Nucleophilic addition/elimination on substituted methyl cations. Analysis of factors that affect thermochemistry and barrier heights

Einar Uggerud

Department of Chemistry, University of Oslo, PO Box 1033 Blindern, N-0315 Oslo, Norway

The title reactions were shown by *ab initio* molecular orbital methods to occur *via* three step mechanisms: $CH_2B^+ + AH \longrightarrow B\text{–}H_2C\text{–}AH^+ \longrightarrow {}^+HB\text{–}H_2C\text{–}A \longrightarrow CH_2A^+ + BH$ (all possible combinations of A = H, F, OH, NH_2 and B = H, F, OH, NH_2 were investigated). A p-donation stabilization constant for each group A and B, E_{stab}, is introduced. By applying these constants it is shown that a balance between the p-donation powers of B and A (expressed as $E_{stab}[A] - E_{stab}[B]$) regulates the well depths as well as the barrier heights. Simple expressions for the relationships between these quantities are derived.

Introduction

Mechanistic schemes with addition followed by elimination are invoked to describe many substitution reactions in organic chemistry.[1–3] One typical example is acid-catalysed Schiff base formation from aldehydes. Other examples include a range of related carbonyl substitutions including acidic ester hydrolysis. Addition/elimination mechanisms are also relevant to electrophilic aromatic substitution reactions.

The purpose of this paper is to investigate more closely some prototype addition/elimination reactions of the type shown in Fig. 1. The results will be directly applicable to the gas phase, and may have some relevance in solution chemistry.

Examination of Fig. 1 reveals that transfer of a proton from the incoming group, AH, to the outgoing group, BH, (step two) is critical. Formally, this is a 1,3-intramolecular proton transfer. When the reaction takes place in solution it is reasonable to assume that the proton transfer takes place *via* solvent molecules or other molecules in the neighbourhood. In the gas phase no solvent assistance is available and proton transfer must occur intramolecularly. A 1,3-intramolecular proton transfer is usually considered to be entropically unfavourable because it requires a tight transition state. When in addition the energy barrier is substantial this step will, therefore, be rate limiting.

The reactant ion (CH_2B^+) and the product ion (CH_2A^+) are substituted methyl cations. For example, when B = OH and A = NH_2 the reactant ion (electrophile) is protonated formaldehyde and the nucleophile is ammonia. In that case Fig. 1 corresponds to the accepted mechanism for Schiff base formation. One should note that for the cases when A, B = F, OH, NH_2 the substituents have lone pair electrons with variable ability to donate p-electron density to the carbocationic centre.

Several important aspects of the general mechanism of Scheme 1 will be addressed here. It will be of great interest to see how the electronic properties of A and B influence the energetics of each reaction step and the overall thermochemistry. The barrier height of the critical 1,3-proton transfer will be a matter of particular concern. In an attempt to unravel the factors affecting this parameter a systematic analysis of a possible connection with the thermochemistry of the two other steps will be performed.

The thermochemical data necessary for the present study are in most cases not easily obtained through experiment. For this reason literature data are sparse, and it is difficult to imagine methods of measurement which would be sufficiently precise. However, as will be demonstrated below, the problem is ideally suited for quantum chemical treatment. The relatively small size of the chemical systems makes this approach attractive.

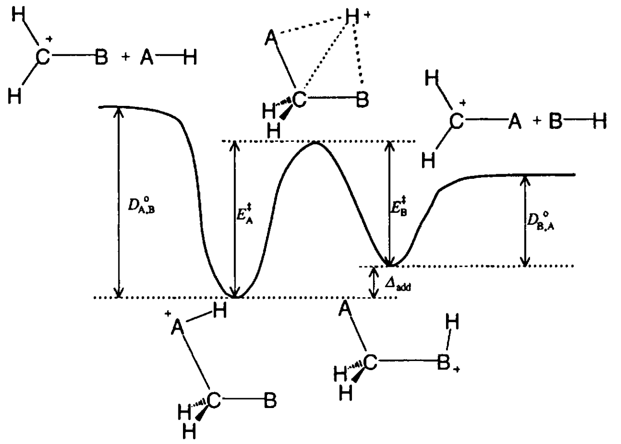
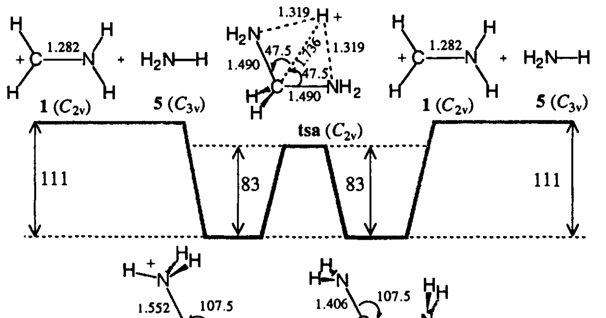


Fig. 1 General potential diagram of the three step addition/elimination (all possible combinations of A = H, F, OH, NH_2 and B = H, F, OH, NH_2)



