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The loss of $NH_2O^•$ from the *N*-hydroxyacetamide radical cation $CH_3C(=O)NHOH^{•+}$: An ion-catalysed rearrangement

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In memory of Professor Chava Lifshitz, whose seminal contributions to our mass spectrometric studies have been a continual source of inspiration.

Abstract

A previous study [Ch. Lifshitz, P.J.A. Ruttink, G. Schaftenaar, J.K. Terlouw, Rapid Commun. Mass Spectrom. 1 (1987) 61] shows that *metastable* *N*-hydroxyacetamide ions $CH_3C(=O)NHOH^{•+}$ (**HA-1**) do not dissociate into $CH_3C{=}O^+ + NHOH^•$ by direct bond cleavage but rather yield $CH_3C{=}O^+ + NH_2O^•$. The tandem mass spectrometry based experiments of the present study on the isotopologue $CH_3C(=O)NDOD^{•+}$ reveal that the majority of the metastable ions lose the $NH_2O^•$ radical as $NHDO^•$ rather than $ND_2O^•$.

A mechanistic analysis using the CBS-QB3 model chemistry shows that the molecular ions **HA-1** rearrange into hydrogen-bridged radical cations $[O{=}C{-}C(H_2){-}H\cdots N(H)OH]^{•+}$ whose acetyl cation component then catalyses the transformation $NHOH^• \rightarrow NH_2O^•$ prior to dissociation. The high barrier for the unassisted 1,2-H shift in the free radical, 43 kcal mol^{-1}, is reduced to a mere 7 kcal mol^{-1} for the catalysed transformation which can be viewed as a quid-pro-quo reaction involving two proton transfers.
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Keywords: Ion-catalysis; Tandem mass spectrometry; CBS-QB3 model chemistry; Quid-pro-quo mechanism

1. Introduction

Almost 20 years ago, in a joint project with the late Professor Chava Lifshitz, we reported a study [1], which dealt with the generation and characterization of the prototype nitroxyl radical $NH_2O^•$ and its isomer $NHOH^•$. Using the technique of Neutralization Reionization Mass Spectrometry (NRMS) [2] and related experiments, it was shown that both $NH_2O^•$ and $NHOH^•$ are stable radicals in the gas phase separated by a high barrier towards interconversion. The $NH_2O^•$ radical has also been identified by far infrared laser magnetic resonance [3], microwave [4] and UV photoelectron [5] spectroscopy. In contrast, its isomer $NHOH^•$ remains an elusive species, which may inter alia be generated in the reaction of $HCO^•$ with HNO [6]. Experimental enthalpies of formation are not available for either radical. However, the most recent theoretical study [7] yields 298 K enthalpies of formation of 17.5 ± 2 and 23.7 ± 2 kcal mol^{-1} for $NH_2O^•$ and *trans*-$NHOH^•$ and a high interconversion barrier at 70 kcal mol^{-1}; these values are close to those obtained with the computational methods of the present study.

The study of Ref. [1] further shows that the *ionic* counterparts of the two radicals are also stable species in the gas-phase. Ions NH_2O^+ and $NHOH^+$ can conveniently be generated by the dissociative ionization of CH_3ONH_2 and $CH_3C(=O)NHOH$, respectively. They can be readily characterized by the unique *m/z* 14–18 peak profiles of their collision induced dissociation (CID) mass spectra. As with the neutral species, the isomerization barrier $NH_2O^+ \rightarrow NHOH^+$ is also high: a subsequent theoretical study at the Gaussian-1 level of theory [8] yields an activation energy of 65.5 kcal mol^{-1}. The more sophisticated model chemistry of this study (see below) predicts the same barrier height and 298 K enthalpies of formation of 224 and 242 kcal mol^{-1} for NH_2O^+ and *trans*-$NHOH^+$, respectively. Experimental values are only available for the NH_2O^+ isomer: they range from 224 to 225 kcal mol^{-1} [1] and agree quite well with the theoretical results.

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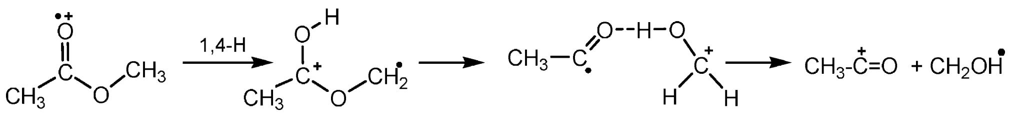


Scheme 1.

Finally, the study of Ref. [1] reports the intriguing experimental observation that *metastable* *N*-hydroxyacetamide ions $CH_3C(=O)NHOH^{\bullet+}$ (**HA-1**) do not dissociate into $CH_3C=O^+ + NHOH^\bullet$ by direct bond cleavage but rather yield $CH_3C=O^+ + NH_2O^\bullet$. This became clear when the connectivity of the $[N,H_2,O]^\bullet$ neutral was probed with a CIDI (collision induced dissociative ionization) experiment (see Section 2).

