case of ref 16b is the range of validity of eq B9. In the adiabatic case the amplitude A is much smaller than in the diabatic case (where A is given by the reorganization energy α). Thus, eq B9 is expected to be valid in the adiabatic cases on a wider range of τ_u than in the diabatic cases.

The acf $\langle u(0)\, u(t)\rangle_g$ can be obtained directly by simulations. However, significant formal insight can be gained by examining analytical autocorrelation functions for a given effective equation of motion for $u(t)$. This point will be explored in subsequent publications.

How Does a Dication Lose a Proton?

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Abstract: A detailed study of the mechanism by which a proton is lost from a dication reveals that such processes are more complicated than is often assumed. In many cases, a deprotonation reaction is best viewed as a two-stage process: Initially, the departing unit is better described as a hydrogen atom than as a proton and only later, at some point further along the decomposition pathway, does a spontaneous electron transfer take place to form the eventual products. Consequently, it is found that, contrary to conventional wisdom, *restricted* Hartree–Fock (RHF) theory does not necessarily offer a satisfactory theoretical treatment of such fragmentations. The circumstances under which it is appropriate to use RHF or UHF procedures (and the Møller–Plesset perturbation theories based on these) are examined in light of a recent model for dication dissociation, and it is found that the Δ parameter of that model is a useful aid in choosing the theoretical formalism appropriate to a given dication.

The chemistry of gas-phase dications has received considerable attention in recent years, from both theoreticians and experimentalists.[1] Such species are usually thermodynamically unstable with respect to dissociation into two monocations, but significant kinetic stability may result if sufficiently high barriers impede fragmentation. For this reason, the accurate assessment of such barriers is of paramount importance in the theoretical investigations of dications.

One ubiquitous fragmentation route for dications is proton loss (eq 1). The observation that the transition structure for such

$$\mathrm{AH}^{2+} \rightarrow \mathrm{A}^{+} + \mathrm{H}^{\bullet +} \qquad (1)$$

reactions often occurs very late along the reaction path has recently been rationalized[3] in terms of a model[2–4] in which the potential curve for the fragmentation is viewed as arising from an avoided crossing between an ion–ion repulsive state, which correlates with $\mathrm{A}^+ + \mathrm{H}^+$, and an ion–induced-dipole attractive state, which correlates with $\mathrm{A}^{2+} + \mathrm{H}$. This model may be used, for example, to show that if the second ionization energy of A is a little larger than 13.6 eV (the ionization energy of H), a late-transition structure for proton loss may be anticipated.

Further inspection of this model can give considerable insight into the dissociation process and reveals certain features that have previously been overlooked. In particular, if AH^{2+} is a closed-shell singlet species, it is conventionally assumed[5] that the proton loss may be treated within the framework of restricted (RHF), as opposed to unrestricted (UHF), Hartree–Fock theory. However, as we show in this paper, the choice between these alternatives is less straightforward than is normally realized, and indeed, for late-transition structures, RHF ought not be used.

Table I. Calculated Bond Lengths (Å) and Total Energies (Hartrees) of the Equilibrium and Transition Structures of AlH^{2+} and Corresponding Barriers for Deprotonation (kJ mol^{-1})[a]

	r_{eq}	E_{eq}	r_{TS}	E_{TS}	barrier[b]
RHF	1.614	−241.562 64	3.009	−241.511 15	135
RMP2	1.641	−241.595 18	3.118	−241.549 00	121
RMP3[c]	1.653	−241.594 39	3.169	−241.545 43	129
RMP4[c]	1.660	−241.597 29	3.142	−241.549 39	126
RCISD[c,d]	1.669	−241.599 80	3.206	−241.550 29	130
TCSCF[e]	1.671	−241.589 99	3.415	−241.530 45	156
UHF	1.645	−241.562 84	3.589	−241.520 68	111
UMP2	1.641	−241.595 18	3.309	−241.539 53	146
UMP3[c]	1.653	−241.594 39	3.276	−241.533 97	159
UMP4[c]	1.660	−241.597 29	3.250	−241.535 72	162
UCISD[c,d]	1.669	−241.599 80	3.206	−241.550 23	130

[a] 6-31G* basis set used throughout. [b] $E_{\mathrm{TS}} - E_{\mathrm{eq}}$. [c] Frozen-core approximation used. [d] Corresponds to full CI for the valence electrons. [e] 4σ and 5σ molecular orbitals were active.

