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Experimental Evidence for the Existence of the Protonitronium Dication ($HONO^{2+}$) in the Gas Phase and ab Initio Molecular Orbital Calculations of Its Potential Energy Surface[1]

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Abstract: As conjectured by Olah et al. (*J. Am. Chem. Soc.* **1992,** *114,* 5608), the protonitronium dication ($HONO^{2+}$) is indeed a viable molecule which can be generated in the gas phase by dissociative electron impact ionization of HNO_3. Charge stripping of $HONO^{\bullet+}$ does not result in the formation of a detectable dication, as the vertical removal of an electron leads to a vibrationally hot $HONO^{2+}$ molecule which undergoes spontaneous Coulombic explosion to generate H^+ and NO_2^+. The kinetic energy release associated with this fragmentation has been determined experimentally to $T_k = 3.48$ eV. State-of-the-art ab initio MO calculations of the complete active space SCF/multireference CI type are used to calculate the relevant parts of the potential energy surface of $HONO^{2+}$, including its transition structures for the two charge separation reactions, i.e. formation of H^+/NO_2^+ and OH^+/NO^+. Special emphasis is paid to the recently described model of Gill and Radom (*J. Am. Chem. Soc.* **1988,** *110,* 5311; *Chem. Phys. Lett.* **1988,** *147,* 213) for deprotonation of dications, and a detailed analysis is provided to explain why this, otherwise useful, approach is not applicable in the present system.

The protonitronium dication (**1**, $HONO^{2+}$), the prototype of a superelectrophile,[2] is assumed to be responsible for the nitration of strongly deactivated arenes[3] as well as alkanes.[4] While lower level ab initio MO calculations indicated[5] that **1** may not correspond to a minimum, more recent HF/6-31G* and MP2/6-31G** calculations do not confirm these predictions.[6] However, attempts to experimentally observe $HONO^{2+}$ by both ^{15}NMR spectroscopy and fast IR and Raman spectroscopy of ^{15}N-enriched samples did not provide any evidence that $HONO^{2+}$ is generated in solution at a sufficiently high concentration. As conjectured by the authors,[6] extremely facile, irreversible proton transfer of the type $HONO^{2+} + B \rightarrow NO_2^+ + BH^+$ possibly explains why **1** escaped experimental verification in solution. Obviously, the method of choice is to generate **1** in the dilute gas phase under conditions which prevent the proton transfer. In fact, there is ample evidence that numerous dications can be conveniently generated and structurally characterized in the gas phase by means of mass spectrometric methods,[7] and as outlined in recent reviews,[7b,c,8] the experiments can be ideally complemented by MO calculations, provided an appropriate level of theory is employed.

In the following we will demonstrate that $HONO^{2+}$ is indeed a viable dication in the gas phase, having a *minimal* lifetime of 20 μs. In addition, the kinetic energy release (T_k) associate with the Coulombic explosion[7,8] of the reaction $HONO^{2+} \rightarrow H^+ + NO_2^+$ has been determined experimentally and related to the intercharge separation (r_{TS})[9] at the transition structure of proton loss from **1**. The experimental results have been complemented by detailed ab initio MO calculations of the relevant parts of the potential energy surface (PES) of **1** using several levels of theories. Our analysis is briefly compared with Gill and Radom's interesting model[10] of how to properly describe proton loss from a dication in the gas phase.

Experimental Section and Computational Details

The mass spectrometric experiments were carried out with a modified VG Instruments ZAB mass spectrometer. This is a four-sector machine of BEBE configuration (B stands for magnetic and E for electric sector) built by AMD Intectra of Harpstedt, Germany, by combining the BE part of a ZAB-HF-3F machine (MSI) with an AMD 604 double-focusing mass spectrometer (MSII).[11] Three different types of experiments were conducted aimed at generating $HONO^{2+}$ and also probing its Coulombic explosion: (i) $HNO_2^{\bullet+}$ was generated by evaporating NH_4NO_3 (150 °C) in the ion source and bombarding the neutrals generated with 70-eV electrons. The ions were accelerated to 8 keV, and the beam of ions with m/z 47 were mass-selected by means of B(1)E(1) at a resolution sufficient to separate any possible isobaric ions with an elemental composition different from $[NO_2H]^{\bullet+}$. Charge-stripping (CS) experiments[7a–c,12] were performed in the field-free region between E(1) and B(2) by colliding the singly charged ions $[NO_2H]^{\bullet+}$ with several stationary gases (e.g. He, O_2) at a pressure such that the primary ion beam intensity was reduced to ca. 40% transmission. Signals due to the reactions $[NO_2H]^{\bullet+} \rightarrow [NO_2H]^{2+} + e^-$ were searched for by scanning B(2) at maximal sensitivity of the instrument. (ii) Dissociative ionization of HNO_3 (generated by

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(1) Dedicated to Professor George A. Olah, an inspirational scientist and colleague, in honor of his fundamental contributions to the chemistry of electrophiles.

