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Loss of DN≡C from ionized 4-hydroxypyridine-OD: An intriguing reaction unravelled by theory and experiment

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Abstract

Low energy 4-hydroxypyridine ions (**HP-1**) decarbonylate but also readily lose hydrogen (*iso*)cyanide. Surprisingly, this reaction leads to a specific loss of the label from the OD-labelled isotopomer. Our tandem mass spectrometry experiments show that ionized vinylketene, CH_2=CHCH=C=O$^{\bullet+}$ (**1**), is the product ion. This ion is also generated by the decarbonylation of 4-cyclopentene-1,3-dione ions (**CP-1**) and a computational analysis using the CBS-QB3 model chemistry indicates that these seemingly unrelated ionic systems share similar dissociation mechanisms.

In this study, a mechanism is presented for the decarbonylation of metastable ions **CP-1** that satisfies the energy requirement dictated by its appearance energy. Our computational analysis further shows that ions **HP-1** may isomerize into the (*iso*)imino analogues of **CP-1**, by consecutive H-shift, ring-opening and cyclization steps. The **CP-1** analogues serve as the immediate precursors for the specific loss of DNC (rather than DCN) from OD-labelled **HP-1** and also its decarbonylation into the vinyl(*iso*)ketenimine ions CH_2=CHCH=N=CH$^{\bullet+}$ (**3**) and CH_2=CHCH=C=NH$^{\bullet+}$ (**4**).

Keywords: Tandem mass spectrometry; CBS-QB3 model chemistry; Reaction mechanism

1. Introduction

Electron ionization (EI) mass spectrometry is a powerful method for the structure analysis of organic molecules and since its inception, the gas-phase ion chemistry of a wide range of molecules has been studied. A variety of experimental procedures has been designed to establish the structure, stability, reactivity and dissociation characteristics of a great many (novel) radical cations [1]. Experiments have also been widely used to study the associated reaction mechanisms but experimental results alone frequently lead to tentative proposals at best. It was realized at an early stage that synergy between experiment and theory would be an ideal approach to probe reaction mechanisms but it was not until recently that the so-called Gaussian and CBS model chemistries became available as powerful tools for such studies [2].

Loss of water from ionized ethyl acetate provides a good illustration: its mechanism has been heavily scrutinized by experiment but was only fully understood when modern electronic structure theory was brought to bear [3].

In the same vein, the loss of hydrogen (*iso*)cyanide from ionized 4-hydroxypyridine (**HP-1**) presents itself as yet another unexplained reaction. Maquestiau et al. [4] and then later Nibbering in a more detailed study [5], reported the surprising observation that low energy 4-hydroxypyridine-OD ions specifically lose DCN or DNC. This intriguing example of a "hidden" hydrogen rearrangement [6] has never been described mechanistically.

In agreement with the results of earlier studies involving EI mass spectrometry [4] and photoelectron spectroscopy [7], Neutralization–Reionization (NRMS) experiments [8] leave little doubt that electron ionization of 4-hydroxypyridine (predominantly) yields the 4-hydroxypyridine ion (**HP-1**) rather than its keto tautomer, ionized 4(1*H*)-pyridone. The latter ion was independently generated and upon collisional activation it does not lose HCN but rather decarbonylates [8].

Although many $C_4H_4O^{\bullet+}$ isomeric ions have been characterized by high energy collision induced dissocation (CID) mass spectrometry [9], the identity of the isomer generated by loss of HCN from **HP-1** has not yet been established. Neither has it been

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established whether the neutral lost is HCN or its higher energy isomer HNC. Metastable **HP-1** ions also decarbonylate, with a substantial kinetic energy release, to yield $C_4H_5N^{\bullet+}$ ions whose structure has not been established either. The *source* generated $C_4H_5N^{\bullet+}$ product ions of the decarbonylation have tentatively been assigned the 3*H*-pyrrole structure [10].

The present study describes the results of tandem mass spectrometry based experiments aimed to identify the ionic and neutral products of the two dissociations of **HP-1** in the μs time-frame and combines this information with a detailed computational analysis of plausible mechanisms. Computational results for the previously studied [9] decarbonylation of ionized 4-cyclopentene-1,3-dione (**CP-1**) will also be discussed and it will be shown that the mechanism of this reaction provides an important clue for the complex yet transparent dissociations of **HP-1**.

2. Experimental and theoretical methods

All experiments were performed with the VG Analytical ZAB-R mass spectrometer of BEE geometry (B, magnet; E, electric sector) [11] using an electron ionization source at an accelerating voltage of 6–10 kV. Metastable ion (MI) and collision induced dissociation (CID) mass spectra were recorded in the second field free region (2ffr). In all collision experiments helium was used as the collision gas. Collision Induced Dissociative Ionization (CIDI) experiments aimed to establish the identity of the neutral species lost (see ref. [12] for a brief description of the technique) were also performed in the 2ffr. The CIDI spectrum of Fig. 2d was obtained from mass selected *m/z* 95 ions **HP-1** having 10 keV translational energy. All spectra were recorded using a PC-based data system developed by Mommers Technologies Inc. (Ottawa). Kinetic energy release measurements were obtained according to standard procedures [1,13].

The 4-hydroxypyridine and 4-cyclopentene-1,3-dione samples were of research grade (Aldrich) and used without further purification. The deuterium labelled isotopomer 4-hydroxypyridine-OD was obtained therefrom by repeated exchange with methanol-OD. The samples were introduced into the source (kept at 120 °C) with the solids probe.

The calculations were performed with the CBS-QB3 model chemistry [14]; for selected species the (computationally much more demanding) CBS-APNO method [15] was also used. All calculations were run with the Gaussian 2003, Rev C.02 suite of programs [16]. In the CBS-QB3 model chemistry the geometries of minima and connecting transition states are obtained from B3LYP density functional theory in combination with the 6-311G(2d,d,p) basis set (also denoted as the CBSB7 basis set). The resulting total energies and enthalpies of formation for minima and connecting transition states (TS) in the 4-hydroxypyridine (HP) and 4-cyclopentene-1,3-dione (CP) systems of ions are presented in Tables 1a and 1b. Computational data pertaining to the dissociation products are found in Table 2. Several of the CBS-QB3 results for the HP system of ions showed a degree of spin contamination above the acceptable limit of 0.79. It is difficult to estimate the effects of spin contaminated enthalpies of formation, but it is gratifying to note that the B3LYP/CBSB7 derived potential energy surface, for which spin contamination plays no prominent role, is not significantly different from that of the CBS-QB3 derived surface. Unless stated otherwise, all enthalpies presented in the text and in the Schemes (numbers in square brackets) refer to $\Delta_f H^0_{298}$ values in kcal mol^{-1} derived from the CBS-QB3 calculations. The complete set of computational results is available from the authors upon request.

3. Results and discussion

3.1. The ionic and neutral products generated from metastable 4-hydroxypyridine ions

The MI spectrum of Fig. 1a shows that low energy 4-hydroxypyridine ions (**HP-1**) lose both CO (*m/z* 67) and HCN or HNC (*m/z* 68). Loss of the isobaric $C_2H_3^{\bullet}$ radical does not occur: the MI spectrum of the $M+1$ molecular ions (not shown) is only compatible with the loss of a 27 Da neutral containing one carbon atom. The spectrum of Fig. 1b confirms [4,5] that metastable 4-hydroxypyridine-OD ions specifically lose DCN or DNC.

