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Endothermic Proton Transfer Reactions from Three $[C_6H_6]^{+\cdot}$ Isomers

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A triple quadrupole mass spectrometer was used to establish the proton affinities of phenyl, $CH_3C{\equiv}CC{\equiv}CCH_2^{\cdot}$, and $HC{\equiv}CCH_2CH^{\cdot}C{\equiv}CH$ radicals as 870±29, 824±25, and 757±21 kJ mol^{-1}, respectively, from the kinetic energy of benzene, 2,4-hexadiyne, and 1,5-hexadiyne molecular ions at which the onset of proton transfer to less basic species occurs in the second rod assembly. These values were confirmed by other triple quadrupole experiments involving bracketing of exothermic proton transfers.

INTRODUCTION

Thermochemistry and dissociation are the principal methods for investigating gaseous ion structure.[1] By comparing experimental data with data from the literature[2,3] or theory[4] quantitative comparisons using ion thermochemistry can be made, while fragmentation patterns are interpreted on a largely qualitative basis.

The proton affinity (PA) of a given neutral is $-\Delta H_r^\circ$ for Eqn (1), its protonation. Proton affinities are most accurately determined by measuring the positions of equilibrium of proton transfer (Eqn (2)) of a series of compounds and correcting for the $T\Delta S^\circ$ contribution to the ΔG_r° for Eqn (2).

$$M + H^+ \rightarrow MH^+ \tag{1}$$

$$MH^+ + N \rightarrow NH^+ + M \tag{2}$$

An older method with a larger associated error is by bracketing. Since ΔH_r° for Eqn 2 equals the PA of N minus the PA of M, the PA of an unknown can be measured by comparison with a known compound whose PA is close enough to allow measurement of the intensities of both MH^+ and NH^+.

Sometimes Eqn (2) is so unfavorable that the amount of NH^+ formed does not exceed noise. On a scale measured roughly to the nearest kJ, the ion-molecule reactions observed in either a high-pressure source or an ion cyclotron resonance (ICR) spectrometer are thus limited to exothermic or thermoneutral reactions. The PA of N can therefore be bracketed as greater than the PA of a standard M if Eqn (2) is observed, and less than the PA of another standard M′ if $M'H^+$ does not protonate N. The uncertainty of the measurement is determined by the difference in the proton affinities of the bracketing standards. In some portions of the proton affinity scale this difference can be more than 8.4 kJ. More accurate measurements require standards with more closely spaced proton affinities.

We have recently reported[5] the behavior of exothermic and endothermic ion/molecule reactions in a triple quadrupole experiment where the product ion yield is measured as a function of ion kinetic energy (energy-resolved tandem mass spectrometry).[6] The dependence of product yield on ion translational energy differs for endothermic and exothermic reactions. The product ion yield of an exothermic reaction is greatest for ion kinetic energy approaching zero and decreases with increasing ion kinetic energy. This diminution is believed[5] to be the result of a decrease in the lifetime of the collision complex as the translational energy increases. For endothermic reactions the product ion yield is generally undetectable at low ion kinetic energy, and there is a threshold above which a roughly linear increase in product ion intensity is observed. This difference allows a slight improvement over the results of our conventional reaction bracketing experiment.

In addition, the numerical value of the ion translational energy at the threshold can be determined for an endothermic reaction.[5] For reactions that are simple atom or molecular fragment transfers, these thresholds have been consonant with thermochemistry to within ±0.2 eV in our early experiments. Since proton transfer is such a simple process, it is useful to establish whether PA values acquired by endothermic reaction onsets are consistent with those acquired by the more traditional route.

The structure of the $[C_6H_6]^{+\cdot}$ isomers, benzene molecular ion, and its isomers, have been the subject of extensive investigation.[7-10] We apply this new experimental method, threshold bracketing, to determine proton affinities of the conjugate bases $[C_6H_5]^{\cdot}$ of the acids benzene molecular ion, 2,4-hexadiyne molecular ion, and 1,5-hexadiyne molecular ion.

