Examples of S_N2 reactions with small or non-existent energy barriers

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Received (in Cambridge) 13th January 1999, Accepted 11th March 1999

The potential energy profiles of the following S_N2 reactions were obtained using the G2 quantum chemical method: $H_3N + CH_3OH_2^+ \rightarrow {}^+H_3NCH_3 + H_2O$, $H_2O + CH_3FH^+ \rightarrow {}^+H_2OCH_3 + FH$ and $H_3N + CH_3FH^+ \rightarrow {}^+H_3NCH_3 + FH$. The activation energy for the first is only $\Delta E° = 6.9$ kJ mol^{-1}, while the others have no energy barrier. These findings are discussed in the light of Marcus theory.

Introduction

In the preceding paper we reported results from quantum chemical calculations on the following cationic identity S_N2 reactions [eqn. (1)],[1] for which we found that the barrier heights

$$A + CH_3A^+ \rightarrow {}^+ACH_3 + A \ (A = NH_3, H_2O, HF) \quad (1)$$

increase linearly with the proton affinity of the nucleophile A. In this paper we report new data from quantum chemical calculations of the reactions in eqns. (2)–(4) where the nucleophile and nucleofuge (leaving group) are different.

$$H_3N + CH_3OH_2^+ \rightarrow {}^+H_3NCH_3 + H_2O \quad (2)$$

$$H_2O + CH_3FH^+ \rightarrow {}^+H_2OCH_3 + FH \quad (3)$$

$$H_3N + CH_3FH^+ \rightarrow {}^+H_3NCH_3 + FH \quad (4)$$

We want to examine if it is possible to extract information about the barrier heights of these reactions from the corresponding identity reactions using Marcus theory.[2,3] Previously, it has been reported that the barriers of anionic S_N2 reactions, where the nucleophile and the nucleofuge are different, can be quite precisely estimated using Marcus theory.[4–6] One important difference between a cationic and an anionic S_N2 reaction is that in the former case the nucleophile is much weaker. In addition, reactions (2)–(4) are quite exothermic, so it would be of great interest to see if this affects the validity regime of Marcus theory.

Methods

Quantum chemical calculations were carried out using the program system GAUSSIAN 94.[7] The methods used were Møller–Plesset perturbation theory to second order (MP2)[8] with the 6-31G(d,p) basis set,[9] and the compound G2 method.[10] Only the G2 results are reported here. More detailed data of the MP2 and G2 calculations may be obtained from the author upon request.

All critical points found (reactants, transition structures, intermediates and products) of the potential energy surface were characterized by complete optimization of the molecular geometries [MP2/6-31G(d,p)]. Harmonic frequencies were obtained by diagonalizing the mass-weighed Cartesian force constant matrix, calculated from the analytical second derivatives of the total energy (the Hessian). Harmonic frequencies obtained in this manner were used to calculate the zero point vibrational energies (zpve).

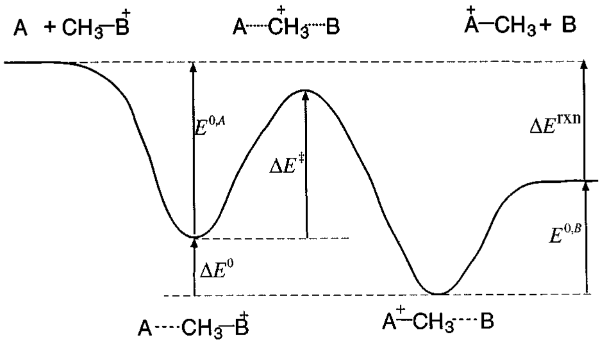

Fig. 1 Schematic potential energy diagram for a general cationic S_N2 reaction, including definitions of the energy parameters used.

Results and discussion

Fig. 1 shows a schematic potential energy diagram of a general gas phase cationic S_N2 reaction.[11] It has the characteristic double well form found for a wide variety of ion–molecule reactions. The two wells correspond to the stable ion–neutral configurations, $A \cdots CH_3B^+$ and $ACH_3^+ \cdots B$, which are usually referred to as the reactant complex and product complex, respectively. The transition structure, $A \cdots CH_3 \cdots B^+$, is located between these two stable ion structures. Fig. 1 also includes definitions of the potential energy parameters necessary for the following discussion.