Fig. 2a displays the CID mass spectrum of the *m/z* 68 product ions generated from metastable ions **HP-1**. The spectrum is identical with that of the well characterized $C_4H_4O^{\bullet+}$ isomer $CH_2{=}CHCH{=}C{=}O^{\bullet+}$ (**1**), ionized vinylketene [9], shown in Fig. 2b.

A CIDI experiment was conducted with the aim of identifying the product neutrals as either HCN or HNC (or in admixture). The HCN/HNC pair of isomers can be differentiated on the basis of the *m/z* 12–15 [17] and the *m/z* 24–27 [18] peak intensity patterns of their CIDI spectra. However, in the spectrum obtained in our experiments (see Fig. 2d) a significant portion of the *m/z* 12 signal stems from $CO^{\bullet+}$ co-generated in the re-ionization step, thus hindering a secure structure assignment based on the *m/z* 12–15 signals. Analysis of the *m/z* 26:27 ratio was also obscured: by peaks at *m/z* 24, 25 and 26 stemming from collisionally ionized hydrocarbon neutrals generated by collision induced dissociation of ions **HP-1** with He in front of the deflector electrode. Attempts to reduce these hydrocarbon interferences by lowering the He pressure failed; the resulting spectra contained too much noise for a meaningful analysis and thus the identity of the H, C, N isomer remains uncertain.

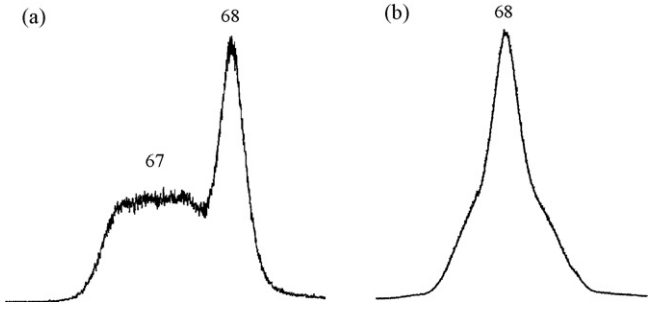


Fig. 1. (a) Partial MI spectrum of ionized 4-hydroxypyridine (**HP-1**); (b) partial MI spectrum of OD-labelled ions **HP-1**.

Table 1a
Energetic data[a] derived from CBS-QB3 calculations of stable isomers and connecting transition states involved in the loss of HCN from the 4-hydroxypyridine radical cation (**HP-1**)

Ionic species	B3LYP/CBSB7 $E_{(total)}$	CBS-QB3 $E_{(total)}$ [0 K]	ZPE	QB3 $\Delta_f H_0^0$	QB3 $\Delta_f H_{298}^0$
HP-1 (Scheme 1)	−323.26525	−322.64397	56.6	206.8	202.5
HP-2 (Scheme 1)	−323.22405	−322.60257	55.1	232.7	228.7
TS HP 1 → 2	−323.14892	−322.53392	51.8	275.8	271.5
HP-3 (Scheme 2)	−323.21773	−322.59721	56.3	236.1	232.0
HP-4a (Scheme 2)	−323.17842	−322.56317	54.0	257.5	254.3
HP-5 (Scheme 2)	−323.19340	−322.57057	53.5	252.8	249.8
TS HP 1 → 3	−323.17720	−322.56065	54.1	259.0	254.7
TS HP 3 → 4a	−323.16414	−322.55022	53.5	265.6	261.9
TS HP 4a → 5	−323.14096	−322.53171	50.5	277.2	273.8
HP-3a (Scheme 3)	−323.19644	−322.57443	51.9	250.4	247.2
HP-3a$_1$ (Scheme 3)	−323.20016	−322.57876	54.6	247.7	244.4
HP-3b (Scheme 3)	−323.20445	−322.58959	53.4	240.9	237.6
HP-3c (Scheme 3)	−323.20067	−322.58671	55.7	242.7	238.6
HP-4a$_1$ (Scheme 3)	−323.18320	−322.56897	54.1	253.8	250.6
HP-4b (Scheme 3)	−323.18681	−322.57671	52.5	249.0	246.1
HP-4c (Scheme 3)	−323.23550	−322.61042	55.0	227.8	223.9
TS HP 3 → 3a	−323.17744	−322.56015	54.7	259.4	255.4
TS HP 3a$_1$ → 3b	−323.16682	−322.55032	51.8	265.0	261.0
TS HP 3b → 3c	−323.16439	−322.54881	52.4	266.5	258.1
TS HP 4a$_1$ → 4b	−323.15213	−322.54044	50.8	271.7	268.2
TS HP 4b → 4c	−323.18058	−322.56787	52.0	254.5	251.2
HP-3d (Scheme 5)	−323.17117	−322.56096	52.9	258.8	255.8
HP-3e (Scheme 5)	−323.23401	−322.61263	52.3	226.4	222.4
HP-4d (Scheme 5)	−323.21026	−322.59120	53.9	239.9	236.6
HP-4e (Scheme 5)	−323.22669	−322.60656	53.3	230.2	227.4
HP-4e *ion-dipole*	−323.21271	−322.59001	52.3	240.6	238.5
TS HP 3d → 3e	−323.10817	−322.48603	52.3	305.9	297.5
TS HP 4c → 4d	−323.20654	−322.58771	53.8	242.1	238.2
TS HP 4d → 4e	−323.18649	−322.56609	53.1	255.6	252.2
HP-3f (text Section 3.5)	−323.18298	−322.57183	53.8	252.0	248.4
HP-3g (Scheme 7)	−323.20104	−322.58174	53.3	245.8	242.9
HP-4f (Scheme 7)	−323.22176	−322.60336	53.2	232.2	229.2
HP-4g (Scheme 7)	−323.22400	−322.59650	53.3	236.5	233.7
TS HP 3b → 3f	−323.12784	−322.51689	51.9	286.5	282.9
TS HP 3b → 3g	−323.16479	−322.55045	51.9	265.4	262.1
TS HP 4c → 4f	−323.19664	−322.58153	52.7	245.9	242.3
TS HP 4f → 4g	−323.18670	−322.56592	51.9	255.7	252.6

[a] $E_{(total)}$ in Hartrees, all other components, including the ZPE scaled by 0.99, are in kcal mol^{-1}.

Table 1b
Energetic data[a] derived from CBS-QB3 calculations of stable isomers and connecting transition states involved in the decarbonylation of 4-cyclopentene-1,3-dione ions **CP-1**

Ionic species	B3LYP/CBSB7 $E_{(total)}$	CBS-QB3 $E_{(total)}$ [0 K]	ZPE	QB3 $\Delta_f H_0^0$	QB3 $\Delta_f H_{298}^0$
CP-1	−343.10878	−342.49161	47.8	176.7	173.6
CP-2	−343.08211	−342.46114	46.2	195.8	193.6
CP-3	−343.05544	−342.43994	45.3	209.1	207.0
CP-4	−343.10798	−342.47914	46.7	184.5	182.4
CP-5	−343.06877	−342.45419	47.7	200.1	197.4
CP-6	−343.06600	−342.44753	45.4	204.3	202.4
TS CP 1 → 2	−343.07371	−342.45480	46.1	199.8	196.9
TS CP 2 → 4	−343.06105	−342.43868	45.6	209.9	207.3
TS CP 2 → 5	−343.03409	−342.41713	45.3	223.4	220.6
TS CP 5 → 6	−343.04051	−342.42537	47.3	218.2	215.6

[a] $E_{(total)}$ in Hartrees, all other components, including the ZPE scaled by 0.99, are in kcal mol^{-1}.

