Helionitronium trication (NO_2He^{3+}) and helionitrosonium trication ($HeNO^{3+}$)

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Contributed by George. A. Olah, February 2, 1999

ABSTRACT The structures and stabilities of helionitronium trication NO_2He^{3+} and helionitrosonium trication $HeNO^{3+}$ were calculated at the *ab initio* MP2/6–31G** level. The C_s symmetry structure was found to be a minimum for the NO_2He^{3+} trication, which is isoelectronic and isostructural with the previously studied NO_2H^{2+}. Dissociation of the C_s symmetry structure into NO^+ and OHe^{2+} is thermodynamically preferred by 183.1 kcal/mol (1 cal = 4.18 J), although a kinetic barrier of 12.4 kcal/mol has to be overcome. The $C_{\infty v}$ symmetry structure was also found to be a minimum for the $HeNO^{3+}$ trication.

Nitronium ion (NO_2^+) is the electrophile in the acid-catalyzed nitration of aromatics and activated aromatics with nitric acid (1, 2). Superelectrophilic (3) protonitronium dication (NO_2H^{2+}), on the other hand, is responsible for nitration of highly deactivated aromatics with $NO_2^+BF_4^-$ in superacids, as shown by Olah *et al.* (4–7). Lower level calculations carried out by Simonetta (8) on the protonitronium dication indicated that the dication may not correspond to a minimum. However, our HF/6–31G*, MP2/6–31G**, and B3LYP/6–31G** levels calculations show that NO_2H^{2+} corresponds to a minimum (9, 10). Schwarz *et al.* (11) were indeed able to generate NO_2H^{2+} in the gas phase by dissociative electron impact ionization of HNO_3. The ^{17}O NMR studies of nitronium ion in strong acid media have also been reported (10). The ^{17}O NMR line broadening of nitronium ion peak in HSO_3F:SbF_5 has been attributed to proton exchange involving protonitronium dication NO_2H^{2+} (10).

Similar to NO_2^+, NO^+ can also be acitivated to give superelectrophilic protonitrosonium dication in superacids (12). Calculations show that only the N-protonated form HNO^{2+} corresponds to a stable minimum and the O-protonated form is unstable and dissociates into the nitrosonium ion and a proton (12).

The structures and stabilities of helium-containing polyatomic ions (13) were calculated by Wilson *et al.* (14, 15), Schleyer *et al.* (16), Koch and Frenking (17, 18), and Radom *et al.* (19). Unencumbered He^{2+} is an even stronger acid than H^+.[‡] *Ab initio* calculations show that helium is capable of forming strong bonds with carbon in cations such as in $HeCCHe^{2+}$, as reported by Koch and Frenking (17, 18). Schleyer *et al.* (16) first calculated the quadruply charged tetraheliomethane tetracation CHe_4^{4+}. Radom *et al.* have also presented theoretical evidence for the remarkable stability of CHe_4^{4+} (19). Olah *et al.* have also reported *ab initio* calculations that show that helium is capable of forming strong bond with carbon in heliomethonium dication CH_4He^{2+}.

In continuation of our study of protonated onium dications (superelectrophiles) (3) we have now extended our theoretical investigations to helionitronium trication (NO_2He^{3+}) and helionitrosonium trication ($HeNO^{3+}$) and report our findings.
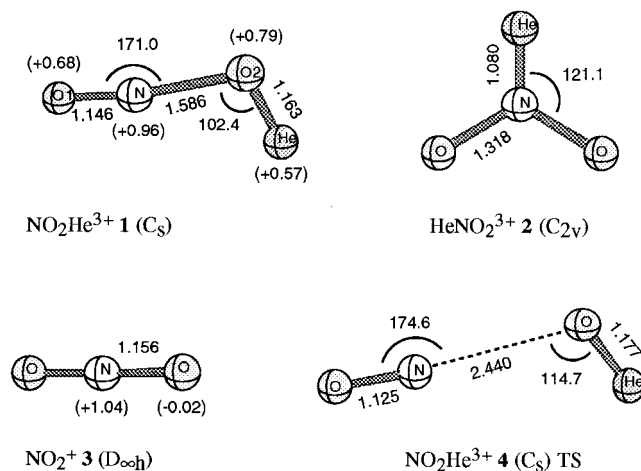
FIG. 1. Calculated structures of **1–4** (calculated NBO charges).

RESULTS AND DISCUSSION

Geometry optimizations and frequency calculations were carried out by *ab initio* method using the correlated MP2/6–31G** level (20). From calculated frequencies, the optimized structures were characterized as minima, saddle point, or transition structure. The Gaussian-2 (G2) method (21) was used for accurate energy calculations. The G2 theory is a composite method based on MP2(FU)/6–31G* geometry that is treated in single-point calculations with a variety of basis sets at the post-self-consistent field level. Atomic charges at the MP2/6–31G**//MP2/6–31G** were obtained by using the natural bond orbital analysis (22) (NBO) method.

NO_2He^{3+}. The C_s structure **1** and C_{2v} structure **2** (Fig. 1) were found to be minima on the potential energy surface of NO_2He^{3+} at the MP2/6–31G** level as indicated by frequency calculations (no. of imaginary frequencies = 0) at the same level. Calculated energies and frequencies are listed in Table 1 and Table 2, respectively. With the G2 theory, helium oxygen bonded **1**, however, was found to be 99.3 kcal/mol (1 cal = 4.18 J) more stable than helium nitrogen bonded **2**. Calculated structure of **1** and **2** together with NO_2^+ **3** are given in Fig. 1.