Method of calculation

The calculations were performed using standard routines of the program suite GAUSSIAN 92.[4] The choice of the quantum chemical method was a matter of careful consideration. Previous calculations of similar systems had shown that the relatively economic MP2/6-31G(d,p) procedure is sufficiently flexible and precise to reproduce barrier heights and bond dissociation energies within approximately 20 kJ mol^{-1} of the corresponding experimental figure.[5,6] The MP2/6-31G(d,p) procedure combines a medium sized basis set with inclusion of dynamic electron correlation. All relevant critical points (minima and transition structures) of the potential energy surface were fully characterized at the MP2/6-31G(d,p) level by complete optimization of the molecular geometries and explicit consideration of the calculated harmonic vibrational frequencies. All relative energies were calculated by including the zero-point vibrational energies scaled by a factor of 0.94. This factor was chosen to give a best fit to the well known zero-point vibrational energies of H_2, HF, H_2O and NH_3.[5,7] The results of the quantum chemical calculations have been summarized in tables which can be obtained from the author upon request, and are also displayed in reactions (1)–(10) (energies are given in kJ mol^{-1} throughout).

$$\underset{\mathbf{1}}{CH_2NH_2^+} + \underset{\mathbf{5}}{NH_3} \longrightarrow CH_2NH_2^+ + NH_3 \quad (1)$$

$$\underset{\mathbf{2}}{CH_2OH^+} + NH_3 \longrightarrow CH_2NH_2^+ + \underset{\mathbf{6}}{H_2O} \quad (2)$$

$$\underset{\mathbf{3}}{CH_2F^+} + NH_3 \longrightarrow CH_2NH_2^+ + \underset{\mathbf{7}}{HF} \quad (3)$$

$$\underset{\mathbf{4}}{CH_3^+} + NH_3 \longrightarrow CH_2NH_2^+ + \underset{\mathbf{8}}{H_2} \quad (4)$$

$$CH_2OH^+ + H_2O \longrightarrow CH_2OH^+ + H_2O \quad (5)$$

$$CH_2F^+ + H_2O \longrightarrow CH_2OH^+ + HF \quad (6)$$

$$CH_3^+ + H_2O \longrightarrow CH_2OH^+ + H_2 \quad (7)$$

$$CH_2F^+ + HF \longrightarrow CH_2F^+ + HF \quad (8)$$

$$CH_3^+ + HF \longrightarrow CH_2F^+ + H_2 \quad (9)$$

$$CH_3^+ + H_2 \longrightarrow CH_3^+ + H_2 \quad (10)$$

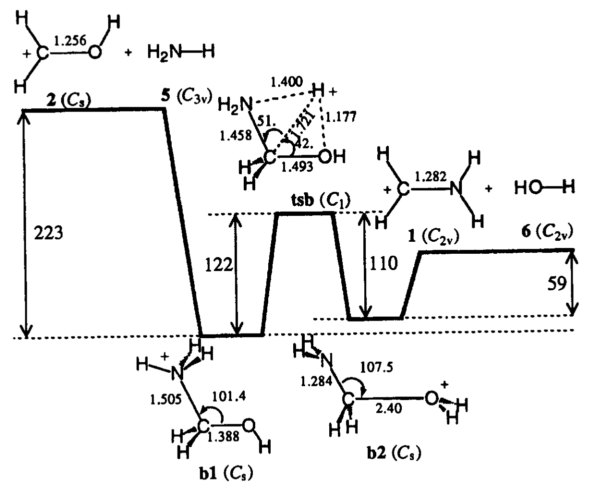
Results

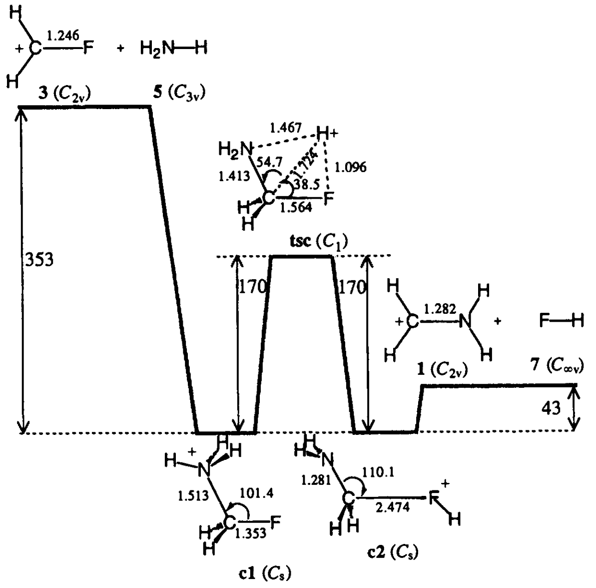
The potential energy diagram shows that the intermediate **a1** is formed directly from the reactants by addition of ammonia to the carbocationic centre of the methyleneammonium ion. The potential energy gained amounts to 111 kJ mol^{-1}. The tight transition structure **tsa** for the intramolecular proton transfer to the identical structure **a2** is 28 kJ mol^{-1} below that of the reactants. Despite the tightness of **tsa** there is therefore a chance that this reaction could be observed in a gas-phase experiment with $^{15}NH_3$. One literature reference has been found on an *ab initio* study of the intermediate 1,3-proton transfer step.[8] Experimental data for the unimolecular dissociation of ^{15}N-labelled protonated glycinamide indicate the intermediacy of **a1**, which decomposes to give $CH_2NH_2^+$ and NH_3.[9]

