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H_2Te_2 Is Stable in the Gas Phase

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Hydrogen peroxide, HOOH, has a strongly oxidizing nature and is consequently widely used as an oxidant in the chemical industry. HSSH has been obtained by cracking and fractionating of higher sulfanes.[1] "Although the sulfanes are all thermodynamically unstable with respect to the reaction

$$H_2S_n(l) = H_2S(g) + (n-1)S(s)$$

these reactions, which are believed to be free-radical in nature, are sufficiently slow for the compounds to be stable for considerable periods."[2] Indeed, the photoelectron spectrum of HSSH has been reported.[3] Experimental data concerning the properties of the higher homologues, HSeSeH and HTeTeH, are rather limited, due to the species' high tendency toward dissociation into H_2Se + Se and H_2Te + Te, respectively. It has been suggested that HTeTeH is formed at the tellurium cathode in 0.003–0.02 N HCl solutions, but the evidence is not conclusive.[4] HTeTeH has been the subject of two theoretical studies.[5,6] The optimized structure in the most recent study[6] has a TeTeH angle of only 72° and a dihedral angle of 76°. The cis and trans rotational barriers were calculated to be only 13 and 6 $kJ \cdot mol^{-1}$, respectively. These data suggest (i) that the potential energy curve is rather flat around the minimum and (ii) that the structural deformation required for dissociation into H_2Te + Te or H_2 + Te_2 is remarkably small. No data have been presented regarding the stability of HTeTeH relative to the dissociation products H_2Te + Te or H_2 + Te_2. In this communication, the gas-phase stability of HTeTeH will be examined. If stable HTeTeH can be produced in large quantities, it could be used for creating high-quality Te optical recording films in a glow discharge device and as a precursor for gas-phase deposition of tellurium in the semiconductor industry.

Neutralization–reionization (NR) mass spectrometry[7] has established itself as an effective technique for examining the stability of supposedly marginally stable species in the gas phase. For example, NR mass spectrometry has been used to show that species such as carbonic acid, H_2CO_3,[8] and O=C=C=S,[9] which have eluded direct observation in solution, are stable in the gas phase. In the NR mass spectrum, a recovery signal at the same m/z value as that of the mass-selected ions usually indicates that the neutral counterparts of the mass-selected ions are stable on the microsecond time scale of neutralization–reionization experiments.

All metastable ion (MI) and collision-induced dissociation (CID) mass spectra were recorded with a VG Analytical ZAB-2F mass spectrometer of reversed geometry (BE).[10] Samples were introduced via the direct insertion probe, and 70-eV electrons were used for ionization. The source temperature was 150 °C. MI and CID mass spectra were recorded using procedures described in detail in ref 11. The CID mass spectra were obtained using He as the target gas, and the gas pressure was adjusted to give a main ion beam transmission of 80%. The NR mass spectra were obtained with a VG Analytical ZAB-R[12] at McMaster University. *N*,*N*-Dimethylaniline was the neutralization gas and O_2 the reionization gas (80% transmission for both compounds). All results presented here refer to ions containing two ^{130}Te atoms, the heaviest isotope of Te. Although this is not the most abundant combination for two Te atoms, the signals due to ions containing two ^{130}Te atoms are isotopically pure and are not contaminated by isobaric ions having a different atomic composition.

The first step in the synthesis of di-*sec*-butylditellurium, $CH_3CH_2CH(CH_3)$-Te-Te-$CH(CH_3)CH_2CH_3$, was addition of sodium to liquid ammonia. After the sodium was completely dissolved, tellurium was added. Addition of *sec*-butyl bromide to this solution gave $CH_3CH_2CH(CH_3)$-Te-Te-$CH(CH_3)CH_2CH_3$. Analysis of the product via ^{13}C and ^{125}Te NMR and mass spectrometry confirmed the structure and showed no detectable impurities.

