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Does ionized diacetylene have a positive proton affinity?

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Dedicated to John H. Beynon FRS for his outstanding contributions to mass spectrometry on the occasion of his 80th birthday

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Abstract

Singly and doubly charged $C_4H_3{}^{+/2+}$ ions generated upon electron ionization (EI) of the neutral precursors 1,3-butadiene, benzene, and *exo*-methylene cyclopropane, respectively, are examined by sector-field mass-spectrometry. Charge stripping of the mass-selected monocations affords the corresponding dications and charge exchange of the $C_4H_3{}^{2+}$ dications allows for the reverse redox process. Refined analysis and additional MS/MS studies suggest that the monocations are mixtures of isomeric ions formed upon ionization, whereas only a single type of dication seems to be formed. As an average of energy-resolved measurements, a vertical ionization energy of $IE_v(C_4H_3{}^+) = 16.5 \pm 0.4$ eV is derived. In addition to the experimental work, density functional theory is used for a computational exploration of the mono- and dicationic species. The best theoretical estimates are $IE_a(C_4H_3{}^+) = 16.33$ eV and $IE_v(C_4H_3{}^+) = 16.49$ eV for the most stable isomer $H_2C{=}C{-}C{\equiv}CH^+$. Combination of the experimental and theoretical findings leads to the conclusion that the diacetylene cation $C_4H_2{}^+$ has indeed a positive proton affinity of $PA(C_4H_2{}^+) = 1.50 \pm 0.42$ eV.

Keywords: Charge reversal; Charge stripping; Density functional theory; Dications; Proton affinities

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1. Introduction

The properties of small multiply charged ions attract ongoing attention, ranging from fundamental aspects to reactivity studies and solvation phenomena. Charge stripping (CS) was pioneered in John H. Beynon's laboratory about three decades ago [1] and still is a leading method for the generation and characterization of unusual dications in the gas phase [2,3]. In the context of multiply charged ions, we became interested in the existence of small monocations which formally bear positive proton affinities in that reaction (1) is exothermic; obviously, protonation of a cation is additionally hindered by a Coulomb barrier.

$$A^+ + H^+ \rightarrow AH^{2+} \quad (1)$$

For some diatomic metal-oxide cations (e.g., A = ScO [4] and LaO [5]), this condition is fulfilled. Here, we extend this search to small organic ions, pure hydrocarbon species in particular. We have chosen the $C_4H_3{}^{+/2+}$ system because (i) relatively intense $C_4H_3{}^{2+}$ signals are observed in the electron ionization (EI) mass spectra of many hydrocarbons [6,7], (ii) the monocation experiences a particular stabilization of the formal vinyl cation $H_2C{=}C^+{-}C{\equiv}CH$ due to the presence of the alkinyl substituent [8,9], which might eventually stabilize the corresponding dication as well, and (iii) the size of the system is still reasonably small (seven atoms). To this end, various mass spectrometric and theoretical methods are used for an estimation of the thermochemistry of reaction (1) with $A = C_4H_2$.

2. Experimental methods

The experiments were performed with a modified VG-ZAB/HF/AMD-604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sector) which has been described elsewhere [10]. The $C_4H_3{}^+$ monocations were generated by EI of several neutral precursor molecules (see below). After acceleration to

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a kinetic energy of 8 keV, the CS spectra of the B(1)/E(1) mass-selected monocations were recorded by scanning B(2); in CS, oxygen was used as a collision gas (80% transmission, *T*). Likewise, the B(1)/E(1) mass-selected $C_4H_3^{2+}$ dications (16 keV) were characterized by metastable ion (MI), collisional activation (CA), and charge exchange (CE) spectra; collision gases: helium (80% *T*) in CA and oxygen (80% *T*) in CE. The last sector E(2) was not used in this study.

As neutral precursors, 1,3-butadiene, benzene, and *exo*-methylene cyclopropane were employed. While some other compounds (i.e., 1,4-butynediol, 1,4-dichloro-1,3-butadiene, iodobenzene, and toluene) were studied also, their results were very similar to those reported for the three former precursors and therefore omitted. Deuterium-labeled $C_4HD_2^{2+}$ dications were generated by EI of [1,1,4,4-D_4]-1,3-butadiene and [1,3,5-D_3]-benzene, respectively.

Because of the superior energy resolution of E(1), energy-resolved CS experiments were conducted with B(1)-only mass-selected ions [11]. To this end, the mono- and dication signals were scanned at energy resolutions $E/\Delta E \geq 4000$ and $Q_{\min}$ values were determined from the differences between the high-energy onsets of the mono- and the dication peaks [4]. The kinetic energy scale was calibrated in a multiplicative manner [12,13] with respect to CS of the molecular ion of toluene, $C_7H_8^+ \rightarrow C_7H_8^{2+}$. While Beynon and coworkers recommend an additive calibration scheme [14], the difference of the two approaches is within the experimental accuracy in the present case, because the $Q_{\min}$ values are close to $Q_{\min}(C_7H_8^+)$. Further, it is important to note that instead of the older value $Q_{\min}(C_7H_8^+) = 15.7 \pm 0.2$ eV [15] which has been applied in many previous CS studies [12], we use a value of $Q_{\min}(C_7H_8^+) = 15.2 \pm 0.2$ eV, very recently determined by photoionization experiments [16].

The theoretical studies employed the density functional method B3LYP [17,18] in conjunction with Dunning's correlation-consistent triple-zeta basis sets (cc-pVTZ) [19–21] as implemented in the Gaussian 98 suite of programs [22]. For all optimized structures, frequency analysis at the same level of theory was carried out in order to assign them as genuine minima and to evaluate the zero-point vibrational energies (ZPVEs). In the evaluation of vertical ionization energies, the ZPVEs of the corresponding structurally "nearest" dication minima were used (see below). Likewise, the adiabatic values given further below refer to these "nearest" dication minima, and must therefore be considered as reaction enthalpies of the associated redox processes if rearrangements are involved.

