Two-Center Three-Electron Bonding Involving Tellurium

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The first known experimental studies of two-center three-electron bonding involving tellurium in the gas, liquid, or solid state are reported. Ions studied include: $[(CH_3)_2Te\therefore Te(CH_3)_2]^+$, $[(CH_3)_2Te\therefore Se(CH_3)_2]^+$, $[(CH_3)_2Te\therefore S(CH_3)_2]^+$, and $[(CH_3)_2Te\therefore ICH_3]^+$. Metastable and collision-induced dissociation tandem mass spectrometry methods were employed to investigate the structures of the ions. The metastable spectra show direct cleavage of the Te∴Te, Te∴Se, Te∴S, and Te∴I bonds yielding product ions with the charge on the Te containing moiety (that with the lowest ionization energy). Collision-induced dissociation spectra show intense peaks for these same fragments. The collision-induced dissociation spectra also show peaks for almost every possible methyl loss, suggesting large collision-induced dissociation cross sections for the methyl losses and/or weak Te−CH_3, Se−CH_3, S−CH_3, and I−CH_3 bonds. These spectra are consistent with Te∴Te, Te∴Se, Te∴S, and Te∴I hypervalent interactions. Equilibrium experiments on $(CH_3)_2Te^{\bullet+} + Te(CH_3)_2 + M \rightleftarrows [(CH_3)_2Te\therefore Te(CH_3)_2]^+ + M$ resulted in $\Delta H_{rxn}° = -97 \pm 2$ kJ/mol and $\Delta S_{rxn}° = -81 \pm 3$ J/(K·mol). Since in this specific reaction, $\Delta H_{rxn}° = -\Delta H_{bond}°$, the experiment yields a bond enthalpy of 97 ± 2 kJ/mol at 516 K. We believe that these are the first experiments on 2c-3e bonding involving tellurium and thus this article includes the first known experimental Te∴Te bond enthalpy.

Introduction

Odd-electron bonding is of great interest from both fundamental and practical perspectives, as odd-electron species exist as intermediates in many chemical reactions.[1] The one-electron bond may occur with a single electron in a σ bonding orbital, while three-electron bonds may occur with two electrons in a σ bonding orbital and one electron in a σ antibonding orbital.[2] Nominally both one- and three-electron bonds of these types have a bond order of $^1/_2$, although the three-electron bond is expected to be weaker than the one-electron bond due to greater antibonding orbital destabilization relative to the bonding orbital stabilization.[3] In one of his classic papers on chemical bonding, Linus Pauling in 1931[2] first described these odd-electron covalent bonds. For the bonds to form, the orbital energies (usually the first ionization energies) of the two moieties involved in the bond should be close.

The three-electron bonds are often referred to as two-center three-electron (2c-3e) bonds. The 2c-3e bonds involve hypervalent bonding and will be the subject of this paper. One of our group's interests has been the study of three-electron interactions in the gas phase using tandem mass spectrometry and high-pressure mass spectrometry (HPMS). The goals of our work are to measure bond strengths and to better understand the chemistry and structure from a fundamental standpoint. We have published experimental gas-phase evidence for a wide range of association adducts that exhibit 2c-3e bonding. They include interactions between S∴S, X∴X, X∴Y, S∴X, Se∴Se, Se∴S, and Se∴I, where X and Y are the halogens F, Cl, Br, and I.[4−13] Other groups, such as Nibbering's[14] and Baer's,[15] have also investigated gas-phase 2c-3e bonding.

Asmus has been a main contributor to solution studies of 2c-3e bonded systems. Using pulsed-radiolysis, his group has studied systems which include S∴X (X = Cl, Br, I), S∴O, N∴N, X∴X (X = Br, I, Cl), and Se∴Se.[16] Symons and others have also published ESR results on S∴S, P∴P, As∴As, O∴O, and N∴N.[17−21] Finally, X-ray crystallography has been employed to study such bonding; examples include studies of the N∴N[22] and the Xe∴Xe[23] bonds.