The high-resolution mass spectrum of $CH_3CH_2CH(CH_3)$-Te-Te-$CH(CH_3)CH_2CH_3$ displays intense signals corresponding with the molecular ion, $C_4H_{10}Te_2^{\bullet+}$, $He_2Te_2^{\bullet+}$, and $Te_2^{\bullet+}$ (loss of one C_4H_8 molecule, loss of two C_4H_8 molecules and loss of one C_4H_8 plus one C_4H_{10} molecule, respectively). The $H_2Te_2^{\bullet+}$:$Te_2^{\bullet+}$ ratio is 58:42. Loss of Te from the molecular ions is not observed. This behavior contrasts with that of other ditellurium compounds such as diphenylditellurium, ditolylditellurium, di-(α,α'-naphthyl)ditellurium, and di-(β,β'-naphthyl)ditellurium.[13] The mass spectra of the latter compounds display intense signals due to loss of one and two Te atoms.

The molecular ions of $CH_3CH_2CH(CH_3)$-Te-Te-$CH(CH_3)CH_2CH_3$ lose butene metastably. The [M − butene]$^{\bullet+}$ ions lose butene and butane metastably in the ratio 10:8. The fragment ions due to the loss of two butene molecules must have the formula $H_2Te_2^{\bullet+}$, which is confirmed by accurate mass measurements. The MI mass spectrum of these $H_2Te_2^{\bullet+}$ ions is dominated by H_2 loss. Thermodynamic data from ref 14 show that H_2 loss is more favorable than $HTe^{\bullet}$, H_2Te, and Te loss:

$$
\begin{array}{ll}
H_2Te_2^{\bullet+} \rightarrow & \\
\quad Te_2^{\bullet+} + H_2 & \sum \Delta H_f(\text{products}) = 933\ kJ \cdot mol^{-1} \\
\quad HTe^{+} + HTe^{\bullet} & \sum \Delta H_f(\text{products}) = 1163\ kJ \cdot mol^{-1} \\
\quad Te^{\bullet+} + H_2Te & \sum \Delta H_f(\text{products}) = 1166\ kJ \cdot mol^{-1} \\
\quad H_2Te^{\bullet+} + Te & \sum \Delta H_f(\text{products}) = 1179\ kJ \cdot mol^{-1}
\end{array}
$$

The CID mass spectrum of the $H_2Te_2^{\bullet+}$ ions is shown in Figure 1a. Since the HTe^{+} signal is much more intense than the $Te^{\bullet+}$ signal and no $H_2Te^{\bullet+}$ is observed, we assume that these ions have

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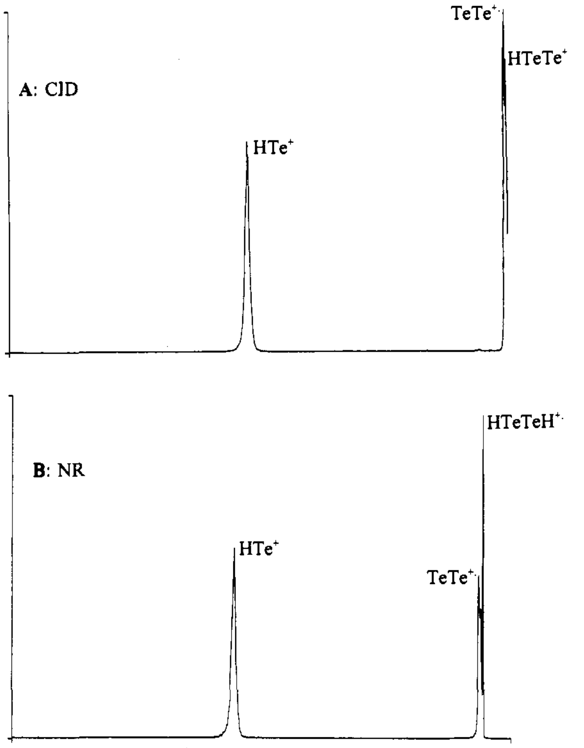

