation radical chemistry.

Acknowledgements

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¶ Of course the spacer will also induce through-bond coupling as shown by Paddon-Row.¹⁶ The through-space overlap in our case is three times as large as through-bond (owing to the $-\text{CH}_2-$).

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