

with the same number of carbon atoms, the unsaturated one is more strongly bound; for example, C_2H_2 and C_2H_4 are more strongly bound than C_2H_6 , but enhanced stabilization with hydrocarbon size is the same magnitude as the binding due to metal to π^* donation so that larger saturated hydrocarbons can be more stable than smaller unsaturated ones. In addition to enhanced stabilization due to large polarization, bigger ligands can interact with the metal ion at more than one site. For example in C_3H_8 , if Sc^{2+} approaches the bond midpoint of one C-C bond, the binding energy is 6.7 kcal/mol larger than for C_2H_6 , but if the Sc^{2+} interacts with both terminal CH_3 groups at the same time, the binding energy is increased by an additional 3.4 kcal/mol—compare Figure 1d and 1f. It is interesting to note that the Sc^{2+} binding energies would follow the order suggested by the IPs if the Sc^{2+} approached the C-C midpoint (i.e., that shown in Figure 1d). Thus, the ligand size effects are only a few kilocalories per mole, but this is sufficient to change the order from that expected based on electrostatic arguments.

The smaller metal to π^* binding for the dipositive ion is not unexpected since a dipositive ion is much less able to donate charge than a singly charged ion. This reduced metal to π^* donation is also responsible for the asymmetric and symmetric forms of $MC_2H_2^{2+}$ and $MC_2H_4^{2+}$ for Sc and Y having similar energies; a large metal to π^* donation naturally favors a symmetric structure.

While some of the changes in the binding energies arise from the difference in the size of the metal ions, we feel that the difference in the ligand bonding order between the singly charged Cu^+ and doubly charged Sc^{2+} or Y^{2+} arises from the metal to π^* donation for the singly charged ion. We are able to test our hypothesis by comparing the bonding of Sc^{2+} and Sc^+ in its first

excited triplet state to C_2H_2 and C_2H_6 . We should note that the Sc^+ is constrained to be electrostatically bound to the ligands and, therefore, does not represent the lowest triplet excited state of a $ScC_2H_n^+$ ion; this type of bonding is, therefore, analogous to that in Cu^+ . If the bonding was only electrostatic, the ratio of the ligand binding energies would be similar for Sc^+ and Sc^{2+} . However, if the importance of metal to π^* donation increased as expected for the singly charged ion, the ratio will change. The binding energies for $ScC_2H_2^+$ and $ScC_2H_6^+$ are 17.8 and 9.2 kcal/mol, respectively. This is smaller than half that found for Sc^{2+} , since Sc^+ , with an occupied 4s orbital, is larger in size, so that the metal-ligand bond distance is larger than for the dipositive ion. The difference in the metal C_2H_2 and C_2H_6 binding energies is larger for Sc^+ than Sc^{2+} , which is a clear indication of enhanced metal to π^* donation in the singly charged ion relative to the dipositive ion. The ratio of the binding energies (C_2H_2/C_2H_6) is 1.9 for Sc^+ , compared to 2.1 for Cu^+ . This is quite different from 1.2 and 1.3 for Sc^{2+} and Y^{2+} , respectively. Therefore, we conclude that the differences in ligand binding energies between Sc^{2+} and Cu^+ are due both to the charge and to the degree of metal to π^* donation. Thus, the order of ligand binding energies is expected to be quite different for singly charged and dipositive ions in general. These results are in excellent agreement with the experimental observations described in this study.

Acknowledgment. Y.D.H. and B.S.F. acknowledge the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (Grant DE-FG02-87ER13766) for supporting this research and the National Science Foundation (Grant CHE-8920085) for continued support of FTMS methodology.

Estimate of the Iodine-Iodine Two-Center Three-Electron Bond Energy in $[CH_3-I-I-CH_3]^+$

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Abstract: The gas-phase ion-molecule association reaction $CH_3I^+ + CH_3I \rightleftharpoons [CH_3-I-I-CH_3]^+$ in various bath gases was studied at 503 K. The iodine-iodine bond in the association product is an example of a two-center three-electron (2c-3e) or a $2\sigma/1\sigma^*$ bond. The bond energy was estimated from ΔG° of reaction, which was in turn determined from equilibrium experiments. Assuming a value for ΔS° of reaction of -20 to -25 cal/(mol K), a bond strength of 23–26 kcal/mol is estimated. This is the first experimental gas-phase binding energy estimate for a 2c-3e bond in an organic molecule involving an iodine-iodine interaction and one of only a few experimental studies of well-characterized gas-phase 2c-3e bonding interactions between heteroatoms in organic molecules. A study of the ion-molecule reactions occurring at low ionizing energies leading to $(CH_3)_2I^+$, $[C_2H_5I_2]^+$, and $[CH_3-I-I-CH_3]^+$ is discussed.