3. Experimental results

Our aim is to address the title question about the proton affinity of small $C_mH_n^+$ cations by means of Born–Haber cycles. In the specific case of the $C_4H_3^{2+}$ dication, reaction (2) is considered; deliberately, we refrain from assigning any particular ion structures at this point.

$$C_4H_2^+ + H^+ \rightarrow C_4H_3^{2+} \tag{2}$$

With the heat of formation of diacetylene $\Delta H_f(C_4H_2) = 4.81$ eV [23] and its ionization energy $IE(C_4H_2) = 10.17 \pm 0.02$ eV [23], the ion energetics can be derived as $\Delta H_f(C_4H_2^+) = 14.98$ eV. Combination with $\Delta H_f(H^+) = 15.86$ eV leads to $\sum \Delta H_f = 30.84$ eV for the left-hand side of reaction (2). For the monocation $C_4H_3^+$, a value of $\Delta H_f(C_4H_3^+) = 13.02 \pm 0.04$ eV [24] can be derived from $\Delta H_f(C_4H_2)$, $\Delta H_f(H^+)$, and the proton affinity $PA(C_4H_2) = 7.65 \pm 0.04$ eV [25,26].[1,2] With the missing quantity $IE(C_4H_3^+)$, the proton affinity of the $C_4H_2^+$ monocation can accordingly be derived via the thermochemical cycle defined in Eq. (3).

$$\begin{aligned} PA(C_4H_2^+) &= [\Delta H_f(C_4H_2) + IE(C_4H_2) + \Delta H_f(H^+)] \\ &\quad - [\Delta H_f(C_4H_2) + \Delta H_f(H^+) \\ &\quad - PA(C_4H_2) + IE(C_4H_3^+)] \\ &= IE(C_4H_2) + PA(C_4H_2) - IE(C_4H_3^+) \\ &= 10.17 \pm 0.02\,\text{eV} + 7.65 \\ &\quad \pm 0.04\,\text{eV} - IE(C_4H_3^+) \\ &= 17.82 \pm 0.05\,\text{eV} - IE(C_4H_3^+) \end{aligned} \tag{3}$$

In an earlier charge-stripping study, Beynon and coworkers [14] reported $Q_{\min}(C_4H_3^+) = 17.5 \pm 0.5$ eV as the average for $C_4H_3^+$ ions generated by dissociative EI of four different precursors. If we further assume $Q_{\min} \approx IE(C_4H_3^+)$ as a first approximation, the proton affinity of the $C_4H_2^+$ monocation is in fact predicted to be slightly positive, $PA(C_4H_2^+) = 0.32 \pm 0.5$ eV. An ultimate decision cannot be made, however, because the neglect of vertical ionization in charge stripping may be unjustified and the experimental error is too large to exclude a negative PA. Therefore, we decided to re-investigate the $C_4H_3^{+/2+}$ system. We note in passing that Beynon's data [14] further imply negative PAs for smaller $C_mH_n^+$ species, whereas larger hydrocarbon ions certainly bear positive PAs, e.g., $PA(C_2H_2^+) \approx -2.1$ eV versus $PA(C_6H_6^+) \approx 1.0$ eV. The $C_4H_3^{+/2+}$ system appears to be a borderline case and is therefore particularly interesting.

Here, we have used butadiene, benzene, and *exo*-methylene cyclopropane as neutral precursors in dissociative EI. The choice of the precursors was influenced by the following considerations. At first, some structural proximity of the neutral compounds to the $C_4H_3^{+/2+}$ ions is considered an advantage. Secondly, prior to a directed synthesis of more stringent precursors, e.g., chlorobutenyne isomers [27] or *exo*-chloromethylene cyclopropene [28], we

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[1] Taken from Ref. [25]; $PA(C_4H_2) = 7.69 \pm 0.04$ eV is given in the original quotation [26].

[2] $\Delta H_f(C_4H_3^+) = 12.49$ eV given in Ref. [24] is based on the same literature thermochemistry and differs due to an algebraic mistake.

wanted to explore the potential-energy surface using readily available substances. Specifically, butadiene was chosen because the two methylene groups present may lead to $H_2C{=}C{-}C{\equiv}CH^{+/2+}$ upon dissociative EI. Along the same line of reasoning, benzene could allow for the formation of ions without two hydrogen atoms at one carbon, e.g., $HC{=}CH{-}C{\equiv}CH^{+/2+}$. *Exo*-methylene cyclopropane could potentially yield ions with a branched or cyclic carbon skeleton. Of course, all three precursors must undergo multiple bond cleavages en route to the $C_4H_3^{+/2+}$ ions, which may also include hydrogen migrations as well as skeletal rearrangements. Therefore, it is first to be investigated whether distinct ion structures evolve or if all $C_4H_3^{+/2+}$ species collapse to a single isomer (or identical mixtures of ions).