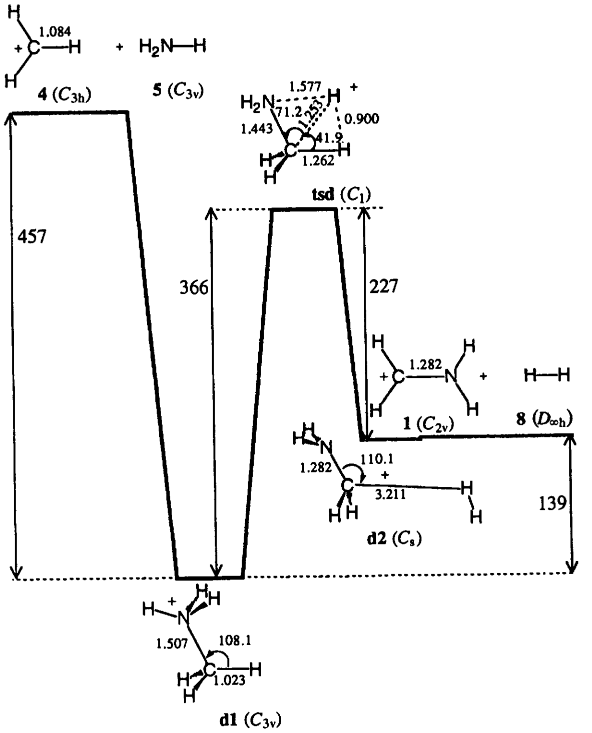
Reaction (2) is exothermic by 152 kJ mol^{-1} and it is clear that the route to the products is available as shown in the potential energy diagram. However, experiments by us[10] and others[11] demonstrate that only the direct proton transfer: $CH_2OH^+ + NH_3 \longrightarrow CH_2O + NH_4^+$ is observed. This route is exothermic by 159 kJ mol^{-1} and is probably taken because it requires a more direct and therefore far less entropically restricted pathway. For reaction (2) the addition step (which gives **b1**) is more favourable than the corresponding step in reaction (1), while the subsequent 1,3-intramolecular proton transfer is more demanding.

No reference to reaction (3) is found in the literature, but the electrophilicity of **3** has been demonstrated in gas-phase reactions with alkenes[12] and benzene.[13] Our calculations show that the reaction is likely, because **tsc** is 183 kJ mol^{-1} lower in energy than the reactants. The reaction exothermicity is calculated to be 310 kJ mol^{-1}.

Huntress *et al.*[14] have shown that reaction (4) occurs readily in the gas phase, and the present results are in good agreement



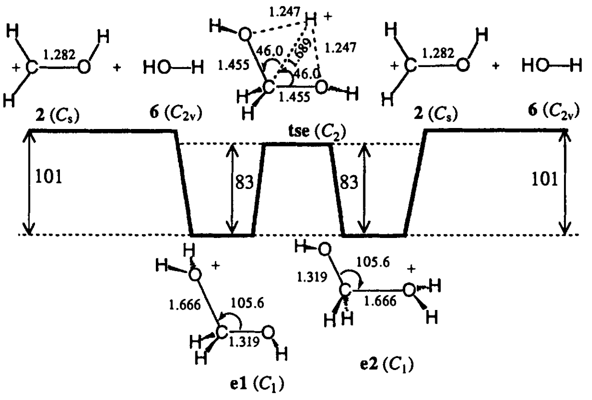




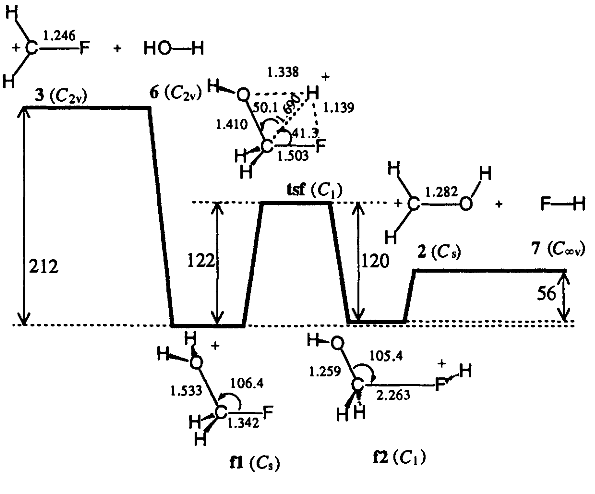
with previous *ab initio* calculations.[6,15] The initial nucleophilic addition and the subsequent 1,3-proton transfer lead to the species **d2** which is very loosely bonded and its existence is for this reason only transient. Once the transition structure is reached the fragmentation to the final products occurs directly with a substantial translational energy release.[6]

By comparison of reactions (1)–(4) it is evident that the exothermicities of the nucleophilic addition steps: $CH_2B^+ + NH_3 \longrightarrow BH_2C\text{-}NH_3^+$ increase down the series B = NH_2- < OH < F < H. A parallel behaviour in the heights of the proton transfer barriers is observed. This will be discussed below.