Introduction

Two-center three-electron (2c-3e) bonding or $2\sigma/1\sigma^*$ bonding was first described by Linus Pauling in 1931.¹ More recently Clark^{2a} and Radom^{2b} have published theoretical descriptions of these bonds. Asmus³ has published extensive experimental results for molecules containing 2c-3e bonds formed in solution by pulse

radiolysis, and we reported what we believe is the best experimental gas-phase binding estimate for a 2c-3e bond, namely, the sulfur-sulfur interaction in $[(CH_3)_2-S-S-(CH_3)_2]^+$.⁴ Yet in spite of the early description by Pauling and the flurry of recent interest in these bonds, gas-phase experimental data on 2c-3e bonding involving organic molecules are extremely sparse.⁵

(1) Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 3225.

(2) For leading references to theoretical work on 2c-3e bonding, see: (a) Clark, T. *J. Am. Chem. Soc.* **1988**, *110*, 1672. (b) Gill, P. M. W.; Weatherall, P.; Radom, L. *J. Am. Chem. Soc.* **1989**, *111*, 2783.

(3) For recent leading references, see: (a) Anklam, E.; Mohan, H.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1297. (b) Kishore, K.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1989**, 2079. (c) Drowello, T.; Lebrilla, C. B.; Asmus, K.-D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1275. (d) Anklam, E.; Asmus, K.-D.; Mohan, H. *J. Phys. Org. Chem.* **1990**, *3*, 17.

(4) Illies, A. J.; Livant, P.; McKee, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 7980.

(5) The bonding in many diatomic cations, including He_2^+ , Ne_2^+ , Kr_2^+ , and Xe_2^+ , is of course well-characterized and involves 2c-3e electron bonds. These simple systems will not be considered here; rather, the present focus is on 2c-3e bonding through heteroatoms in organic molecules. Additionally, though the binding energies for a great number of gas-phase ion-molecule association complexes have been reported (see ref 17), in most cases the nature of the binding interaction and even the atomic connectivity is unknown; hence, these systems are not well-characterized and will also not be further considered.

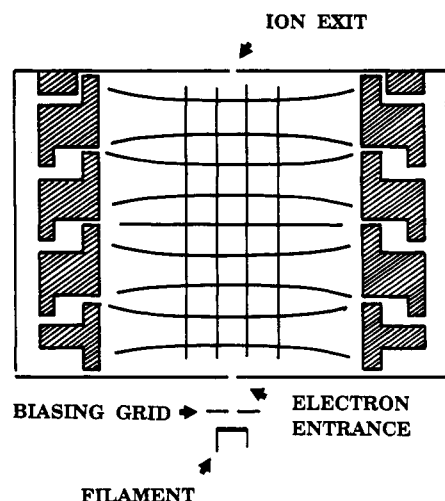
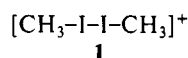


Figure 1. Schematic cross-section of the ion source showing internal drift guard rings (shaded regions), equipotential lines (horizontal curves) and electric field lines (vertical lines).

The present paper focuses on the iodine-iodine 2c-3e bond in gas-phase $[\text{CH}_3\text{-I-I-CH}_3]^+$, which was studied by ion-molecule equilibrium experiments on reaction 1. Both iodine-iodine and sulfur-iodine 2c-3e bonding in solution have been reported by Asmus, though no bond strength estimates were reported.⁶ The



goal of our studies is to determine ΔG° of reaction from equilibrium studies and, if possible, estimate ΔH° of reaction. ΔH° for an association reaction is related to the energy of the bond formed between the two reacting moieties. Although the structure of the association product has not been unequivocally proven, it is in accord with chemical common sense to depict the product as having the atom connectivity seen in 1. Indeed, one is hard pressed to postulate a reasonable alternative structure.⁷



The remainder of this paper is organized in the following manner. Following the Experimental Section, the ion-molecule reactions that take place between CH_3I^+ and CH_3I and CH_2I^+ and CH_3I are summarized in part A of the Results and Discussion section followed by the ion-molecule equilibrium results and interpretation for reaction 1 in part B.