This finding parallels observations on the formation of acetyl cations, $CH_3–C=O^+$, from methyl acetate radical cations, $CH_3C(=O)OCH_3^{\bullet+}$. For the high-energy source generated ions, the process involves loss of $CH_3O^\bullet$ by (simple) direct bond cleavage. In contrast, the low-energy *metastable* ions [9] lose the energetically more favourable isomeric $CH_2OH^\bullet$ radical [10], obviously via a rearrangement. The mechanism of this reaction has been studied in detail using ab initio calculations [11]. It features a hydrogen-bridged radical cation (HBRC [12]), $CH_3C=O\cdots H\cdots O=CH_2^{\bullet+}$, as the key intermediate (Scheme 1).

In contrast, the mechanism for the loss of $NH_2O^\bullet$ from *metastable* ions HA-1 has never been studied. An intriguing possibility is that it involves an (acetyl) ion-catalysed isomerization of the $NHOH^\bullet$ radical into its thermodynamically more stable counterpart $NH_2O^\bullet$. The study of molecular transformations catalysed by ions in the gas-phase is a topic of considerable current interest [13]. This prompted us to probe the mechanism of this reaction by performing additional tandem mass spectrometry based experiments in conjunction with computational chemistry. During the past 5 years we have successfully used the CBS-QB3 method [14] in mechanistic studies of **ionic** transformations catalysed by **molecules** in the gas-phase [15,16]. We therefore decided to use this CBS (complete basis set) variant, which uses density functional geometries and frequencies in the calculations, as the primary computational tool in probing the mechanism for the $NH_2O^\bullet$ elimination from metastable ions $CH_3C(=O)NHOH^{\bullet+}$ (**HA-1**).

2. Experimental and theoretical methods

The experiments were performed with the VG Analytical ZAB-R mass spectrometer of BEE geometry (B, magnet; E, electric sector) [17] 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 He was used as the collision gas. The CIDI [10] spectra were also obtained in the 2ffr. A CIDI experiment is performed with the instrumental setup for CID but with charging of the deflector electrode located in front of the collision gas chamber. A small fraction of the beam of fast moving ions m_1^+ under investigation will dissociate unimolecularly, $m_1^+ \rightarrow m_2^+ + N$, during the flight to the collision gas chamber. Upon arrival at the charged deflector electrode all ions, m_1^+ and the *ionic* dissociation products m_2^+, are deflected away so that the only species entering the collision chamber are the fast moving neutrals N. Within the cell the neutrals are ionized by collision with helium. Part of the ionized neutrals dissociate and the spectrum of their ionic dissociation products is registered as the CIDI spectrum. The CIDI spectrum of Fig. 1d and e was obtained from mass selected *m/z* 75 ions **HA-1** having 10 keV translational energy. The reference CID mass spectrum of the $NHOH^+$ ion of Fig. 1f was obtained from 5 keV ions generated in the source by dissociative ionization of *N*-hydroxyacetamide. Kinetic energy release ($T_{0.5}$) values were measured following standard procedures [18] without correcting for the main beam width. All spectra were recorded using a PC-based data system developed by Mommers Technologies Inc. (Ottawa).

The *N*-hydroxyacetamide sample was of research grade (Aldrich) and used without further purification. The deuterium labelled isotopomer $CH_3C(=O)NDOD$ 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 [14a] was also used. All calculations were run with the Gaussian 2003, Rev C.02 suite of programs [19]. 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 6-31 1G(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 *N*-hydroxyacetamide system of ions are presented in Tables 1 and 2. Spin contaminations were within an acceptable range (0.75–0.79). For two of the isomerizations depicted in Fig. 3, the CBS-QB3 energy of the TS is calculated to be slightly lower than that of the least stable of the connecting isomers. This may happen since transition states are more sensitive to correlation effects than minima and the ZPE also tends to favour transition states. Fig. 2 displays the optimized geometries for the principal species. Unless stated otherwise, all enthalpies presented in the text and in the Schemes (numbers in square brackets) refer to $\Delta_f H^\circ_{298}$ 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

The MI spectrum of $CH_3C(=O)NHOH^{\bullet+}$ (**HA-1**), see Fig. 1a, contains only one peak, at *m/z* 43, which results from the dissociation **HA-1** $\rightarrow CH_3C=O^+ + [N,H_2,O]^\bullet$. The CIDI spectrum of the corresponding $[N,H_2,O]^\bullet$ neutral is shown in Fig. 1d and e.