3.1. Charge-stripping experiments

The CS spectra of B(l)/E(1) mass-selected $C_4H_3^+$ monocations generated from different precursors give clearly resolved dication signals at $m/z = 25.5$. Energy-resolved experiments lead to $Q_{\min} = 16.48 \pm 0.41$ eV as the average of 20 independent measurements. Considering both the experimental error margins and the fact that our reference value for the CS of toluene is about 0.5 eV lower than the one used previously, this result is consistent with $Q_{\min} = 17.5 \pm 0.5$ eV reported by Beynon and coworkers [14]. Based on our experience in $Q_{\min}$ measurements [3], however, the uncertainty of our value appears surprisingly large. Usually, statistical errors below ±0.3 eV are achieved in five to eight separate determinations [13], provided that the dication signals are reasonably intense which is the case for $C_4H_3^{2+}$. In fact, if one re-assigns the data to the different precursors used, the errors decrease to the expected range (Table 1). This deviation indicates the generation of different isomers (or different mixtures of these) dependent on the choice of the neutral precursor. Unfortunately, however, the differences between the $Q_{\min}$ values are close or even within the experimental uncertainties. Thus, $Q_{\min} = 16.43 \pm 0.26$ eV for the $C_4H_3^+$ species generated upon EI of benzene agrees with $Q_{\min} = 16.13 \pm 0.25$ eV for the ion from *exo*-methylene cyclopropane and $Q_{\min} = 16.89 \pm 0.27$ eV for that from butadiene. Before continuing, let us return to $Q_{\min} = 17.5 \pm 0.5$ eV determined by Beynon and coworkers, who used butane, hexane, toluene, and cycloheptatriene as neutral precursors [14]. If we assume that the two former lead to similar $C_4H_3^+$ species as butadiene, the two latter are similar to benzene as a precursor, and use the old value of $Q_{\min}(C_7H_8^+) = 15.7$ eV for anchoring of the energy scale, the average $Q_{\min} = 17.2 \pm 0.4$ eV of our values for butadiene and benzene is in even better agreement with Beynon's results. Apparently, however, the situation is not as simple as might have been anticipated in that the $Q_{\min}$ values show a significant dependence from the choice of the neutral precursor. Accordingly, the inherent assumption in the previous work of Beynon and coworkers that several hydrocarbon precursors always lead to the same monocationic manifold [14,29] appears somewhat questionable. Therefore, we reconsidered the ionic species by means of MS/MS experiments.

Table 1
Separate $Q_{\min}$ measurements (in eV) of mass-selected $C_4H_3^+$ monocations generated from three different neutral precursors and the corresponding averages

Entry	1,3-Butadiene	Benzene	$C_3H_4CH_2$[a]
1	17.22	16.46	16.29
2	16.78	16.02	16.36
3	16.60	16.40	15.88
4	16.49	16.73	15.98
5	17.01	16.29	15.81
6	17.12	16.68	16.13
7	16.98		16.44
Average[b]	16.89 ± 0.27	16.43 ± 0.26	16.13 ± 0.25
IE_v[c]	16.89 ± 0.34	16.43 ± 0.34	16.13 ± 0.32
Average[c,d]	$IE_v(C_4H_3^+) = 16.48 \pm 0.41$[e]		
	$IE_a(C_4H_3^+) = 16.32 \pm 0.41$[f]		

[a] Simplified notation for *exo*-methylene cyclopropane.

[b] Numerical average of the $Q_{\min}$ values with one standard deviation.

[c] Vertical ionization energies with the assumption $Q_{\min} = IE_v \pm 0.2$ eV derived from the data in Ref. [35].

[d] Average of all IE_v values with one standard deviation.

[e] With the previously used value $Q_{\min}(C_7H_8^+) = 15.7 \pm 0.2$ eV for CS of toluene molecular ion as a reference in the calibration of energy scale the average is $IE_v(C_4H_3^+) = 17.03 \pm 0.47$ eV.

[f] Derived using the computed $\Delta IE_{v/a} = 0.16$ eV (see text).

3.2. MS/MS studies of $C_4H_3^+$ monocations

As a first method for the characterization of the monocations, we have chosen the charge-stripping (CS) technique, that is fragmentation of mass-selected $C_4H_3^+$ upon collision with O_2 at 8 keV kinetic energy. In general, the CS spectra of the $C_4H_3^+$ ions generated from the three neutral precursors examined here are quite similar (Table 2). Thus, losses of atomic and molecular hydrogen largely predominate and fragments due to C–C bond cleavages do not exceed a few percent relative to the base peak (loss of $H^\bullet$). More careful inspection reveals minor, but clearly significant differences for the three precursors examined. As a characteristic ratio, the abundances of fragment ions C_4^+ and C_3H^+ are compared with that of $C_4H_3^{2+}$. Particularly the ions generated upon EI of benzene show a somewhat decreased dication signal, when compared to the ions generated from butadiene and *exo*-methylene cyclopropane, respectively. It is obvious, however, that these differences are too small for structural assignments. The lack of specificity in cation fragmentation can be traced back to the large energy demands of the conceivable dissociation channels of unsaturated $C_mH_n^+$ ions [30].

An alternative approach for the characterization of hydrocarbon cations is charge-reversal (CR) to anionic species [31,32]. Even though CR of cations is very endothermic and

Table 2
CS and CR spectra of B(1)/E(1) mass-selected $C_4H_3^+$ monocations generated from three different neutral precursors

	Fragments: m/z (abundance)
1,3-Butadiene	
CS	50 (100), 49 (17), 48 (1.6), 38 (0.4), 37 (2.1), 36 (0.6), 26(0.5), 25.5 (2.3), 25 (1.0); characteristic ratio[a]: C_4^+:C_3H^+:$C_4H_3^{2+}$ ≈ 7:9:10
CR	51 (4), 50 (19), 49 (100), 48 (59), 38 (1), 37 (4), 36 (10), 25 (9), 24 (12); characteristic ratios[b,c]: $C_3/C_2 = 0.76 \pm 0.05$, $C_2H^-/C_2^- = 0.73 \pm 0.02$
Benzene	
CS	50 (100), 49 (16), 48 (1.5), 38 (0.4), 37 (1.9), 36 (0.5), 26 (0.4), 25.5 (1.3), 25 (0.8); characteristic ratio[a]: C_4^+:C_3H^+:$C_4H_3^{2+}$ ≈ 8:10:7
CR	51(4), 50 (18), 49 (100), 48 (66), 38 (2), 37 (6), 36 (14), 25 (12), 24 (17); characteristic ratios[b,c]: $C_3/C_2 = 0.59 \pm 0.03$, $C_2H^-/C_2^- = 0.60 \pm 0.04$
$C_3H_4CH_2$[d]	
CS	50 (100), 49(16), 48 (1.8), 38 (0.4), 37(1.8), 36 (0.5), 26(0.4), 25.5 (2.0), 25 (0.9); characteristic ratio[a]: C_4^+:C_3H^+:$C_4H_3^{2+}$ ≈ 9:9:10
CR	51 (3), 50 (21), 49 (100), 48 (58), 38 (1), 37 (3), 36 (6). 25 (5), 24 (7); characteristic ratios[b,c]: $C_3/C_2 = 0.68 \pm 0.05$, $C_2H^-/C_2^- = 0.63 \pm 0.03$