As already stated, much research has contributed to understanding these bonds; however, interactions between only a few atoms have been studied. In this paper, we will continue the story in Group 16 to report on reaction products that contain tellurium. A summary of a few important uses of tellurium is worth mentioning. First, the main industrial use of tellurium is as an alloying element. It is added to free-machining steel, usually with lead, to improve machinability.[24] Second, tellurium-containing catalysts are used for the oxidization of organic compounds, where they are also used mainly in hydrogenation and halogenation reactions.[24] Finally, semiconductor applications of the metalloid are found in thermoelectric and photoelectric devices.[24] It is our intent to contribute to the fundamental understanding of the bonding of tellurium in general and, where possible, to measure new bonding enthalpies.

Experimental Section

Experiments were carried out on two mass spectrometers. Tandem mass spectrometry experiments were carried out on a modified ZAB-1F. These modifications have been described in detail previously.[5] This instrument has three modifications which impact the work presented here. First, there is a collision cell added in the second field-free region, second, the electron multiplier is placed on-axis to reduce discrimination in the MIKES scan, and finally a home-built ion source is installed.

The ZAB ion source, built from a large oxygen-free copper block, is optimized for high-pressure and variable-temperature operation. The source has a coaxial electron beam and ion-exit

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geometry and utilizes an ion extraction potential between the front plate and the rear plate. The inside source cross-section is large, resulting in a uniform ion extraction electric field drop in the ion drift region. Ions generated at the electron entrance drift through the 1-cm drift length to the ion exit slit; hence they undergo numerous reactive collisions.

The metastable and CID experiments were carried out under chemical ionization conditions at about 315 K. In all experiments only the association adducts with the following isotopes were investigated: ^{130}Te, ^{80}Se, and ^{32}S. We cannot determine the ZAB ion source pressures exactly, but we estimate that they were approximately 0.05−0.1 Torr. Kinetic energy release distributions (KERD's) were obtained by standard methods from metastable peak shape analysis.[25] CID spectra were recorded with helium as the stationary gas at pressures needed to reduce the main beam intensity by approximately 40%.

Thermodynamic measurements were carried out on a DuPont 491 fitted with a high-pressure, variable-temperature ion source that resembles a miniature drift tube.[5,6,26] This source also has a coaxial electron entrance/ion exit geometry; it contains four internal drift guard rings that shape the electric drift field, and has a total drift length of 2 cm. Experiments on the equilibrium forming $[(CH_3)_2Te\therefore Te(CH_3)_2]^+$ were carried out between 0.025 and 0.034 Torr of $Te(CH_3)_2$ in research-grade CO_2 as a bath gas. The total source pressure ranged from 0.297 to 0.358 Torr; higher ion source pressures resulted in CID in the ion acceleration region and hence incorrect measurements of dimer ion intensities, while at lower ion source pressures equilibrium was not established. The ion source pressures in this instrument were directly measured with a MKS type 270B capacitance manometer. The source temperature ranged from 473 to 540 K and was measured with a platinum resistance element imbedded in the ion source copper wall. This ion source was designed and built with special attention for uniform temperature, especially at the ion source exit. The ion exit slit is placed inside the massive copper block; this provides excellent heat transfer and eliminates a temperature gradient at the exit slit. Both continuous and pulsed experiments were conducted.

In all experiments, the association adducts were formed by introducing gas samples into the ion source and forming the ions of interest by ion−molecule reactions. In every case, spectra of only the ^{130}Te isotopes were examined; however, those measurements were corrected by the natural abundances of all the isotopes to reflect the entire ion intensity.

All chemicals were commercially available and used as purchased. Sample preparation was accomplished by simple outgassing through several freeze−pump−thaw cycles with a Pyrex vacuum line with a base pressure of approximately 5×10^{-3} Torr.

CO_2 was purchased from MG Industries, $Te(CH_3)_2$ and $Se(CH_3)_2$ from Strem, and CH_3I and $S(CH_3)_2$ and from *Aldrich.* Due to the toxicity of the selenium and tellurium compounds, great care was taken to properly vent all vacuum pumps into hoods.

Results and Discussion

Metastable MS/MS Results. Metastable and CID experiments were carried out on the four association adducts; $[(CH_3)_2Te\therefore Te(CH_3)_2]^+$, $[(CH_3)_2Te\therefore Se(CH_3)_2]^+$, $[(CH_3)_2Te\therefore S(CH_3)_2]^+$, and $[(CH_3)_2Te\therefore ICH_3]^+$. Though the metastable results are all similar and will be presented together, we note that the bonding in the first three adducts is between two atoms in Group 16 while the bonding in the last adduct is between atoms in Groups 16 and 17.