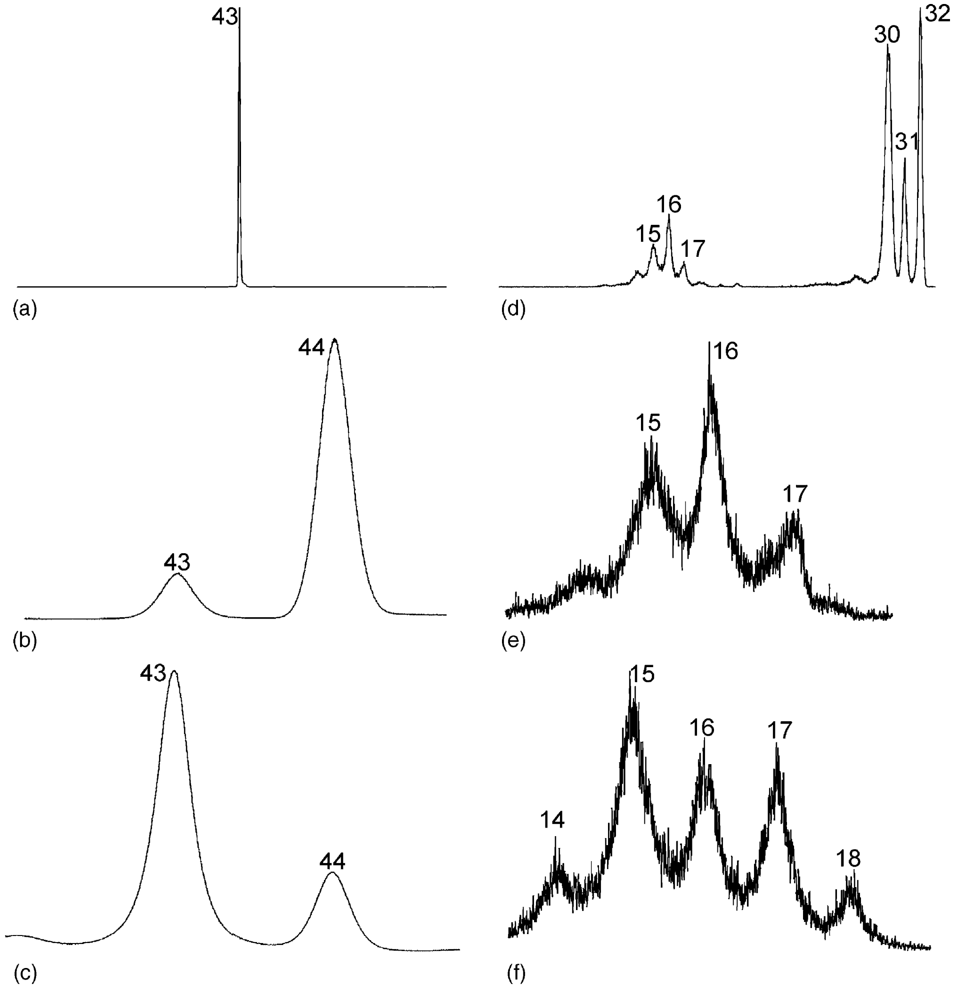


Fig. 1. (a) MI spectrum of ionized *N*-hydroxyacetamide, $CH_3C(=O)NHOH^{\bullet+}$ (**HA-1**); (b) partial MI spectrum of $CH_3C(=O)NDOD^{\bullet+}$ (**HA-1**d_2); (c) partial CID spectrum of $CH_3C(=O)NDOD^{\bullet+}$ (**HA-1**d_2); (d) CIDI spectrum of the $m = 32$ neutrals generated from metastable ions **HA-1**; (e) the *m/z* 14–18 region in the CIDI spectrum of the $m = 32$ neutrals generated from metastable ions **HA-1**; (f) the *m/z* 14–18 region in the CID spectrum of *m/z* 32 reference ions of structure $NHOH^+$.

These spectra are very close to those reported in Ref. [1] where, based upon additional experimental observations in conjunction with a detailed analysis of the CID spectra of $NHOH^+$ and NH_2O^+, compelling evidence is presented that the (majority of) the neutrals lost in the dissociation of metastable ions **HA-1** have the $NH_2O^\bullet$ connectivity.

To gain more insight in the mechanism of the reaction, the (slightly acidic) N–H and O–H hydrogens of $CH_3C(=O)NHOH$ were exchanged with deuterium using methanol-OD. The MI spectrum of the resulting isotopomer **HA-1**d_2 (*m/z* 77) is shown in Fig. 1b. It is seen that the *m/z* 43 peak is largely shifted to *m/z* 44, indicating that $NHDO^\bullet$ rather than $ND_2O^\bullet$ is preferentially lost. We further note that the intensity of the minor *m/z* 43 peak in the MI spectrum of Fig. 1b is very sensitive to the presence of (residual) collision gas: when the 2ffr collision cell was pressurized with He its intensity, see Fig. 1c, increased strongly – by a factor of 40 – whereas the *m/z* 44 peak only increased by a factor of 2. From this result, we conclude that *metastable* ions **HA-1**d_2 largely dissociate into $CH_2DC{=}O^+ + NHDO^\bullet$, whereas collision induced dissociation of stable ions **HA-1**d_2 – which may account for (part of) the *m/z* 43 peak in the MI spectrum of Fig. 1b – leads to the formation of $CH_3C{=}O^+ + NDOD^\bullet$, by direct bond cleavage.

We further note that if part of the *m/z* 43 peak in the spectrum of Fig. 1b is indeed of metastable origin, a second mechanism for the $NH_2O^\bullet$ loss may play a (minor) role. Analysis of the shapes [18] of the MI and CID peaks of Fig. 1b and c does not provide conclusive evidence for this proposal. The $T_{0.5}$ values of the Gaussian shaped metastable peaks at *m/z* 43 and 44 (18.2 and 17.4 meV) are not significantly different and the same obtains for the corresponding CID peaks, which are only marginally broader (~5%).

Overall, we can assert that during the loss of $NH_2O^\bullet$ from *metastable* ions **HA-1**, one of the hydrogen atoms of the NHOH moiety is exchanged with a methylic hydrogen.

