The bonding strength of $Ag^+(C_2H_4)$ and $Ag^+(C_2H_4)_2$ complexes

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Received 29 January 1991; in final form 27 March 1991

The association reactions $Ag^+(C_2H_4)_{n-1}+C_2H_4=Ag^+(C_2H_4)_n(n=1 \text{ or } 2)$ were studied using high pressure mass spectrometry (HPMS). The enthalpy and entropy changes determined are $-\Delta H^0 = 32.4$ kcal/mol, and $-\Delta S^0 = 30.2$ cal/mol K for the n=2reaction. In the case of the n=1 reaction, the Gibbs free energy change at 750 K is measured to be $-\Delta G^0 = 17.1$ kcal/mol. Using the free energy change and the calculated entropy change $-\Delta S^0 = 22.1$ cal/mol K, we derive an enthalpy change $-\Delta H^0 = 33.7$ kcal/mol for the n=1 reaction. The bonding in both $Ag^+(C_2H_4)$ and $Ag^+(C_2H_4)_2$ complexes is extremely strong, and much higher than expected based on the simple electrostatic-interaction considerations. The strong bonding suggests that covalent interaction or a two-way donor-acceptor interaction dominates in the complexes.

1. Introduction

Understanding the structure and bonding of transition metals to unsaturated hydrocarbon is of significant importance in the fields of organometallic chemistry, catalysis, and surface chemistry, etc. [1]. In 1951, Dewar [2] first proposed a so-called twoway donor-acceptor interaction model to interpret the structure and bonding of metal-olefin complexes. In his model, Dewar suggested that the metal is located symmetrically above the plane of the olefin, and that σ bonding charge donation takes place from the filled π orbital of the olefin to the empty s orbital of the metal, while π bonding back donation occurs from the filled d orbital of the metal to the empty π^* orbital of the olefin. Since then, a large number of theoretical calculations [3-10] have been made to explore the nature of the bonding in metalunsaturated hydrocarbon complexes.

Numerous calculations [3–6] have tended not to support Dewar's two-way donor-acceptor interaction model and have instead indicated that electrostatic interactions are the major forces responsible for the stability of the complexes, especially in ones formed by group 11 monoions bound to unsaturated hydrocarbons. In fact, these are the systems for which Dewar's model would be expected to be particularly applicable. For instance, the ab initio calculations conducted by Basch [3] demonstrated that pure electrostatic interaction instead of two-way donoracceptor bonding dominates in $Ag^+(C_2H_4)$. In recent work [4], Miralles-Sabater et al. have employed a CI level calculation to analyze the bonding in $Cu^+(C_2H_2)$ and $Ag^+(C_2H_2)$. Again, their work indicated that the contribution of the two-way donoracceptor interaction to the bonding is negligible and that the main contribution comes from electrostatic forces.

Evidently, gaining a complete perspective on the bonding of group 11 monoion-unsaturated hydrocarbon complexes is difficult, and the subject remains a controversial one. With this in mind, we have undertaken some new experiments in order to provide further information on the bonding of systems relevant to the above issue. One property of the complexes which could be derived from both experiment and calculation is the bonding strength which is expected to be weak in the case of the electrostatic interactions, and strong for ones in which covalent effects dominate.

During the past years, high pressure mass spectrometry has been one of the most powerful methods [11] to measure the thermochemical properties of ion-neutral complexes, especially, the bonding enthalpies. In the present work, using high pressure mass spectrometry we investigate the following association reactions to determine the bonding strength of Ag^+ to C_2H_4 , which is one of the most simple unsaturated hydrocarbons

$$Ag^{+}(C_{2}H_{4})_{n-1} + C_{2}H_{4} = Ag^{+}(C_{2}H_{4})_{n},$$

n=1 or 2. (1)

2. Experimental

The high pressure mass spectrometry (HPMS) in operation in our laboratory has been described in detail previously [12]. Briefly, Ag^+ is produced by resistively heating a coated thermionic filament. The coating consists of one part Al_2O_3 , two parts of SiO₂, and one part of AgNO₃. Since Ag has a much higher ionization potential and melting point than sodium and potassium [13], the Ag⁺ filament is carefully prepared in such a manner as to prevent subsequent contamination from sodium and potassium. Therefore, high purity starting materials and distilled and deionized water are used to make the filament as a source of Ag⁺.

