Single-Electron Self-Exchange between Cage Hydrocarbons and Their Radical Cations in the Gas Phase**


We show that the radical cations of adamantane (C\textsubscript{10}H\textsubscript{16}+, 1H\textsuperscript{+}) and perdeuteroadamantane (C\textsubscript{10}D\textsubscript{16}+, 1D\textsuperscript{+}) are stable species in the gas phase. The radical cation of adamantylidenedeadamantane (C\textsubscript{20}H\textsubscript{28}+, 2H\textsuperscript{+}) is also stable (as in solution). By using the natural \textsuperscript{13}C abundances of the ions, we determine the rate constants for the reversible isergonic single-electron transfer (SET) processes involving the dyads 1H\textsuperscript{+}+/1H, 1D\textsuperscript{+}/1D and 2H\textsuperscript{+}/2H. Rate constants for the reaction 1H\textsuperscript{+}+/1D\textsuperscript{+}+/1H\textsuperscript{+} are also determined and Marcus’ cross-term equation is shown to hold in this case. The rate constants for the isergonic processes are extremely high, practically collision-controlled. Ab initio computations of the electronic coupling (\textit{H}_\text{int}) and the reorganization energy (\textit{\lambda}) allow rationalization of the mechanism of the process and give insights into the possible role of intermediate complexes in the reaction mechanism.

1. Introduction

Electron transfer (ET)[1] and/or proton-coupled electron transfer (PCET)[2] mediate fundamental biological processes such as cell respiration[3] and photosynthesis[4]. The study of ET at electrode surfaces[5] has played a key role in the development of theoretical models for ET processes.[6] Presently, these processes are being studied at the single-molecule level[7] and they still pose a challenge for both experimentalists and theoreticians.

Figure 1. Structures of 1H and 1H\textsuperscript{+}. Distances (\textgreek{A}) in parentheses and brackets were computed at the UMP2/6-311G(d,p) and B3LYP/aug-cc-pVTZ levels, respectively. Experimental geometry from ref. [8]. For high-level studies on 1H, see, for example, ref. [9].

Herein, we focus on the gas-phase isergonic self-exchange single-electron transfer (SET) reaction between the radical cations derived from the hydrocarbons adamantane (C\textsubscript{10}H\textsubscript{16}, 1H) and adamantylidenedeadamantane (C\textsubscript{20}H\textsubscript{28}, 2H) and the corresponding parent hydrocarbons (see Figures 1 and 2). The role of these species in different chemical processes such as selective functionalization of aliphatic and alicyclic hydrocarbon cations derived from their radical cations[11–13] or the recently demonstrated ability of a family of diamondoids (1H is the smallest diamondoid structure) to act as good electron emitters[14] (presumably due to the stability of the diamondoid radical cations on metal surfaces) makes ET processes involving this kind of molecules an interesting research topic.

The dyads 1H\textsuperscript{+}/1H and 2H\textsuperscript{+}/2H are characterized by three-dimensional rigidity and stability. Moreover, and at variance with the radical cations of many other aliphatic and alicyclic hydrocarbons,[15] fast reactions such as loss of H\textsuperscript{+} and H\textsuperscript{+} do not efficiently compete with ET. Indeed, although 1H\textsuperscript{+} irreversibly loses H\textsuperscript{+} (as shown in this work and also by direct electron-impact experiments)[16] the rate of this process is slower than that of ET.

** A Combined Fourier Transform Ion Cyclotron Resonance (FT-ICR) and Computational Study

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In particular, $\text{1H}^+$ has been identified as an intermediate in the oxidation of $\text{1H}_2$ and in the transition states for the reaction of $\text{1H}$ with polyhalogen electrophiles and other highly oxidizing species in solution displaying considerable radical character.\[1,10\] Radical cation $\text{2H}^+$ appears as a long-lived one-electron, two-center $\pi$-bonded species\[11\] in different chemical processes, and this has allowed its characterization by near-UV/Vis spectroscopy.\[12,13\] It has also been identified in the epoxidation of $\text{2H}$ by $\text{O}_2$ catalyzed by nitrogen oxides, as well as in the direct epoxidation of $\text{2H}$ by $\text{NO}_2$.\[14\] Interestingly, however, these ions show very different reactivity, whereby $\text{2H}^+$ is less reactive than $\text{1H}^+$ due to the difference between the adiabatic ionization energy ($\text{IE}_a$) of $\text{1H}$ (9.40 eV)\[15\] and that of $\text{2H}$, which is less than or equal to the vertical ionization energy ($\text{IE}_v$) of 7.84 eV\[16\].