Table 2
Energetic data derived from CBS-QB3 calculations for various dissociation products of ionized 4-hydroxypyridine and 4-cyclopentene-1,3-dione

Species	*m/z*	CBS-QB3 $E_{(total)}$ [0 K]	QB3 $\Delta_f H^0_0$	QB3 $\Delta_f H^0_{298}$	APNO $\Delta_f H^0_{298}$	Expt $\Delta_f H^0_{298}$
CH_2=CHCH=C=O$^{\bullet+}$ (**1a**) (*trans*)	68	−229.31146	203.1	201.0	198.8	198[a]
CH_2=CHCH=C=O$^{\bullet+}$ (**1b**) (*cis*)	68	−229.30851	205.0	202.8		
3-*H* pyrrole ion (**2**)	67	−209.41897	261.4	257.6		
CH_2=CHCH=N=CH$^{\bullet+}$ (**3a**) (*trans*)	67	−209.42317	258.8	255.9		
CH_2=CHCH=N=CH$^{\bullet+}$ (**3b**) (*cis*)	67	−209.42080	260.2	257.3		
CH_2=CHCH=C=NH$^{\bullet+}$ (**4a**) (*trans*)	67	−209.44218	246.8	244.2		
CH_2=CHCH=C=NH$^{\bullet+}$ (**4b**) (*cis*)	67	−209.43935	248.6	245.9		
CH_2=CH–C=O$^+$	55	−190.70217	184.9	183.2	182.0	182[b]
$^{\bullet}CH_2C{\equiv}N$		−131.87592	63.2	62.5	62.0	61.6[b]
CO		−113.18201	−27.7	−26.9	−26.4	−26.4[c]
HCN		−93.28754	31.8	31.7	32.0	32.3[c]
HNC		−93.26511	45.9	46.0	46.5	48[c]
CH_2=CHCH=C=O (*trans*)		−229.62053	9.2	7.0	5.5	4[d]
4-Cyclopentene-1,3-dione		−343.45257	−43.6	−46.7	−47.9	−53[e]

$E_{(total)}$ in Hartrees, all other components, including the ZPE scaled by 0.99, are in kcal mol^{-1}.
[a] From IE = 8.34 ± 0.05 eV (ref. [9b]) and $\Delta_f H^0_{298}$ (neutral) = 5.5 kcal mol^{-1} (CBS APNO).
[b] Refs. [1,20] has 179 kcal mol^{-1}.
[c] Ref. [20].
[d] Estimate from ref. [9b].
[e] Estimate from ref. [9a,20].

HP-1 ions decarbonylate into $C_4H_5N^{\bullet+}$ ions in both the ion source and the field free regions of the instrument. An elaborate study [10] aimed to differentiate the isomeric 1*H*-, 2*H*- and 3*H*-pyrrole ions on the basis of their similar CID mass spectra, proposes that the source generated ions from **HP-1** are 3*H*-pyrrole ions **2**. Based on the tentative assignment, this study proposes the mechanism of Scheme 1 for the decarbonylation.

In this proposal **HP-1** ketonizes via a 1,3-H shift to **HP-2** which then eliminates CO by extrusion to yield the 3*H*-pyrrole ion **2**.

As will be discussed in Section 3.6, our computations indicate that the decarbonylation of *metastable* **HP-1** ions probably does not take place via ketonization. The barrier for the associated 1,3-H shift is very high (69 kcal mol^{-1}, see Table 1a) and decarbonylation pathways of lower energy are available. These do not yield 3*H*-pyrrole ions **2** but rather vinyl(*iso*)ketenimine ions CH_2=CHCH=N=CH$^{\bullet+}$ (**3**) and CH_2=CHCH=C=NH$^{\bullet+}$ (**4**).

The CID mass spectrum of the *m/z* 67 product ions generated from *metastable* **HP-1** ions is shown in Fig. 2c. The weak spectrum resembles that reported [10] for the 3*H*-pyrrole ion (**2**) but that does not imply that this cyclic isomer is generated. Our calculations show that ring-opening of ion **2** into the more stable vinyl(*iso*)keteneimine ion **3** proceeds with a low activation barrier and thus the CID mass spectra of **2** and **3** are most likely indistinguishable. A recent theoretical study [19] has further shown that the various pyrrole tautomeric ions, including the ring-closed form of vinylketenimine (**4**), have low interconversion barriers with respect to their dissociation pathways of lowest energy, loss of acetylene. This may explain why the reported CID mass spectra of 1*H*-, 2*H*- and 3*H*-pyrrole ions are only marginally different. The above computations also indicate that the CID mass spectra of $C_4H_5N^{\bullet+}$ ions having the structure of the hitherto not studied ketene type ions **3** or **4** will be very similar to those of 1*H*-, 2*H*- and 3*H*-pyrrole ions.

3.2. The energy requirement for the competitive loss of H, C, N and CO from ions *HP-1*

Knowledge of the appearance energy of the dissociation(s) that metastable ions undergo provides an important (energetic) criterion to judge the feasibility of mechanistic proposals derived from calculations [1,2]. Unfortunately, this information is not available or easily obtainable for the dissociations of metastable ions **HP-1**.

As an alternative we have used the criterion that all calculated minima and transition states involved in the loss of CO and H, C, N from **HP-1** must be lower in energy than that required for the formation of *m/z* 55 ions CH_2=CHCO$^+$ by loss of $^{\bullet}CH_2CN$. This reaction only occurs when (meta)stable **HP-1** ions are energized by collisions. The *m/z* 55 peak generated in the CID mass spectrum [5,8] shifts cleanly to *m/z* 56 in the CID mass spectrum of 4-hydroxypyridine-OD, which is in support of the proposed mechanism of Scheme 2.

HP-1 ions first undergo a 1,2-H shift to yield **HP-3**, followed by cleavage of the carbon-nitrogen bond yielding **HP-4a**. A subsequent rate determining 1,4-H shift yields **HP-5** which can readily dissociate into CH_2=CHC=O$^+$ + $^{\bullet}CH_2CN$. The overall energy requirement for this reaction is (see Scheme 2): 274 − 203 = 71 kcal mol^{-1} and thus the highest barrier in any mechanistic proposal for the dissociations of the metastable **HP-1** ions should lie below this number.

3.3. The specific loss of D, C, N from 4-hydroxypyridine-OD ions

The challenging aspect of this mechanistic problem lies in the fact that the hydroxyl hydrogen is lost specifically. This implies that the transfer of the hydroxyl hydrogen to either the carbon or nitrogen involved in the loss of HCN/HNC, must occur in a