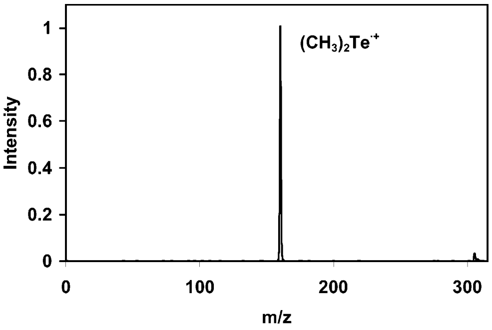

Figure 1. The metastable spectrum of $[(CH_3)_2Te\therefore Te(CH_3)_2]^+$ showing direct cleavage of the 2c-3e bond yielding *m/z* 160 $(CH_3)_2Te^{\bullet+}$.

All association products were formed by the following scheme of ion−molecule reactions where we use the tellurium association adduct as an illustrative example:

$$(CH_3)_2Te + e^- \rightarrow (CH_3)_2Te^{\bullet+} + 2e^-$$

$$(CH_3)_2Te^{\bullet+} + (CH_3)_2Te + M \rightarrow [(CH_3)_2Te\therefore Te(CH_3)_2]^+ + M \quad (1)$$

In each case only one metastable reaction pathway was observed for the decomposition of the adduct, that being the direct cleavage of the (2c-3e) bond. For example, the metastable spectrum of $[(CH_3)_2Te\therefore Te(CH_3)_2]^+$ (shown in Figure 1) has one major peak at *m/z* of 160 corresponding to the following metastable fragmentation reaction

$$[(CH_3)_2Te\therefore Te(CH_3)_2]^+ \rightarrow (CH_3)_2Te^{\bullet+} + (CH_3)_2Te \quad (2)$$

The kinetic energy release distribution, KERD, for this process was measured and found to have an average kinetic energy release, aKER, of 34 meV. Small aKERs such as this one are indicative of reactions that possess small or no reverse activation barriers, as is expected for the direct cleavage of an ion−molecule association bond. The measured aKER reported above is consistent with many other direct cleavage reactions we have observed for 2c-3e bonded systems. We propose that the value determined for the aKER implies direct cleavage of a bond involving a $Te\therefore Te$ interaction resulting in the $(CH_3)_2Te^{\bullet+}$ fragment.

The metastable spectra of $[(CH_3)_2Te\therefore Se(CH_3)_2]^+$, $[(CH_3)_2Te\therefore S(CH_3)_2]^+$, and $[(CH_3)_2Te\therefore ICH_3]^+$ all also display just one metastable peak at *m/z* 160, which corresponds to the fragment $(CH_3)_2Te^{\bullet+}$. This finding is consistent with simple bond cleavage where the charge resides on the moiety with the lowest ionization potential, in all cases that being the $(CH_3)_2Te^{\bullet+}$ moiety. The aKER for direct cleavage reactions of $[(CH_3)_2Te\therefore Se(CH_3)_2]^+$, $[(CH_3)_2Te\therefore S(CH_3)_2]^+$, and $[(CH_3)_2Te\therefore ICH_3]^+$ are 23, 23, and 9 meV, respectively. These are all relatively small aKERs, and the data are consistent with metastable cleavage of a bond involving Te for the four adducts.

We note that the kinetic energy release for cleavage of the 2c-3e bond in the $[(CH_3)_2Te\therefore ICH_3]^+$ adduct is substantially smaller (less than half) than those for the analogous KERs for the $[(CH_3)_2Te\therefore Te(CH_3)_2]^+$, $[(CH_3)_2Te\therefore Se(CH_3)_2]^+$, and $[(CH_3)_2Te\therefore S(CH_3)_2]^+$ adducts. We had previously proposed that small aKERs were observed when the neutral leaving group had a large polarizability.[10] However, in the present study we find that the aKER for cleavage of the 2c-3e bond in $[(CH_3)_2Te\therefore Te$-

$(CH_3)_2]^+$ results in an aKER of 34 meV, more than 3 times that for $[(CH_3)_2Te\therefore ICH_3]^+$. Yet, tellurium has a larger polarizabilty than either iodine or bromine,[27] thus some other factor, in addition to the polarizabilty, might contribute to the smaller aKER observed for the $[(CH_3)_2Te\therefore ICH_3]^+$ adduct.