According to Marcus theory the potential energy barrier of a reaction—formulated in eqn. (5) for a general cationic S_N2

$$A + CH_3B^+ \rightarrow {}^+ACH_3 + B \quad (5)$$

reaction—may be expressed with reference to the potential energy barriers of the two identity reactions [eqn. (1) and (6)] ($A \neq B$) and the reaction energy.

$$B + CH_3B^+ \rightarrow {}^+BCH_3 + B \quad (6)$$

The potential energy barrier, $\Delta E^‡$, the energy difference between the transition structure, $[A \cdots CH_3 \cdots B]^+$, and the reactant complex, $A \cdots CH_3B^+$, is then given by eqn. (7).[12] In

$$\Delta E^‡ = \Delta E^‡_o \left(1 + \frac{\Delta E°}{4E^‡_o}\right)^2 \quad (7)$$

this equation the reaction energy, $\Delta E°$ is the energy difference between the product and reactant complexes involved, *i.e.* between $B \cdots CH_3A^+$ and $A \cdots CH_3B^+$. The so-called intrinsic

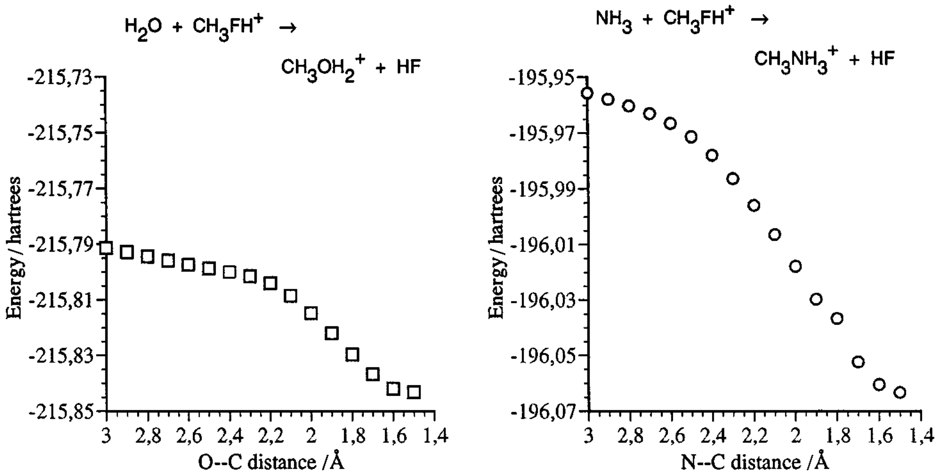

Fig. 2 Potential energy profiles of reaction (3) (left panel) and reaction (4) (right panel). The ordinate axis corresponds to the energy obtained with MP2/6-31G(d,p), but without zero point vibrational energy correction. Each data point was obtained by subjecting the system to energy minimization, keeping the indicated reaction co-ordinate fixed as explained in the text.

Table 1 G2 reaction energies

	Energy/kJ mol^{-1}					
Reaction	ΔE^{rxn}	$\Delta E^{\circ,\mathrm{A}}$	$\Delta E^{\circ,\mathrm{B}}$	$\Delta E^{\ddagger}$	ΔE°	$\Delta E^{\ddagger}_{\mathrm{o}}$
NH_3/H_2O (6)	160.2	45.2	33.0	6.9	148.0	65.1[a]
H_2O/HF (7)	151.6	—	30.0	—	—	24.4[a]
NH_3/HF (8)	311.8	—	25.5	—	—	49.3[a]

[a] Taken from ref. 1.

barrier, $\Delta E^{\ddagger}_{\mathrm{o}}$, is given by eqn. (8), where $\Delta E^{\ddagger}_{\mathrm{o},\mathrm{AA}}$ and $\Delta E^{\ddagger}_{\mathrm{o},\mathrm{BB}}$ are the barriers for the identity reactions (1) and (6), respectively.

$$\Delta E^{\ddagger}_{\mathrm{o}} = \tfrac{1}{2}(\Delta E^{\ddagger}_{\mathrm{o},\mathrm{AA}} + \Delta E^{\ddagger}_{\mathrm{o},\mathrm{BB}}) \qquad (8)$$

In the case of the nucleophilic displacement of water by ammonia in protonated methanol, reaction (2), it was possible to locate the minima corresponding to the complexes $H_3N\cdots CH_3OH_2^+$ and $H_3NCH_3^+\cdots OH_2$. Both these structures have the features typical of species where the interaction between the ionic and the neutral part to a large degree is due to ion–dipole and ion–induced dipole forces. For example, the C–O bond of 1.567 Å in the $H_3N\cdots CH_3OH_2^+$ complex is 0.051 Å longer than in free $CH_3OH_2^+$, while the C–N bond of 1.516 Å in the $H_3NCH_3^+\cdots OH_2$ complex is 0.006 Å longer than in free $CH_3NH_3^+$. Although the interaction is mainly electrostatic, there is a small but noticeable degree of covalent interaction between H_3N and $CH_3OH_2^+$ in the $H_3N\cdots CH_3OH_2^+$ reactant complex. The bond distances are r(C–O) = 1.756 Å and r(C–N) = 2.264 Å. The potential energy barrier (Table 1) measured from the reactant complex is only $\Delta E^{\circ} = 6.9$ kJ mol^{-1}. This is in good qualitative agreement with Okada *et al.* who have reported results of MP3/6-31G(d)//HF/3-21G calculations for this reaction.[13]