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evaporation of NH_4NO_3) was attempted at higher ionization energies (ca. 100 eV), and the mass spectrum of the resulting metastable $[HONO]^{2+}$ ion (MI) was recorded by scanning B(2). (iii) The kinetic energy release (T_k) associated with proton loss from $HONO^{2+}$ ("Coulombic explosion") was determined by mass-selecting the ions at *m/z* 23.5 with B(1), at 4-keV acceleration voltage, followed by scanning of E(1) in order to record the products formed in the unimolecular dissociation $HONO^{2+} \rightarrow H^+ + NO_2^+$. By using established procedures,[7] T_k was determined from the "horns" of the dished-top signal.

The geometries of the stationary points on the $^1A'$ $[NO_2H]^{2+}$ potential energy surface were initially located at the restricted Hartree–Fock level employing the triple-valence d,p-polarized 6-311G** basis set (RHF/6-311G**) and at the MP2(fc)/6-311G** level, where the effects of dynamical electron correlation were accounted for through second-order Møller/Plesset perturbation theory. At the latter level, the harmonic frequencies were obtained to characterize the stationary points as minima or as saddle points and to facilitate zero-point vibration energy (ZPVE) corrections to the relative energies. Using the MP2/6-311G**-optimized geometries, energy calculations using full fourth-order Møller/Plesset perturbation theory (MP4sdtq/6-311G**) were performed.[13] However, it turned out that the RHF/6-311G** wave function, on which the correlation treatment is based, shows an RHF → UHF instability;[14] i.e., there exists a UHF wave function for the closed-shell system with lower energy (see below). The use of unstable zeroth-order wave functions for subsequent perturbational treatments is at least questionable and may produce not only erratic relative energies but also dubious geometry data.[15] Thus, we decided to employ a multireference approach not only for the energy determinations but also for the optimization step. The geometries of the minimum and the saddle points were reoptimized using a complete active space SCF (CASSCF) wave function[16] in which the orbitals 6–12a′ and 1–3a″ were chosen to be active. The five inactive orbitals included the 1s-like orbitals on oxygen and nitrogen, 1–3a′, and orbitals 4a′ and 5a′, which describe mostly the 2s orbitals of the oxygen atoms. Thus, the active space consisted of 12 electrons distributed in 11 orbitals leading to a CI expansion of 30 744 spin- and symmetry-adapted configurations (CSF). To keep the optimizations manageable, we used the somewhat smaller split-valence, d-polarized (i.e. no p-polarization functions on H) 6-31G* one-particle basis set. Relative energies were obtained with these geometries by using a full-valence CASSCF expansion (16 electrons distributed in 4–12a′ and 1–3a″, i.e. 13 orbitals), generating a CI expansion of 216 249 CSF. The CASSCF orbitals were then subjected to multireference CI-SD (MRCI) calculations, where the four to six most important CSF's were taken as a reference. The effects of higher than double excitations were estimated using the multireference analog of the Davidson correction (MRCI + D). These CAS and MRCI calculations employed a fairly large atomic natural orbital (ANO) basis set of 4s3p2d and 3s2p quality as introduced by Taylor and Almlöf[17] and as described by Widmark et al.,[18] on O, N, and H, respectively. In order to obtain information about vertical and adiabatic ionization energies of the monocation, the $^2A'$ ground state of $NO_2H^{\bullet+}$ was treated in the same way. It could be expected on this level of approximation not only that the RHF → UHF instability problem (which essentially is an indication of the inadequacy of a one-determinant-based approach) would be resolved but also that the resulting geometry and energy data would provide an accurate description of the $[NO_2H]^{2+}$ potential energy surface. If not noted otherwise, all theoretically predicted data mentioned hereafter refer to the CASSCF geometries and MRCI + D energies. Programs employed in this study include Gaussian92[19] (Møller/Plesset calculations), Gamess[20] (CASSCF geometry determinations), and Molcas-2[21] (CASSCF and MRCI energies). All calculations were performed on an IBM RS/6000 Model 550 workstation.