Method and Results

A modified version[6] of the GAUSSIAN 82 system of programs[7] was used to carry out standard ab initio calculations[8] on AlH^{2+} and $\mathrm{N_2H_6}^{2+}$ with the 6-31G* basis set, both for the equilibrium structures and for the transition structures for deprotonation. The equilibrium and transition structure bond lengths in AlH^{2+} were optimized at the Hartree–Fock (HF), second-, third-, and fourth-order Møller–Plesset perturbation theory (MP2, MP3, and MP4, respectively), and singles-and-doubles configuration interaction (CISD) levels, within both the spin-restricted (leading to RHF, RMP, and RCISD) and spin-unrestricted (leading to UHF, UMP, and UCISD) frameworks. The bond lengths were also optimized at the two-configuration SCF (TCSCF) level with the 4σ and 5σ molecular orbitals as the active space. The results, including corresponding barrier heights, are summarized in Table I. Because AlH^{2+}

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Table II. Calculated[a] Lengths of the Breaking N–H Bond (Å) and Total Energies (Hartrees) of the Equilibrium and Transition Structures for Deprotonation of $N_2H_6^{2+}$

	r_{eq}	E_{eq}	r_{TS}	E_{TS}	barrier[b]	$E(N_2H_5^{\cdot 2+})$ + $E(H^{\cdot})$[c]
RHF	1.026	−111.61330	3.110	−111.41955	509	−111.44888
RMP2	1.045	−111.94785	3.305	−111.75602	504	−111.74425

[a] 6-31G* basis set used throughout. [b] $E_{TS} - E_{eq}$. [c] Calculated using unrestricted (UHF or UMP2) theory (hartrees).

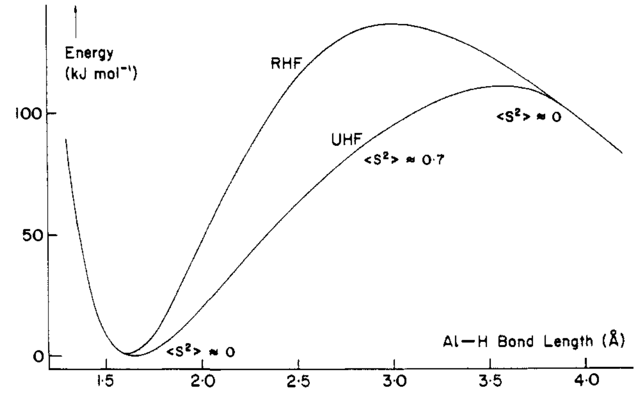

Figure 1. RHF/6-31G* and UHF/6-31G* potential curves describing the deprotonation of AlH^{2+}.

has only two valence electrons, CISD calculations are equivalent to full-valence CI. Consequently, the CISD results provide a standard by which to judge the performance of both TCSCF and Møller–Plesset perturbation theory. Additionally, RHF and UHF potential curves for AlH^{2+} were calculated and are plotted in Figure 1. Similar curves, with the molecular energy given as a function of the N–H bond length, were calculated for the deprotonation of $N_2H_6^{2+}$ and are plotted in Figure 2. These energies were obtained by optimizing *all* structural parameters in the molecule for a series of values of the length of the breaking N–H bond. The equilibrium and transition-structure geometries of $N_2H_6^{2+}$ were also calculated with RHF and RMP2, and the results are summarized in Table II.