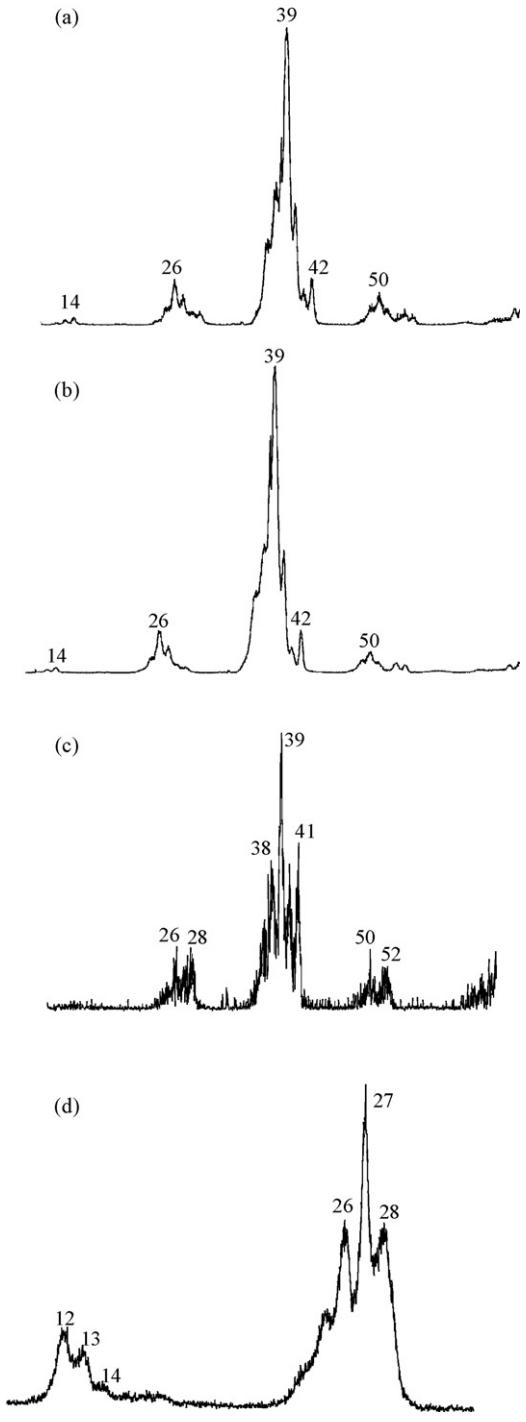


Fig. 2. CID mass spectra (3ffr) of (a) *m/z* 68 C_4H_4O ions generated from metastable 4-hydroxypyridine ions **HP-1**; (b) *m/z* 68 vinylketene ions generated from metastable 2-cyclo-hexene-1-one ions [9]; (c) *m/z* 67 C_4H_5N ions generated from metastable ions **HP-1**. Item (d) is the CIDI spectrum of the *m* = 27 neutrals generated from metastable ions **HP-1**.

single step. Our calculations show that this is achievable if **HP-1** first rearranges into **HP-3** as depicted in Scheme 2. We note in passing that this rearrangement is far less energy demanding than the ketonization of **HP-1** into **HP-2**. Ion **HP-3** then acts as the reaction configuration for the two pathways depicted in Scheme 3.

Scheme 3 shows that bond cleavage of **HP-3** at either the α-position (route **a**) or the β-position (route **b**) yields the open chain structures **HP-3a** and **HP-4a**. Direct deuterium transfer via either a 1,5-D shift or a 1,6-D shift generates ions **HP-3b** and **HP-4b**. These intermediates have the desired D, C, N connectivity but will not lose DCN or DNC by direct bond cleavage because the resulting product ion, although a minimum on the $C_4H_4O^{\bullet+}$ potential energy surface, is far too high in energy. However, our computations indicate that **HP-3b** and **HP-4b** can easily cyclize into **HP-3c** and **HP-4c** which can be viewed as the (*iso*)imino analogues of 4-cyclopentene-1,3-dione (**CP-1**). Metastable ions **CP-1** readily decarbonylate yielding the same product ion [9], ionized vinylketene, as generated by loss of H, C, N from **HP-1**. This analogy is relevant because the mechanism(s) by which **CP-1** decarbonylates may well provide insight as to how **HP-3c** and **HP-4c** and hence **HP-1**, lose both H, C, N and CO. This point will be addressed in the next section.

Finally, we note that the highest barriers of the two routes in Scheme 3 – the 1,5-D shift of route **a** and the 1,6-D shift of route **b** – both satisfy the energetic criterion discussed in the previous section.

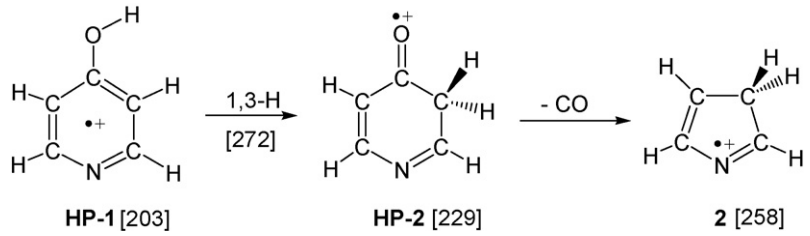
*3.4. The decarbonylation of 4-cyclopentene-1,3-dione ions **CP-1**: what can this reaction tell us about the dissociation of **HP-1** ions?*

In a previous study [9a] it is stated that the decarbonylation of 4-cyclopentene-1,3-dione ions **CP-1** was investigated, because this reaction might well be expected to generate cyclobutenone ions.

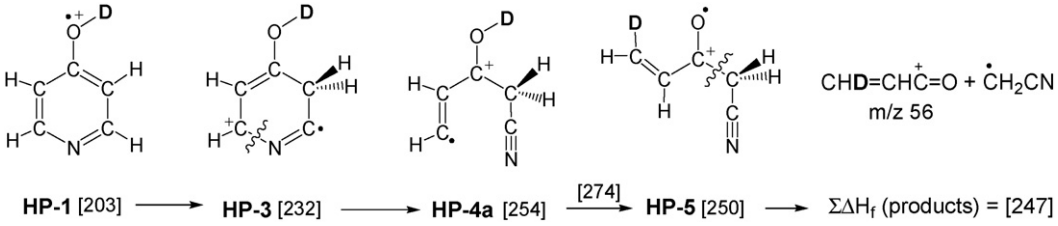
Based upon a measured appearance energy of 10.88 eV and an estimated heat of formation of the neutral dione: $\Delta_f H^0$ **CP-1**(N) = −53 kcal mol^{-1}, the C_4H_4O product ion was proposed to have a $\Delta_f H^0$ of 224 kcal mol^{-1}. The CBS-QB3 and CBS-APNO model chemistries of our study yield $\Delta_f H^0_{298}$ values for the neutral dione of −47 and −48 kcal mol^{-1}, respectively, while subtraction of the measured IE (9.6 eV [20]) from the CBS-QB3 derived enthalpy of the **CP-1** ion yields −48 kcal mol^{-1}. We propose that $\Delta_f H^0_{298}$ **CP-1**(N) = −48 kcal mol^{-1} provides a better estimate so that the apparent $\Delta_f H^0$ of the C_4H_4O product ion becomes 230 kcal mol^{-1}. It was argued [9a] that this value must be an *upper limit* for the $\Delta_f H^0$ because the above reaction showed a metastable peak of dished shape with an associated T_{min} value of 0.19 eV (4 kcal mol^{-1}).

It was further noted that the CID mass spectrum of the *m/z* 68 product ions was closely similar to that of the ring-opened vinylketene ion **1**. This led the authors of ref. [9a] to conclude that *if* it is generated, the cyclobutenone ion has a CID mass spectrum essentially indistinguishable from that of its valence isomer **1**, i.e., although the cyclic ion could be generated at threshold, it readily ring-opens with little energy requirement.