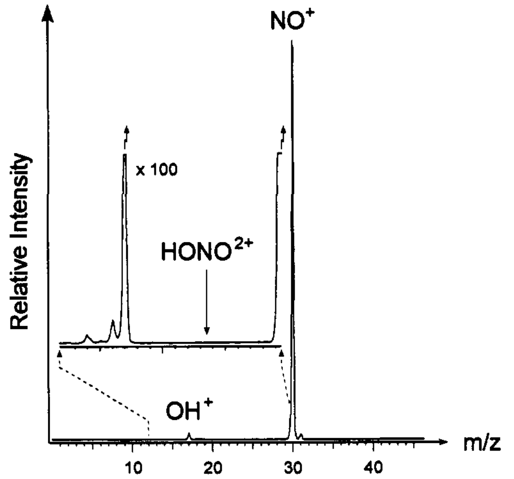

Figure 1. Collisional activation mass spectrum of B(1)E(1) mass-selected $HONO^{\bullet+}$ (B(2) scan, collision gas O_2, 40% transmission). The arrow indicates the *m/z* position at which one would expect a signal for the charge-stripping process $HONO^{\bullet+} \rightarrow HONO^{2+}$.

Results and Discussion

All attempts to generate the protonitronium dication, $HONO^{2+}$, by charge stripping of the mass-selected monocation $HONO^{\bullet+}$ failed. Irrespective of the nature of the collision gas, we were not able to observe a signal for $HONO^{2+}$ (*m/z* 23.5) at the sensitivity level of our machine (see Figure 1). However, this negative result by no means implies that $HONO^{2+}$ does not correspond to a minimum. As will be shown further below in the discussion of the potential energy surface of $HONO^{2+}$, vertical removal of an electron from $HONO^{\bullet+}$ (i.e. charge stripping) results in a vibrationally "hot" $HONO^{2+}$ dication having enough internal energy to undergo rapid proton loss prior to detection of the dication. In addition, collision-induced dissociation of $HONO^{\bullet+}$ competes with the charge-stripping process, and a typical collision spectrum for an 8-keV beam of $HONO^{\bullet+}$ collided with O_2 is given in Figure 1. In line with thermochemical data, the major process corresponds to the loss of $OH^\bullet$ to generate NO^+.

The mass spectrum obtained by bombarding HNO_3 (generated by thermolysis of NH_4NO_3) with 100-eV electrons is shown in Figure 2, and there is no doubt that the dissociative ionization of HNO_3 results in the formation of a clearly detectable signal having the elemental composition $[NO_2H]^{2+}$. As the protonitronium dication $HONO^{2+}$ is the only minimum on the singlet potential energy surface of $[NO_2H]^{2+}$,[6] we conclude that the ion at *m/z* 23.5 does indeed correspond to the long-sought-after protonitronium dication. As predicted by Olah et al.,[6] this species is indeed viable, and the failure to detect it in solution does not reflect an intrinsic instability. As already indicated by the MO calculations from the Olah group[6] and confirmed by our more detailed theoretical studies at a significantly higher level of theory, $HONO^{2+}$ is prevented by substantial barriers from undergoing spontaneous Coulombic explosion.

Dissociative ionization of HNO_3 is expected to generate $HONO^{2+}$ with a range of internal energies; consequently, one can safely predict that a fraction of the dications will undergo unimolecular dissociation. This expectation is borne out by the

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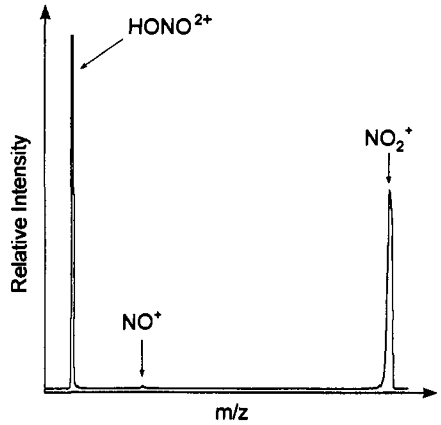

Figure 2. Metastable ion (MI) mass spectrum of B(1)E(1) mass-selected $[NO_2H]^{2+}$ ions generated by 100-eV electron impact ionization of HNO_3 (B(2) scan).