Discussion

A large number of singlet dications have been characterized, both theoretically and experimentally.[1] The bond lengths in most of these are similar to those found in comparable neutral molecules, and, for this reason, restricted Hartree–Fock (RHF) theory is often assumed to provide a suitable starting point for theoretical studies of such species. For example, we find that AlH^{2+} has a bond length (1.67 Å, Table I) that is roughly 0.2 Å shorter than that in the isoelectronic (and well-behaved) NaH molecule (1.887 Å, exptl), and this might well lead us to conclude that RHF should be used to describe this species. Surprisingly, however, we find that the RHF wave function for AlH^{2+} at the RHF equilibrium structure is UHF unstable and that the UHF equilibrium bond length is more than 0.03 Å longer than the RHF value.

Likewise, the loss of a proton from AlH^{2+} produces the closed-shell singlet Al^+ ion (isoelectronic with Mg atom), and therefore the very stretched $Al^+\cdots H^+$ system is also expected to be well described by an RHF wave function. This is indeed found to be the case for $r > 4$ Å, but, curiously, the RHF wave function at the RHF transition structure (3.009 Å, Table I) is UHF unstable. Moreover, if the RHF spin restriction is relaxed, a UHF transition structure, with a bond length nearly 0.6 Å longer and giving a barrier 24 kJ mol⁻¹ lower, is obtained.

Dorman and Morrison suggested[2] some time ago that the ground-state potential curve for a diatomic dication AB^{2+} could be viewed as arising from the interaction between a state that correlates with $A^+ + B^+$ and another that correlates with A^{2+} + B, and such a description has been used subsequently by several other workers.[9] More recently, we have extended this approach by proposing two semiquantitative avoided-crossing models for describing dicationic fragmentation. Our simpler avoided-crossing (AC) model[3] neglects the polarization attraction between A^{2+} and B and also neglects coupling between the diabatic potential curves, while our more refined ACDCP (avoided crossing with diabatic coupling and polarization) model[4] takes account of both of these effects. Within each of these models, an important parameter is Δ, the asymptotic energy difference between the diabatic states, given by the energy difference between the pairs of fragmentation products (eq 2). The simpler AC model is applicable when there

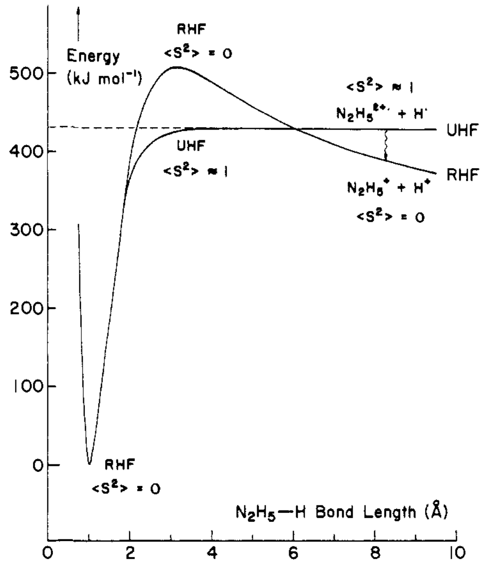

Figure 2. RHF/6-31G* and UHF/6-31G* potential curves describing the deprotonation of $N_2H_6^{2+}$. The arrow shows the point at which the spontaneous electron transfer can take place from the $N_2H_5^{\cdot 2+}$ + H· potential curve to the $N_2H_5^+$ + H^+ potential curve (see text).

$$\Delta(AB^{2+}) = E(A^{2+}) + E(B) - E(A^+) - E(B^+) = IE(A^+) - IE(B) \qquad (2)$$

is little coupling between the diabatic curves involved and when the quantity Δ is small (less than ≃2–3 eV). Under such conditions, we have shown[3] that the transition-structure bond length for fragmentation of diatomic dications may be usefully estimated via eq 3, r_{TS} being the bond length at which the A^{2+} + B curve

$$r_{TS} \simeq \Delta^{-1} \qquad (3)$$

(assumed flat) and the $A^+ + B^+$ curve (assumed hyperbolic) cross. For AlH^{2+}, Δ = 0.146 hartrees (HF/6-31G*), and hence the predicted value of r_{TS} is 6.8 au ≡ 3.6 Å. This is in good agreement with the UHF/6-31G* value (3.589 Å) in Table I but not with the RHF/6-31G* value (3.009 Å). This surprising state of affairs is illustrated in Figure 1 from which it is clear that the RHF and UHF potential curves for AlH^{2+}, while identical for $r < 1.6$ Å or $r > 3.9$ Å, are significantly different in the intermediate (and chemically interesting) region.