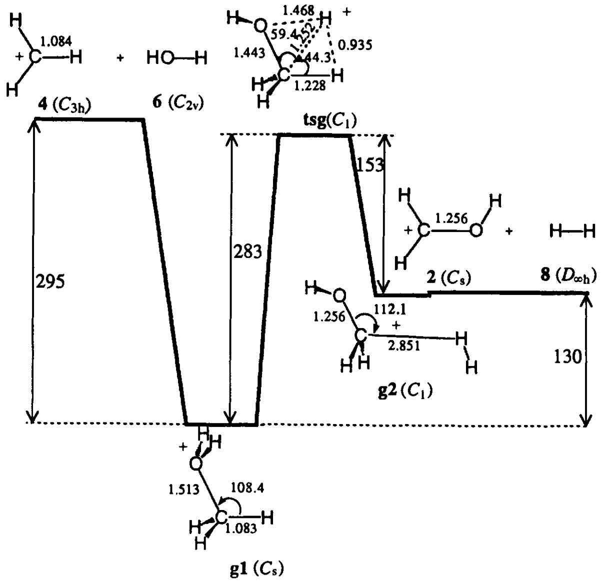
As in reaction (1) the reactants and the products are identical in reaction (5). The results are in complete agreement with one previous *ab initio* study[16] and indicate a reaction which is not very likely to occur, due to the severe energetic and entropic bottleneck provided by **tse**. Failure to observe isotope exchange in the reaction between protonated formaldehyde and $H_2{}^{18}O$ in ICR experiments substantiates this theoretical finding.[10]



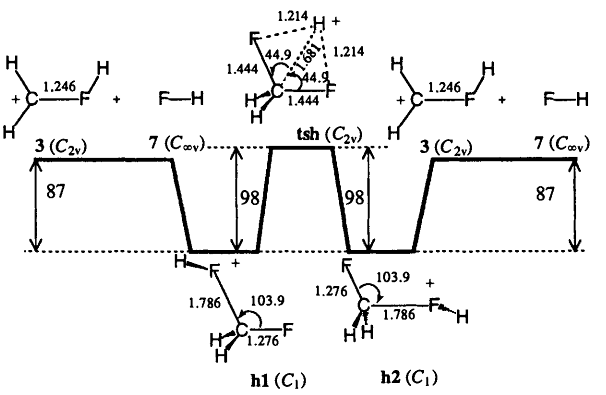
The reactivity of CH_2F^+ towards water [reaction (6)] is so far unknown, judging from what we find in the literature. According to the potential energy diagram the reaction should be feasible, in that the transition structure is 90 kJ mol⁻¹ below the reactants in potential energy.

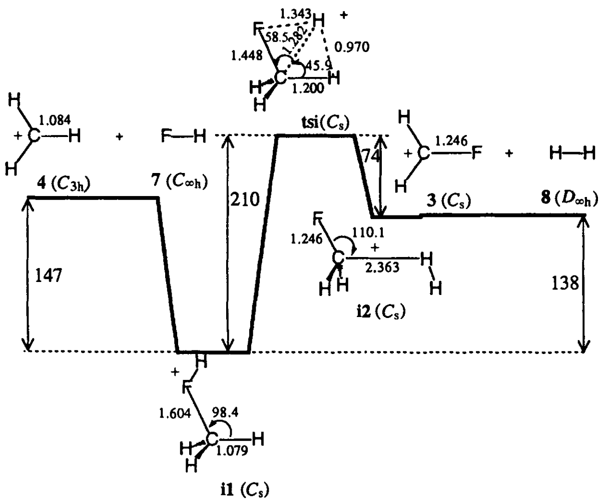


In contrast to the isoelectronic reaction between the methyl cation and ammonia [reaction (4)] reaction (7) does not occur at thermal energies.[14,17,18] The reason for this is evident from the figures. Despite the fact that the overall reaction is exothermic by 165 kJ mol⁻¹ the tight transition structure for the proton transfer which is only 12 kJ mol⁻¹ lower in energy than the reactants effectively blocks transition into the product region. This finding is in complete accord with previous theoretical calculations. However, the transition into products can be achieved by activated **g1** ions (protonated methanol) which are observed to dissociate to give the products CH_2OH^+ and H_2 directly. A substantial translational energy release accompanies this fragmentation reaction.[6] Formation of the reactants, $CH_3{}^+$ and H_2O, is also found to occur from **g1**. Interestingly, the analogous reactions between the methyl cation and methanol and ethanol, respectively, occur readily.[19]