We note that in many of our previously published results[28] on 2c-3e bonded adducts, as well as the results presented here, when a mono-methyl-substituted heteroatom with large polarizability is involved in the association adduct, the aKERs are always less than 10 meV while when di-methyl-substituted moieties are involved, the aKERs are always greater than 20 meV. This observation leads us to suggest that a key factor in determining the aKERs for these adducts may be the greater angular momentum associated with the disubstituted moieties relative to the monosubstituted ones. The larger angular momenta lead to larger centrifugal barriers and hence larger kinetic energy releases. Hence, ions with the generic structure $[(R)_2X\therefore Y(R)_2]^+$ will result in larger aKERs than those with the following structures:$[(R)_2X\therefore YR]^+$ or $[RX\therefore YR]^+$. This leads us to suggest that adducts involving 2c-3e bonding with group 16 moieties will have larger aKERs than adducts involving Group 16 and 17 or just Group 17 moieties.

CID Results. The CID spectra for the association adducts are shown in Figure 2 and are described below. In the spectrum of $[(CH_3)_2Te\therefore Te(CH_3)_2]^+$, Figure 2a, the most intense peak is at *m/z* 160 corresponding to $(CH_3)_2Te^{\bullet+}$. This result implies facile cleavage of the $Te\therefore Te$ bond and supports the metastable result, which suggests that the$(CH_3)_2Te^{\bullet+}$ results from direct bond cleavage. The CID spectrum of $[(CH_3)_2Te\therefore Te(CH_3)_2]^+$ also shows peaks for all possible methyl losses; these include $Te^{\bullet+}$ *m/z* 130, CH_3Te^+ *m/z* 145, $Te_2^{\bullet+}$ *m/z* 260, $CH_3Te_2^+$ *m/z* 275, $(CH_3)_2Te_2^{\bullet+}$ *m/z* 290, and $(CH_3)_3Te_2^{\bullet+}$ *m/z* 305. The intensities of these peaks decrease as the total number of methyl losses increases. These methyl losses suggest that the C−Te bonds may be relatively weak and/or that they have large collision-induced dissociation cross sections.

The largest peak in the CID spectrum of $[(CH_3)_2Te\therefore Se(CH_3)_2]^+$, Figure 2b, is at *m/z* 160; this again corresponds to $(CH_3)_2Te^{\bullet+}$, the adduct moiety with the lowest ionization energy. Other peaks observed are CH_3Se^+ *m/z* 95, $(CH_3)_2Se^{\bullet+}$*m/z* 110, $Te^{\bullet+}$ *m/z* 130, CH_3Te^+ *m/z* 145, $SeTe^{\bullet+}$ *m/z* 210, CH_3SeTe^+ *m/z* 225, $(CH_3)_2SeTe^{\bullet+}$ *m/z* 240, and $(CH_3)_3$ $SeTe^+$ *m/z* 255. The spectrum demonstrates that fragmentation of the $Te\therefore Se$ bond is the prominent fragmentation route. The intensity for loss of one methyl from the adduct at *m/z* 240 is the next most intense peak demonstrating that this loss is also a facile process. Finally, there is a weak peak present in this spectrum near *m/z* 158 that appears as a shoulder on the low mass side of the peak at *m/z* 160. This peak might correspond to $C_2H_4Te^{\bullet+}$; precedents for ions with analogous molecular formulas exist. The analogous Group 16 containing ions of $C_2H_4S^{\bullet+}$ and $C_2H_4Se^{\bullet+}$ are both documented in the literature; however, the structures of these ions are unspecified.[29−31]

Figure 2c shows the spectrum of $[(CH_3)_2Te\therefore S(CH_3)_2]^+$; the largest peak is again at *m/z* 160 corresponding to the fragment with the lowest IP in the adduct. The spectrum shows peaks for most possible methyl losses, including the CH_3S^+ *m/z* 47, $(CH_3)_2S^{\bullet+}$ *m/z* 62, $Te^{\bullet+}$ *m/z* 130, CH_3Te^+ *m/z* 160, CH_3STe^+ *m/z* 222, $(CH_3)_2STe^{\bullet+}$ *m/z* 192, and $(CH_3)_3STe^+$ *m/z* 207. The only peak not observed in this series is $S^{\bullet+}$, which would result from loss of both methyl groups from the S-containing moiety. Again there is a small peak at *m/z* 158, which as stated above could be $C_2H_4Te^{\bullet+}$. We note that a peak representing the $TeS^{\bullet+}$ moiety would be hidden in the CID peak broadening of the $(CH_3)_2Te^{\bullet+}$ peak.