[a] Approximate ratios (±1) of the fragments at $m/z = 48$ and $m/z = 37$ as well as the dication signal at $m/z = 25.5$.

[b] C_3/C_2 stands for the ratio of the sum of anionic $C_3H_n^-$ and $C_2H_n^-$ fragments ($n = 0$–2), i.e., the integral intensities of the mass ranges $m/z = 36$–38 and $m/z = 24$–26, respectively. The ratios are determined from 3 to 4 independent scans of these mass regions, and the error is given as one standard deviation.

[c] Ratio of the fragments C_2H^- ($m/z = 25$) and C_2^- ($m/z = 24$). The ratios are determined from 3 to 4 independent scans of this mass region, and the error is given as one standard deviation.

[d] Simplified notation for *exo*-methylene cyclopropane.

pretty inefficient, it can provide more specific structural information because only those anionic fragments are likely to be formed in a high-energy collision which bear significant electron binding energies [33,34]. Similar to the CS spectra, the CR spectra of the $C_4H_3^+$ ions under study are quite alike in general, but reveal characteristic differences upon more detailed inspection of the fragments arising from C–C bond cleavages. Thus, significant differences in the C_3/C_2 and C_2H^-/C_2^- ratios are observed for the ions generated from the three precursors (Table 2). It is quite obvious, however, that these differences do not permit to draw any distinct conclusion as far as specific cation structures are concerned. Hence, we end up in a dilemma often found for hydrocarbon cations: although the spectral features indicate the presence of isomeric species, no clear structural assignments can be made. In fact, it even cannot be assessed whether different ions or mixtures of isomers with variable compositions are formed. Last but not least, one may involve different internal energy contents of the monocations formed upon dissociative EI. Therefore, all what can be extracted from the experiments is the average of $IE_v = 16.48 \pm 0.41$ eV for the three precursors, where the error also includes an ±0.2 eV uncertainty of the assumption $Q_{min} = IE_v$ [35]. To a first approximation, this value shall further on be regarded as an average screening of $C_4H_3^+$ isomers. The unsatisfying outcome of the CS and CR experiments led us to abandon attempts towards the synthesis of more specific precursors to be used in EI.

3.3. MS/MS studies of $C_4H_3^{2+}$ dications

In contrast to the monocationic species, the metastable ion (MI), collisional activation (CA), and charge exchange (CE) mass spectra of the mass-selected $C_4H_3^{2+}$ dications generated from the different neutral precursors are identical within experimental error. In order to illustrate the processes observed, we refer to the spectra of the dication made upon EI of *exo*-methylene cyclopropane (Fig. 1).

Not unexpected for a system comprising only seven atoms, metastable-ion decomposition of $C_4H_3^{2+}$ is relatively weak; in Fig. 1a, the base peak $C_4H_3^{2+}$ is off scale and more than three orders of magnitude more intense than the fragments. The unimolecular processes observed can be attributed to the charge-separation reactions (4a) and (4b) with predominance of the former.

$$C_4H_3^{2+} \rightarrow C_4H_2^+ + H^+ \tag{4a}$$

$$C_4H_3^{2+} \rightarrow C_3H^+ + CH_2^+ \tag{4b}$$

In both cases, the lighter fragments H^+ and CH_2^+, respectively, are not observed which is assigned to inefficient collection of these low-mass ions in conjunction with the considerable kinetic energy releases associated with Coulomb explosions [12]. Reaction (4b) has previously been reported by March et al. [36], whereas these authors denied the occurrence of reaction (4a). The present results clearly disprove the latter statement. In particular, artifacts which could have masked the occurrence of reaction (4a) in the two-sector experiments of March et al. can be excluded rigorously for the B(1)/E(1) mass-selected $C_4H_3^{2+}$ species studied here [11]. The occurrence of a genuine charge separation according to reaction (4a) is further supported by the characteristically broadened peak shape of the resulting $C_4H_2^+$ monocation (see inset in Fig. 1a).