Is such UHF instability over a finite, but important, range of the fragmentation pathway a general feature of proton losses from dications? If so, what is its origin? Indeed, if such behavior is the rule rather than the exception, is is possible to decide which, of RHF and UHF, is the more chemically reasonable? The answer to the first of these questions is that this type of UHF instability is common, and we shall present examples elsewhere.[10] In the present paper, we present a resolution of the question of the origin of the phenomenon, from which it becomes clear that such be-

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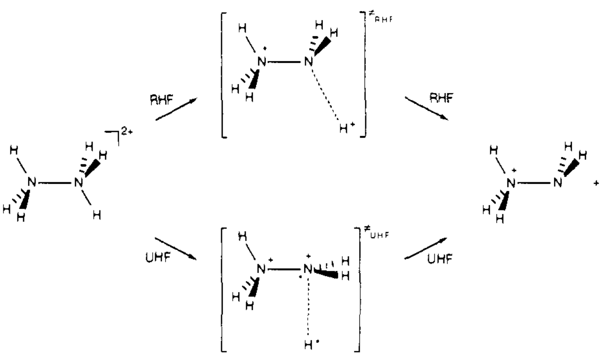

Figure 3. Different paths prescribed through coordinate space by RHF and UHF procedures for the deprotonation of $N_2H_6^{2+}$.

havior should be widespread. We also suggest circumstances under which an RHF or UHF approach is more appropriate.

The key to the problem is found by considering the changes in the molecular wave function as the dication is stretched from the equilibrium to the transition structure. Near the equilibrium structure, the molecular charge in AH^{2+} is shared between A and H, to an extent determined in part by the internuclear separation. However, as the bond is lengthened, it becomes progressively more possible for the departing fragments to resemble the (lower lying) pure diabatic $A^{2+}\cdots H^{\bullet}$ state. *Thus, before the transition structure is reached (and especially when* Δ *is small so that the crossing point is late), the fragmentation process is better described as a hydrogen atom loss than as a proton loss.* Only beyond the transition structure, after an electron transfer has taken place, does the system resemble $A^{+}\cdots H^{+}$.

Now of course, as is well-known, RHF cannot satisfactorily describe hydrogen atom loss because, in this process, an electron pair is split. Accordingly, we can now understand the significantly different descriptions afforded by RHF and UHF in the intermediate region of the fragmentation process. We note that the size of this intermediate region may be very small (or, possibly, even nonexistent) if Δ is large, and when this is the case, the use of RHF to describe proton loss may be justifiable. Nevertheless, in the general case, it appears that the use of UHF is essential.

A second example is provided by the hydrazinium dication, $N_2H_6^{2+}$. We mentioned this species in our earlier paper,[3] presenting its proton loss as an example of a fragmentation with a very late-transition structure (N$\cdots$H = 3.11 Å, RHF/6-31G*). It now appears that we actually understated the case since if we plot the energy of the system as a function of the length of the breaking N–H bond (fully optimizing all other geometric parameters) using UHF rather than RHF (Figure 2), we find that the UHF transition structure is not reached until the length of the breaking bond is more than 7 Å. Moreover, at the HF/6-31G* level, Δ for the system is only 69 mhartrees, which, according to eq 3, should give rise to a transition-structure bond length of roughly 8 Å. It is clear that the UHF description seems to accord much better with the avoided-crossing model than does the RHF treatment.