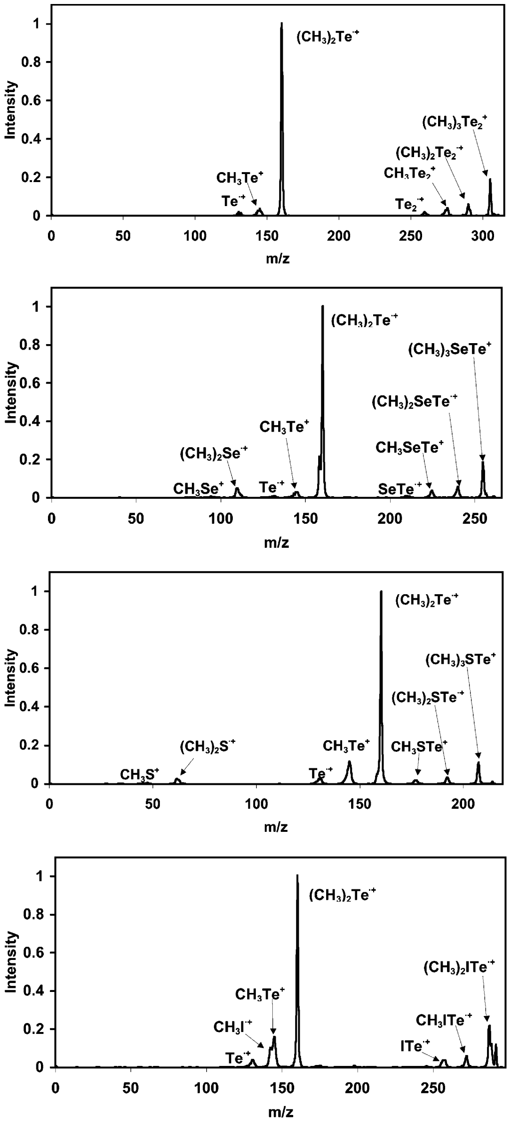

Figure 2. The CID spectra of $[(CH_3)_2Te\therefore Te(CH_3)_2]^+$, $[(CH_3)_2Te\therefore Se(CH_3)_2]^+$, $[(CH_3)_2Te\therefore S\ (CH_3)_2]^+$, and $[(CH_3)_2Te\therefore ICH_3]^+$. The largest peak is always *m/z* 160 $(CH_3)_2Te^{\bullet+}$ arising from the $Te\therefore Te$ bond cleavage.

Figure 2d shows the CID spectrum of $[(CH_3)_2Te\therefore ICH_3]^{+\cdot}$, Again, in this case, the predominant fragmentation leads to $(CH_3)_2Te^{\bullet+}$ at 160 *m/z*. Other peaks observed include $Te^{\bullet+}$ *m/z* 130, $CH_3I^{\bullet+}$ *m/z* 142, CH_3Te^+ *m/z* 145, ITe^+ *m/z* 257, $CH_3ITe^{\bullet+}$ *m/z* 272, and $(CH_3)_2ITe^+$ *m/z* 287. There also appears to be a shoulder on the peak at *m/z* 130 ($Te^{\bullet+}$) that could be *m/z* 127 I^+. The peak at *m/z* 291 that cannot be reasonably assigned to the adduct and is probably an artifact peak.[32]

In summary of the CID results, the spectra of the association adducts all show major fragmentation of the adduct bond. The spectra also show almost all sequential methyl losses. These losses suggest that the Te−C, Se−C, S−C, and I−C bonds in these adducts may be relatively weak. It is also possible that the adducts have relatively large CID fragmentation cross sections for methyl loss. We were not able to carry out studies to determine if the sequential methyl losses arise from single or multiple collisions. Finally, all four CID and metastable spectra support $Te\therefore$(Te, Se, S, and I) connectivity.