EXPERIMENTAL

All experiments were performed using an ExtrEL Corporation (Pittsburgh, Pennsylvania) triple quadrupole mass spectrometer as previously described.[5] The ion

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kinetic energies were varied from 0 to 15 eV (in the laboratory frame) by changing the pole zero of the second quadrupole relative to the source potential. The collision cell pressure was in the range of $2\text{-}4 \times 10^{-6}$ Torr (ion gauge), and corresponded to single collision conditions.[11] All reagents were obtained from commercial sources and used without further purification. Gas chromatographic ion trap detector (Finnigan Instruments, Sunnyvale, California) analyses of the benzene, 2,4-hexadiyne and 1,5-hexadiyne confirmed the absence of cross-contamination. The parent ions were formed by impact of 18-20-eV electrons. Experimental data were deconvoluted for Doppler broadening from thermal motion of the neutral by the method of Chantry using the linear cross-section model.[12] Curves were fitted to the nearest 0.1 eV (in the center of mass, COM, frame of reference) for experimental data in a 2.0-eV (COM) window around an approximate threshold determined by inspection of the raw data.

RESULTS AND DISCUSSION

Four collision gases were used: dimethylamine (from a 40% aqueous solution), $(CH_3)_2NH$, PA = 925 kJ mol^{-1}; NH_3, PA = 853.5 kJ mol^{-1}; CH_3OH, PA = 761 kJ mol^{-1}; and H_2O, PA = 699 kJ mol^{-1}.[3] The reactions of interest are Eqns (3) and (4). The intensities of $[(CH_3)_2NH_2]^+$, $[NH_4]^+$, $[CH_3OH_2]$ and $[H_3O]^+$, produced by the reaction of the benzene molecular ion with dimethylamine, ammonia, methanol and water are shown as a function of ion translational energy in Fig. 1. These curves illustrate the behavior of exothermic and endothermic reactions as previously described; the reaction of benzene molecular ion with dimethylamine is exothermic by 0.5 eV, and its reaction with ammonia is endothermic by 0.2 eV (Eqns (3), (4)).

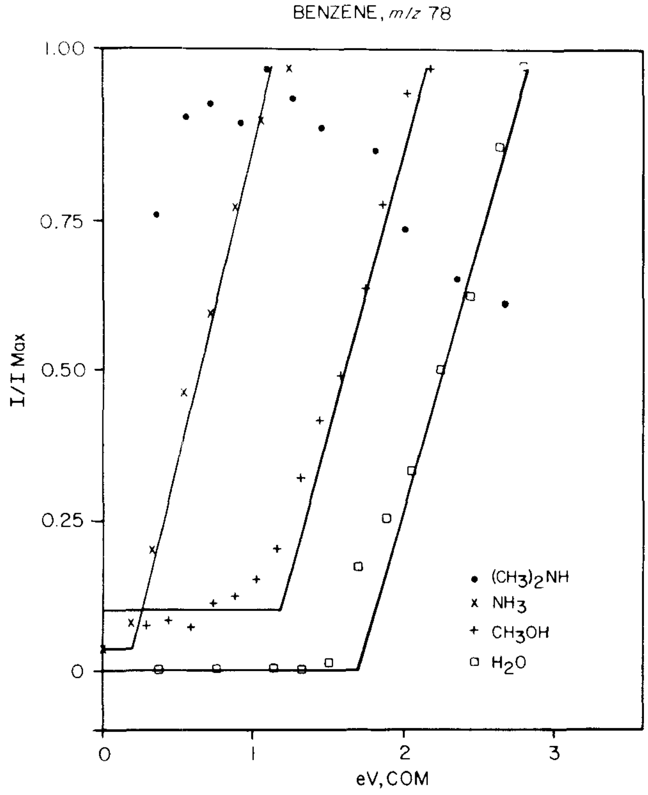

Figure 1. Product ion MH^+ intensities for the reaction of benzene molecular ion and M defined as (a) $(CH_3)_2NH$, (b) NH_3, (c) CH_3OH and (d) H_2O.