Examination of the proton loss from $N_2H_6^{2+}$ also reveals that even the *qualitative* description provided by RHF of the way in which the rest of the molecule behaves during proton loss from a polyatomic dication may be different from that afforded by UHF. As the system approaches the transition structure, it resembles $N_2H_5^{+}\cdots H^{+}$ within the RHF framework (a consequence of the RHF constraint) while, within the UHF framework, it becomes essentially $N_2H_5^{\bullet 2+}\cdots H^{\bullet}$. Structurally, these are very different because the $N_2H_5^{\bullet 2+}$ dication, unlike the monocation, contains a trigonal rather than a pyramidal nitrogen (Figure 3). *Consequently, for proton losses from polyatomic dications, RHF and UHF generally prescribe distinctly different paths through coordinate space.*

In view of the success of the avoided-crossing model in describing proton losses,[2-4] it might appear that a multiconfiguration SCF treatment would be a natural way to address such problems. While this may well be true for diatomic systems, or where full-valence MCSCF is possible, smaller MCSCF models do not generally give an equally satisfactory account of all parts of the potential surface of a polyatomic molecule and, therefore, do not satisfy the criteria of uniqueness and unbiasedness, which are desirable in a theoretical model.[8] Moreover, full-valence MCSCF rapidly becomes very computationally expensive, even for moderate-sized systems, particularly if the treatment is augmented with CISD in order to correct for the effects of dynamical electron correlation. For these reasons, and because we note additionally that TCSCF (without augmentation by CISD) does not give particularly good results even for the simple AlH^{2+} dication (Table I), we will henceforth confine our attention to single-configuration-based methods.

We have determined that UHF is preferable to RHF for modeling proton loss from dications, but this has solved only one of the problems involved. At this point we face a second dilemma. Suppose that we were also interested in obtaining improved estimates of the deprotonation barrier height using Møller–Plesset perturbation theory. Given that we have used unrestricted Hartree–Fock theory to find the transition structure, should we then employ unrestricted Møller–Plesset (UMP) perturbation theory to correct for the effects of electron correlation? Unfortunately this would be very unwise because, as indicated in Figures 1 and 2, in the region before the transition structure is reached, the expectation value of the spin-squared operator (i.e. $\langle S^2 \rangle$) for the UHF wave function may deviate considerably from the correct singlet value of zero, indicating that the UHF wave function may be heavily spin-contaminated in the vicinity of the transition structure. We have confirmed the recent finding[11] that UMP theory converges extremely slowly under such circumstances and, at the normally accessible levels (MP2, MP3, MP4), gives rise to *deceptively convergent barriers* for dicationic dissociations.[12] Consequently, for example, the progression of UMP barrier heights for the fragmentation of AlH^{2+} is 111, 146, 159, and 162 kJ mol^{-1} while the correct value with the 6-31G* basis set (full-valence CI) is 130 kJ mol^{-1} (Table I). Furthermore, in cases where Δ is smaller and the transition structure occurs even later (e.g. proton loss from $N_2H_6^{2+}$), the spin-contamination problem (and hence the UMP convergence problem) will be so serious that any attempt to use UMP barrier estimates would be completely futile.

Likewise, although for different reasons, the straightforward application of restricted Møller–Plesset (RMP) perturbation theory also appears unpromising. It is obvious from Figure 2 that, at least for dications where Δ is small, RHF gives an exceedingly poor estimate of the transition-structure geometry, the error in the case of $N_2H_6^{2+}$ being roughly 4 Å. Moreover, RMP2 reduces this error by less than 0.2 Å (Table II), suggesting that only extremely high orders of RMP theory could possibly produce realistic geometries. Furthermore, the RHF energy rises well above even the energy of separated $N_2H_5^{\bullet 2+}$ + $H^{\bullet}$ (Table II, Figure 2), implying, presumably incorrectly, that a hydrogen atom is *easier* to remove from the dication than is a proton.