From the point of view of the mechanisms underlying the ET processes, different formulations of intermolecular ET between freely diffusing neutral or charged electron donors (D) and acceptors (A) rely on the formation of transient 1:1 precursor complexes (D, A) that play a key mechanistic role\[17\] (see Scheme 1).

$$D + A \rightleftharpoons (D, A) \rightleftharpoons (D^-, A^+) \rightleftharpoons D^- + A$$

**Scheme 1.** Electron transfer between freely diffusing neutral or charged electron donors (D) and acceptors (A).

From the standpoint of theoretical analysis, ET has remained a challenge since the seminal works of Mulliken, Marcus, and Hush. Mechanistically, ET processes can be classified as adiabatic, weakly adiabatic or non-adiabatic, depending on the value (high, intermediate or low, respectively) of the coupling ($\text{H}_{\text{DA}}$) between the electronic states involved in the reaction, which determines the role that non-adiabaticity plays in the process. This has important mechanistic consequences, whereby hopping between surfaces leads to lower ET rates in non-adiabatic ET processes than would be obtained were they adiabatic. Between the two extreme cases, the weakly adiabatic ET regime displays intermediate characteristics. The nature of ET—adiabatic, weakly adiabatic or non-adiabatic—determines the kind of computational approach that is more appropriate for its description. In the case of the rate constant for adiabatic ET, the Marcus expression (Eq. (1)) usually provides a good description of the kinetics:

$$k_{\text{ET}} = \nu_0 e^{-\frac{\Delta G^0}{RT}}$$

(1)

Here, $\nu_0$ is the nuclear frequency factor, $\Delta G^0$ the change in free energy in the reaction, and $\lambda$ the reorganization energy for ET, defined as the energy required to distort the reactants and the associated solvent shell from their initial nuclear equilibrium configuration to that of the products, which, together with $\text{H}_{\text{DA}}$ is a key parameter in the classification and description of ET processes. The $\lambda$ value is evaluated as the sum of two independent components: the internal (solvent-independent) term $\lambda_{\text{int}}$ emerging from the structural differences of reactants and products, and the solvent-dependent term $\lambda_s$ originating in the different configurations (orientation and polarization) of the solvent molecules around the reactants and products. In Equation (1), it is implicitly assumed that the transmission coefficient is unity.

On the other hand, for the non-adiabatic process a different expression for the rate constant is used (Eq. (2)):

$$k_{\text{ET}} = \frac{4\pi^2|\text{H}_{\text{DA}}|^2}{\hbar} \left( \frac{1}{4\pi^2k_B T} \right)^{1/2} e^{-\frac{\lambda^2}{4\pi^2k_B T}}$$

(2)

The existence of surface hopping between energetically close potential-energy surfaces leads to a transmission coefficient less than unity, that is, not every trajectory leads to formation of the products of the process.

Among the different ET processes, SET reactions (3) and (4) are the simplest class of reactions in chemistry because of 1) elimination of the relative thermodynamic stability of reactants and products and 2) the fact that no chemical bonds are broken or formed in simple electron-transfer reactions.\[18\]

$$\text{A}^+ + \text{A} \rightleftharpoons \text{A} + \text{A}^+ \quad (3)$$

$$\text{A}^+ + \text{A} \rightleftharpoons \text{A} + \text{A}^+ \quad (4)$$

Line broadening of ESR spectra\[19\] has provided numerous rate constants for self-exchange processes in solution involving dyads of neutral species and radical cations or radical anions derived therefrom.\[20,21\] X-rays were used to determine the structures of the corresponding precursor complexes.\[22,23\] UV/ NIRSpectrophotometry\[24\] allowed determination of $\text{H}_{\text{DA}}$ within the precursor complex. In the case of intramolecular ET,\[25\] spectrophotometric methods allowed experimental determination of $\text{H}_{\text{DA}}$ and also delimited the scope of Hush model.\[26\]