Experimental Section

The experimental methods employed here were similar to those used in our previous work^{4,8} and will be only briefly reviewed here. The studies were all carried out in a high-pressure (0–1.5 Torr) ion source in a Du Pont 21-491B mass spectrometer. The mass spectrometer has been significantly modified by increasing the pumping speed, installing an ion source designed in these laboratories, and modernizing much of the electronics. The mass spectrometer ion source has coaxial ionizing electron-entrance and ion-exit apertures and four overlapping internal drift guard rings, which shape the electric fields in the source. Figure 1 shows a schematic diagram of a cross-section of the mass spectrometer ion source and the equipotential electric field lines. Ions drift through the source at a constant velocity due to the uniform potential drop and the collisions that take place as they travel through the source. The

energy gained by the ions between collisions is small compared to thermal energies.⁹

The total ion-source pressure ranged from 0.2 to 1.0 Torr. The CH_3I concentration in the source covered the range 1.3–10.0 mol %. In some experiments, the CH_3I and bath gas were mixed in the ion source inlet system by introducing the gases through separate leak valves. In other cases, gas mixtures were premixed on a vacuum line and introduced through a single leak valve. The ion-source gas pressure was measured with an MKS capacitance manometer. Mass spectra were recorded with conventional analogue-recording techniques, while residence time distributions and ion intensity measurements for the determination of equilibrium constants were collected with use of previously described pulse-counting techniques.⁸

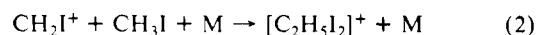
The coaxial arrangement of the electron-entrance and ion-exit apertures results in high sensitivities when very low ionizing electron energies are used, even at high pressures. Hence, it is often possible to study ion-molecule reactions of primary ions uncomplicated by reactions of higher energy ions (fragment ions formed at higher ionizing electron energies). Time-resolved experiments are performed by pulsing the ionizing electron beam with a biasing grid placed between the filament and the source. The time-resolved studies result in kinetic information that is useful in determining whether equilibrium is established.

Experiments were carried out with Aldrich Gold Label CH_3I , which was dried by condensing onto activated type 3A molecular sieves, followed by two bulb-to-bulb distillations. Ar (research grade, Air Products), Kr (research grade, MG Scientific) and SF_6 (instrument grade, Air Products) were used as received from the suppliers. All gas connections other than the primary connection to the cylinders were made with Ultra-Torr connectors. Some gas mixtures were prepared with use of a gas vacuum rack with a base pressure of 10^{-5} Torr. The sample pressures in the vacuum line were measured with an MKS capacitance manometer.

Results and Discussion

A. Ion-Molecule Reaction Pathways. Upon ionization of molecules by high-energy electrons, molecular and fragment ions may be formed. At low ion-source pressures, these ions give rise to the normal mass spectrum. At elevated pressures, ion-molecule collisions and hence reactions occur. In the mass spectrum of CH_3I at low ion-source pressures approximating standard electron-impact conditions, the two major peaks are $m/z = 141$ and 142 , corresponding to CH_2I^+ and CH_3I^+ . As the ionizing electron energy is lowered, the peak corresponding to CH_2I^+ decreases in intensity relative to that for CH_3I^+ . This is in perfect accord with the fact that the appearance potential for CH_2I^+ is higher (12.08 eV) than the ionization potential for CH_3I^+ (9.538 eV).¹⁰

As the ion-source pressure is increased with addition of CH_3I , reactive collisions between ions and neutrals result in ion-molecule reactions. At the higher pressures and high ionizing electron energies, major ions (within 1 order of magnitude in intensity) at $m/z = 141, 142, 157, 283,$ and 284 are observed. The relative intensities of these peaks depend on the ion source conditions, namely, the ionizing electron energy, the ion residence times, and the neutral-reactant partial pressure. The new ions appearing at $m/z = 157, 283,$ and 284 correspond to $(\text{CH}_3)_2\text{I}^+$, $[\text{C}_2\text{H}_5\text{I}_2]^+$, and $[\text{CH}_3\text{-I-I-CH}_3]^+$. As the electron energy is decreased, the peak for $[\text{C}_2\text{H}_5\text{I}_2]^+$ decreases relative to those for CH_3I^+ , $(\text{CH}_3)_2\text{I}^+$, and $[\text{CH}_3\text{-I-I-CH}_3]^+$. On this basis, we postulate that $[\text{C}_2\text{H}_5\text{I}_2]^+$ arises from the reaction