The computations of our study confirm the suspicion that ionized cyclobutenone is not a local minimum on the $C_4H_4O^{\bullet+}$ potential energy surface: geometry optimizations starting from its (stable) neutral counterpart invariably lead to the vinylketene isomer. Removal of an electron from the fixed geometry



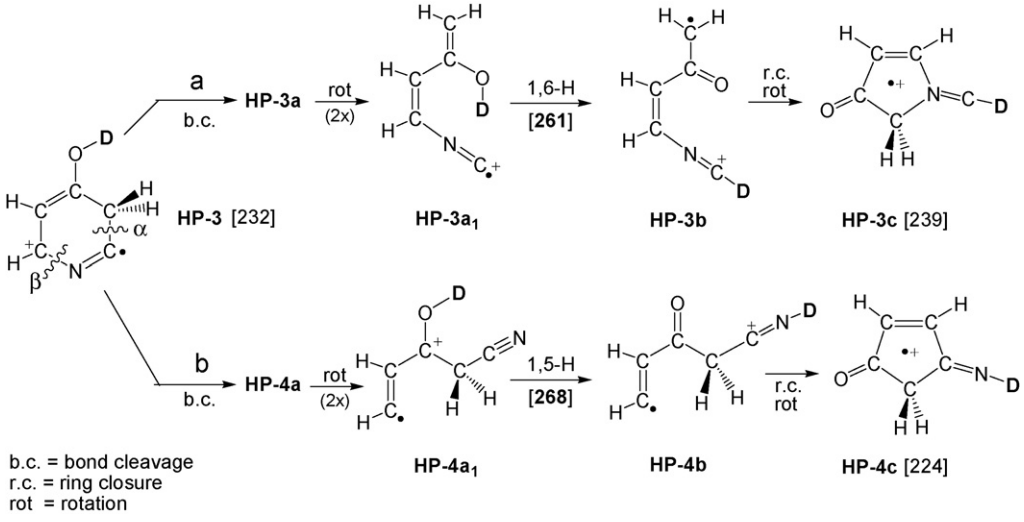
Scheme 1.



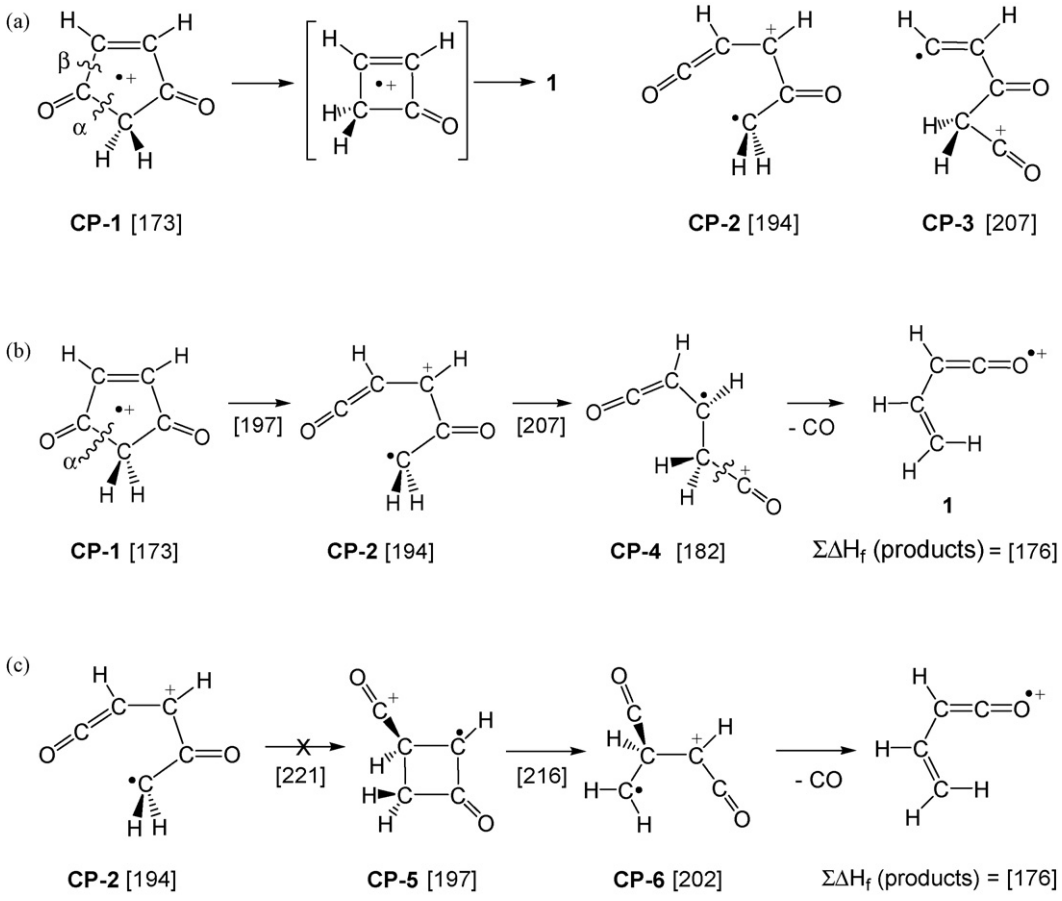
Scheme 2. Proposal for the collision induced loss of $^{\bullet}CH_2CN$ from 4-hydroxypyridine ions (**HP-1**). The full set of enthalpies for intermediates and transition states is presented in Table 1a.

of the neutral (whose $\Delta_f H^0_{298}$ is 10.7 kcal mol^{-1}) yields a crude $\Delta_f H$ estimate of ∼230 kcal mol^{-1} for an unstable ionic cyclobutenone intermediate. Extrusion of a CO molecule from **CP-1** as depicted in Scheme 4a could yield such an intermediate. However, a scan of the potential energy surface indicates that a concerted extrusion reaction would be even higher in energy than the transition state linking **CP-2** → **CP-5** in Scheme 4c. This leaves us with the option that the decarbonylation of **CP-1** takes place from either of its stable ring-opened isomers, **CP-2** or **CP-3** in Scheme 4a. The appearance energy of the previous study would then prescribe that the highest transition state in a plausible decarbonylation mechanism from either of these ions should lie at ∼203 kcal mol^{-1}. This makes it unlikely that the reaction takes place via **CP-3**: its enthalpy is relatively high (207 kcal mol^{-1}) and exploratory calculations indicate that further transformations leading to the loss of CO have barriers far in excess of the 203 kcal mol^{-1} dictated by experiment. We therefore focused on the more stable isomer **CP-2** and our proposed route for the decarbonylation of **CP-1** is shown in Scheme 4b.

The reaction starts with ring-opening of ion **CP-1** by cleavage of the α-bond to generate ion **CP-2**. The next step involves attack of the methylene group on the charged methine moiety of the ion which leads to a three membered ring transition state structure. Ring-opening of this structure yields the stable **CP-4** ion, which can be viewed as a vinylketene ion bound covalently to a CO molecule. The TS for the transformation **CP-2** → **CP-4** represents the most energy demanding step of the reaction. It is calculated to lie at 207 kcal mol^{-1} and may well correspond with the above experimentally derived energy requirement of 203 kcal mol^{-1} for the decarbonylation reaction. In this context we note that we affix ±4 kcal mol^{-1} as a conservative estimate for the uncertainty in the computed barrier heights [21]. The continuously endothermic loss of CO from **CP-4** completes the



Scheme 3. Energy diagram depicting the isomerization of **HP-3** ions into **HP-3c** and **HP-4c**, the (*iso*)imino analogues of 4-cyclopentene-1,3-dione (**CP-1**). The full set of enthalpies for intermediates and transition states is presented in Table 1a.



Scheme 4. (a) Extrusion of a CO molecule from **CP-1**. (b) The proposed mechanism for the decarbonylation of 4-cyclopentene-1,3-dione ions **CP-1**. (c) An alternative pathway for the decarbonylation of **CP-2**.

reaction. In this mechanistic proposal, theory and experiment are clearly in concert.