$$C_4H_3^{2+} \rightarrow C_4H_2^{2+} + H^\bullet \tag{5}$$

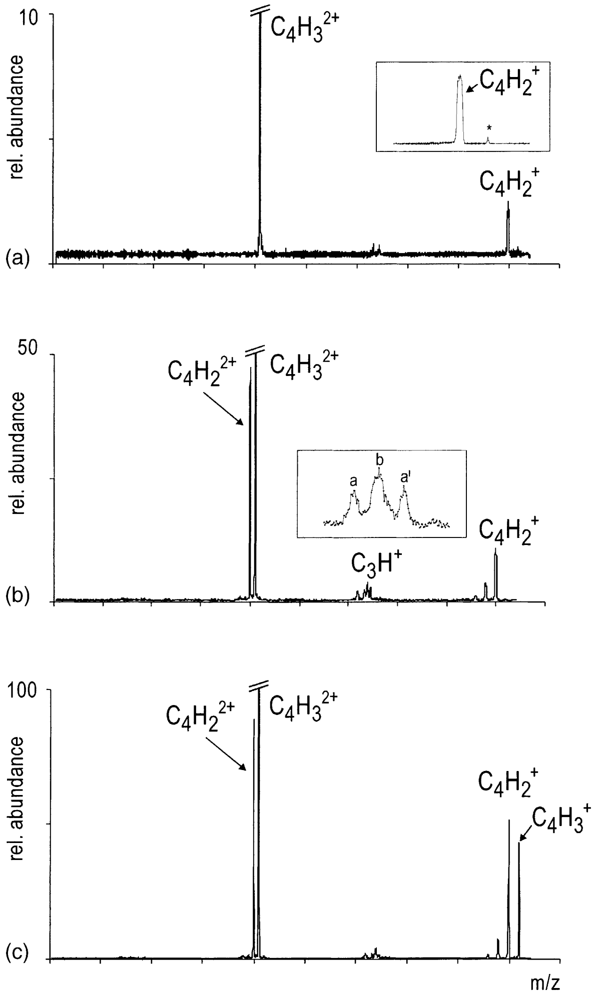

Fig. 1. (a) MI, (b) CA, and (c) CE spectra of B(1)/E(1) mass-selected $C_4H_3^{2+}$ dications generated by dissociative EI of *exo*-methylene cyclopropane; the kinetic energy of the incident beam is 16 keV. The inset in panel (a) shows a separate scan around the $C_4H_2^+$ signal on an expanded scale. The inset in panel (b) shows an expansion of the C_3H^+ signal. The denoted scaling of the vertical axis allows for a comparison of the fragment-ion intensities in MI, CA, and CE experiments.

While collisional activation of $C_4H_3^{2+}$ with helium further enforces reactions (4a) and (4b), the CA spectrum (Fig. 1b) is dominated by loss of atomic hydrogen (reaction (5)), suggesting that direct C–H bond cleavage can effectively compete with charge separation. Further, although quite endothermic for helium ($\text{IE} = 24.587\,\text{eV}$), also dissociative charge exchange according to reaction (6) is observed to some extent.

$$C_4H_3^{2+} + \text{He} \rightarrow C_3H^+ + \text{He}^+ + CH_2 \tag{6}$$

Even though reactions (4b) and (6) both lead to C_3H^+ fragments ($m/z = 37$), they can readily be distinguished by the associated peak shapes. Occurrence of charge-separation in reaction (4b) is associated with a considerable release of kinetic energy giving rise to a signal with low- and high-energy components centered around $m/z = 37$ (a and a′ in the inset of Fig. 1b). In contrast, the third peak appears at the center of mass (denoted as b in the inset) and can thus only be explained by invoking reaction (6).

$$C_4H_3^{2+} + O_2 \rightarrow C_4H_3^+ + O_2^{\bullet+} \tag{7a}$$

$$C_4H_3^{2+} + O_2 \rightarrow C_4H_2^+ + O_2^{\bullet+} + H^\bullet \tag{7b}$$

Because $\text{IE}(C_4H_3^+)$ exceeds $\text{IE}(O_2) = 12.071\,\text{eV}$ by about 5 eV (see above) and the exoergicity is close to the reaction window, single electron-transfer processes prevail in the CE spectrum (Fig. 1c). Most specifically, reaction (7a) gives rise to a pronounced signal for the $C_4H_3^+$ monocation, which corresponds to the reversal of the charge-stripping process described above. In addition, dissociative charge exchange takes place, e.g., reaction (7b) rather than charge separation (reaction (4a)), as implied by the narrow shape of the $C_4H_2^+$ fragment. Nevertheless, hydrogen-atom loss (reaction (5)) can compete with charge-exchange to a considerable extent because the former can occur as a continuously endothermic process lacking a barrier in excess of the reaction endothermicity, whereas charge separation as well as charge exchange are both subject to Coulomb barriers. Occurrence of reaction (7b) may also provide an explanation why March et al. [36] could not observe reaction (4a). For charge separation according to reaction (4a), a characteristically broadened peak shape is expected and indeed is observed in Fig. 1a. However, our MI experiments also show a small, narrow signal due to $C_4H_3^+$ (denoted by an asterisk in the inset of Fig. 1a) which is attributed to charge exchange with a small amount of residual gas (viz. air) present in the field-free region (reaction (7b)). Slightly larger background pressures may therefore mask the occurrence of reaction (4a). The significance of this argument evolves from a consideration of relative intensities in that the monocationic $C_4H_2^+$ fragment is about 25 times larger in Fig. 1c compared to Fig. 1a.

Further insight into the potential-energy surface of the $C_4H_3^{+/2+}$ system is gained from examination of the partially deuterated dication $C_4HD_2^{2+}$. Like for the unlabeled dications, no significant differences were found when using either [1,1,4,4-D_4]-l,3-butadiene or [1,3,5-D_3]-benzene as neutral precursors in dissociative EI. For example, a ratio of 0.82 ± 0.03 of the $C_4D_2^+$ and C_4HD^+ fragments evolves in the CE spectrum of $C_4HD_2^{2+}$ ion generated upon EI of [1,1,4,4-D_4]-1,3-butadiene compared to 0.85 ± 0.03 for the ion generated from [1,3,5-D_3]-benzene. With respect to the role of H/D kinetic isotope effects (KIEs), consideration of Fig. 2 has the following implications.[3]

(i) Collision-induced C–H(D) cleavage of the dication (reaction (5)) to $C_4D_2^{2+}$ and C_4HD^{2+}, respectively, is associated with a modest isotope effect, $\text{KIE}(5) = 1.9 \pm 0.2$. (ii) A similar value, $\text{KIE}(7b) = 1.6 \pm 0.2$, is obtained for dissocia-

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[3] Here, a statistical correction is applied in order to account for the number of H and D atoms in $C_4HD_2^{2+}$, while the effect of differential collection efficiencies for H and D losses is neglected.