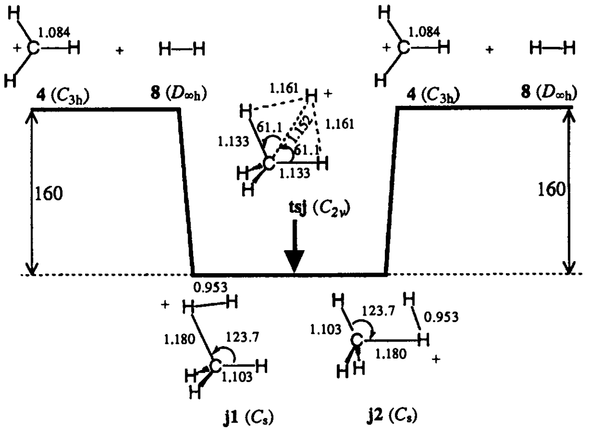
Our calculations predict that reaction (8) is not likely to occur under normal conditions. Both the height of the barrier and the nature of the transition structure should prevent isotopically substituted hydrogen fluoride from exchanging according to reaction (8).





Reaction (9) is clearly unfavourable, despite the fact that it is slightly exothermic. Unimolecular decomposition of energetic protonated methyl fluoride molecules (intermediate **i1**) only gives rise to CH_3^+ and FH, and no $CH_2F^+ + H_2$.[6] This experimental finding was predicted by previous theoretical calculations of this reaction.[15] The present calculations are in complete agreement with this.

Reaction (10) is different from the others in several respects.



The exceptionally strong bond between CH_3^+ and H_2 which leads to formation of the complex CH_5^+ (protonated methane) is the result of a 'non-classical' three-centre two-electron interaction. The H_2 moiety binds to the methyl cation in a side-on fashion by partial donation of σ-electrons to the empty p-orbital of the carbon atom. In striking contrast to this behaviour H_2 is virtually non-bonded to the three other carbocations, CH_2B^+, where $B \neq H$. The reason for this appears to be the interference of the 2p-electrons present on the central atom of each of the substituents $B \neq H$. One of the 2p-orbitals of B mixes with the 2p-orbital of the carbon atom and partial p-electron donation from B to the carbon atom takes place. By accepting p-electron density from B the p-orbital of the carbon atom loses its ability to act as an acceptor for the σ-electrons of H_2.

The chemistry of CH_5^+ has been subject of some quite extensive theoretical[20,21] and experimental[22] studies. Despite this, the present calculations reveal some interesting new features. In complete agreement with the previous calculations the C_s species **j1** is a minimum energy structure. Previous calculations have shown that there also exists another C_s structure corresponding to the transition structure for rotation of the H_2 moiety around the quasirotational axis of the methyl cation moiety. The present calculations show that in addition there is a third stationary structure of C_{2v} symmetry, **tsj**, corresponding to the transition structure for internal transfer of one of the hydrogens of the H_2 moiety to one of the methyl hydrogens, and thereby formation of a new H_2 moiety. At **tsj** the internal coordinate for this movement has a strong component of displacement normal to the C–H bond of the moving hydrogen. This transition structure is therefore seen to provide a mechanism for rapid scrambling of the five hydrogen atoms. The imaginary frequency of vibration for this movement is 615 cm^{-1}, and at the MP2 level **tsj** is only 3 kJ mol^{-1} above CH_5^+ **j1**. By inclusion of zero-point vibrational energy the barrier disappears completely. It should, however, be pointed out that the potential energy surface of the CH_5^+ system is highly non-quadratic. For this reason great caution should be taken in using the calculated harmonic frequencies for the purpose of deriving precise zero-point vibrational energies. The situation is probably that there is a small, but for practical purposes negligible, barrier to the proton transfer.

One common feature of the transition structures **tsa**–**tsj** is that they all clearly correspond to the indicated 1,3-proton transfers. When one analyses the reaction coordinates calculated for the transition structures, it is seen that the most significant contribution is the displacement of the hydrogen atom tangential to the path of its movement from A to B, and perpendicular to the line which connects the hydrogen atom to the central carbon atom. The imaginary frequencies (unscaled, in cm^{-1}) are 1620 (**tsa**), 1470 (**tsb**), 1310 (**tsc**), 1284 (**tsd**), 1539 (**tse**), 1414 (**tsf**), 1316 (**tsg**), 1433 (**tsh**), 1351 (**tsi**) and 615 (**tsj**).