However, our prognosis of the problem need not be entirely pessimistic. We have observed that the serious problems in applying Møller–Plesset perturbation theory to proton losses arise only when Δ is rather small. For systems with large Δ (e.g. the BH^{2+} dication, for which Δ = 425 mhartrees from experimental ionization energies), restricted theory (RHF or RMP) is suitable for *all* bond lengths. For systems with intermediate Δ values (e.g. the AlH^{2+} dication considered earlier), although UHF is preferable to RHF, the use of moderate levels of RMP theory (e.g. RMP3 or RMP4, Table I) should give satisfactory results (see also, ref 13). Only for systems with small Δ do both RMP and UMP lose their usefulness for transition-structure determination. Nonetheless, a physical appreciation of the problem can help us at this point.

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We noted above that, for deprotonations involving small Δ values, the fragmentations are best viewed as being initially hydrogen atom losses, followed by an instantaneous electron transfer at the curve crossing point, at which stage a coulomb repulsion between the nascent A^+ and H^+ moieties becomes dominant. For this reason, the energy profile for proton loss from $N_2H_6^{2+}$ (Figure 2) should be typical of those for small-Δ proton losses generally: an early steeply rising section during which the A–H bond is *homolytically* cleaved; an almost flat plateau, due to the very weak (r^{-4}) attraction between $A^{\bullet 2+}$ and $H^\bullet$, which extends to the crossing point; and a downward hyperbolic section beyond the crossing point. Consequently, the barrier to proton loss in such cases is essentially equal to the barrier to hydrogen atom loss, despite the fact that the net endothermicities for proton loss and hydrogen atom loss differ substantially. Formulating this in terms of energies that can be satisfactorily estimated by Hartree–Fock or Møller–Plesset theory gives as the barrier for deprotonation (E_{deprot})

$$E_{\text{deprot}} \simeq E(A^{\bullet 2+}) + E(H^\bullet) - E(AH^{2+}) \qquad (4)$$

if Δ is small. Indeed, even when Δ is not particularly small, eq 4 will still give an upper bound to the true barrier. Using eq 4 in conjunction with the total energies in Table II gives modified RHF and RMP2 barriers for proton loss (and, of course, for hydrogen atom loss) from $N_2H_6^{2+}$ as 432 and 535 kJ mol^{-1}, respectively.

Our argument is relevant to the suggestion of Beynon and co-workers[14] that the experimental kinetic energy release in the fragmentation of dications can be roughly equated to $1/r_{TS}$ where r_{TS} is the intercharge separation at the transition structure. One assumption that underlies this idea is that, at the transition structure, the charges on each of the incipient fragments are close to unity. We observed in a previous paper that the avoided-crossing model provided a theoretical basis for such an assumption.[3] We now suggest that, for proton losses from systems in which the plateau is reached before the electron transfer takes place (for example, see Figure 2), the kinetic energy release should be almost equal to Δ. Consequently, using the definition of Δ (eq 2), we find that the kinetic energy release (T) for deprotonation of the dication AH^{2+} is given by eq 5. The principal assumptions

$$\begin{aligned} T &\simeq \Delta(AH^{2+}) \\ &= E(A^{\bullet 2+}) + E(H^\bullet) - E(A^+) - E(H^+) \\ &= \text{IE}(A^+) - 13.60 \text{ eV} \end{aligned} \qquad (5)$$

made in the derivation of this relationship between the kinetic energy release accompanying deprotonation and the second ionization energy of the remaining fragment are that the diabatic coupling between the diabatic $A^{\bullet 2+} + H^\bullet$ and $A^+ + H^+$ curves is small and that the electron transfer occurs late, both of which will be the case if Δ is small.[4]

The prediction of eq 5 may be compared with the observed kinetic energy release in the case of the $SiH^{\bullet 2+}$ dication, which has been carefully studied both theoretically[15] and experimentally[16] by Koch et al. The experimental kinetic energy release T was measured to be 2.42 eV.[16] The second ionization energy of Si is 16.35 eV,[17] and eq 5 therefore predicts that T should be approximately equal to (and certainly no greater than) 2.75 eV, which is consistent with the experimental value. Because the ion–induced-dipole interaction of Si^{2+} with $H^\bullet$ is very small at the point of electron transfer ($E_{\text{pol}} < 0.04$ eV), that is, the plateau is *very* flat, and because the diabatic coupling is also very small,[4] the small discrepancy between the prediction of eq 5 and the measured value may not be attributed to either of these effects. It may be associated with experimental uncertainty or nonadiabatic coupling effects.