The fact that $[\text{C}_2\text{H}_5\text{I}_2]^+$ was not observed in previous ICR experiments on the ion-molecule chemistry of methyl iodide^{11,12} but is observed in our experiments is in accord with the fact that the reaction requires a stabilizing collision, which would not occur at the lower pressures typical of ICR experiments. This also explains why the association to $[\text{CH}_3\text{-I-I-CH}_3]^+$ (reaction 1) was also not observed in the earlier studies. As the electron energy

(6) (a) Anklam, E.; Mohan, H.; Asmus, K.-D. *Helv. Chim. Acta* **1987**, *70*, 2110. (b) Mohan, H.; Asmus, K.-D. *J. Am. Chem. Soc.* **1987**, *109*, 4745. (c) Mohan, H.; Asmus, K.-D. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1795. (d) Mohan, H.; Asmus, K.-D. *J. Phys. Chem.* **1988**, *92*, 118. (e) Anklam, E.; Mohan, H.; Asmus, K.-D. *J. Chem. Soc., Chem. Commun.* **1987**, 629.

(7) In a recent ab initio study, Hess and Zahradnik (*J. Am. Chem. Soc.* **1990**, *112*, 5731) concluded that the bonding between CH_2F^+ and CH_3F involved an -H-H- interaction, namely, $[\text{H}_2\text{FC-H-H-CH}_2\text{F}]^+$. However, they did not explore the -F-F- interaction, which might also result in an energy minimum. Moreover, in light of the tremendous difference in electronegativities, polarizabilities, and ionization potentials between fluorine and iodine, the calculations on the fluorine system probably do not pertain to the present case.

(8) Illies, A. J. *J. Phys. Chem.* **1988**, *92*, 2889.

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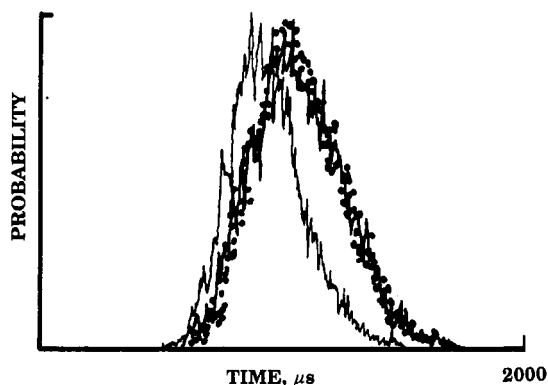
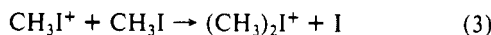


Figure 2. Normalized residence time distributions for CH_3I^+ (heavy line) and $[\text{CH}_3\text{-I-I-CH}_3]^+$ (points), which show that reaction 1 is at equilibrium, and the distribution for $(\text{CH}_3)_2\text{I}^+$ (lighter line), which is not involved in the $\text{CH}_3\text{I}^+ / [\text{CH}_3\text{-I-I-CH}_3]^+$ equilibrium.

is increased from 0 eV, $m/z = 142, 157,$ and 284 all appear at the same nominal energy.¹³ This is consistent with the known ion-molecule chemistry of methyl iodide reported by Beauchamp,¹¹ who observed that $(\text{CH}_3)_2\text{I}^+$ is generated by reaction 3. Fortu-



nately for the present study of reaction 1, the rate constant for reaction 3 is a factor of 5.5×10^{-3} smaller than the ADO (average dipole orientation) collision rate constant¹⁴ and hence should result in only a minor perturbation of the equilibrium reaction (1).