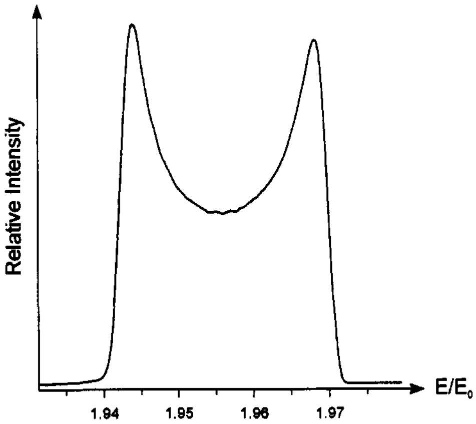

Figure 3. Kinetic energy release (T_k) associated with the process $HONO^{2+} \rightarrow H^+ + NO_2^+$ (mass selection of $[NO_2H]^{2+}$ by B(1), unimolecular reaction in the second field-free region, E(1) scan over a narrow range of electric sector voltage).

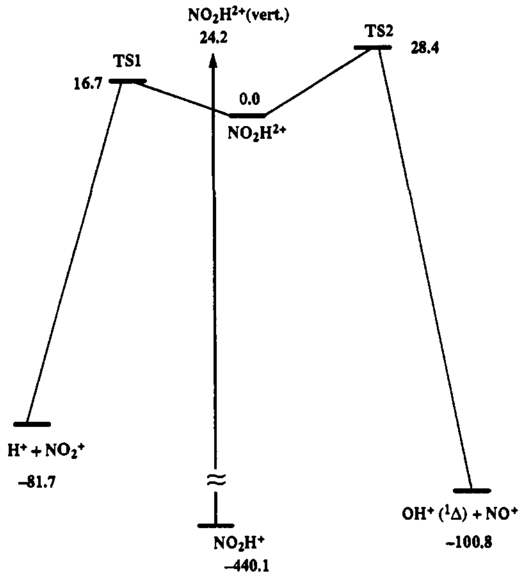

Figure 4. Schematic potential energy surface of $[NO_2H]^{2+}$ computed at MRCI + D + ZPVE. Relative energies are given in kcal/mol. Energy values are not on scale.

Table I. Results of Geometry Optimizations at MP2/6-311G** and [CASSCF/6-31G*] for $HONO^{2+}$, $HONO^{\bullet+}$, TS1, and TS2 (Distances in Å; Angles in deg)[a]

	O_1–N	N–O_2	O_2–H	O_1–N–O_2	N–O_2–H
$HONO^{2+}$	1.125	1.175	1.074	169.1	125.2
C_s $^1A'$	[1.109]	[1.196]	[1.061]	[169.8]	[120.6]
TS1	1.134	1.147	1.745	176.5	157.8
C_s $^1A'$	[1.121]	[1.154]	[1.671]	[176.1]	[151.0]
TS2	1.090	1.821	1.031	164.8	102.6
C_s $^1A'$	[1.083]	[1.752]	[1.047]	[166.3]	[102.6]
$HONO^{\bullet+}$	1.116	1.294	0.989	132.8	108.4
C_s $^2A'$	[1.154]	[1.328]	[0.997]	[124.9]	[105.4]

[a] Key: TS1, proton loss; TS2, OH^+ loss; O_1–N–O_2–H, *trans* arrangement.

MI spectrum of $HONO^{2+}$ (Figure 2), which also demonstrates that proton loss to generate NO_2^+ is favored over the loss of OH^+ to form NO^+. For the former reaction we have also determined the kinetic energy release (Figure 3), for which one obtains a value of $T_k = 3.48$ eV. On sensitivity grounds it was not possible to perform the same measurement for the OH^+ loss from 1. If one employs the suggestion of Beynon and co-workers[9] that the experimental kinetic energy release, T_k, in the fragmentation of dications can be roughly equated to $1/r_{TS}$ where r_{TS} is the intercharge separation at the transition structure, one obtains for the process $HONO^{2+} \rightarrow H^+ + NO_2^+$ an intercharge distance of 4.14 Å. This number as well as the kinetic energy release will be discussed in the next section in relation to the Gill/Radom concept[10] for proton loss in dications.