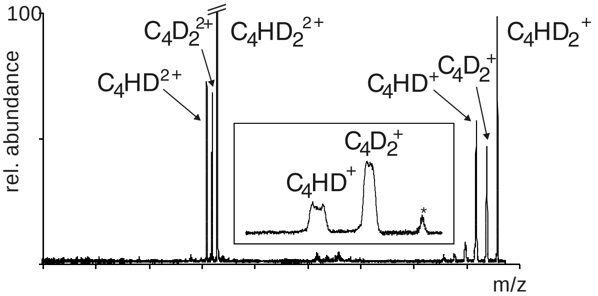

Fig. 2. CE spectrum of B(1)/E(1) mass-selected $C_4HD_2^{2+}$ dications generated by dissociative EI of [1,1,4,4-D_4]-1,3-butadiene; the kinetic energy of the incident beam is 16 keV. The inset shows a separate scan of the unimolecularly formed C_4D_2 and C_4HD^+ fragments on an expanded scale.

Table 3
Energetic properties of some selected $C_4H_3^+$ monocations[a] calculated at the B3LYP/cc-pVTZ level of theory

	E_{rel}[b]	$E_{rel,0\,K}$[c]	IE_v[d]	IE_a[e]
$^{1}1^{+}$	0.00[f]	0.00[f]	16.49	16.33 ($^{2}1^{2+}$)
$^{3}1^{+}$	1.37	1.32	15.04	15.02 ($^{2}1^{2+}$)
$^{1}2^{+}$	1.50	1.57	16.64	16.06 ($^{2}1^{2+}$)
$^{1}3^{+}$	1.53	1.54	16.37[g]	14.79 ($^{2}1^{2+}$)[h]
$^{3}4^{+}$	1.67	1.70	16.26	15.30 ($^{2}4^{2+}$)
$^{1}5^{+}$	2.00	2.01	17.39	17.26 ($^{2}3^{2+}$)
$^{3}6^{+}$[i]	2.03	2.03	16.66[g]	14.30 ($^{2}1^{2+}$)[h]

[a] For ion structures, see Fig. 3.
[b] Total energy relative to $^{1}1^{+}$ (in eV).
[c] Energy relative to $^{1}1^{+}$ at 0 K (in eV).
[d] Energy of the dicationic species at the geometry of the respective monocation. Here, the computed ZPVE of the "nearest" dication minimum was used.
[e] Adiabatic ionization energy at 0 K of the monocations after relaxation to the "nearest" dication structure (the latter is given in brackets).
[f] $E_{tot}(^{1}1^{+}) = -153.8395008$ H, ZPVE($^{1}1^{+}$) = 0 : 046572 H.
[g] Because the corresponding dication is not a minimum, ZPVE was neglected.
[h] No structurally related minimum was found. Therefore, the adiabatic value is given assuming a rearrangement to structure $^{2}1^{2+}$.
[i] The structure is not a minimum on the singlet surface and rearranges to $^{1}1^{+}$ upon geometry optimization.

tive charge exchange to afford the monocations $C_4D_2^+$ and C_4HD^+. (iii) In contrast, the isotope effect is significantly larger in the unimolecular dissociation of the dication (see inset in Fig. 2), i.e., KIE(4a)$_{height}$ = 4.7 ± 0.5 from consideration of peak heights and KIE(4a)$_{area}$ = 3.8 ± 0.4 from peak areas, where the latter is considered more meaningful for this particular dissociation due to Coulomb broadening [37]. To a first approximation, the larger magnitude of the KIE associated with charge separation of the dication according to reaction (4a) can be understood as a reflection of H(D) atom tunneling in the passage of the barrier associated with Coulomb explosion.

4. Theoretical results

With regard to the ambiguous structures of the experimentally generated $C_4H_3^+$ monocations, a considerable number of isomers needs to be addressed in a concise theoretical study and the same applies for the resulting dicationic species which could be accessible upon charge stripping. Moreover, a computational evaluation of the experimental results would also require the treatment of all relevant barriers involved. While such a more comprehensive study of the $C_4H_3^{+/2+}$ system is in progress, here, we limit ourselves to the most stable structures **1**–**6** of the monocation (Fig. 3), the corresponding dicationic minima, and the vertical electron-transfer processes involved between them. As a pragmatic approach, the hybrid functional B3LYP is employed in conjunction with Dunning's correlation-consistent polarized triple-valence basis sets.

In agreement with earlier studies at lower levels of theory [7,26,38,39], the but-3-yn-l-en-2-yl cation in its singlet ground state, $^{1}\mathbf{1}^{+}$, is found as the most stable monocation (Table 3). Due to interaction of the π-type orbitals at all four carbon atoms, the carbon backbone is strictly linear with three relatively short C–C bonds. While the triplet $^{3}\mathbf{1}^{+}$ bears a similar geometry, it is more than 1 eV higher in energy. Irrespective of the spin state, the same applies for the other cationic species. Until about 2 eV above $^{1}\mathbf{1}^{+}$, five other minima were located. Of these, the energetically least demanding isomers are the cyclic structures $^{1}\mathbf{2}^{+}$, $^{1}\mathbf{3}^{+}$, and $^{3}\mathbf{4}^{+}$. Based upon a qualitative inspection of the bond lengths, these three structures can be described as cyclobutadienyl cation [40], 3-(*exo*-methylene) cyclopropen-1-yl cation, and carbinyl cyclopropenylium ion, respectively; assignment of the latter structure $^{3}\mathbf{4}^{+}$ as a carbene also accounts for the triplet state. The acyclic isomers $^{1}\mathbf{5}^{+}$ and $^{3}\mathbf{6}^{+}$ are ca. 2 eV above $^{1}\mathbf{1}^{+}$; on the singlet surface, structure $\mathbf{6}^{+}$ is not a minimum and undergoes hydrogen rearrangement to $^{1}\mathbf{1}^{+}$ instead.