In the gas phase, ET involving hydrocarbons is also well known and experimental kinetic and thermodynamic data for electron exchange in mixtures of radical cations and anions derived from aliphatic and alicyclic hydrocarbons and neutral hydrocarbon molecules have been obtained by ion cyclotron...
Experimental and Computational Methods

Materials: Adamantane (1H) and perdeuteroadamantane (1D, C\textsubscript{10}D\textsubscript{16}) were Aldrich products. Both were crystallized from hexane and sublimed twice. Our sample of C\textsubscript{10}D\textsubscript{16} contained 12\% of C\textsubscript{10}HD\textsubscript{15}, which could not be separated from C\textsubscript{10}D\textsubscript{16}. The experimental results were corrected accordingly.

Resonance (ICR) spectroscopy \[48\] and high-pressure mass spectrometry (HPMS)\[49,50\]. However, these techniques do not yield direct information about H\textsubscript{\alpha} and/or the range of distances between the species A and D in which electron transfer most likely take place. We show below that computational methods can contribute to providing an enhanced picture of this and other aspects of the ET process.

Dunning correlation-consistent basis set such as cc-pVTZ\[56\] reproduce experimental isotope effects remarkably well. Here, we used the B3LYP/aug-cc-pVTZ level, which contains diffuse functions\[58,59\] to study these effects in the analyzed systems. All computations have been performed with the Gaussian 03 software package.\[59\]

2. Results and Discussion

2.1. Experimental Results

We have experimentally found that in the gas phase and in the presence of an excess of a cooling gas, the radical cations 1H\textsuperscript{+}(g) (C\textsubscript{10}H\textsubscript{16}\textsuperscript{+}), and 2H\textsuperscript{+}(g) (C\textsubscript{10}D\textsubscript{16}\textsuperscript{+}) are rather stable species. Further, we have developed a simple experimental method allowing the determination of the reaction rate constants k\textsubscript{1} and k\textsubscript{2} for isergic single-electron transfer (SET) reactions (5) and (6), respectively:

\[1H\textsuperscript{+}(g) + 1H(g) \rightarrow 1H(g) + 1H\textsuperscript{+}(g) \quad (5)\]

\[2H\textsuperscript{+}(g) + 2H(g) \rightarrow 2H(g) + 2H\textsuperscript{+}(g) \quad (6)\]

Two much slower processes, namely, reactions (7) and (8), are also observed:

\[1H\textsuperscript{+}(g) + 1H(g) \rightarrow C\textsubscript{10}H\textsubscript{14}\textsuperscript{+}(g) + H\textsubscript{2}(g) + C\textsubscript{10}H\textsubscript{15}(g) \quad (7)\]

\[1H\textsuperscript{+}(g) + 1H(g) \rightarrow C\textsubscript{10}H\textsubscript{14}\textsuperscript{+}(g) + H\textsubscript{2}(g) + 1H\textsuperscript{+}(g) \quad (8)\]

Reactions (7) is endoergic\[60\] and some of its features are discussed in the Supporting Information section. Ion-selection experiments show that C\textsubscript{10}H\textsubscript{14}\textsuperscript{+}(g) essentially originates from decomposition of 1H\textsuperscript{+}(g). As we discuss below, k\textsubscript{1d} ≪ k\textsubscript{1a} ≪ k\textsubscript{1} and, most importantly, we show that k\textsubscript{1}, the relevant rate constant for the study of SET process (5) can be rigorously separated from k\textsubscript{1a} and k\textsubscript{1d}.