The relevant part of the PES of the $^1A'$ ground state of $[NO_2H]^{2+}$ as computed at the MRCI + D level corrected for ZPVE (computed at MP2/6-311G** and scaled by 0.95) is shown in Figure 4. The possibility of a low-lying triplet state was also examined, but the corresponding $^3A'$ minimum was some 80 kcal/mol higher in energy. According to Olah et al.,[6] merely the *trans* isomer of $HONO^{2+}$ is a minimum; neither the *cis* form nor any other $[NO_2H]^{2+}$ species could be located in their theoretical study. We thus concentrated solely on *trans*-$HONO^{2+}$. The MP2/6-311G** and CASSCF/6-31G* optimized geometries are presented in Table I while the total, relative, and ZPV energies and the weights of the MRCI reference spaces are summarized in Table II.

$HONO^{2+}$ resides in a potential well separated from the charge separation channels leading to $H^+ + NO_2^+$ ($^1\Sigma_g^+$) or OH^+ ($^1\Delta$) + NO^+ ($^1\Sigma^+$) by barriers of 16.7 (TS1) and 28.4 (TS2) kcal/mol, respectively. The former value is in good agreement with the deprotonation activation barrier of 17.0 kcal/mol obtained at RHF/6-31G*, by Olah et al.[6] (however, without ZPVE corrections). Fragmentation into $OH^+ + NO^+$ was not considered in Olah's study.[6] While proton loss is exothermic by 81.7 kcal/mol, fragmentation into OH^+ ($^1\Delta$) and NO^+ is still more exothermic, the products lying 100.8 kcal/mol below NO_2H^{2+}. It should be emphasized that, assuming spin conservation, fragmentation of singlet ($^1A'$) NO_2H^{2+} *cannot* produce $^3\Sigma^-$ ground-state hydroxyl cations. According to our calculations, the lowest accessible OH^+ state ($^1\Delta$) is 56.7 kcal/mol above the triplet ground state, followed by OH^+ ($^1\Sigma^+$), 87.7 kcal/mol above $^3\Sigma^-$ (exptl: 83 kcal/mol). Thus, only if spin–orbit coupling is small, will dissociation into singlet $OH^+ + NO^+$ take place. This is probably the case since spin–orbit interactions increase with increasing mass of the participating atoms and are usually small for first-row atoms. Even though the thermochemistry favors dissociation into the hydroxyl cation and NO^+, the computed barrier heights predict that deprotonation should be the dominant fragmentation seen in the gas phase at low internal energies of the dication, in accord with the experimental results described above.

The results presented in Figure 4 provide an immediate explanation as to why charge-stripping experiments failed in producing a signal corresponding to the target dication. Charge stripping is a very fast, i.e. vertical, ionization process, and the dication produced will initially still have the geometry of the parent monocation.[7] The computed differences in the equilibrium geometries of the singly and doubly charged HONO species are substantial, as evidenced from the data in Table I. Removal of

Table II. Total (hartrees), Relative, and ZPV (kcal/mol) Energies of $HONO^{2+}$

	$HONO^{2+}$	TS1	TS2	$HONO^{2+\,e}$	$HONO^{\bullet+}$
RMP2/6-311G**	−204.206 86	−204.177 79	−204.116 05	N/A	−204.884 79
rel energy	0	18.2	57.0	N/A	−425.4 = −18.4 eV
RMP4/6-311G** [a]	−204.236 57	−204.207 55	−204.157 78	−204.193 48	−204.918 46
rel energy	0	18.2	49.4	27.0	−427.9 = −18.4 eV
CAS/6-31G*	−203.803 08	−203.776 87	−203.752 08	N/A	−204.466 65
rel energy	0	16.4	32.0	N/A	−416.4 = −17.9 eV
CAS/ANO[b]	−203.916 61	−203.877 80	−203.868 46	−203.861 70	−204.569 05
rel energy	0	24.3	30.2	34.5	−409.4 = −17.6 eV
MRCI + D[b]	−204.258 45	−204.225 54	−204.210 33	−204.202 19	−204.964 71
no. of ref CSF	4	6	6	4	3
weight of ref, %	89.6	89.7	89.6	88.8	88.7
rel energy	0	20.7	30.2	35.3	−443.2 = −19.1 eV
ZPVE[c]	11.1	7.1	9.3	N/A	14.2
"best"[d] E_{rel}	0	16.7	28.4	24.2	−440.1 = −19.0 eV