As far as vertical ionization to dications is concerned, the computed IE_v spread around 16.5 eV for most monocations, with the exceptions of a significantly lower value for $^{3}\mathbf{1}^{+}$ (because it converges to the same dication state like $^{1}\mathbf{1}^{+}$) and the somewhat larger IE_v of $^{1}\mathbf{5}^{+}$. Geometry optimization of the resulting dications can be used to derive the corresponding adiabatic IEs. Note, however, that upon ion generation in the experiments hydrogen migrations as well as skeletal rearrangement may compete with relaxation to the respective local minima, and we cannot assess this aspect for the time being. With regard to the transition $^{1}\mathbf{1}^{+} \rightarrow {}^{2}\mathbf{1}^{2+}$ some, but overall minor changes in geometry are observed. The most notable feature is that the lengths of the C(1)–C(2) and C(2)–C(3) bonds reverse in order. The associated difference between vertical and adiabatic ionization is computed as $\Delta IE_{v/a}$ = 0.16 eV. Not surprisingly, quite different effects evolve for the other dications. In the present context, however, let us focus on the computational finding that much like the monocation $^{1}\mathbf{1}^{+}$, the congener $^{2}\mathbf{1}^{2+}$ also is the most stable structure on the dication surface. With regard to the title question, we further computed the energy of ion-

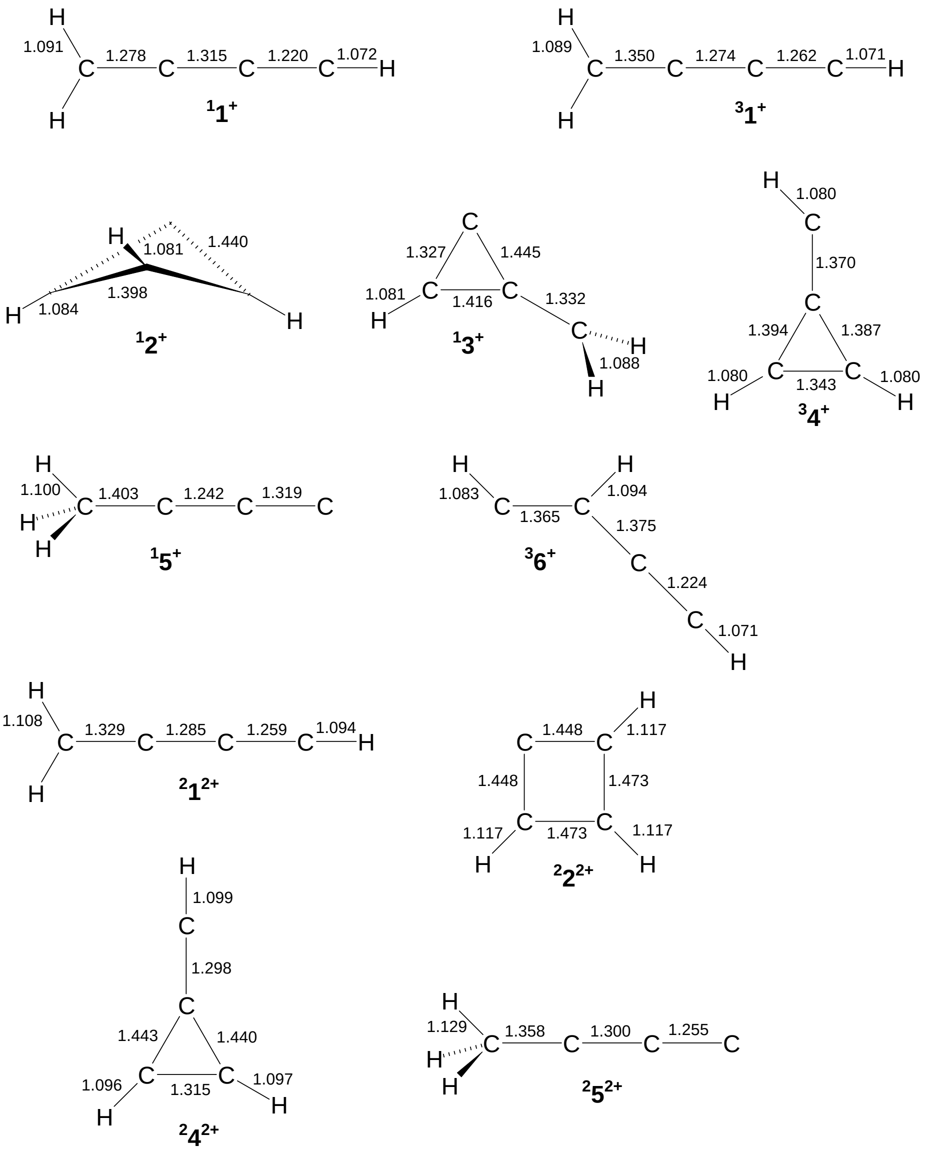

Fig. 3. Optimized structures of several $C_4H_3{}^{+/2+}$ mono- and dications obtained at the B3LYP/cc-pVTZ level of theory (bond lengths given are given in Å).

ized diacetylene $C_4H_2{}^+$ ($E_{tot} = -153.183572$ H, ZPVE $= 0.036302$ H), whose combination with the data of $^2\mathbf{1}^{2+}$ ($E_{tot} = -153.2373267$ H, ZPVE $= 0.044654$ H) leads to a computational prediction of PA($C_4H_3{}^+$) = 1.24 eV at 0 K.