In the context of our computational quest of plausible mechanisms for the $NH_2O^\bullet$ elimination from metastable ions **HA-1**, an important criterion is that none of the stable intermediates or connecting transition states of a viable proposal should lie significantly above the energy level for the direct bond cleavage **HA-1** → $CH_3C{=}O^+ + NHOH^\bullet$. Our calculations, see Table 1, indicate that $\sum \Delta_f H^\circ_{298}$ ($CH_3C{=}O^+$ + *trans*-$NHOH^\bullet$)

Table 1
Energetic data for various dissociation products of ionized *N*-hydroxyacetamide derived from CBS-QB3 and selected CBS-APNO calculations[a]

Species	*m*/*z*	CBS-QB3, $E_{(\mathrm{total})}$ (0 K)	QB3, $\Delta_f H^\circ_0$	QB3, $\Delta_f H^\circ_{298}$	APNO, $\Delta_f H^\circ_{298}$	Expt, $\Delta_f H^\circ_{298}$	Ref./note
$CH_3C{=}O^+ + NHOH^\bullet$	43			180.2	181.3	–	
$CH_3C{=}O^+$		−152.68586	159.8	158.1	158.7	156	[24a]
$NHOH^\bullet$ (*trans*)		−130.90786	23.7	22.1	22.6	–	
$NHOH^\bullet$(*cis*)		−130.89944	29.0	27.5	27.9	–	
$CH_3C{=}O^+ + NH_2O^\bullet$	43			172.4	174.1	–	
$NH_2O^\bullet$		−130.92056	15.8	14.3	15.4	–	
TS $NH_2O^\bullet \rightarrow NHOH^\bullet$ (*trans*)		−130.83876	67.1	65.5	65.4	–	
$CH_2{=}C{=}O^{\bullet +} + NH_2OH$	42			199.8	199.4	200	
$CH_2{=}C{=}O^{\bullet +}$		−152.02211	211.0	210.3	209.3	210	[24a]
NH_2OH		−131.54158	−8.7	−11.2	−9.9	−10	[24a]
$NH_2OH^{\bullet +} + CH_2{=}C{=}O$	33			190.5	189.7	200	
$NH_2OH^{\bullet +}$		−131.20170	204.6	202.2	201.9	211	[b]
$CH_2{=}C{=}O$		−152.37579	−11.0	−11.7	−12.2	−11	[24a]
$NHOH^+ + CH_3C{=}O^\bullet$	32			238.9	238.6	–	
$NHOH^+$(*trans*)		−130.55794	243.3	241.6	242.1	–	
$NHOH^+$(*cis*)		−130.54705	250.2	248.5	249.0	–	
TS $NH_2O \rightarrow NHOH^+$(*trans*)		−130.48116	291.5	289.8	288.9	–	
$CH_3C{=}O^\bullet$		−152.94168	−0.7	−2.7	−3.5	−2.4	[24b]
$NH_2O^+ + CH_3C{=}O^\bullet$	32			220.8	220.8	222.6	
NH_2O^+		−130.58679	225.2	223.5	224.3	225	

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

[b] Using IE = 9.6 eV as proposed in the photoionization study of Ref. [24c]; the unusually large discrepancy between theory and experiment probably originates from large differences in the geometries of the ion and the neutral so that the true adiabatic IE cannot be measured, see also Ref. [24d].

Table 2
Energetic data[a] derived from CBS-QB3 calculations of stable isomers and connecting transition states involved in the loss of $NH_2O^\bullet$ from the *N*-hydroxyacetamide radical cation (HA-1)

Ionic species	B3LYP/CBSB7, $E_{(\mathrm{total})}$	CBS-QB3, $E_{(\mathrm{total})}$ (0 K)	ZPE	$\Delta_f H^\circ_0$	$\Delta_f H^\circ_{298}$
HA-1a $CH_3C({=}O)NHOH^{\bullet +}$	−284.136268	−283.640009	47.6	154.5	150.1
HA-1b conformer of above	−284.122151	−283.626406	46.9	163.0	159.1
HA-2a $CH_3C(OH)NHO^{\bullet +}$	−284.148324	−283.646792	48.6	150.2	145.6
HA-2b conformer of above	−284.144380	−283.642561	48.4	152.9	148.4
HA-3 $CH_3C(OH)ONH^{\bullet +}$	−284.121695	−283.624535	47.6	164.2	159.8
HA-3a conformer of above	−284.126329	−283.629495	47.6	161.1	156.6
HA-4 $CH_3C({=}O)ONH_2^{\bullet +}$	−284.144105	−283.645333	46.8	151.2	147.8
HA-5a $CH_2{=}C(OH)NHOH^{\bullet +}$	−284.135389	−283.638448	48.0	155.5	151.0
HA-5b conformer of above	−284.133062	−283.637363	47.8	156.2	151.8
HA-6 $CH_2C({=}O)NH_2OH^{\bullet +}$	−284.110470	−283.614910	48.1	170.3	165.9
HA-7 $O{=}C{=}C(H_2)NH_2OH^{\bullet +}$	−284.104738	−283.596194	46.5	182.0	178.5
HBRC-1	−284.107804	−283.609736	45.2	173.5	170.1
HBRC-2	−284.101810	−283.600772	44.3	179.1	175.8
HBRC-3	Collapses to **HA-4**				
HBRC-4	−284.051387	−283.557534	43.5	206.3	202.8
TSHA-1a → 2a	−284.128069	−283.633569	45.6	158.5	153.8
TSHA-1b → 5b	−284.057507	−283.564903	44.7	201.6	197.0
TS HA-2a → 3	−284.079590	−283.588701	46.6	186.7	181.9
TS HA-2b → 5a	−284.082397	−283.586945	45.3	187.8	182.7
TS HA-6 → 7	−284.092226	−283.589281	45.7	186.3	182.5
TS HA-1a → HBRC-1	−284.105535	−283.610176	45.4	173.2	169.5
TS HBRC-1 → 2	−284.101470	−283.601980	42.8	178.3	174.7
TS HBRC-2 → HA-4	−284.099095	−283.598089	45.3	180.8	176.9
TS HBRC-2 → HA-7	−284.096193	−283.587935	44.7	187.2	183.9
TS HA-3 → 4	−284.115422	−283.622998	45.1	165.2	160.5