B. $[\text{CH}_3\text{-I-I-CH}_3]^+$ Bond Energy. The thermodynamic bond energy for $[\text{CH}_3\text{-I-I-CH}_3]^+$ can be found from equilibrium measurements of the reversible reaction (1). Specifically the van't Hoff equation results in the enthalpy and entropy of reaction. For

$$\ln K_p = -\Delta H^\circ_{rx} / RT + \Delta S^\circ_{rx} / R \quad (4)$$

association reactions, the enthalpy of reaction is the negative of the bond enthalpy. The values for bond enthalpy and bond energy are nearly identical.

In order to correctly determine the experimental equilibrium constant, it must be demonstrated that the system is at true chemical equilibrium. In our laboratory, we apply three criteria to test for equilibrium: (1) The ion residence time distributions for the reactant and product ions must be identical. Residence time distributions of ions in equilibrium are the same since the charge that is eventually mass-analyzed and detected undergoes many switching reactions as it traverses the source, resulting in an averaging of the drift properties.⁸ (2) The measured apparent equilibrium constant (K_{app}) must be independent of the ion extraction potential. This potential is applied to move the ions through the source. If the potential is too high, it is possible to translationally heat the ions along the direction of ion motion. However, in our experiments the energy gained per collision is small compared to kT and changes in K_{app} with the extraction voltage can usually be attributed to kinetic effects from changes in the ion residence times.^{9,15} (3) K_{app} must be independent of the total ion-source pressure and reactant partial pressure. This is a standard test, which if possible should be applied to all equilibrium studies.

All attempts to demonstrate equilibrium for reaction 1 with Ar and Kr as bath gases were unsuccessful. Residence time distributions showed that equilibrium was not being established. As the total ion-source pressure was increased and as the CH_3I partial pressure was increased, the CH_3I^+ and $[\text{CH}_3\text{-I-I-CH}_3]^+$

(13) The peak intensities for $m/z = 142, 157,$ and 284 were all of the same order of magnitude but depended on the ion-source conditions controlling the ion-molecule kinetics, namely, the CH_3I partial pressure, the total ion-source pressure, and the reaction time.

(14) (a) Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1975**, *212*, 211. (b) Rothe, E. W.; Bernstein, R. B. *J. Chem. Phys.* **1959**, *31*, 1619.

(15) These experiments are carried out in an extraction regime where ions are not translationally pumped (see ref 9); however, the average ion residence time is strongly dependent on the extraction potential.

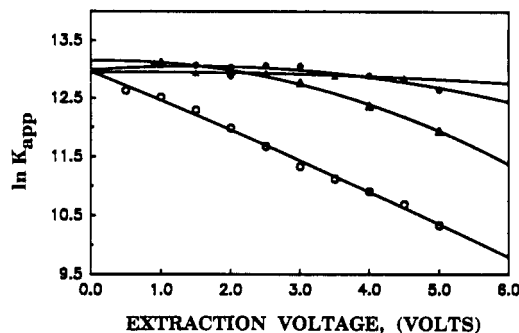


Figure 3. $\ln K_{app}$ vs the extraction voltage in. The CH_3I partial pressure was 0.014 Torr in SF_6 bath gas. The total pressures were 0.17 Torr (open circles), 0.28 Torr (open triangles), 0.37 Torr (closed circles), and 0.48 Torr (closed triangles). The data for 0.60 Torr (see text) are not shown for clarity. The data for 0.28, 0.37, and 0.48 Torr merge at the lower ion-extraction voltages.

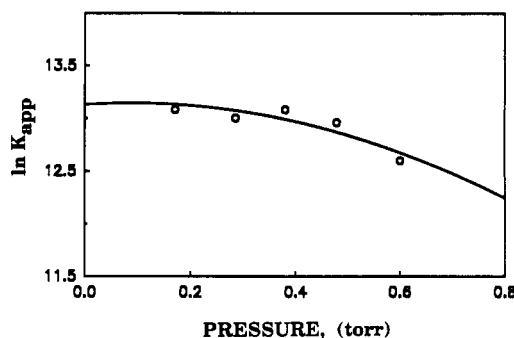


Figure 4. Extrapolated $\ln K_{app}$ vs the total ion-source pressure with a fixed CH_3I partial pressure of 0.014 Torr in SF_6 bath gas.

residence time distributions became more similar but could not be made to superimpose.