5. Thermochemistry

The combined experimental and theoretical data permit to address the title question of the proton affinity of $C_4H_2{}^+$ more specifically by consideration of the redox chemistry of the $C_4H_3{}^{+/2+}$ system in conjunction with the relevant dissociation channels (Fig. 4). Here, $\Delta H_f(C_4H_2) = 4.81$ eV (and $\Delta H_f(H) = 15.859$ eV) may be used for anchoring the relative energies to heats of formation; any change in this value would alter the absolute heats of formation whereas the relative energetics remain unaffected.

Most $[C_4H_2 + H]^{+/2+}$ dissociation asymptotes are settled reasonably well with IE(C_4H_2) = 10.17 ± 0.02 eV and IE(H) = 13.598 eV. With regard to the $C_4H_2{}^{2+}$ + H asymptote (reaction (5)), IE(C_4H_2) $\approx Q_{min} = 17.8 \pm 0.5$ eV determined by Beynon and coworkers [14] is re-scaled to IE($C_4H_2{}^+$) $\approx Q_{min} = 17.2 \pm 0.5$ eV on the basis of the revised reference energy for CS of ionized toluene (see experimental section). As outlined above, $\Delta H_f(C_4H_3{}^+) = 13.02 \pm 0.04$ eV can be derived from $\Delta H_f(C_4H_2)$, $\Delta H_f(H^+)$, and PA(C_4H_2) by means of an Born–Haber cycle. Using the average $IE_v(C_4H_3{}^+) = 16.48 \pm 0.41$ eV and the computed $\Delta IE_{v/a}(C_4H_3{}^+) = 0.16$ eV, we arrive at $IE_a(C_4H_3{}^+) = 16.32 \pm 0.41$ eV. Accordingly, the resulting thermochemical cycle (Fig. 4) demonstrates that ionized diacetylene does

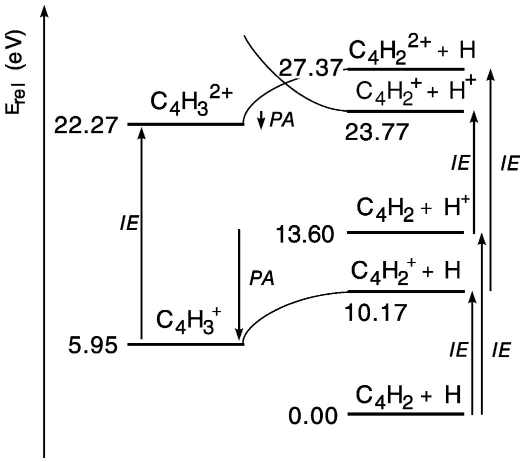

Fig. 4. Potential-energy surface of the $C_4H_3^{+/2+}$system (relative energies are given in eV).

indeed have a positive proton affinity of $PA(C_4H_2^+) = 1.50 \pm 0.42$ eV. Hence, protonation of $C_4H_2^+$ is exothermic, but yet prevented by a kinetic barrier due to Coulomb repulsion of the positively charged reactants. This hindrance is reflected by the effectively competing loss of atomic hydrogen from the dication upon CA, even though reaction (5) is considerably more endothermic. The corresponding C–H bond strengths can be derived as $D_0(C_4H_2^+–H) = 4.22 \pm 0.04$ eV and $D_0(C_4H_2^{2+}–H) = 5.1 \pm 0.7$ eV, respectively.

As a result of these thermochemical considerations, unimolecular dissociation of $C_4H_3^{2+}$ via reaction (4a) is nascent from internally excited dications, whereas ground state $C_4H_3^{2+}$ is thermochemically stable with respect to loss of a proton. Similar endothermicities are found for reaction (4b), which is situated at about 23.8 eV in terms of Fig. 4 [41]. Similar considerations apply for other, not observed, but conceivable dissociation asymptotes of $C_4H_3^{2+}$, e.g., $C_4^+ + H_3^+$ (27.0 eV), $C_3^+ + CH_3^+$ (25.0 eV), $C_2H_2^+ + C_2H^+$ (24.3 eV), $C_2H_3^+ + C_2^+$ (25.0 eV). Thus, $C_4H_3^{2+}$ seems to add to the set of thermochemically stable dications existing in the gas phase [2,3].

6. Conclusions

The present experimental and theoretical results demonstrate that the $C_4H_2^+$ monocation has a positive proton affinity and that the resulting $C_4H_3^{2+}$ dication is thermochemically stable with respect to all conceivable dissociation asymptotes. Despite this success, the results also point to some deficiencies in both experiment and theory. As far as experiment is concerned, EI clearly does not represent a suitable means for the generation of well-defined $C_4H_3^+$ ions. While this conclusion is neither new nor surprising as such, the suspicion that mixtures of isomeric ions are formed upon EI sheds also some doubt on several flow-tube studies concerning the bimolecular reactivity of mass-selected $C_mH_n^+$ ions with EI used for reactant-ion generation [42,43]. Even though equilibration to room temperature can safely be assumed in flow-tube experiments, for a set of isomers separated by reasonably large barriers this might lead to a situation in which each isomer is trapped in its potential-energy well, while the overall population has not reached any thermal equilibrium. Specific consideration of the structures of the $C_4H_3^{+/2+}$ ions, however, resembles opening of Pandora's box. Thus, the experimental findings suggest that several structural isomers contribute to the monocation manifold. Even otherwise powerful methods, like charge stripping or charge reversal, do not permit any distinct structural assignments. The lack of specificity in these experiments can be attributed to the high energy demands of all fragmentation channels available for the monocations. Even the vertical transition to the dications in charge stripping is not sensitive enough in this case which can be understood by the similar IEs of the various isomers as predicted by theory. Therefore, a more comprehensive investigation of the $C_4H_3^{+/2+}$ system represents a formidable challenge for future studies.

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