Thermochemical Equilibrium Experiments. We attempted the first quantitative measurements of gas-phase Te∴Te bonding interactions. Equilibrium experiments on reaction 3 were carried

$$(CH_3)_2Te^{\bullet +} + (CH_3)_2Te + M \rightleftarrows [(CH_3)_2Te\therefore Te(CH_3)_2]^+ + M \quad (3)$$

out as a function of temperature in a bath gas of CO_2. Such studies can yield $\Delta H_{rxn}°$ and $\Delta S_{rxn}°$ from the van't Hoff equation:

$$\ln K_{rxn} = \frac{-\Delta H_{rxn}°}{RT} + \frac{\Delta S_{rxn}°}{R}$$

To collect meaningful thermodynamic data, it is necessary to show that equilibrium can be achieved. We carried out four tests to demonstrate attainment of equilibrium. (1) The equilibrium quotient is measured as a function of the ion source extraction potential. (2) The equilibrium quotient is measured as a function of the neutral reagent gas pressure, in this case the $(CH_3)_2Te$ pressure. (3) The equilibrium quotient is measured as a function of the total ion source pressure by varying the bath gas pressure, in this case CO_2. (4) Ion source residence time distributions are collected to demonstrate constant ion current−time profiles. Identical distributions provide rigorous evidence for equilibrium.

In the first test where the reaction quotient is measured as a function of ion extraction potential, the equilibrium quotient curved downward at the higher potentials but was constant at the lower extraction potentials. The downward curve can be attributed to nonattainment of equilibrium at the shorter ion source residence times. Our final data came from an average equilibrium quotient in the region of low extraction voltages.

The second test for equilibrium is to measure the reaction quotient while varying the gas composition. The equilibrium expression for reaction 3 is

$$K_{eq} = \frac{[(CH_3)_2Te\therefore Te(CH_3)_2]_i^{\ +}}{[(CH_3)_2Te]_i^{\bullet +}\,[(CH_3)_2Te]_{atm}}$$

When true equilibrium is achieved, different gas compositions will not change the reaction quotient but the ion ratio will change. Hence, we changed the pressure of $(CH_3)_2Te$ and we were able to achieve equilibrium from 0.025 to 0.034 Torr. Larger $(CH_3)_2Te$ pressures shifted the equilibrium to the right and made the monomer intensity too small to measure accurately.

We also changed the bath gas CO_2 pressure; since CO_2 does not enter into the equilibrium expression, the reaction quotient should be constant with changing CO_2 pressure at equilibrium. At high pressures of CO_2 we did observe CID outside the source breaking up the dimer thus making the reactant quotient smaller.

The final test of equilibrium comes from the residence time distributions. If equilibrium is attained, the residence times in the ion source will be the same. This test is shown in Figure 3 where the $(CH_3)_2Te^{\bullet +}$, represented by a line, and $[(CH_3)_2Te\therefore Te(CH_3)_2]^+$, represented by points, are completely superimposable.

With the above evidence for equilibrium, the data for the van't Hoff plot were collected. These data covered a range of temperatures from 473 to 559 K; the resulting plot is shown in Figure 4. The slope of this plot yields $\Delta H_{rxn}° = -97 \pm 2$ kJ/mol and the intercept yields $\Delta S_{rxn}° = -81 \pm 3$ J/(K·mol). In these association reactions, $\Delta H_{rxn}° = -\Delta H_{bond}°$, thus the experiment yields a bond enthalpy of 97 ± 2 kJ/mol at 516 K.

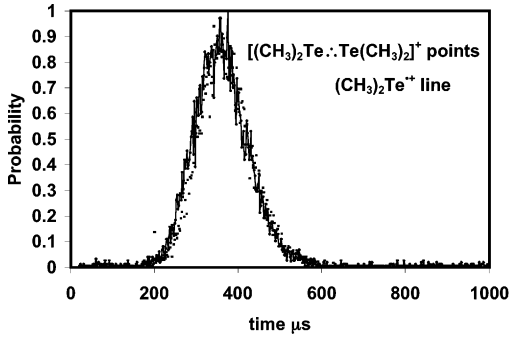

Figure 3. Residence time distributions of the $(CH_3)_2Te^{\bullet +}$ line and $[(CH_3)_2Te\therefore Te(CH_3)_2]^+$ points. The overlapping distributions demonstrate rigorous evidence of the achievement of equilibrium.