From the intrinsic barriers of the identity reactions [eqn. (9)

$$H_2O + CH_3OH_2^+ \rightarrow {}^+H_2OCH_3 + H_2O \qquad (9)$$

and (10)] (see the preceding paper), we obtain [eqn. (8)] an

$$H_3N + CH_3NH_3^+ \rightarrow {}^+H_3NCH_3 + NH_3 \qquad (10)$$

intrinsic barrier of $\Delta E^{\ddagger}_{\mathrm{o}} = 65.1$ kJ mol^{-1} for reaction (2). We are now in the position of using Marcus theory [eqn. (7)] when we also introduce the G2 value for the reaction exoergicity, $\Delta E^{\circ} = -148$ kJ mol^{-1}. This gives an estimated barrier of 12.1 kJ mol^{-1}, which should be compared to the G2 barrier of $\Delta E^{\circ} = 6.9$ kJ mol^{-1}. Although the deviation is not large, it implies that simple Marcus theory has some limitations in this case. The reason for this may be that in Marcus theory, energy is truncated after the second order term, which may be inappropriate in this case. Alternatively, and perhaps more likely, the reaction requires the use of a two-dimensional reaction co-ordinate.[14–20]

In the transition structure of reaction (2), $H_3N\cdots CH_3\cdots OH_2^+$, an imaginary frequency of vibration, corresponding to the antisymmetric vibration of the reaction co-ordinate, of $\nu = 423i$ cm^{-1} was found. This should be compared with the values $\nu = 499i$ and $614i$ cm^{-1} for reactions (9) and (10), respectively, which reflects the lower and flatter TS region of reaction (2).

Quite surprisingly to us, reactions (3) and (4) turned out to be barrier-less. This means that the reactant complexes $H_2O\cdots CH_3FH^+$ [reaction (3)] and $H_3N\cdots CH_3FH^+$ [reaction (4)] do not exist as stable species, which also implies that there are no S_N2 transition structures on any of the two potential energy surfaces. Despite serious attempts to locate the reactant complexes and the transition structures they could not be found. Potential energy scans were then performed. In the scan for reaction (3), the distance O···C was taken as the reaction co-ordinate and it was varied in steps of −0.1 Å, starting from the local minimum of the product complex $^+H_2OCH_3\cdots FH$. Redundant internal co-ordinates[21] were used, and the energy was minimized with respect to all degrees of freedom, except the reaction co-ordinate. The scan for reaction (4) was performed analogously, using the distance N···C as the reaction co-ordinate. The scans give rise to the potential energy profiles of Fig. 2. It is clear from these findings that reactions (3) and (4) are without barriers. To the best of our knowledge these are the first examples of S_N2 reactions with this property.

It should be realized, however, that the absence of an energy barrier does not necessarily imply absence of a free energy barrier.[13]

Marcus theory was also applied to reactions (3) and (4). The intrinsic barriers obtained from the identity reactions are $\Delta E^{\ddagger}_{\mathrm{o}} = 49.3$ kJ mol^{-1} [reaction (3)] and $\Delta E^{\ddagger}_{\mathrm{o}} = 24.4$ kJ mol^{-1} [reaction (4)]. Because stable reactant complexes do not exist on the potential energy surfaces of the two reactions, ΔE° is not defined, and eqn. (7) can therefore not be applied rigorously. Instead we approximate this figure with $\Delta E^{\circ} \approx \Delta E^{\mathrm{rxn}}$. This gives $-\Delta E^{\circ} > 4\Delta E^{\ddagger}_{\mathrm{o}}$, which means that the expression within the parenthesis of eqn. (7) is negative for both reactions. The outcome of this situation is that simple Marcus theory “breaks down”; a result which is in good accord with the finding that $\Delta E^{\circ} = 0$.

According to Ingold the digit “2” in the term S_N2 designates the molecularity of the reaction, and not the kinetic order.[22]

Molecularity is “a salient feature of the mechanism, meaning the number of molecules undergoing covalency change”. We therefore see that the apparently peculiar barrier-less reactions reported here are still S_N2 reactions in Ingold’s sense.

In conclusion, the results given here show that, for some reactions, the combination of a moderate intrinsic barrier and a large exothermicity result in a small or vanishing reaction barrier.

Acknowledgements

The author wishes to thank the Norwegian Research Council (NRF) and VISTA for the grants which made this work possible. The calculations were made possible thanks to support through the NFR (The Norwegian Research Council) Programme for Supercomputing.

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Paper 9/00380K