An alternative pathway for the decarbonylation of **CP-2** is shown in Scheme 4c. It involves cyclization followed by a simple bond cleavage to yield **CP-6** which then decomposes into the vinylketene ion and CO. It is interesting to note that the carbonylated cyclobutenone ion **CP-5** is a stable species, but the high barrier for its formation precludes the route of Scheme 4c as a feasible pathway.

3.5. The specific loss of DCN and DNC from 4-hydroxypyridine-OD ions

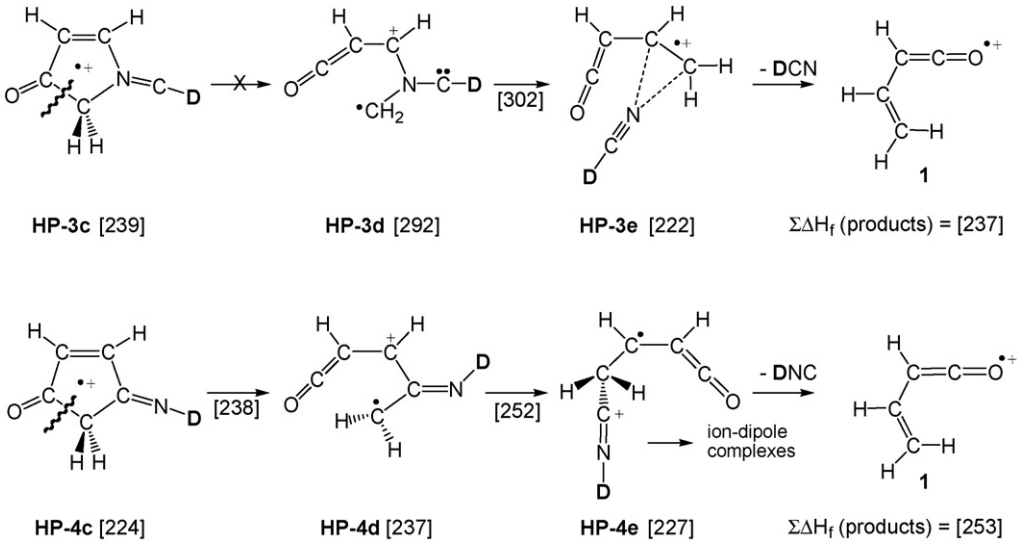
In Section 3.3, it was shown that **HP-1** ions could isomerize into the (*iso*)imino analogues of the dione **CP-1**. In Section 3.4, a mechanism for the decarbonylation of **CP-1** ions was presented. Armed with this information, we will now discuss mechanistic proposals for the loss of DCN and DNC from **HP-1**.

By analogy with the proposal of Scheme 4b, ions **HP-3c** and **HP-4c** would lose either HCN or HNC via the routes depicted in Scheme 5. Ions **HP-3c** and **HP-4c** first undergo cleavage of the α-bond to yield ions **HP-3d** and **HP-4d**, respectively. The second transformation leads to three membered ring transition states that decompose into ions **HP-3e** and **HP-4e**. Ion **HP-3e** represents an ion-dipole complex of HCN with the vinylketene ion whereas the HNC and vinylketene moieties of **HP-4e** are connected by a covalent bond. However, HNC has a significant dipole moment ($\mu = 3.1$ D) and its loss from **HP-4e** undoubtedly occurs via ion-dipole configurations. This point will be further discussed in Section 3.6.

The bottom route of Scheme 5, depicting the loss of DNC from ions **HP-4c**, is energetically attractive. Its energy requirement lies at 252 kcal mol^{-1}, which is 16 kcal mol^{-1} lower in energy than the pathway linking ionized 4-hydroxypyridine with its iminocylopentenone isomer **HP-4c**. Hence, as is shown in the energy diagram of Scheme 6, the loss of DNC from 4-hydroxypyridine via the intermediate **HP-4c** ion is feasible on energetic grounds: the rate limiting step requires 5 kcal mol^{-1} less energy than the collision induced reaction yielding the vinyl carbonyl cation at *m/z* 55. In addition, this reaction satisfies the deuterium labeling results.

In contrast, the overall energy requirement for the loss of DCN from **HP-3c** is so high (TS **HP-3d** → **HP-3e** lies at 302 kcal mol^{-1}) that this reaction can effectively be ruled out for the dissociation of the metastable ions. The (resonance) structure of **HP-3d** depicted in Scheme 5 provides a rationale for the high energy requirement. The extra pair of non-bonding electrons relative to **HP-3c** suggests that in the transformation **HP-3c** to **HP-3d** a bond is broken which is never reformed, resulting in a drastic loss of stabilization energy.

We have also examined the possibility that the DCN loss takes place by analogy with **CP-1**'s decarbonylation mechanism of

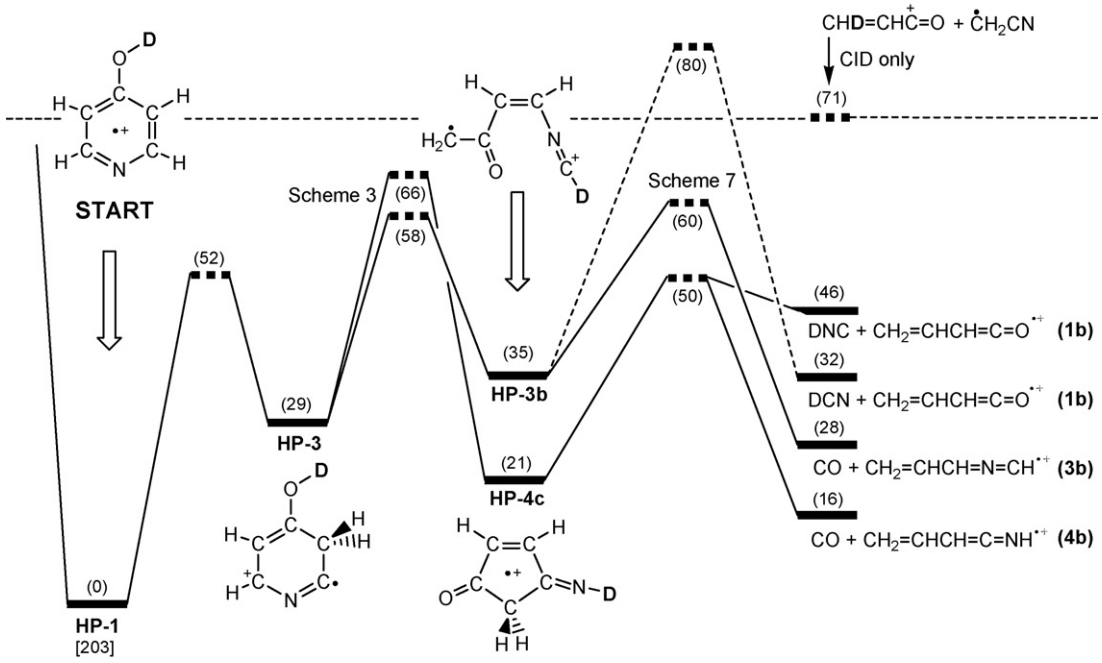


Scheme 5. Mechanistic pathways for the loss of DCN from **HP-3c** and DNC from **HP-4c**.