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

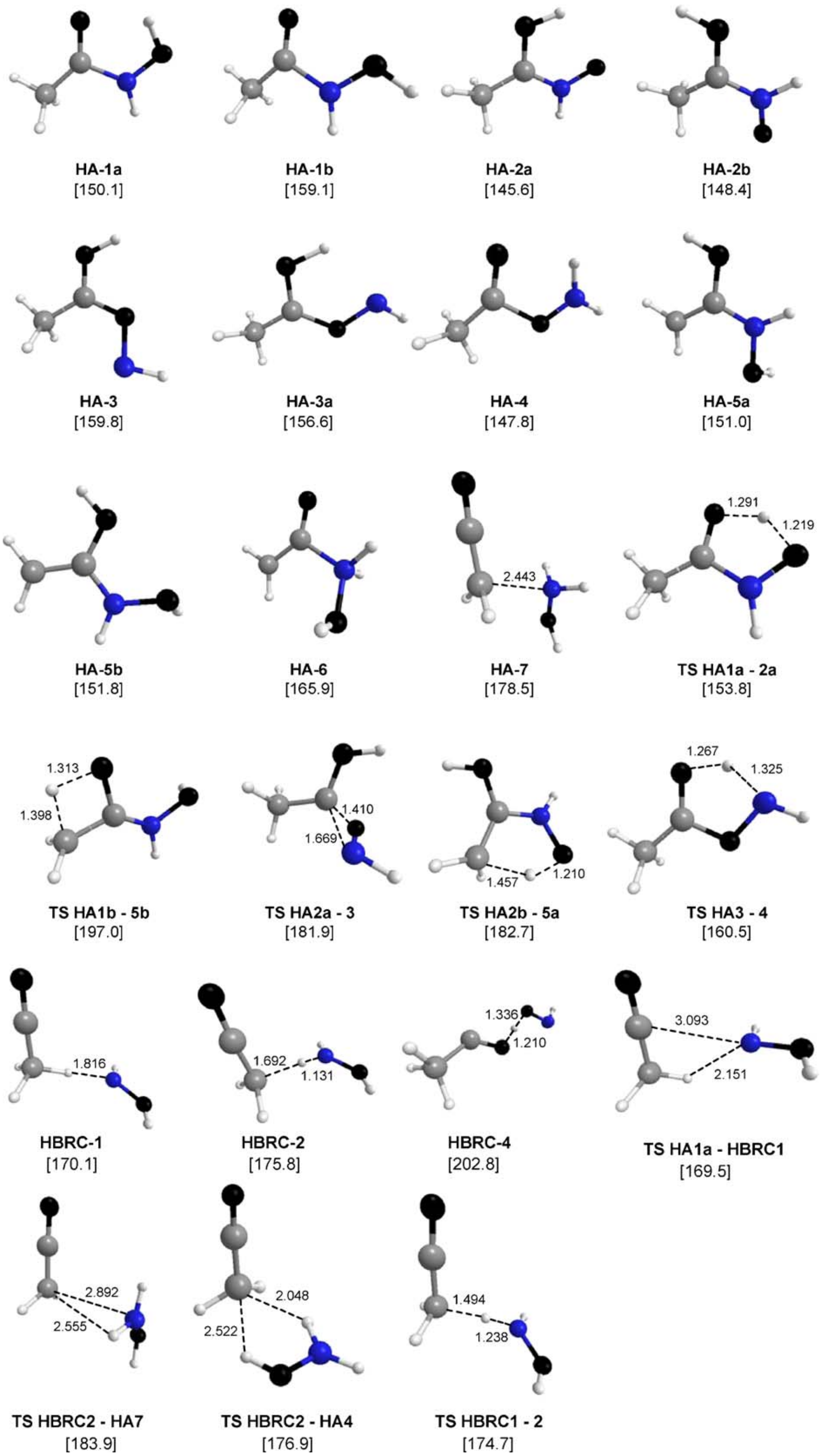
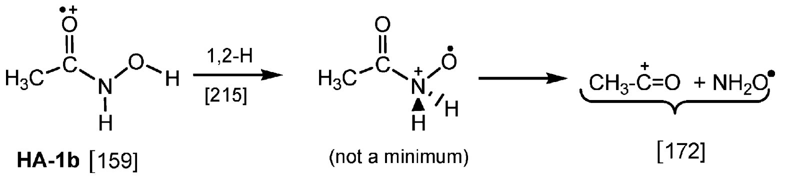
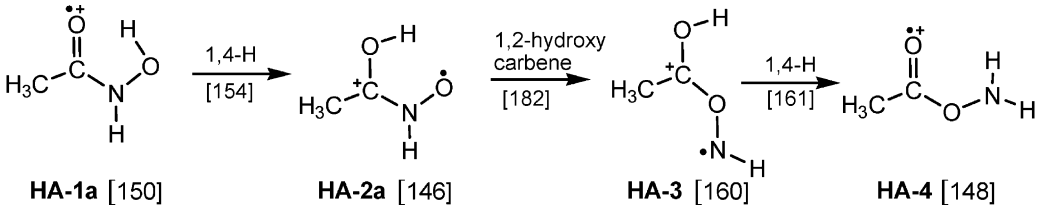