[a] At RMP2/6-311G**-optimized geometries. [b] At CASSCF/6-31G*-optimized geometries. [c] At RMP2/6-311G**, scaled by 0.95. [d] MRCI + D corrected for ZPVE. [e] Geometry of $HONO^{\bullet+}$.

an additional electron from $HONO^{\bullet+}$ leads to a significant shortening of the N–OH bond from 1.328 to 1.196 Å with concomitant opening of the bond angles of 15.2 and 44.9° for the N–O–H and O–N–O angles, respectively. The total energy of the dication computed at the equilibrium geometry of the monocation is 24.2 kcal/mol above the zero point of the ground state and even 7.5 kcal/mol above the zero-point vibration energy of the deprotonation barrier (TS1). Thus, the so-produced dication is highly vibrationally excited and will within a few vibrations decompose into H^+ and NO_2^+, preventing its experimental detection.

As already mentioned under Computational Details, the RHF wave functions of all three stationary points investigated on the $[NO_2H]^{2+}$ PES showed an RHF → UHF instability, rendering the use of standard one-determinant-based theoretical methods questionable. It was recently pointed out by Gill and Radom[10] in their discussion of proton loss reactions in dications that RHF wave functions of closed-shell dications AH^{2+} often exhibit this problem, particularly if the difference Δ in ionization energies of H and A^+ is small. In the course of the deprotonation reaction, the hydrogen departs initially as a hydrogen atom, i.e. in a homolytic way. Only at a later stage of the reaction does electron transfer take place to yield the usually energetically favored $A^+ + H^+$ charge-separated dissociation limit. This situation resembles the fundamental inability to describe the homolytic H_2 dissociation in the RHF/SCF scheme. A UHF wave function does partly remedy the situation since it allows dissociation toward the correct energetic limit of two hydrogen atoms but for the price of a highly triplet-contaminated wave function.[22] For the $HONO^{2+}$ species the RHF → UHF instability is only modest for the proton loss saddle point TS1, as indicated by the small $\langle S^2 \rangle$ expectation value of 0.236 of the UHF wave function and an energy lowering of only 0.8 kcal/mol. The effect is much larger for TS2 where $\langle S^2 \rangle$ assumes a value of 0.959 and the energy lowering, on going from RHF to UHF, is as large as 33.9 kcal/mol! Even the minimum structure is not RHF stable, but a lower UHF wave function with $\langle S^2 \rangle = 0.380$ exists, being 2.7 kcal/mol more favorable than the RHF solution (all stability tests performed at the RMP2/6-311G** optimized geometries). The most appropriate way to address such problems is the use of multiconfigurational SCF schemes such as the CASSCF approach adopted here. For all three $HONO^{2+}$ species, the CASSCF and MRCI expansions revealed that besides the Hartree–Fock configuration at least three other configurations have coefficients larger than 0.1, mostly describing double excitations from the highest a′ and a″ orbitals into the respective lowest virtual orbitals of the HF configuration. The data shown in Table I reveal, however, that the use of unstable wave functions for the RMP2 geometry optimizations did not have a significant effect on the structural data. The CASSCF/6-31G* optimized structures are similar to the RMP2/6-311G** ones; only in the saddle points are the bonds being broken computed to be shorter by some 0.07 Å at the CASSCF level. Since the differences in geometries between MP2/6-311G** and CASSCF were only minor, we still used the harmonic frequencies determined at the former level for estimating the ZPVE contributions. That the RHF wave function of TS2 is indeed flawed is demonstrated by the relative energies computed at MP4/6-311G** and CASSCF/MRCI, respectively. It is known that the validity of restricted Møller/Plesset energies based on wave functions which are unstable with respect to becoming UHF is questionable.[15] MP4/6-311G** yields a barrier height of 49.4 kcal/mol (using the ANO 4s3p2d/3s2p basis set gives 46.9 kcal/mol), while the barrier shrinks dramatically to 29.7 kcal/mol using the CASSCF/MRCI approach (but using the same RMP2/6-311G** optimized geometry). For TS1, where only moderate instability is found, no significant effect on the energy is observed, in accord with the analysis given in ref 15.