Experiments with SF_6 as a bath gas were much more successful. As shown in Figure 2, the normalized residence time distributions for CH_3I^+ and $[\text{CH}_3\text{-I-I-CH}_3]^+$ were the same but that for the $(\text{CH}_3)_2\text{I}^+$ ion, which was also always present, was quite different. The superimposable residence time distributions for CH_3I^+ and $[\text{CH}_3\text{-I-I-CH}_3]^+$ meet criterion 1 as the first test for equilibrium. That the distributions are superimposable in SF_6 while they are not in Ar and Kr is most probably due to SF_6 being a much better third body (energy sink) than Ar or Kr. This would result in better stabilization in reaction 1 and allow reaction 1 to compete more favorably with reaction 3. That the distributions for CH_3I^+ and $[\text{CH}_3\text{-I-I-CH}_3]^+$ are superimposable also signifies that the forward and reverse reactions in reaction 1 are fast relative to the depletion of CH_3I^+ by reaction 3.

The results of experiments to test the second and third criteria are shown in Figures 3 and 4. These data were collected at 503 K by first establishing a CH_3I partial pressure of 0.014 Torr in the ion source and then adding various partial pressures of SF_6 . As shown in Figure 3, at the lowest SF_6 partial pressure (and hence total ion-source pressure) the plot of K_{app} vs extraction voltage shows a marked voltage dependence. At the low pressures, equilibrium is not fully established and the plots show the kinetic approach to K_{app} as the ion residence times increase with decreasing extraction voltage. As the SF_6 pressure is increased, the voltage dependence lessens and a limit is reached. These data extrapolate, by a second-degree polynomial least squares, to a value of 13.0 ± 0.3 for the $\ln K_{app}$ at zero extraction voltage. The extrapolated values from Figure 3 are plotted in Figure 4 as a function of the total ion-source pressure. At the highest pressure (0.60 Torr), the extrapolated $\ln K_{app}$ drops to ca. 12.6. This drop in the apparent equilibrium constant is now known to be due to a change in the gas flow characteristics from the ion source.¹⁶ As the pressure is increased, the gas flow changes from molecular to

(16) Kemper, P. R.; Bowers, M. T. *J. Am. Soc. Mass Spectrom.* **1990**, *1*, 197.

enthalpy-limited flow resulting in a drop in the CH_3I partial pressure in the ion source;¹⁷ hence, the calculated K_{app} is in error since an incorrect value for the partial pressure of CH_3I is used. Similar experiments with the CH_3I partial pressure ranging from 0.008 to 0.021 Torr were carried out, and extrapolated values for $\ln K_{\text{app}}$ ranged from 12.8 to 13.1.

In another set of studies, premixed gases of 1.9 and 2.9 mol % CH_3I in SF_6 were studied as a function of ion-source pressure. Experiments with premixed gases often result in an unknown composition in the ion source due to mass discrimination of the gases as they travel through the leak valves and plumbing to the ion source. Discrimination of this sort depends upon the ratio of the square root of the masses. This value is 0.986 for $\text{CH}_3\text{I}/\text{SF}_6$, meaning that very little mass discrimination should occur as long as the flow is in the effusive regime. The data at 1.9 mol % imply a limit of 13.0 for the value of $\ln K_{\text{app}}$, while the data at 2.9 mol % imply a limit of 12.9. In these experiments, a drop in the K_{app} at higher ion-source pressures was also observed. Again, this is due to changes in the gas flow from the ion source. These results are in excellent agreement with those described in the previous paragraphs.

In the present experiment, the bonding in $[\text{CH}_3\text{-I-I-CH}_3]^+$ is strong relative to the bonding range that can be measured in our apparatus and it was simply not possible to measure equilibrium constants over a large enough temperature range to determine a reliable van't Hoff plot. The binding interaction in $[\text{CH}_3\text{-I-I-CH}_3]^+$ can, however, still be estimated from our data. The present data lead to K_{app} in the range of 12.8–13.1 at an average temperature of 503 K (the temperature in these experiments actually ranged from 500 to 505 K). On the basis of examination of extensive data for ion-molecule association reactions,¹⁸ an estimate of -20 to -25 cal/(mol K) is reasonable for $\Delta S^\circ_{\text{rx}}$. The measured free energy of reaction and the estimated entropy of reaction result in $\Delta H^\circ_{\text{rx},503} = -23$ to -26 kcal/mol for reaction 1, where both the experimental error in the determination of $\Delta G^\circ_{\text{rx}}$ and the range for the estimate of $\Delta S^\circ_{\text{rx}}$ have been incorporated into the reported range. $\Delta H^\circ_{\text{rx}}$ is nearly equivalent to minus the bond energy formed in the reaction (neglecting heat capacity differences between reactants and products). The present data thus result in a bond energy range of 23–26 kcal/mol. This, to the best of our knowledge, represents the only gas-phase experimental value for a 2c-3e iodine-iodine heteroatom interaction involving organic molecules.