Radical cation 2H\textsuperscript{+} does not seem to undergo loss of H\textsubscript{\alpha} but extremely slow loss of dihydrogen (reaction (9)):

\[C\textsubscript{10}H\textsubscript{26}\textsuperscript{+}(g) + C\textsubscript{2}H\textsubscript{6}(g) \rightarrow C\textsubscript{10}H\textsubscript{24}\textsuperscript{+}(g) + H\textsubscript{2}(g) + C\textsubscript{2}H\textsubscript{6}(g) \quad (9)\]

Similarly, k\textsubscript{1}\textsubscript{a} ≪ k\textsubscript{1}\textsubscript{d} here, and k\textsubscript{2} (the relevant rate constant for the SET study) can be rigorously separated from k\textsubscript{1}\textsubscript{d}.

Reactions (5) to (9) involve all the isotopologues\[61\] of the radical cations and their respective neutral hydrocarbons, namely, the dyads 1H\textsuperscript{+}/1H and 2H\textsuperscript{+}/2H. The process begins with electron-impact ionization of 1H(g) under very mild conditions (nominal ionization energies of 9.2–10.0 eV) and leads to the formation of 1H\textsuperscript{+}(g), together with smaller amounts of 1-adamantyl cation (1-Ad\textsuperscript{+}). Similarly, mild electron ionization of 2H(g) (nominal ionization energies of 8.2–9.5 eV) leads to formation of 2H\textsuperscript{+}(g). The mass spectra of these species are presented in Figure 3 and Figures S1 and S2 of the Supporting Information.
respectively. It follows that the most abundant isotopologues of species $1^{+}$ (g) have $m/z$ values and relative abundances (taking 100% for the most abundant one) of 136 (100%, $^{12}$C$_{10}$H$_{18}^{+}$), 137 (11.00%; $^{12}$C$_{10}$H$_{18}^{+}$ and 0.184% from $^{12}$C$_{10}$H$_{18}^{+}$), 138 (0.53%, $^{12}$C$_{10}$H$_{18}^{+}$ and 0.32% from $^{12}$C$_{10}$H$_{18}^{+}$). In the case of 2$^{+}$ (g), these values become 268 (100%, $^{13}$C$_{12}$H$_{28}^{+}$), 269 (21.95%; 21.63% from $^{13}$C$_{12}$H$_{28}^{+}$ and 0.32% from $^{12}$C$_{10}$H$_{18}^{+}$), 270 (2.22%, $^{13}$C$_{12}$H$_{28}^{+}$). The FT-ICR technique allows selective ejection of ions. For instance, in the case of 1$^{+}$, it is possible to eject ions with $m/z = 137$ and 138 while the ion with $m/z = 136$ remains in the cell (Figure 4).

In the case of 1H, taken as an example, ions in the ICR cell are surrounded by neutral molecules of 1H and an excess of argon (cooling agent). The neutral molecules of 1H are also a mixture of isotopologues, and their relative proportions are those indicated above for 1$^{+}$ (g). When the mass spectrum is monitored for times ranging from about a few tenths of a second to one hundred seconds or more after selection, ions with $m/z = 137$ and 138 are seen to reappear, and their relative abundances increase until they reach (within the limits of experimental error) the values they had prior to ejection, and then level off. In the same vein, if the ion with $m/z = 136$ is ejected, it appears again, and the limiting values of the relative intensities are the same as in the previous experiment. This is best seen by considering the temporal evolution of the ratio $\rho$, defined by Equation (10):

$$\rho(t) = \frac{[I_{137} - I_{138}]}{I_{136}}$$  \hspace{1cm} (10) $$

where $I_{137}$, $I_{137}$, and $I_{138}$ stand for the relative abundances of the various ions (corrected as indicated in the Supporting Information) at time $t$ after selection (relative ion intensities are taken as directly proportional to the partial pressures of the ions). Figure 5 shows an example. The same method can also be applied to 2$^{+}$ (see Supporting Information). It is also possible to isolate ions with $m/z$ values of 137 and 138 and then monitor the growth of the isotopologue with $m/z = 136$. Figure S3 (see Supporting Information) portrays the results of experiments in which the two kinds of ion selection were applied to the same system. As it can be seen, the limiting values of $\rho$ are the same in both cases (within the experimental uncertainty limits).