We have already pointed out that the RHF- and UHF-based descriptions of proton loss from dications lead to different paths through coordinate space implying, for example, that the curves in Figure 2 only *appear* to cross (because they are projections onto the energy–reaction-coordinate plane) while in full-coordinate space they do not. However, this now appears to present a paradox. We have suggested that UHF gives a satisfactory qualitative description of the system before the transition structure and that RHF is qualitatively correct after the transition structure, but if they prescribe paths which are not joined, how does the system pass from one path onto the other in the vicinity of the transition structure? There appears to be a continuity problem, but we offer the following explanation, which is illustrated in the specific case of $N_2H_6^{2+}$ deprotonation in Figure 2. At some point along the $A^{\bullet 2+} + H^\bullet$ path it becomes energetically feasible for a spontaneous electron transfer to take place, thereby momentarily forming $A^+ + H^+$ at the $A^{\bullet 2+} + H^\bullet$ geometry. At this point the dissociation becomes inevitable, for the system will then rapidly roll down onto the hyperbolic $A^+ + H^+$ path and fragment. From this it is clear that "geometry of the transition structure" is not very well-defined for deprotonation of polyatomic dications with small Δ values. Nonetheless, the geometry at the point at which electron transfer becomes energetically feasible (which will be the highest point on the lowest dissociation pathway but which will not be a stationary point) *is* well-defined. On the assumption that, in the vicinity of the electron transfer, there is little coupling in either diabatic state between the length of the fragmenting bond and the other internal modes of A, it is straightforward to show that the electron transfer will occur somewhat later than eq 3 predicts. Specifically, if the difference between the vertical and adiabatic electron affinities of A^{2+} is δ (a positive number), then eq 6 applies. This r_{TS} refers to the distance from the departing

$$r_{TS} \simeq (\Delta - \delta)^{-1} \qquad (6)$$

proton to the *center of charge* of A rather than the distance to the particular nucleus to which the proton was formerly bonded. Equation 6 represents the polyatomic analogue of eq 3.

Conclusions

Several important results emerge from this study:

(1) Dication deprotonation is a more complicated process than is often assumed. In cases where the transition structure for deprotonation occurs late on the reaction pathway, the deprotonation process for AH^{2+} involves (i) *homolytic* cleavage of the A–H bond to give $A^{\bullet 2+}\cdots H^\bullet$; (ii) further stretching of $A^{\bullet 2+}\cdots H^\bullet$, now dominated by a (weak) ion–induced-dipole potential with little change in energy; and (iii) a crossing to the $A^+ + H^+$ diabatic potential curve yielding the dissociation products $A^+ + H^+$. Generally, it is necessary to use *unrestricted*, not restricted, Hartree–Fock theory to examine such fragmentations.

(2) A simple but reliable "back of the envelope" indicator of the lateness of the transition structure for deprotonation of a dication AH^{2+} is provided by the Δ parameter, i.e. the difference between the second ionization energy of A and the (first) ionization energy of H (13.6 eV). A small Δ value implies a late-transition structure.

(3) Proton losses should be treated theoretically according to the magnitude of Δ: (a) Δ large (several hundred millihartrees), RHF and RMP may be used; (b) Δ intermediate (100–300 mhartrees), UHF is preferable to RHF but RMP is preferable to UMP; (c) Δ small (<100 mhartrees), UHF (not RHF) is mandatory for obtaining transition-structure *geometries* while proton loss *barrier heights* should be equated to hydrogen atom loss barriers.

(4) For deprotonations of polyatomic dications, RHF and UHF generally prescribe different paths through coordinate space.

(5) The kinetic energy release from the fragmentation of a dication AH^{2+} with small Δ should be approximately 13.6 eV less than the second ionization energy of A.

Registry No. AlH^{2+}, 115162-35-1; $N_2H_6^{2+}$, 31479-14-8.

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