Discussion

Reaction energies

The first subject to be discussed is the overall thermochemistry of the reactions, in reaction (11).

$$CH_2B^+ + A\text{-}H \longrightarrow CH_2A^+ + B\text{-}H \quad \Delta E_{B,A} \quad (11)$$

The calculated reaction energies are in good agreement with experimental data.[23] Because the relative p-electron donating ability of each of the substituents F, OH and NH_2 is central in the preceding discussion, it is necessary to obtain a measure of this property. A good starting point comes from consideration of the reactions (12)–(15).

$$CH_2H^+ + H\text{-}H \longrightarrow CH_2H^+ + H\text{-}H \qquad \Delta E_{H,H} = 0 \text{ kJ mol}^{-1} \quad (12)$$

$$CH_2H^+ + F\text{-}H \longrightarrow CH_2F^+ + H\text{-}H \qquad \Delta E_{H,F} = -11 \text{ kJ mol}^{-1} \quad (13)$$

$$CH_2H^+ + HO\text{-}H \longrightarrow CH_2OH^+ + H\text{-}H \qquad \Delta E_{H,OH} = -165 \text{ kJ mol}^{-1} \quad (14)$$

$$CH_2H^+ + H_2N\text{-}H \longrightarrow CH_2NH_2^+ + H\text{-}H \qquad \Delta E_{H,NH_2} = -318 \text{ kJ mol}^{-1} \quad (15)$$

The energetics of these reactions depend primarily on the strengths of the two bonds which are broken (C–H and A–H) and the two which are formed (C–A and H–H). The C–A bonds possess a varying degree of double-bond character, which will depend on the p-electron donating ability of the substituents A. To account for the difference in single-bond energies the following definitions (with MP2/6-31G(d,p) values included) are invoked [reactions (16)–(18)].

$$CH_3\text{-}H + H\text{-}H \longrightarrow CH_3\text{-}H + H\text{-}H, \qquad \Delta E_{\sigma H} = 0 \text{ kJ mol}^{-1} \quad (16)$$

$$CH_3\text{-}H + H\text{-}F \longrightarrow CH_3\text{-}F + H\text{-}H, \qquad \Delta E_{\sigma F} = 97 \text{ kJ mol}^{-1} \quad (17)$$

$$CH_3\text{-}H + H\text{-}OH \longrightarrow CH_3\text{-}OH + H\text{-}H, \qquad \Delta E_{\sigma OH} = 105 \text{ kJ mol}^{-1} \quad (18)$$

$$CH_3\text{-}H + H\text{-}NH_2 \longrightarrow CH_3\text{-}NH_2 + H\text{-}H, \qquad \Delta E_{\sigma NH_2} = 92 \text{ kJ mol}^{-1} \quad (19)$$

The corresponding stabilization energies due to p-donation were then obtained by eqn. (20).

$$E_{stab}[A] = -(\Delta E[H,A] - \Delta E_{\sigma}[A]) \quad (20)$$

The resulting $E_{stab}[A]$ values are 0 (H), 108 (F), 270 (OH) and 410 kJ mol^{-1} (NH_2). These p-donation stabilization constants correlate almost perfectly with the calculated proton affinities (E_{PA}, defined as the negative enthalpy change for the reaction $M + H^+ \longrightarrow MH^+$, values taken from this work) of CH_4 (542), CH_3F (648), CH_3OH (812) and CH_3NH_2 (951 kJ mol^{-1}).

A straight line of the form in eqn. (21) is obtained.

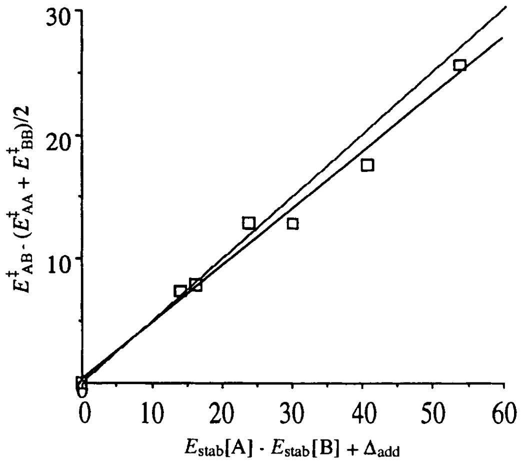


Fig. 2 Plot of the corrected activation energies $E^{\ddagger}_{AB} - (E^{\ddagger}_{AA} + E^{\ddagger}_{BB})/2$ *vs.* the reduced thermochemical quantity $E_{stab}[A] - E_{stab}[B] + \Delta_{add}$. The lower line represents the best least-squares fit to the data, while the upper represents eqn. (29). Units are kJ mol⁻¹.

$$E_{stab}[A] = E_{PA}[CH_3A] - 544\ \text{kJ mol}^{-1} \qquad (21)$$

Association and dissociation energies

The second subject to be discussed is the thermochemistry of the addition and elimination steps. For the addition step (step one) the association energy, $D^0(B,A)$, is defined as the potential energy change of Fig. 1 [reaction (22)].

$$CH_2B^+ + AH \longrightarrow {}^+HA\text{-}CH_2\text{-}B \qquad (22)$$

All association energies are given in reactions (1)–(10). In the case where B = H, CH_2B^+ is the methyl cation, and for this reason $D^0[H,A]$ resembles the methyl cation affinities of the four nucleophiles. Inspection of the data shows that for B = H the association energies, $D^0[B,A]$, decrease in the order NH_3, H_2O, H_2, HF. For the three other B groups the order is NH_3, H_2O, HF, H_2. From the molecular geometries it is seen that there is good correspondence between bond strengths and bond lengths.