The above results show that reaction (5) is reversible and equilibration can be observed within the timeframe of these experiments. The standard Gibbs energy and enthalpy changes $\Delta G^\circ$ (5) and $\Delta H^\circ$ (5), respectively, are zero. Hence, any activation barrier for the process is intrinsic in the sense of Marcus.[37, 41] Furthermore, neither solvent nor counter-ions are involved. The quantitative study of the experimental values of $\rho(t)$ obtained using different partial pressures of 1H provides, through Equations (10) and (11), the reaction rate constant $k_1$ (full details are given in the Supporting Information):

$$k_1 P_{1H} t = \ln \frac{\alpha_1 (1 + \rho_0)}{(\alpha_1 - \rho_0)}$$  \hspace{1cm} (11) $$

where $\alpha_1$ is given by Equation (12):

$$\alpha_1 = \frac{P_{1H(137)} + P_{1H(138)}}{P_{1H(136)}}$$  \hspace{1cm} (12) $$
Applying the same method to 1D and 2H yields the rate constants $k_{1D}$ and $k_1$ (full details of the determination of $k_{1c}$ and $k_{1D}$ are given in the Supporting information). It is important that $\rho_k$, $\rho_{1D}$ and $\rho_1$ are independent of constants $k_{1o}$, $k_{1D}$ and $k_{1o}$ respectively (see Supporting Information).

We last examined SET between species $1H^+$ (g) and $1D$(g) [reaction (13)]:

$$1D^+(g) + 1H(g) \rightarrow 1D(g) + 1H^+(g) \quad (13)$$

where 1D is perdeuterodiamantane ($C_{18}H_{16}$ or $C_{18}D_{16}$). Process (13) is not isergonic, and $K_{13}$ measures the isotope effect on the SET process. Using a number of systems with different total pressures ($P_{1H}$ or $P_{1D}$) and different $P_{1Ha}/P_{1Da}$ ratios provides values of $k_1$ and $k_{13}$. Their ratio $k_1/k_{13}$ gives $K_{13}$ (see Supporting Information). The average $K_{13}$ value is $3.1 \pm 0.6$ and the corresponding standard Gibbs energy change, $\Delta G^*_k_{13}(12)$, is $-0.72 \pm 0.18$ kcal mol$^{-1}$. We calculated $\Delta G^*_k_{13}(12)$ at the B3LYP/aug-cc-pVTZ level and found a value of $-0.79$ kcal mol$^{-1}$, in good agreement with the experimental result.

We also examined the SET processes of dyads $1H^+/1H$, $2H^+/1D$ and $1D^+/1D$ as well as SET in reaction (13). Treatment of the experimental results according to the methods described above leads to the rate constants reported in Table 1. The uncertainties in the rate constants reported in Table 1 are twice the standard deviations involved in the treatment of experimental data, and they do not include the uncertainty in the calibrated pressures (ca. 15%).

Rate constants $k_1$, $k_2$ and $k_3$ (or $k_{13}$) are on the order of magnitude of the collision rate. In general, the activation Gibbs energy $\Delta G^*$ for this kind of reaction is defined through Equation (14a):

$$\Delta G^* = -RT \ln r \quad (14a)$$

where the values of $r=\kappa_{1D}/\kappa_{1o}$ are given in Table 1.

In the case of an isergonic process, the highest rate constant is equal to half of the collision rate. Then, Equation (14b) applies:

$$\Delta G^* = -RT \ln r - \Delta G^* \ln 2 \quad (14b)$$

The results presented in Table 1 (where $r$ and $\Delta G^*$ include the uncertainties originating both in the treatment of the experimental data and in the values of the pressures) indicate that, within the uncertainty limits, $k_1$ and $k_{13(D)}$ are equal to the collision limit. In the case of $k_{13}$, the ratio $k_{13}/\kappa_{13(Da)} = 1.19 \pm 0.48$. This ratio is larger than the collision limit, but this can be justified, at least in part, by the value of $\kappa_{13(Da)}$ being larger than the Langlevin value, for the reasons indicated above. A contribution from a non-adiabatic mechanism cannot be ruled out either.