Fig. 2. Selected optimized geometries (CBSB7 basis set) for stable intermediates and transition states involved in the elimination of NH_2O from ionized *N*-hydroxyacetamide (**HA-1**).



Scheme 2.



Scheme 3.

lies at 180 kcal mol^{-1} whereas $\Delta_f H^\circ_{298}$ (**HA-1a**), the lowest energy conformer of **HA-1**, is 150 kcal mol^{-1}. Hence, a 30 kcal mol^{-1} energy window exists in which the rearrangement **HA-1** → $CH_3C{=}O^+ + NH_2O^\bullet$ occurs.

Loss of $NH_2O^\bullet$ from HA-1 clearly does not involve a simple 1,2-H shift in the NHOH moiety of the ion as depicted in Scheme 2.

The energy requirement for this shift, 56 kcal mol^{-1}, is quite high and considerably larger than that calculated for the dissociation threshold for loss of $NHOH^\bullet$ by direct bond cleavage. In fact, the transformation $NHOH^\bullet \rightarrow NH_2O^\bullet$ in the ion requires even more energy than that in the free radicals, 43 kcal mol^{-1}, see Table 1.

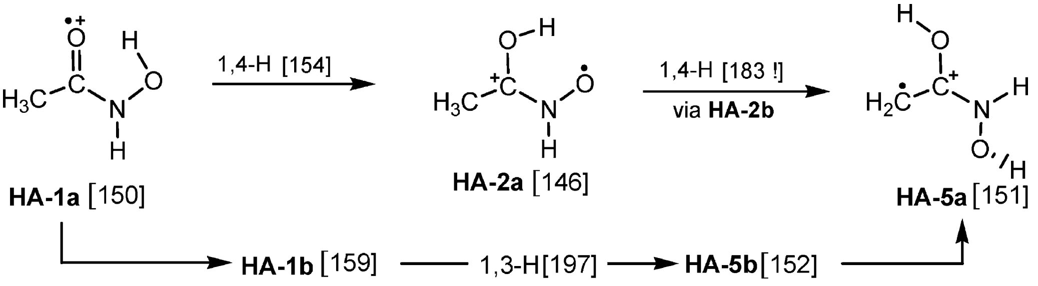
A more plausible route involves the formation of $CH_3C({=}O)ONH_2^{\bullet+}$ (**HA-4**) via a 1,2-hydroxy-carbene shift, a well-documented transformation [10,20] (Scheme 3).

A 1,4-H shift in **HA-1** yields the stable distonic isomer **HA-2a**. Next the 1,2-hydroxycarbene shift takes place yielding a second stable distonic isomer, **HA-3**. A subsequent 1,4-H shift completes the rearrangement to **HA-4** which can readily lose $NH_2O^\bullet$ by direct bond cleavage. The most energy demanding step of this route is the hydroxycarbene shift: its energy barrier slightly exceeds, by 2 kcal mol^{-1}, the thermochemical threshold for the direct bond cleavage **HA-1** → $CH_3C{=}O^+ + NHOH^\bullet$. A conservative estimate of the error in energies derived from the CBS-QB3 method is ±2 kcal mol^{-1} for local minima and ±4 kcal mol^{-1} for transition states [15] and thus from an energetic point of view this mechanism could be operative. It may rationalize the minor loss of $ND_2O^\bullet$ from $CH_3C({=}O)NDOD^{\bullet+}$ (**HA-1**d_2) but cannot easily account for the major pathway which leads to the loss of $NHDO^\bullet$. We note that H/D exchange reactions that could lead to a (partial) randomization of the label do not seem to occur. Our calculations provide a rationale: the key intermediate required for this exchange, the enol ion $CH_2{=}C(OH)NHOH^{\bullet+}$, **HA-5**, cannot readily communicate with its keto counterpart **HA-1**. The associated barriers lie higher in energy than the dissociation level for $CH_3C{=}O^+ + NHOH^\bullet$.

Note that the second 1,4-H transfer in Scheme 4 is quite energy demanding (37 kcal mol^{-1}). This has been observed previously [21] for a process involving a 1,4-H *atom* shift to a trigonal $CH_2^\bullet$ group. Starting from **HA-2**a the large barrier is associated with the change in hybridization of the methyl carbon during the 1,4-H shift, but there is a further consideration. It is a well established phenomenon that ionized enol ions lie below the keto form (by about 14 kcal mol^{-1}), but this is not so for **HA-5**, the enol ion of *N*-hydroxyacetamide. Had ion **HA-5** lain significantly below **HA-2**, then according to Hammond's principle the TS energy of the associated 1,4-H shift might well have been reduced to below the upper limit of 180 kcal mol^{-1} and H/D mixing would have ensued.