The p-donating ability of B appears to regulate the association energies to nucleophiles other than H_2. For a given nucleophile AH forms the strongest bond to CH_3^+ (B = H), while a gradual decrease in the order B = H, F, OH, NH_2 is observed. This trend parallels the increase in the p-donating ability of the B groups given by $E_{stab}[B]$. It can thus be stated that the observed association energy for a pair of A and B substituents, $D^0[B,A]$, is the result of a balance between two opposing forces, namely the donating powers of A and B.

To put this on more quantitative grounds it is useful to take advantage of the thermochemical cycle implicit in Fig. 1, eqn. (23).

$$D^0[B,A] = D^0[A,B] + \Delta_{add} - \Delta E[B,A] \qquad (23)$$

By invoking the definitions given in the section above it is straightforward to rewrite this to eqn. (24).

$$D^0[B,A] - D^0[A,B] = E_{stab}[A] - E_{stab}[B] - (E_{\sigma}[A] - E_{\sigma}[B]) + \Delta_{add} \qquad (24)$$

For A = NH_3, H_2O, HF and B = NH_3, H_2O, HF—and also for A = B = H (this includes seven of the ten reactions)—it turns out to be a good approximation to write eqn. (25).

$$D^0[B,A] - D^0[A,B] = E_{stab}[A] - E_{stab}[B] \qquad (25)$$

The reason for this is that in that Δ_{add} and the expression within the parentheses of eqn. (24) both are close to zero in all these cases. Eqns. (24) and (25) clearly show how the association energies $D^0[B,A]$ and $D^0[A,B]$ are regulated by a compromise based on the relative p-donation powers of A and B.

In the cases where eqn. (25) is valid the two species $^+HA\text{-}CH_2\text{-}B$ and $A\text{-}CH_2\text{-}BH^+$ are equally stable. This has the interesting implication that the two local proton affinities of the species $A\text{-}CH_2\text{-}B$ are the same irrespective of the site of protonation (A or B). For example, the proton affinities corresponding to protonation on F or N of fluoromethylamine ($F\text{-}CH_2\text{-}NH_2$) are the same, despite the fact that the proton affinities of methyl fluoride and methylamine differ by 303 kJ mol⁻¹!

Barrier heights for the 1,3-proton transfers

In this section we will look more closely at the factors determining the barrier of the intramolecular 1,3-proton transfer step. In many respects intramolecular proton transfer resembles intermolecular proton transfer. A gas phase intermolecular proton transfer is formulated by reaction (26).

$$M^1H^+ + M^2 \longrightarrow M^2H^+ + M^1 \qquad (26)$$

The proton donor and the proton acceptor are free to orient themselves in a relative geometric arrangement that allows for maximum electronic overlap between both M^1 and M^2 and the transferring proton during the complete course of the reaction. The result is that one finds that proton transfer reactions in the gas phase usually proceed with zero or negligible activation energy for the central proton transfer step. The thermochemistry of association of M^1H^+ and M^2 and the barriers for proton transfer have been shown to follow Marcus theory for some common examples.[24]

When the proton donor, A, and the proton acceptor, B, are functional groups within the same molecule the barrier heights will be subject to varying degrees of steric strain depending on how close the groups are.[8] In the present case sterically unfavourable geometries must be adapted to accommodate the 1,3-proton transfers. We first tried to apply Marcus theory[25] to the barrier heights, but not surprisingly this turned out to be unsuccessful. Instead we chose to analyse the barriers in light of the above derived p-stabilization constants. The activation energies $E^{\ddagger}_A$ and $E^{\ddagger}_B$ are defined in Fig. 1. We start by taking the average of these [eqn. (27)],

$$E^{\ddagger}_{AB} = (E^{\ddagger}_A + E^{\ddagger}_B)/2 \qquad (27)$$

for each of the ten reactions. The four symmetrical reactions where A = B serve as the common basis on which these are evaluated. Following Marcus theory at this part we subtracted the contribution from the symmetrical reactions, $y = E^{\ddagger}_{AB} - (E^{\ddagger}_{AA} + E^{\ddagger}_{BB})/2$.