Figure 1. (A) Collision-induced dissociation mass spectrum of the $H_2Te_2^{\bullet+}$ ions from di-*sec*-butylditellurium. (B) Neutralization–reionization mass spectrum of the $H_2Te_2^{\bullet+}$ ions from di-*sec*-butylditellurium.

the H–Te–Te–H structure.[15] Based on the CID mass spectrum, the H_2TeTe structure is unlikely. Next, the $HTeTeH^{\bullet+}$ ions were mass selected and subjected to neutralization–reionization (see Figure 1b). An intense recovery signal proves unequivocally that vertical neutralization of these $HTeTeH^{\bullet+}$ ions leads to species which are stable on the microsecond time scale of neutralization–reionization experiments and which we propose to be HTeTeH.[16] Moreover, the NR mass spectrum resembles the CID spectrum quite closely, which indicates that isomerization into structures such as H_2TeTe is unlikely during the neutralization–reionization process. Thus, neutralization–reionization experiments have demonstrated that HTeTeH, the tellurium analogue of hydrogen peroxide, is stable in the gas phase.

The molecular ions of di-*sec*-butylditellerium were examined as well. Neutralization–reionization gave a spectrum which contains the same fragment ions as the CID mass spectrum (loss of one and two butene molecules). However, obviously more extensive fragmentation occurs in the NR mass spectrum, giving rise to low molecular weight fragment ions, such as $C_4H_9^+$. Careful analysis of the recovery signal indicates that the $CH_3CH_2CH(CH_3)\text{-}Te\text{-}Te\text{-}CH(CH_3)CH_2CH_3^{\bullet+}$ ions survive neutralization–reionization intact. The NR mass spectrum of the $[M - \text{butene}]^{\bullet+}$ ions suggests that the neutral counterparts of these ions, which we propose to be $H\text{-}Te\text{-}Te\text{-}CH(CH_3)CH_2CH_3^{\bullet+}$, are stable as well.

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(15) The term "structure" in mass spectrometry terminology is normally used to denote the connectivity of the atoms instead of the exact three-dimensional geometry of the ion.

(16) One of the reviewers suggested that the recovery signal might be due to $^{130}Te_2^{\bullet+}$ (*m/z* 260) instead of $H_2{}^{130}Te_2^{\bullet+}$ (*m/z* 262), because of incomplete mass separation by the magnet (low-resolution conditions are used for neutralization–reionization experiments to obtain maximum signal strength). However, this possibility can be excluded. If a trace amount of $^{130}Te_2^{\bullet+}$ caused the intense recovery signal in the NR mass spectrum of *m/z* 262, the NR efficiency of $Te_2^{\bullet+}$ must be several orders of magnitude higher than that of $H_2Te_2^{\bullet+}$. Consequently, the NR mass spectrum of *m/z* 260 should be dominated by the $^{130}Te_2^{\bullet+}$ recovery signal, since 28% of the *m/z* 260 ions are $^{130}Te_2^{\bullet+}$ (72% is $H_2{}^{128}Te^{130}Te^{\bullet+}$). However, the *m/z* 262:261:260 and *m/z* 260:259:258 ratios in the NR mass spectra of *m/z* 262 and 260, respectively, are quite close: *m/z* 262:261:260 = 100:40:50 and *m/z* 260:259:258 = 100:29:35. Thus, the scenario suggested by the reviewer can be excluded. The hydrogen loss signals at *m/z* 261 and 260 and virtually all of the *m/z* 262 recovery signal in the NR mass spectrum of *m/z* 262 can be assigned to $H_2{}^{130}Te_2^{\bullet+}$, and the contribution from $^{130}Te_2^{\bullet+}$ must be minimal. The slight relative increase of the recovery signal in the NR mass spectrum of *m/z* 260 compared to that of *m/z* 262 is most likely due to neutralized and reionized $^{130}Te_2^{\bullet+}$.