Scheme 4c. The overall energy requirement of this route, **HP-3b** → **HP-3f** → **HP-3e** → **1** + DCN, is determined by the TS of the first step, the cyclization of **HP-3b** into **HP-3f**, whose structure is shown in Fig. 3a. This TS lies lower in energy than that of Scheme 5 (top reaction) but Scheme 6 shows that its value of 283 kcal mol^{-1} is still too high to consider this route as a viable option.

3.6. The decarbonylation of metastable 4-hydroxypyridine ions

The results of our computational study indicate that **HP-1**'s competing decarbonylation reaction may follow a mechanistic pathway similar to that of the HNC loss. Scheme 7 shows mechanistic proposals for the decarbonylation of both **HP-3c** and **HP-4c**. Both are analogous to the decarbonylation mechanism of **CP-1** in Scheme 4b and have energy requirements that lie below that of the collision induced formation of *m/z* 55 ions. Note that the top reaction of Scheme 7 actually starts from **HP-3b** which can be generated directly from **HP-1** (see Scheme 3). This route yields the isoketenimine radical cation **3**, the ring opened isomer of 3*H*-pyrrole (**2**), the structure proposed to be the product of the extrusion reaction of Scheme 1. The product of the decarbonylation of **HP-4c** is the vinylketenimine ion **4**. This $C_4H_5N^{\bullet+}$isomer is more stable than **3** and also than its ring-closed pyrrole tautomer (by 9 kcal mol^{-1}).



Scheme 6. Energy level diagram (CBS-QB3 298 K calculations Table 1a) describing the losses of CO and DNC from metastable ions **HP-1**. The relative energies in round brackets are in kcal mol^{-1}.

As discussed in Section 3.1, the CID mass spectrum (Fig. 2c) of the product ions generated by the decarbonylation of **HP-1** is compatible with the presence of **3** or **4** or a mixture thereof. Scheme 6 indicates that both product ions are energetically accessible. However, from a kinetic point of view formation of the vinyl(*iso*)ketenimine ion **3** is clearly the preferred route: the formation of **4** is more energy demanding by 8 kcal mol^{-1}, faces competition with the loss of HNC and involves an entropically less favoured cyclization step. Thus, we propose that the decarbonylation of metastable **HP-1** ions yields a mixture of vinyl(*iso*)keteneimine ions of which the isoketenimine **3** is the major component.

Finally we note that the fraction of the reverse activation energy (ε_0^r) that is released as kinetic energy (T) is much smaller

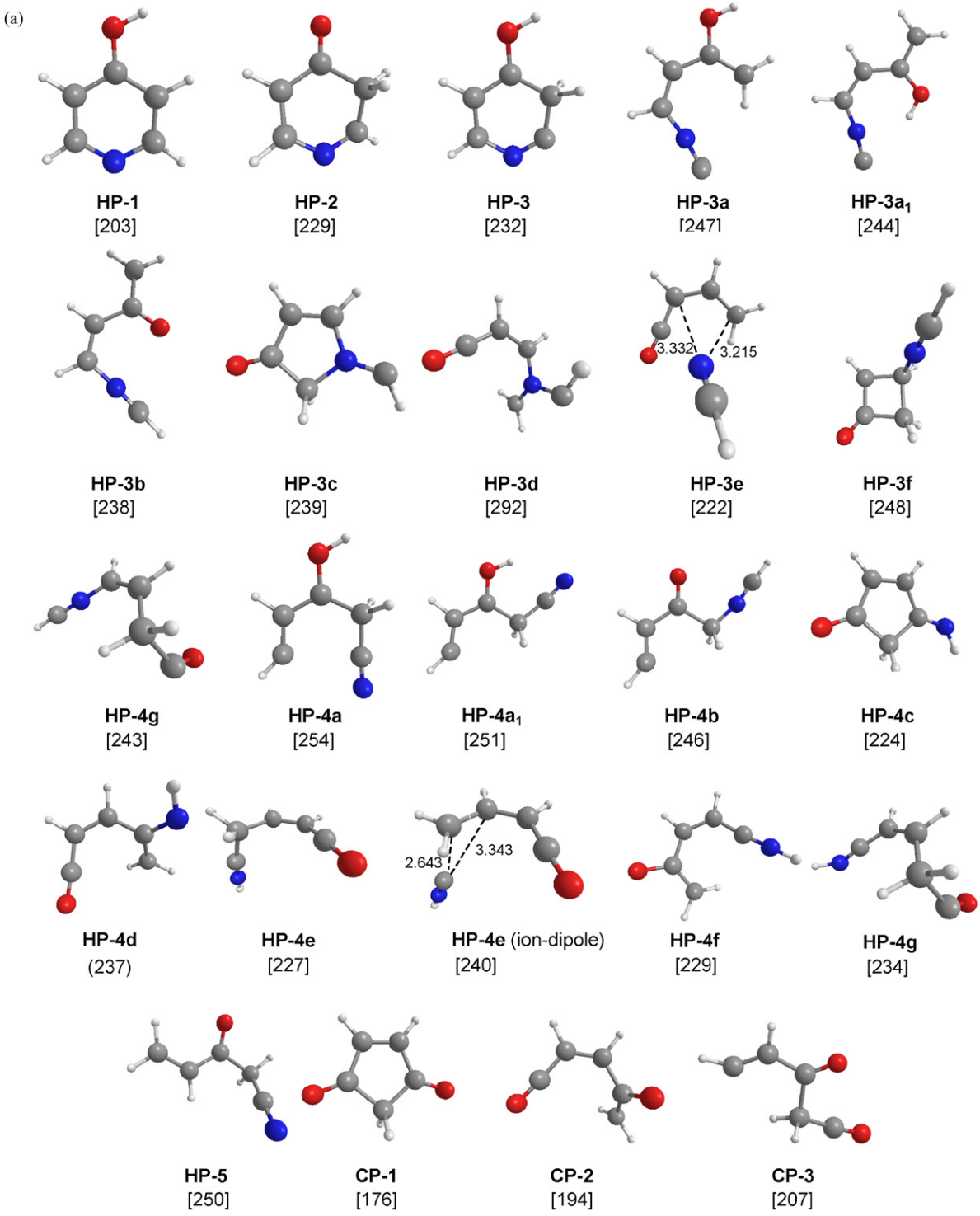


Fig. 3. (a) Selected optimized geometries (CBSB7 basis set) for stable intermediates involved in the elimination of HCN and CO from ionized 4-hydroxypyridine (**HP-1**) and CO from 4-cyclopentene-1,3-dione (**CP-1**). (b) Selected optimized geometries (CBSB7 basis set) for transition states involved in the elimination of HCN from ionized 4-hydroxypyridine (**HP-1**).