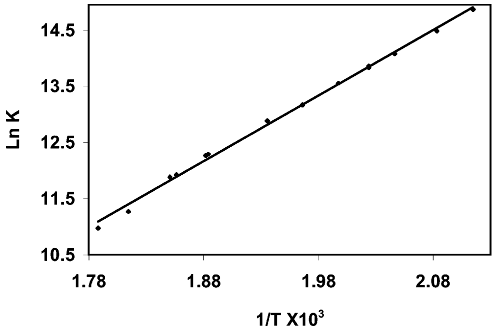

Figure 4. The van't Hoff plot resulting from the equilibrium experiments on reaction 2.

The Te∴Te bond energy is the same, within error, as the previously published Se∴Se bond of 95 ± 3.0 kJ/mol at 511 K.[13] This result does not follow our preconceived notion that the bond dissociation energy should be lower going down a group in the periodic table but the value is in the same range as the values for the other 2c-3e bonded adducts published by our group. In our past work, we have been able to compare our findings to a reliable two-center two-electron bond energy published in the literature since the bond energy for a two-center three-electron bond should be approximately half the bond energy of the two-center two-electron bond in a similar chemical environment. In the present work, we have not been able to find a numerical value for a Te−Te 2c-2e bond.

The entropy of reaction was found to be $\Delta S_{rxn}° = -81 \pm 3$ J/(K·mol). This value is similar to that previously found in the analogous selenium case ($\Delta S_{rxn}° = -76 \pm 6$ J/(K·mol) for $[(CH_3)_2Se\therefore Se(CH_3)_2]^+$).[13] A similar entropy of reaction is anticipated for both the selenium and tellurium adducts since the reactants are similar and the bond connectivity in the two adducts is also similar.

Thermochemical equilibrium experiments on $[(CH_3)_2Te\therefore Se(CH_3)_2]^+$, $[(CH_3)_2Te\therefore S(CH_3)_2]^+$, and $[(CH_3)_2Te\therefore ICH_3]^+$ were not possible due to the difficulty in establishing the appropriate equilibria.

Conclusions

We believe these are the first ever reported results of 2c-3e bonding involving tellurium in the gas or condensed phases. Considerable progress has been made toward understanding 2c-3e interactions between sulfur, iodine, bromine, and selenium described in the Introduction. In this work, we have presented the metastable and CID results for $[(CH_3)_2Te\therefore Te(CH_3)_2]^+$, $[(CH_3)_2Te\therefore Se(CH_3)_2]^+$, $[(CH_3)_2Te\therefore S(CH_3)_2]^+$, and $[(CH_3)_2Te\therefore ICH_3]^+$. These association adducts all display behavior that is consistent with 2c-3e bonding. The behavior includes, (1) a single metastable reaction with the charge residing in the moiety with the lowest ionization potential, (2) a small average kinetic energy release that is indicative of a reaction with little or no reverse activation barrier such as for the direct cleavages proposed, and (3) the CID spectra displaying peaks consistent with the proposed bonding.

A much smaller aKER was determined for $[(CH_3)_2Te\therefore ICH_3]^+$ than for $[(CH_3)_2Te\therefore Te(CH_3)_2]^+$, $[(CH_3)_2Te\therefore Se(CH_3)_2]^+$, and $[(CH_3)_2Te\therefore S(CH_3)_2]^+$. It is suggested that ions with the generic structure $[(R)_2X\therefore Y(R)_2]^+$ result in larger aKERs than those with the generic structures $[(R)_2X\therefore YR]^+$ or $[RX\therefore YR]^+$. The larger aKERs may originate from neutral leaving groups with larger angular momenta. The larger angular momenta should lead to larger centrifugal barriers and hence larger kinetic energy releases.

Finally, the thermochemical results determined here are believed to be the first reported thermodynamic measurements for 2c-3e $Te\therefore Te$ bonding. The experimental values are $\Delta H_{rxn}° = -97 \pm 2$ kJ/mol and $\Delta S_{rxn}° = -81 \pm 3$ J/(K·mol).

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