$$\begin{array}{lcccc} & [C_6H_6]^{+\cdot} + (CH_3)_2NH & \rightarrow & [(CH_3)_2NH_2]^+ + [C_6H_5]^{\cdot} & (3) \\ \Delta H_f^\circ & 975 \quad -21 & & 590 \quad 318\ \text{kJ mol}^{-1} & \\ & & & \Delta H_r^\circ = -46\ \text{kJ mol}^{-1} & \end{array}$$

$$\begin{array}{lcccc} & [C_6H_6]^{+\cdot} + NH_3 & \rightarrow & [NH_4]^+ + [C_6H_5]^{\cdot} & (4) \\ \Delta H_f^\circ & 975 \quad 46 & & 632 \quad 318\ \text{kJ mol}^{-1} & \\ & & & \Delta H_r^\circ = +21\ \text{kJ mol}^{-1} & \end{array}$$

Thus the curves indicate that PA($[C_6H_5]^{\cdot}$) is between 853.5 kJ mol^{-1} and 925 kJ mol^{-1}. More accurately, after deconvolution the threshold observed for the reaction with ammonia is 0.2 eV. If 100% conversion of ion kinetic energy to internal energy is assumed for a simple H^+ transfer, then PA($[C_6H_5]^{\cdot}$) is 21 kJ mol^{-1} greater than the proton affinity of ammonia, thus 874.5 kJ mol^{-1}. The threshold of 21 kJ is in good agreement with the calculated heat of reaction (Eqn (4)); there is no barrier in excess of the endothermicity, and the reaction proceeds with 100% conversion of ion translational energy to internal energy at threshold. The agreement of our results with thermochemical data indicates that the assignment of the phenyl structure to the $[C_6H_5]^{\cdot}$ product of Eqn (4) is also reasonable. The onsets for reactions with methanol and water produce PAs of 879 and 862 kJ mol^{-1} for $[C_6H_5]^{\cdot}$, and the significant conclusion about the efficiency of energy transfer and the lack of a reaction barrier is similar.

The concordance among PA($[C_6H_5]^{\cdot}$) values established against different bases (H_2O, CH_3OH, NH_3) and especially the agreement of the experimental value with the anticipated value from the literature has a parallel with fifteen results we published earlier,[5] and also with numerous results of Dawson and Douglas.[13-17] The mass of evidence bears on the question of the number of collisions the ion undergoes: multiple collisions increase the internal energy of the ultimately reacting system,[18,19] so that onsets could appear below their true values if energy were transferred more than once. Dawson and Douglas have studied the pressure dependence of ion/molecule reactions in a triple quadrupole instrument and determined single-collision conditions there.[20] Our experimental conditions are similar to theirs. The very small attenuation of the primary ion beam[18] supports our contention of operating in single-collision conditions too.

Full conversion from kinetic to internal energy in all of these systems is to be contrasted with V → V transfer, which is inefficient.

The ion yields for the respective proton transfer reactions for each of the hexadiyne isomers reacting with each of the collision gases are shown in Figs 2 and 3. Broadly, Fig. 2 indicates that proton transfer from 2,4-hexadiyne molecular ion to dimethylamine and ammonia is exothermic and proton transfer to methanol and water is endothermic. Figure 3 indicates that the proton transfer from 1,5-hexadiyne molecular ion to dimethylamine, ammonia and methanol is exothermic