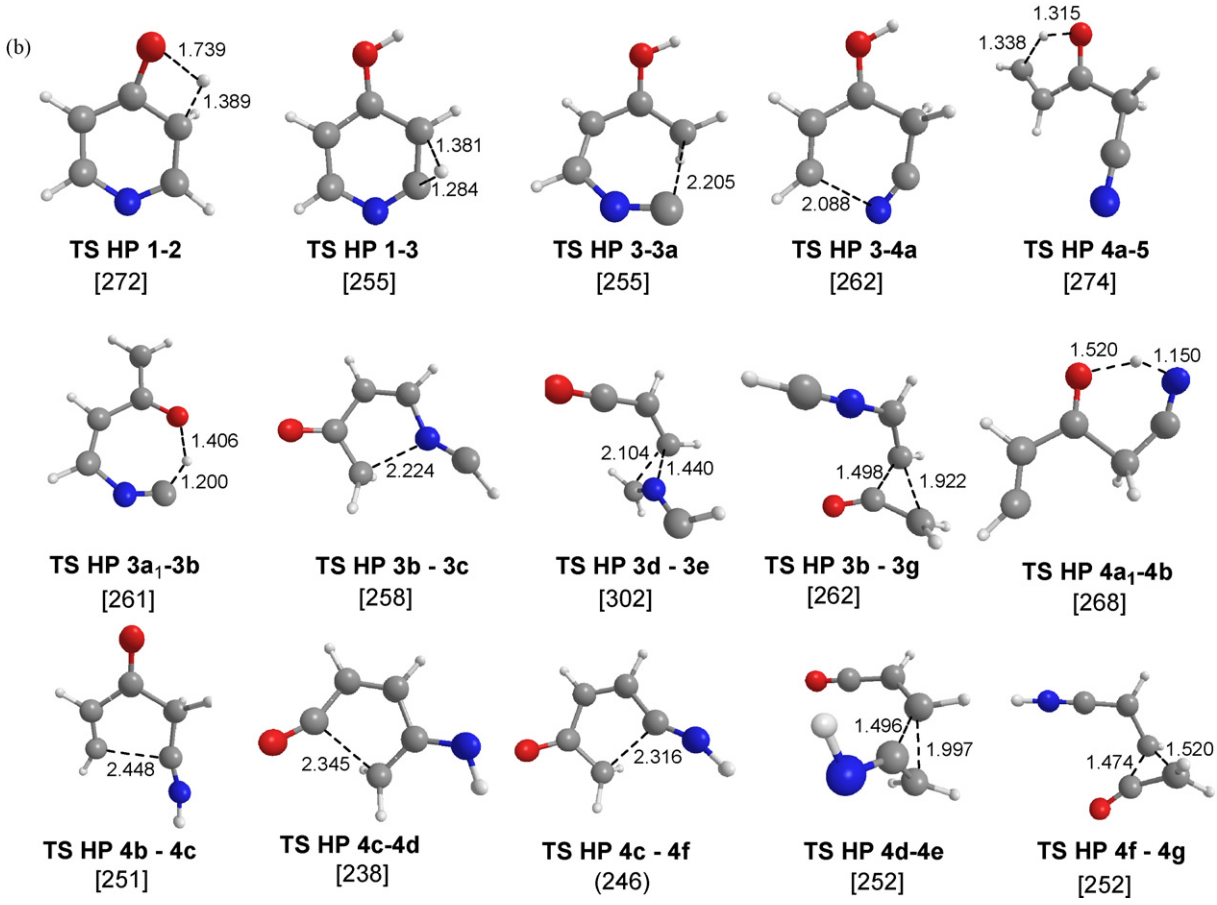
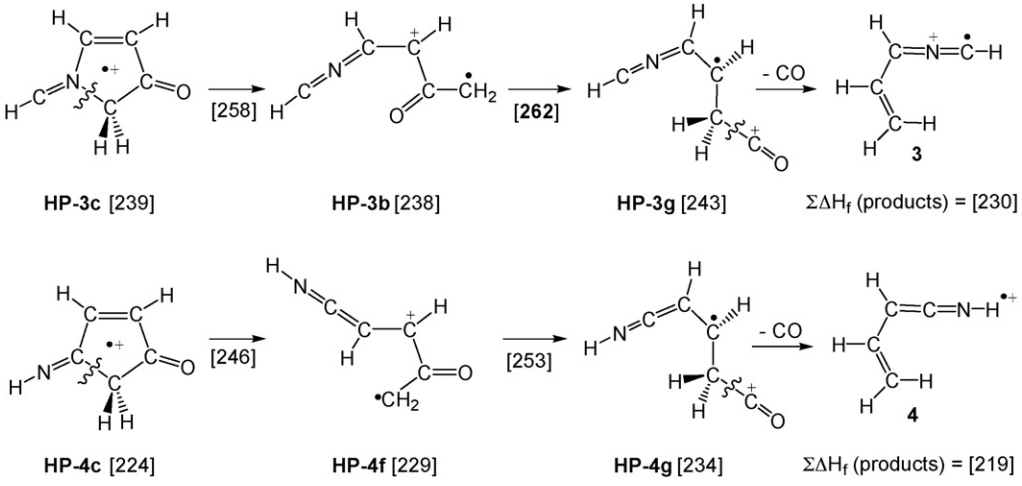


Fig. 3. (*Continued*).

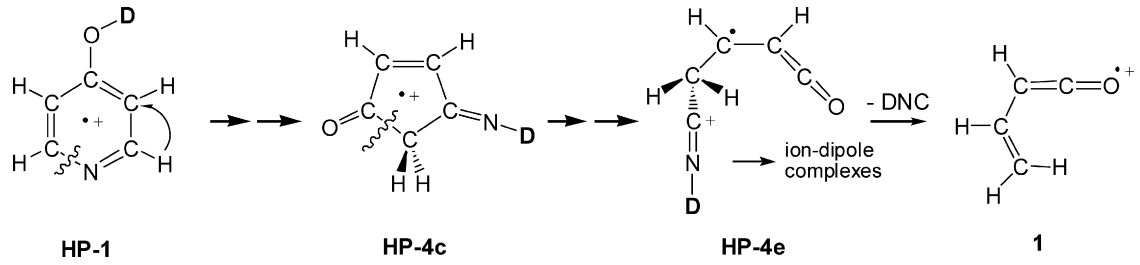
in the loss of HNC than in the loss of CO: the two reactions have ε_0^r values of 16 and 32 kcal mol^{-1} (Scheme 6) and display metastable peaks (Fig. 1a) whose $T_{0.5}$ values are 45 and 540 meV, respectively. We suggest that the relatively low partitioning of excess internal energy among translational degrees of freedom in the loss of HNC reflects the proposed participation of ion–dipole complexes in the final step of the reaction [2,22].

4. Summary

Our experiments leave little doubt that ionized vinylketene is generated as the product ion of the title reaction. The structure of the neutral, DCN versus DNC, remains experimentally uncertain. However, our computational analysis leads to a transparent mechanistic proposal for the specific loss of DNC that satisfies the energetic constraint dictated by experiment:



Scheme 7. Mechanistic pathways for the decarbonylation of ions **HP-3c** and **HP-4c**.



HP-1 **HP-4c** **HP-4e** **1**

The OD-labelled 4-hydroxypyridine ions **HP-1** first isomerize into **HP-4c** in four consecutive steps: a 1,2-H shift, ring-opening by C–N bond cleavage, a 1,5-D transfer to N and cyclization. Ion **HP-4c** is the imino analogue of **CP-1**, the 4-cyclo-pentene-1,3-dione ion. **CP-1** readily decarbonylates in the μs time-frame to produce the vinylketene ion and the transformation of **HP-4c** into **HP-4e** occurs in an analogous fashion. The final step of the reaction involves the loss of DNC from ion-dipole complexes comprised of ionized vinylketene (**1**) and neutral DNC.

Mechanisms leading to the loss of DCN have also been probed but all of these appeared to be too energy demanding for competition with the loss of DNC and the decarbonylation. Our calculations further indicate that the decarbonylation of **HP-1** does not involve loss of CO by extrusion into 3*H*-pyrrole ions but rather dissociation via (*iso*)imino analogues of **CP-1** yielding vinyl(*iso*)keteneimine ions.

Acknowledgement

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