A more promising rearrangement pathway involves hydrogen bridged radical cations (HBRCs) [12] as key intermediates, as depicted in Fig. 3.

In this proposal, **HBRC-1** is generated from **HA-1** via migration of its NHOH moiety towards the methyl group of the acetyl cation, forming a C···H···N bridged species. The bridging H



Scheme 4.

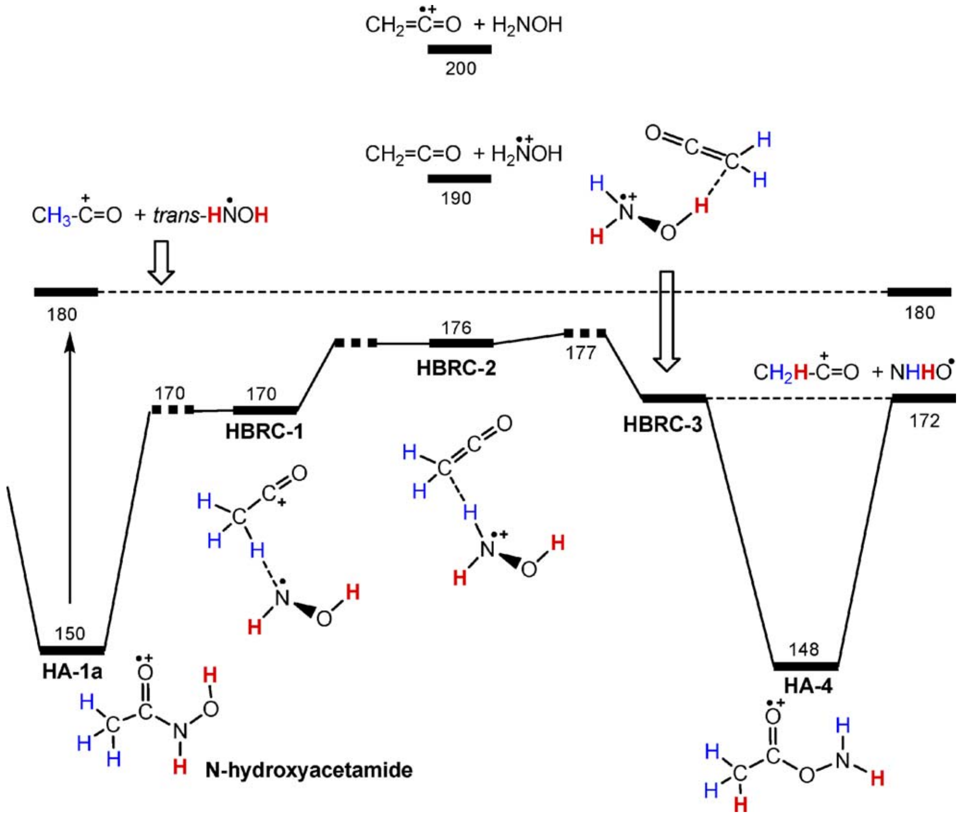


Fig. 3. Energy-level diagram derived from CBS-QB3 calculations describing the elimination of $NH_2O^\bullet$ from metastable *N*-hydroxyacetamide ions **HA-1** via a quid-pro-quo mechanism. The numbers refer to 298 K enthalpy values in kcal mol^{-1}.

is closer to the (methylic) carbon because it has the higher proton affinity. However, it can easily move towards the N(H)–OH moiety as *a proton* yielding **HBRC-2**, a hydroxylamine(ion)-ketene(molecule) complex of slightly higher energy. Hardly any additional energy is required for **HBRC-2** to rearrange into **HBRC-3**. This transformation can be viewed as the movement of the neutral ketene molecule in **HBRC-2** towards the hydroxylic H of the hydroxylamine ion. In this rearrangement the hydroxylic hydrogen *protonates* the ketene molecule transforming it into an acetyl cation. **HBRC-3** is not a minimum on the PES (the TS at 177 kcal mol^{-1} connects **HBRC-2** with ion **HA-4**) but rather a transient species that in the calculation collapses into $CH_3C(=O)ONH_2^{\bullet+}$ (**HA-4**). However, the incipient **HBRC-3** ions have internal energies in excess of that required for dissociation by direct bond cleavage and thus the transformation **HA-1** → **HBRC-1** → **HBRC-2** → **HBRC-3** → $CH_3C{=}O^+ + NH_2O^\bullet$ adequately describes the course of the reaction.