At the temperature of our studies (503 K), the experimental equilibrium constant $K_p = 4.4 \times 10^5 \text{ atm}^{-1}$ results in $K_c = 1.8$

(17) The transition pressure from effusive flow to enthalpy-limited flow depends on the mean free path, which in turn depends inversely on the molecular collision diameter. This same phenomenon was also observed previously in our study on the association of $[(\text{CH}_3)_2\text{-S-S-(CH}_3)_2]^+$; however, at that time we were unable to explain the effect (ref 4). The fact that the dimethyl sulfide and methyl iodide have the largest collision cross-sections of any molecules studied by us to date explains why the effect was not previously observed.

(18) Keese, R. G.; Castleman, A. W., Jr. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1011.

$\times 10^7 \text{ L mol}^{-1}$, where K_p describes the equilibrium constant in terms of pressure and K_c in terms of concentrations (mol/L). This compares with the equilibrium limit ($K_c \geq 5 \times 10^4 \text{ L mol}^{-1}$) from the pulse radiolysis experiments at room temperature in aqueous solution by Asmus et al.^{6c} It is very difficult to compare these two numbers due to solvation effects: In the aqueous system, the molecular radical cation CH_3I^+ is likely to be strongly associated with water as $(\text{CH}_3\text{I-OH}_2)^+$.^{6c} Preferential solvation of the reactant would lead to a smaller equilibrium constant for the studies in aqueous medium relative to the gas-phase studies.

The range determined in this work for the bond in $[\text{CH}_3\text{-I-I-CH}_3]^+$ is very similar to that for the gas-phase 2c-3e iodine-iodine bond energy in I_2^+ , which is 24.3 kcal/mol.¹⁹ The range is also similar to that which we recently reported for the gas-phase sulfur-sulfur 2c-3e bond in $[(\text{CH}_3)_2\text{-S-S-(CH}_3)_2]^+$ (23.9–26.5 kcal/mol).⁴ We chose to study the iodine-iodine bonding in the present study because we expected the bonding to be weaker than that for the sulfur-sulfur interaction and were hopeful that a complete van't Hoff plot could be obtained. We expected a weaker interaction because of the more diffuse nature of the interacting orbitals in iodine compared to those in sulfur. However, the bonding range is very similar, suggesting that the more diffuse nature of the orbitals might be countered by better orbital overlap and/or a stronger electrostatic contribution to the bond. The stronger electrostatic contribution might arise from the larger polarizability of iodine compared to that of sulfur.

Conclusions

Although the equilibrium reaction leading to $[\text{CH}_3\text{-I-I-CH}_3]^+$ must be slightly perturbed by the reaction leading to $(\text{CH}_3)_2\text{I}^+$, we were able to establish a value for the equilibrium constant at 503 K. From this value, $\ln K_{\text{app}} = 13.0$, an estimated range for the iodine-iodine 2c-3e bond in the $[\text{CH}_3\text{-I-I-CH}_3]^+$ cluster was determined to be 23–26 kcal/mol. This value represents the first reliable gas-phase estimate for an iodine-iodine 2c-3e bond in an organic molecule. Appearance potential measurements suggest that $[\text{C}_2\text{H}_5\text{I}_2]^+$, which is observed at higher ionizing electron energies, arises from an ion-molecule reaction involving CH_2I^+ and CH_3I .

Acknowledgment. A.I. is especially grateful to Drs. Paul Kemper and Martin Jarrold for very helpful discussions on gas flow, which led to the understanding of the drop in K_{app} at the higher ion-source pressures. We also acknowledge K.-D. Asmus for stimulating discussions on the subject of 2c-3e bonds during a recent visit. A.I. is also very grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Auburn University Chemistry Department for financial support.

Registry No. CH_3I^+ , 12538-72-6; CH_3I , 74-88-4.

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