In the case of electron exchange between $1H$ ($m/z=136$) and $2H^+$ ($m/z=152$), we applied electron pulses at $m/z = 288$, corresponding to the putative adduct (1H1D)$^+$. This ion was not observed experimentally, and even 5 s ejection pulses failed to show any effect on the exchange process. This result suggests that the equilibrium concentration of (1H1D)$^+$ is vanishingly small and is consistent with electron transfer taking place at very high rates.

For two species in a bimolecular ET process of the type [Eq. (15)]:

$$r^+ + j^- \rightarrow r^+ j^- \quad (15)$$

an important result derived from Marcus theory is that Equation (16) holds:

$$k_j \approx \left(k_j k_0 f_j \right)^{1/2} \quad (16)$$

where $k_j$ and $k_0$ are the self-exchange rate constants, $K_j$ is the thermodynamic equilibrium constant and $f_j$ is given by Equation (17):

$$\ln f_j = -\frac{\left(\ln K_j \right)^2}{4 \ln \left(\frac{Z^*}{2} \right)} \quad (17)$$

where $Z$ is a bimolecular collision frequency. We have applied this method to reaction (13) and used for $k_j/k_0$ the product of the ratios $r$ for $k_1$ and $k_{13(Da)}$. In principle, the values of $k_j$ and $k_0$ should correspond to $k_1$ and $k_{13}$. The values obtained, $1.29 \times 10^{-3}$ and $4.16 \times 10^{-10}$ molec$^{-1}$ cm$^3$ s$^{-1}$, are quite consistent with the experimental values. Nelson and co-workers applied Equation (16) to numerous reactions involving SET between substituted tetraalkyl hydrazines and their radical cations in solution.

Table 1. Experimental rate constants for processes (5)–(8) and (13).a,b,c,d,e

<table>
<thead>
<tr>
<th>Const.</th>
<th>Exp.a,c</th>
<th>Coll.a,c</th>
<th>$\Delta G^*$(a,c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>(7.85±0.94)×10$^{-10}$</td>
<td>1.26</td>
<td>0.62±0.17</td>
</tr>
<tr>
<td>$k_{1D}$</td>
<td>(6.68±0.74)×10$^{-10}$</td>
<td>1.19</td>
<td>0.56±0.16</td>
</tr>
<tr>
<td>$k_{1c}$</td>
<td>(4.41±0.15)×10$^{-12}$</td>
<td>1.26</td>
<td>5.6×10$^{-3}$</td>
</tr>
<tr>
<td>$k_{1D}$</td>
<td>(5.22±0.17)×10$^{-12}$</td>
<td>1.19</td>
<td>4.2×10$^{-3}$</td>
</tr>
<tr>
<td>$k_{1D}$</td>
<td>=10$^{-12}$</td>
<td>1.26</td>
<td>=10$^{-12}$</td>
</tr>
<tr>
<td>$k_{1o}$</td>
<td>=10$^{-13}$</td>
<td>1.19</td>
<td>=10$^{-13}$</td>
</tr>
<tr>
<td>$k_3$</td>
<td>(1.50±0.15)×10$^{-8}$</td>
<td>1.26</td>
<td>1.19±0.48</td>
</tr>
<tr>
<td>$k_1$</td>
<td>(1.20±0.14)×10$^{-9}$</td>
<td>1.22</td>
<td>0.98±0.26</td>
</tr>
<tr>
<td>$k_{13}$</td>
<td>(3.83±0.73)×10$^{-10}$</td>
<td>1.22</td>
<td>0.31±0.11</td>
</tr>
</tbody>
</table>

[a] This work. [b] Defined in the text. [c] In molec$^{-1}$ cm$^3$ s$^{-1}$. [d] In 10$^{-9}$ molec$^{-1}$ cm$^3$ s$^{-1}$. [e] In kcal mol$^{-1}$. [f] Using equation (14b). [g] Using Equation (14a).
and in the gas phase. Equation (16) was shown to successfully apply to both subsets, spanning overall 14 powers of ten in reaction rates. Equation (16) also seems to apply to reaction (13), characterized by a small activation barrier and involving rates close to the collision limit. This agrees with the structure dependence of SET rates being operative even in the case of very small barriers.