The structure **1** is characterized by a long N—O_2 (1.586 Å) bond. This is 0.430 Å longer than N—O bond of NO_2^+ **3**. The O—He bond distance is 1.163 Å, which is slightly longer than that of calculated He_2O^{2+} (1.148 Å) (16). This observation indicates that helium is strongly bonded to the oxygen of **1**. The O1—N—O2 bond angle is 171.0°. The trication **1** is isoelectronic with protonitronium dication NO_2H^{2+}. The trication **1** is also isostructural with the previously calculated structure of NO_2H^{2+} (9, 10).

Table 1. Total energies (Hartree) and relative energies

Structure	Ion	MP2/6-31G** (ZPE)	G2	Relative energy, kcal/mol
1	NO_2He^{3+}	204.98651 (6.6)	205.26923	0.0
2	NO_2He^{3+}	204.88682 (11.7)	205.11102	99.3
3	NO_2^+	204.23933 (6.7)	204.48421	492.6
4	NO_2He^{3+} (TS)	204.96464 (5.3)		12.4†
	OHe^{2+}	76.00562 (1.9)	76.16218	
5	$HeNO^{3+}$	129.73938 (6.2)	129.85375	0.0
6	NO^+	129.24259 (2.8)	129.39888	285.4

Zero point vibrational energies (ZPE) are at MP2/6-31G**//MP2/6-31G** level scaled by a factor of 0.93. Relative energies based on G2. †Based on MP2/6-31G**//MP2/6-31G** + ZPE with G2, self-consistent field values did not converge.

The NBO charge calculations (Fig. 2) show that the helium atom of **1** bears less positive charge than any of the oxygen or nitrogen atoms. The nitrogen atom of trication **1** bears almost the same positive charge as the nitrogen atom of the nitronium monocation NO_2^+ **3**. This observation shows that in the reaction NO_2^+ **3** + He^{2+} → NO_2He^{3+} **1**, most of the charges from helium transfer to the oxygen atoms of **1**. These results also show that the unusually long N—O2 (1.586 Å) bond is probably due to charge–charge repulsion.
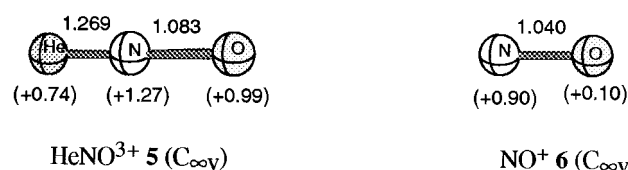
Two possible dissociation paths for the ion **1** were considered, and their energetics were calculated with the G2 method. The dissociation into NO^+ and OHe^{2+} was calculated to be exothermic by 183.1 kcal/mol. We also have located a transition structure, **4** (Fig. 1), for the dissociation process. Structure **4** lies 12.4 kcal/mol higher in energy than **1**. Thus, **1** has considerable kinetic barrier for such dissociation. In comparison, the barrier toward such a dissociation of protonitronium dication NO_2H^{2+} into NO^+ and OH^+ was calculated to be 38.5 kcal/mol. Another possible dissociation of **1** into NO_2^+ **3** and He^{2+}, however, was calculated to be highly unfavorable (endothermic by 492.6 kcal/mol).

$HeNO^{3+}$. Two possible structures, N-heliated and O-heliated forms, can be considered for the helionitrosonium trication. The N-heliated $C_{\infty v}$ structure **5** (Fig. 2) was found to be a minimum on the potential-energy surface of $HeNO^{3+}$ at the MP2/6–31G** level, as indicated by their frequency calculations at the same level. The O-heliated structure is unstable, and dissociate to the NO^+ **6** and He^{2+}. Similar to O-heliated structure, the O-protonated nitrosonium dication NOH^{2+} is also unstable and dissociates into the NO^+ **6** and H^+ on optimization (12). The N—He bond distance of **5** is 1.269 Å, 0.106 Å longer than O—He bond in **1**. The N—O (1.083 Å) bond is 0.043 Å longer than N—O bond in NO^+ **6**. Calculated NBO charges of **5** and **6** are given in Fig. 2. The dissociation

FIG. 2. Calculated structures of **5** and **6** (calculated NBO charges).

of **5** into NO^+ **3** and He^{2+} was calculated to be also highly unfavorable (endothermic by 285.4 kcal/mol).

Present *ab initio* molecular orbital study shows that the helionitronium trication NO_2He^{3+} **1** is a minimum on its potential energy surface. Its dissociation into NO^+ **6** and OHe^{2+} is thermodynamically preferred by 183.1 kcal/mol, although a kinetic barrier of 12.4 kcal/mol has to be overcome. In structure **1**, helium is strongly bonded to the oxygen. Similarly, helionitrosonium trication $HeNO^{3+}$ **5** also was found to be a stable minimum on the potential energy surface of $HeNO^{3+}$.

Table 2. MP2/G-31G** calculated frequencies and IR intensities

Structure	Frequencies, cm^{-1} (IR intensities in K_m/mol)
1	330 (0); 339 (8); 415 (19); 807 (2); 1,347 (40); 1.706 (190)
2	562 (40); 643 (80); 916 (1); 1,269 (26); 2,421 (328); 3,015 (1,351)
4	i236† (268); 248 (2); 257 (1); 379 (7); 1,330 (112); 1,754 (968)
5	800 (1); 1,256 (160); 1,777 (16)

†Imaginary frequency.

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