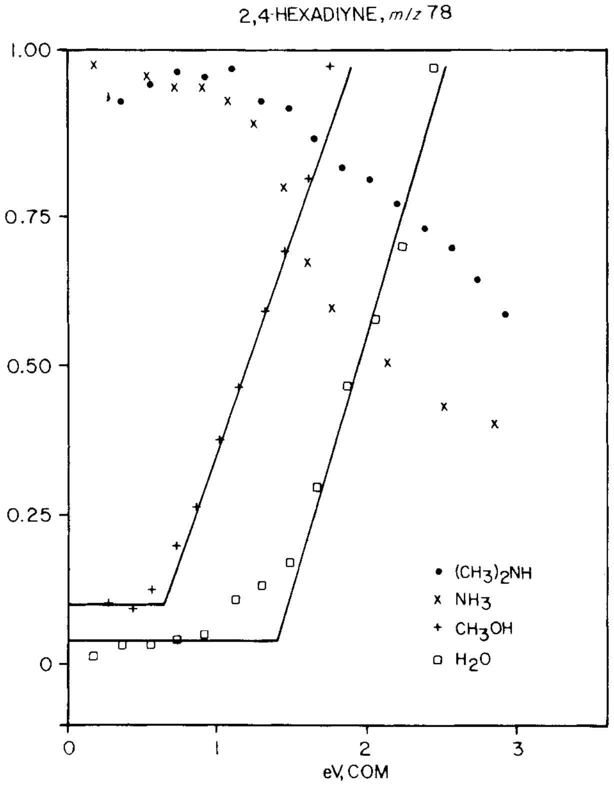

Figure 2. Product ion MH^+ intensities for the reaction of 2,4-hexadiyne molecular ion and M defined as (a) $(CH_3)_2NH$, (b) NH_3, (c) CH_3OH and (d) H_2O.

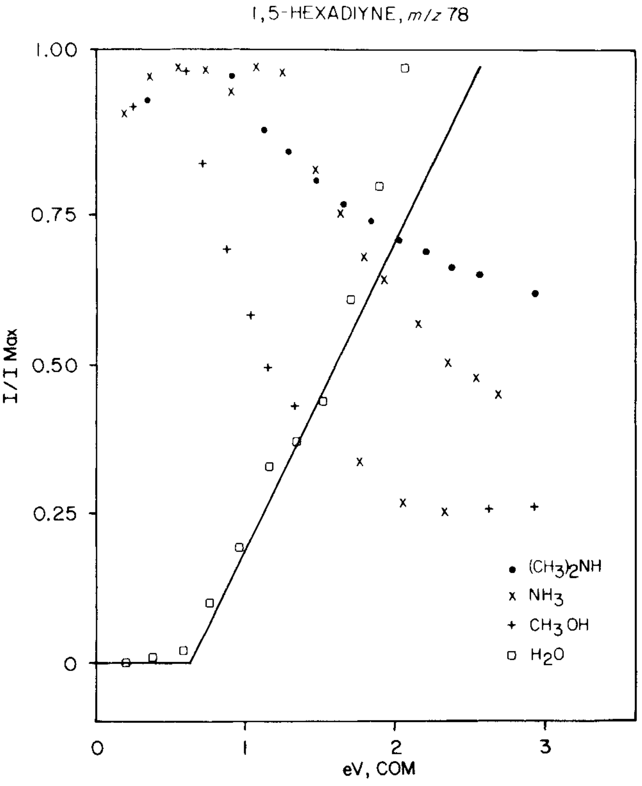

Figure 3. Product ion MH^+ intensities for the reaction of 1,5-hexadiyne molecular ion (a) $(CH_3)_2NH$, (b) NH_3, (c) CH_3OH and (d) H_2O.

Table 1.Threshold ion kinetic energies for observed proton transfer reactions

Collision gas	PA[3] (eV)	Benzene	Thresholds[a] (eV) 2,4-Hexadiyne	1,5-Hexadiyne
$(CH_3)_2NH$	9.6	exothermic	exothermic	exothermic
NH_3	8.8	0.2	exothermic	exothermic
CH_3OH	7.9	1.2	0.6	exothermic
H_2O	7.2	1.7	1.4	0.6

[a] Reproducibility ± 0.2 eV.

and proton transfer to water is endothermic. The threshold ion kinetic energies are summarized in Table 1. These data then yield the proton affinities reported in Table 2.