For electron transfer from c-C₆H₁₂ to c-C₆D₁₂⁺ [reaction (18)]:

\[
\text{c-C₆D₁₂⁺} + \text{c-C₆D₁₂} \rightarrow \text{c-C₆D₁₂} + \text{c-C₆D₁₂⁺} \quad \Delta G_{\text{m}}^\circ(18)
\]

values of \(-0.65\) \(\text{ kcal mol}^{-1}\), \(-0.74\) \(\text{ kcal mol}^{-1}\) and \(-0.76\) \(\text{ kcal mol}^{-1}\) for \(\Delta G_{\text{m}}^\circ(18)\) were obtained by ICR at about 330 K and HPMS at 321 K, respectively. The reaction rate constant for the forward process was found to be \((3.8 \pm 0.3) \times 10^7 \text{ molec}^{-1} \text{cm}^3 \text{s}^{-1}\), a value extremely close to that of \(k_{\text{obs}}\). Thus, there is a clear similarity between 1H and c-C₆H₁₂ as far as the kinetics of SET is concerned.

2.2. Computational Results

For the computational study on these processes we selected the SET reaction 1H⁺/1H as a prototypical model. In the case of ET processes mediated by formation of an encounter complex, the ET mechanism governing the reaction is characterized with the help of \(H_{\text{DA}}\) and \(\lambda\). In particular, and within the twostate Marcus–Hush model, the magnitude of the donor–acceptor binding factor \(Q = 2H_{\text{DA}}/\lambda\) is a key parameter for classification of the ET process \(13, 71\) that, as already mentioned above, determines the nature of the kinetic approach for describing the ET reaction. Values of \(Q < 1\) are characteristic of non-adiabatic or weakly adiabatic ET processes in which the rate is essentially controlled by the intrinsic activation barrier \(\lambda\), while \(Q \geq 1\) identifies those processes for which the reaction is essentially limited by diffusion and not by the electron-transfer step. \(35\) All systems showing values of \(Q\) in the intermediate region display characteristics in between the two extreme behaviours. To determine the type of ET displayed by this reaction, we studied the potential-energy profile that gives rise to formation of the encounter complex in vacuo, using different geometrical arrangements compatible with the process. Figure 6 shows the BSSE-corrected PMP2/6-311G(d,p)//MP2/6-31G(d) profiles for the different geometrical approaches considered. These reaction profiles were built using the protocol described in the Computational Details section by fixing at each point a distance related to the intermolecular separation (see Figure 6 and Supporting Information), while the rest of the internal coordinates were allowed to relax. In the cases of profiles 1–3 full optimization of the structure allowed unconstrained minima (within the symmetry used) to be located in the reaction profiles corresponding to loose (1:1) intermediate complexes (only for the minimum of profile 1 was the Hessian numerically evaluated). This situation is not present in the case of profile 4.
of the geometrical arrangements used in profile 4, where no unconstrained minimum (within the symmetry employed) was found. The most stable complex found (profile 1) can be classified, according to the relation between the values of $\lambda$ and $H_{DA}$ (see Table 2), as a class II intermediate complex within the Robin–Day classification of mixed-valent complexes.\[35, 63, 71\] The nature of the electronic states can also be qualitatively inferred from Mulliken population analysis (MPA). The MPA results indicate that the first three profiles are consistent with the charge distribution found in Class II (localized) self-exchange charge-transfer processes\[35\] (see Supporting Information) with the positive charge located essentially in the radical cation. Profile 4 displays significant charge transfer from the radical to the neutral species in the region of interaction that eventually leads to a charge of 0.5–0.5 au, though no minimum was found on the potential-energy surface. Thus, the nature of the ET process is dependent on the geometrical orientation adopted by the donor and acceptor in their mutual approach.