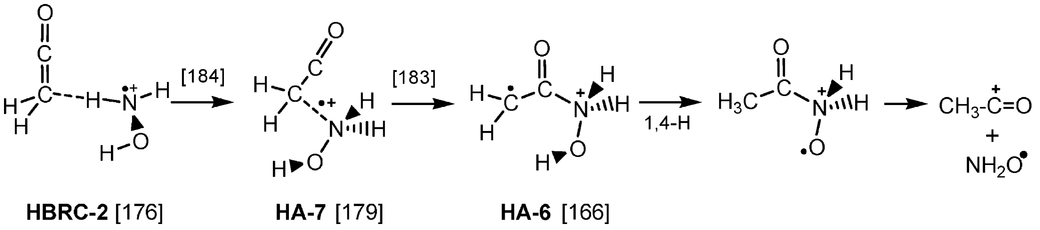
This mechanism satisfies the energetic constraint discussed above and it also readily explains the predominant loss of $NHDO^\bullet$ from metastable ions $CH_3C(=O)NDOD^{\bullet+}$ (**HA-1**d_2). It involves two *proton* transfers: first a methylic hydrogen is abstracted as a proton (**HBRC-1** → **HBRC-2**) and in the next step (**HBRC-2** → **HBRC-3**) the hydroxylic hydrogen is donated back as a proton to the methylene carbon atom of the ketene molecule. This process can be classified as a quid-pro-quo reaction. Several recent studies of (radical cat)ion-molecule reactions have reported this type of reaction [22,23] but so far it has not been shown to occur in a dissociative ionization reaction. We note that this mechanistic proposal also provides a prime example of the role of an ion in catalysing the isomerization of a neutral radical into a more stable hydrogen-shift isomer.

The quid-pro-quo transformation in the proposal of Fig. 3 could in principle also be realized via other routes. One intriguing possibility involves rearrangement of **HBRC-2** into distonic ion **HA-6** which could lose $NH_2O^\bullet$ following a 1,4-H shift as depicted in Scheme 5.

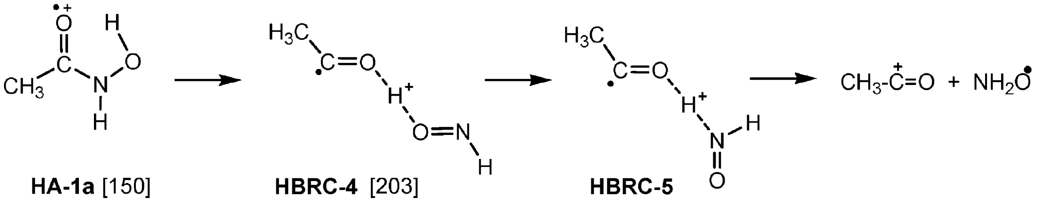
Our calculations indicate that the rearrangement of **HBRC-2** into **HA-6** can take place via intermediate ion **HA-7**, a one-electron bonded species [12] rather than an ion-dipole complex. However, the energy requirement for the route **HBRC-2** → **HA-7** → **HA-6** exceeds that of the direct dissociation **HA-1** → $CH_3C{=}O^+ + NHOH^\bullet$ so that this pathway is not a viable alternative for our proposed mechanism.

One further mechanistic proposal deserves comment. In the mechanism for loss of $CH_2OH^\bullet$ from metastable methyl acetate ions, see Introduction, $CH_3C{=}O\cdots H\cdots O{=}CH_2^{\bullet+}$ is a key intermediate. The analogue of this intermediate in the **HA-1** system is the O–H–O bridged ion **HBRC-4**. This ion could, possibly via proton-transport catalysis [12,16], rearrange into **HBRC-5** which would then dissociate into the desired products (Scheme 6).

However, the first intermediate ion of this proposal, **HBRC-4**, lies so high in energy that this route requires no further consideration.



Scheme 5.



Scheme 6.

4. Conclusions

Tandem mass spectrometry based collision experiments reveal that low energy *N*-hydroxyacetamide radical cations, $CH_3C(=O)NHOH^{\bullet+}$ **HA-1**, dissociate to $CH_3C{=}O^+ + NH_2O^\bullet$ and not to the expected $HNOH^\bullet$ radical. The mechanism of this intriguing "hidden" hydrogen rearrangement has been elucidated with the help of the CBS-QB3 model chemistry. The key transformation is comprised of the ion-catalysed rearrangement $HNOH^\bullet \rightarrow NH_2O^\bullet$ where CH_3–C=O^+ acts as the catalyst in a quid-pro-quo process. In this reaction the acetyl cation donates a *proton* to the N atom of $HNOH^\bullet$ and then the O–H *proton* of the incipient $NH_2OH^{\bullet+}$ radical cation is donated back.

In general terms, the quid-pro-quo process between a protonated molecule MH^+ and a (deuterated) substrate radical A-B-$D^\bullet$ can be represented by: $MH^+ + A\text{-}BD^\bullet \rightarrow M\cdots H^+\cdots A\text{-}BD^\bullet \rightarrow M\cdots D^+\cdots B\text{-}AH^\bullet \rightarrow MD^+ + B\text{-}AH^\bullet$. An important criterion for a smooth reaction is that the PA of M lies between the PA of A-$BD^\bullet$ at A and the PA of B-$AH^\bullet$ at B. This criterion is not met in the system of our study: from the data of Table 1 it follows that the PA of ketene (196 kcal mol^{-1}) is higher than that of both $NH_2O^\bullet$ and $NHOH^\bullet$ (179 and 186 kcal mol^{-1}, respectively). As a result the proton abstraction from CH_3–C=O^+ is endothermic so that the transformation $NHOH^\bullet \rightarrow NH_2O^\bullet$ still has a (small) barrier of 7 kcal mol^{-1}, see Fig. 3.

Finally, we note that a minor fraction of the $NH_2O^\bullet$ loss may take place via a more "classical" transformation, i.e., the well-known 1,2-hydroxycarbene shift.

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