The trend in these proton affinities is consistent with typical C—H bond strengths in neutral molecules, and by inference in the molecular ions. A higher C—H bond dissociation energy in the ion leads to a higher proton affinity in the radical that is its conjugate base. The C—H bond strengths in 2,4-hexadiyne and 1,5-hexadiyne can be estimated from those of structurally similar compounds. The C—H bond strength in a $CH_3{-}C{\equiv}C$ moiety would be estimated to be 393 kJ mol^{-1} from the C—H bond strength of H—propargyl (392.5 kJ mol^{-1})[21] and H—CH_2CN (389 kJ mol^{-1}).[22] The strength of the C—H bond in 2,4-hexadiyne is less than that of the C—H bond in benzene (460 kJ mol^{-1})[23] because of the greater p character of the bond; the proton affinity of 2,4-hexadiyn-1-yl radical is then expected to be less than the proton affinity of phenyl radical, as is confirmed in Table 2.

Proton transfer from the 1,5-hexadiyne molecular ion could occur through loss of either the terminal methine hydrogens or by loss of the interior methene hydrogens. The methine C—H bond strength would be expected to be approximately 460 kJ mol^{-1} from the C—H bond strength of H—CCH;[24] while the methene C—H bond strength should again be about 393 kJ mol^{-1}. The sp^3 C—H bonds should have a lower bond strength than those of sp C—H bonds. The loss of a methene hydrogen should then be the lower energy process. The appearance energies for the formation of $[C_6H_5]^+$ from 1,5-hexadiyne and $[C_6H_3D_2]^+$ (the C_6 ion of lowest appearance energy) from 1,5-hexadiyne-1,6-d_2 were nearly identical: 10.50 ± 0.04 eV and 10.53 ± 0.02 eV, respectively;[7] the H lost at lowest energy is thus the methene H. The C—H bond strength in 1,5-hexadiyne is arguably less than the C—H bond strength in 2,4-hexadiyne because the C—H bond broken in 2,4-hexadiyne involves a primary carbon while the C—H bond broken in 1,5-hexadiyne involves a secondary carbon.

Table 2. Proton affinities determined from threshold ion kinetic energies

Collision gas	Benzene	Proton affinity (kJ mol^{-1}) 2,4-Hexadiyne	1,5-Hexadiyne
$(CH_3)_2NH$	<925	<925	<925
NH_3	874	<854	<854
CH_3OH	879	820	<761
H_2O	862	833	757
Average value	870 ± 29	824 ± 25	757 ± 21

[a] Error of 21 kJ mol^{-1} in onset of endothermic process.

CONCLUSION

The thresholds of endothermic proton transfers are consistent with the thermochemistry of the exothermic processes observed. This agreement is further evidence that the lateral motion of ions in the quadrupole due to motion induced by the rf field is minor and supports previous assessments of its unimportance.[5,18,25] Threshold bracketing in a quadrupole is then a useful method for determining proton affinities.

Ultimately this approach could be used to fill in gaps between the proton affinities of widely separated standards. A general threshold-bracketing scheme for determining proton affinities could then be developed using only a few standards. In the $[C_6H_6]^{+\cdot}$ isomer system the proton affinities obtained indicate that the reactant ion structures differ from each other. It has been shown that they interconvert when they have enough energy to fragment,[10] and our method may be the first chemical method of distinguishing among them. The trend in the proton affinities measured for these species is consistent with C—H bond strengths. The values obtained can be used as clear indicators of the respective ion structures and are in qualitative agreement with the expected trends in C—H bond strengths in the neutrals.

Qualitatively, our results are consistent with previous experiments on non-dissociating molecular ions of benzene, 2,4-hexadiyne and 1,5-hexadiyne. Different reactivity of the molecular ions of benzene and of the two acyclic isomers with 2-propyl iodide distinguishes the first from the others but does not distinguish between the linear isomers.[7,8] Our results point to a threshold for conversion of 1,5-hexadiyne ion to other isomers, the existence of which has not been clear from thermochemistry of unimolecular reactions of these ions.

If our observations occurred under only multiple-collision conditions, there would be far different interpretations. Our adherence to demonstrated[20] single-collision conditions makes further discussion of these irrelevant.

A referee has pointed out that experiments with an ion beam apparatus[26] are philosophical precursors to these. It follows that establishment of thermochemically accurate metal ion chemistry in a triple quadrupole instrument would be interesting.

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