From the kinetic point of view, profile 1 seems consistent with a kinetic pattern of the kind displayed in Scheme 2 for ET reactions in solution. The second-order rate constant for the process, assuming steady-state conditions, takes the form\[35\] of Equation (19):

$$k_{SE} = k_{EF}^{\text{adi}} + k_{ET}^{\text{adi}}$$

(19)

where $k_{SE}$ is the adiabatic rate constant, $k_{ET}$ the first order intracomplex electron-transfer rate constant for an adiabatic process [Eq. (20)]:

$$k_{ET} = \frac{n e^{\Delta G_{\text{ET}}^{0}}}{v_{e}} = \frac{n e^{\Delta G_{\text{ET}}^{0}}}{v_{e}}$$

(20)

where $v_{e}$ is the nuclear vibrational frequency related to the ET. However, as indicated, experimental attempts to isolate and identify the complex were unsuccessful, in agreement with the theoretical predictions, which give a Gibbs free energy of formation $\Delta G_{\text{ET}}^{0}$ of 7.9 kcal mol$^{-1}$ (see Supporting Information). The complex is thermodynamically unstable under the experimental conditions used and plays no role in modulating the ET rate constant as in Equation (19). However, we can expect that this complex will play an important role from the mechanistic and kinetic viewpoints, because it is in this region where the electron transfer will most likely take place due to the distance dependence of $H_{DA}$.\[72\] Thus, we computed the rate constant within the adiabatic approach as Equation (21):

$$k_{ET} = \frac{Z}{\text{Ze}^{-\frac{72}{2}}}$$

(21)

where we evaluated $H_{DA}$ at the encounter-complex minima found in the profile and used a transmission coefficient of unity on the basis of the value of $H_{DA}$ (see Table 2). Within this model, and assuming for the collision frequency $\mu$ under the experimental conditions a value of 1.26 x $10^{-9}$ molec$^{-1}$ cm$^{3}$ s$^{-1}$, the computed rate constant for the electron-transfer process is 5.63 x $10^{-10}$ molec$^{-1}$ cm$^{3}$ s$^{-1}$, which is in good agreement with the experimental value. The use of the $H_{DA}$ value obtained with the GMH method gives a rate constant slightly smaller but within the same order of magnitude (see Supporting Information).

3. Conclusions

It has been experimentally established that the radical cation of adamantane is a stable (albeit very reactive) species. Use of the natural $^{13}$C “labelling” of adamantane and adamantylide- adamantane allowed experimental determination of the rate constants for isergonic electron exchange between these hydrocarbons and their corresponding radical cations. These rate constants are practically collision-controlled in both cases. The rate constants for the forward and reverse reaction in process (13) were also determined, and Marcus’ cross-term equation was shown to hold in this case. Theoretical computations exploring different possible reaction paths have given insight into the role that intermediate complexes may play in this ET reaction. Evaluation of the reorganization energy and the electronic coupling allowed characterization of this reactive process.

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The experimental enthalpy of reaction (7) is 18.8 ± 1.5 kcal mol⁻¹, as obtained from the standard enthalpies of formation of \( ^1\text{H} \), \( ^1\text{H}^+ \), \( ^1\text{H}^+ \), and \( ^1\text{C} \) of (32.2 ± 0.5), (184.6 ± 0.6), (162.3 ± 0.8), and (8.9 ± 1.0) kcal mol⁻¹, respectively. Full details are given in the Supporting Information.

Definition of isotopologue: “A molecular entity that differs only in isotopic composition (number of isotopic substitutions), for example, \( \text{CH}_4 \), \( \text{CH}_3\text{D} \), \( \text{CH}_2\text{D}_2 \).” From P. M. C. Müller, Pure Appl. Chem. 1994, 66, 1077 – 1184. See also: http://www.iupac.org/goldbook103351/103351.pdf.

It is known that the ratio of experimental rates of proton and deuteron exergonic transfers\[64, 65] to the Langevin rate constant are generally larger than unity in these cases.

Assuming that the electronic coupling displays an exponential decay behaviour with the donor–acceptor distance \( R \),\[32\] we searched for geometrical arrangements allowing for the shortest possible distance between the fragments of the encounter complex that simultaneously maximizes the interaction between donor and acceptor and minimizes the steric repulsion between fragments.