The semiquantitative avoided-crossing model for describing dicationic fragmentation of Gill and Radom[10] (which is actually an extension of a model first introduced by Dorman and Morrison[23]), where in AB^{2+} an avoided crossing between a repulsive state correlating with $A^+ + B^+$ and an attractive state correlating with $A^{2+} + B$ is responsible for the fragmentation barrier, allows an estimation of the transition structure bond length r_{TS} as the point where the two diabatic curves cross as $r_{TS} \approx \Delta(AH^{2+})$.[10,24] In combination with the suggestion of Beynon and co-workers[9] that the experimental kinetic energy release in the fragmentation of dications can be roughly equated to $1/r_{TS}$ (see above), Gill and Radom[10,24] arrive at the following equation for the kinetic energy release of deprotonation reactions of dicationic hydrides as a function of the Δ parameter:

$$T_k \approx 1/r_{TS} \approx \Delta(AH^{2+}) = E(A^{2+}) + E(H) - E(A^+) - E(H^+) = IE(A^+) - 13.60 \text{ eV}$$

The whole model and thus also this equation are, however, only valid as long as Δ is small, less then 2–3 eV, due to the

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(22) See, e.g., the dicussion in: Szabo, A.; Ostlund, N. S. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*; Macmillan: New York, 1982; Chapter 3.5.

(23) Dorman, F. H.; Morrison, J. D. *J. Chem. Phys.* **1961**, *35*, 575.

(24) Gill, P. M. W.; Radom, L. *Chem. Phys. Lett.* **1987**, *136*, 294.

complete neglect of coupling between the diabatic potential curves.[25] The computed adiabatic ionization energy of $HONO^{\bullet+}$ amounts to 19.0 eV, and $\Delta = 5.4$ eV. Thus, it falls outside the validity of the Gill/Radom equation.[26] The measured kinetic energy release of 3.48 eV is indeed some 2 eV lower than Δ, but still in the same ballpark. What should be less affected by the magnitude of Δ is the first relation in the equation, i.e., Beynon's suggestion[9] that $T_k \approx 1/r_{TS}$. The underlying idea is that at the saddle point the charge on the incipient fragments is close to unity and that the kinetic energy release is essentially the Coulombic repulsion of the two charges. With $T_k = 3.48$ eV an intercharge separation of 4.14 Å is estimated. However, while this relation can be easily applied to diatomic dications, we are now faced with the problem of defining the intercharge separation for polyatomic molecules. The computed O–H bond length in TS1 is 1.671 Å, but the center of charge is certainly shifted toward the other end of the ONO fragment. A reasonable value of r_{TS} could thus be around 3 Å. The agreement is not perfect but, considering the at best semiquantitative nature of the Beynon suggestion, acceptable. In addition, the departing hydrogen is certainly not a pure proton at the saddle point. Actually, the Mulliken partial charge of H as computed from the MRCI wave function is +0.9 and not +1.

Conclusion

Unequivocal evidence has been presented that the protonitronium dication, $HONO^{2+}$, is indeed a metastable molecule in the gas phase with a minimal lifetime of 2×10^{-5} s. However, the dication can only be produced from dissociative electron impact ionization of suitable neutral precursors (here HNO_3). Direct generation through ionization of the $HONO^+$ monocation via a charge-stripping process is not possible due to unfavorable Franck/Condon factors: The so-generated dication is highly vibrationally excited and dissociates within a few vibrations. The experimental findings are supported and complemented by ab initio calculations employing highly correlated wave functions. The analysis of the theoretical results reveals that, due to the peculiar character of the charge separation fragmentation reactions in dications, the widely used approach of employing many-body perturbation theory based on one single determinant to account for electron correlation is not suitable here, even though all stationary points are closed-shell singlets. A consistent picture can only emerge if multireference-based schemes, such as CASSCF/MRCI, are chosen.

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(25) (a) Gill, P. M. W.; Radom, L. *Chem. Phys. Lett.* **1986**, *147*, 213. (b) For a critical discussion and an alternative interpretation, see: Senekowitsch, J.; O'Neil, S.; Meyer, W. *Theor. Chim. Acta* **1992**, *84*, 85.

(26) For polyatomic dications, Gill and Radom use $\Delta' = \Delta - \delta$, where δ is the difference between the vertical and the adiabatic electron affinities of A^+. This has been omitted here, since this correction will certainly not alter the result that Δ (or Δ') > 2–3 eV.