We then plotted the resulting y values against $x = E_{stab}[A] - E_{stab}[B] + \Delta_{add}$ and obtained the straight line shown in Fig. 2 [eqn. (28)].

$$y = 2 + 0.46\,x\ \text{kJ mol}^{-1} \qquad (28)$$

This indicates an approximate relationship of the form in eqn. (29).

$$E^{\ddagger}_{AB} = (E^{\ddagger}_{AA} + E^{\ddagger}_{BB})/2 + (E_{stab}[A] - E_{stab}[B] + \Delta_{add})/2 \qquad (29)$$

Besides the intrinsic barriers $E^{\ddagger}_{AA} + E^{\ddagger}_{BB}$ we see that the barrier heights are determined by a balance between the p-electron donation powers A and B. In addition there is a thermodynamic factor $\Delta_{add}/2$. Eqn. (29) can be understood by considering the complete reaction from reactants to products as a push–pull type of process. Upon association of A–H to CH_2B^+, the interaction becomes stronger the better donor A is. On the other hand, the interaction becomes weaker the better donor B is. The balance between these tendencies determines both the association energy D^0[B,A] and the molecular geometry of the reactant adduct $^+HA{-}CH_2{-}B$. The stronger the interaction is, the shorter is the distance $r_{(C-A)}$ and the longer is the distance $r_{(C-B)}$. In order to accommodate the transition structure from the reactant adduct one can see from reactions (1)–(10) that this requires that $r_{(C-A)}$ becomes shorter and that $r_{(C-B)}$ becomes longer. In a sense this is a continuation of the route leading from reactants to reactant adduct, but from the minimum to the transition structure this leads to an increase in potential energy. Exactly the same reasoning applies when one instead considers the reverse reaction which is association of the products B–H and CH_2A^+, and subsequent uphill movement to the transition structure. With this in mind it is understandable that the heights of the barrriers are regulated by the same forces that regulate the depths of the wells.

Acknowledgements

The author wishes to thank VISTA (The Norwegian Academy for Science and Letters, and Statoil) for financial support and NFR (The Norwegian Research Council) for computer time.

References

1 R. A. Y. Jones, *Physical and Mechanistic Organic Chemistry*, Cambridge University Press, Cambridge, 1984.
2 F. Ruff and I. G. Csizmadia, *Organic Reactions. Equilibria, Kinetics and Mechanism*, Elsevier, Amsterdam, 1994.
3 T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper and Row, New York, 1981.
4 M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, GAUSSIAN 92, Gaussian Inc., Pittsburgh, PA, 1992.
5 E. Uggerud, *J. Am. Chem. Soc.*, 1994, **116**, 6873.
6 T. Vulpius, E. L. Øiestad, Å. M. L. Øiestad, H. Skaane, K. Ruud, T. Helgaker and E. Uggerud, *Eur. Mass Spectrom.*, 1995, **1**, 121.
7 J. A. Pople, A. P. Scott, M. W. Wong and L. Radom, *Isr. J. Chem.*, 1993, **33**, 345.
8 X. Duan and S. G. Scheiner, *J. Am. Chem. Soc.*, 1992, **114**, 5849.
9 R. D. Kinser, D. P. Ridge, G. Hvistendahl, B. Rasmussen and E. Uggerud, *Chem. Eur. J.*, 1996, in the press.
10 J. K. Pau, J. K. Kim and M. C. Caserio, *J. Am. Chem. Soc.*, 1978, **100**, 3831. Recent experiments by us confirm this (E. Uggerud, unpublished results).
11 M. T. Kinter and M. M. Bursey, *J. Am. Chem. Soc.*, 1986, **108**, 1797.
12 K. Stanney, J. M. Tedder and A. L. Mitchell, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1383.
13 R. Cipollini, N. Pepe, M. Speranza and G. Lilla, *Gazz. Chim. Ital.*, 1978, **108**, 33.
14 W. T. Huntress Jr., R. F. Punizzotto Jr. and J. B. Laudenslager, *J. Am. Chem. Soc.*, 1973, **95**, 4107.
15 R. H. Nobes and L. Radom, *Chem. Phys.*, 1983, **74**, 163.
16 E. M. Evleth and E. Kassab, *NATO ASI Ser., Ser. B*, 1992, **291**, 343.
17 N. G. Adams and D. Smith, *Chem. Phys. Lett.*, 1978, **54**, 530.
18 D. Smith and N. G. Adams, *Chem. Phys. Lett.*, 1977, **47**, 145.
19 R. D. Smith and J. H. Futrell, *Chem. Phys. Lett.*, 1976, **41**, 64.
20 P. C. Hariharan, W. A. Lathan and J. A. Pople, *Chem. Phys. Lett.*, 1972, **14**, 385.
21 A. Komornicki and D. A. Dixon, *J. Chem. Phys.*, 1987, **86**, 5625.
22 A. R. J. Heck, L. J. de Koning and N. M. M. Nibbering, *J. Am. Soc. Mass Spectrom.*, 1991, **2**, 453.
23 S. G. Lias, J. E. Bartmess, J. F. Liebman, J. H. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data*, 1988, **17**, 1.
24 S. Scheiner and P. Redfern, *J. Phys. Chem.*, 1986, **90**, 2969.
25 R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891.

Paper 6/01603K
Received 6*th March* 1996
Accepted 26*th April* 1996