The ions generated from the filament are drifted through a gas mixture of C₂H₄ and He, and focused into a thermally controlled reaction cell by a series of three electrostatic plates. Within the reaction cell, the ions and associated clusters undergo further clustering and achieve both chemical and thermal equilibrium. The sampled ions diffuse out of the cell through a small orifice (100 µm) and are detected by a quadrupole mass spectrometer. From the measured ion intensities and the known partial pressure of the ligand C_2H_4 in the reaction cell, equilibrium constants are determined at the measured temperature using well established methods [12,14]. One atmosphere is chosen as the standard state. A number of measurements at various selected temperatures results in a van 't Hoff plot from which the enthalpy and entropy changes can be deduced using conventional thermodynamic equations.

3. Results

A typical van 't Hoff plot (log K versus 1/T) corresponding to the n=2 reaction is shown in fig. 1.



Fig. 1. Van 't Hoff plot for the association reaction of $Ag^+(C_2H_4)+C_2H_4=Ag^+(C_2H_4)_2$.

Thermochemical properties are deduced from a linear least-square fit [15] to the data. The enthalpy change derived from the slope and the entropy change from the intercept of the van 't Hoff plot are listed in table 1 for the n=2 reaction, along with the Gibbs free energy change at 298 K obtained from the equation

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \,. \tag{2}$$

Since the bonding of Ag⁺(C₂H₄) is very strong, quite high temperatures (above 750 K) are needed to effect the reverse reaction of Ag⁺(C₂H₄) dissociating into Ag⁺ and C₂H₄. Hence, a complete van 't Hoff plot for the n=1 reaction could not be obtained due to the temperature limitation of the current apparatus, so that the enthalpy and entropy changes for the reaction could not be derived directly from the measurement. Fortunately, an equilibrium constant (K=95000) for the reaction was measurable at 750 K (upper temperature limitation). The determined value gives a Gibbs free energy change $-\Delta G^0$ of 17.1 kcal/mol at 750 K.

Considering the fact that the entropy change is one

Table 1 Thermochemical properties for the association reactions of $Ag^+(C_2H_4)_{n-1}+C_2H_4=Ag^+(C_2H_4)_n$

n	$-\Delta H^0$ (kcal/mol)	$-\Delta S^0$ (cal/mol K)	$-\Delta G^{o}$ (kcal/mol)	
1	33.7 ^{a)}	22.1 ^b)	17.1 (750K)	
2	32.4	30.2	23.4 (298K)	

^{a)} Derived from the relation $\Delta H^0 = \Delta G^0 + T \Delta S^0$.

^{b)} Calculated value from the standard statistical methods.

of the thermochemical properties which can be obtained from statistical mechanics [16], we estimated the entropy change in order to deduce ΔH^0 for the n=1 reaction. Details of the procedure to calculate entropy changes for an association reaction have been discussed previously [17,18]. Since both the ion complex and ligand are not expected to be electronically excited under the conditions of the experiment, the contribution from the electronic part is normally zero. Hence, only the translational, rotational, and vibrational entropy changes need to be considered here.

In order to obtain the rotational and vibrational entropy changes, the molecular constants of both the ion complex and ligand must be known. For the $Ag^+(C_2H_4)$ system, constants for the ligand C_2H_4 have been determined experimentally [19], and the values for $Ag^+(C_2H_4)$ are deduced from our ab initio calculations [20] ^{#1}. The various contributions to the entropy changes calculated for the n=1 reaction at the experimental temperature of 750 K are listed in table 2 along with the molecular constants. By using the calculated ΔS^0 and the measured ΔG^0 at 750 K, we also derived the ΔH^0 for the n=1 reaction from eq. (2). These values are also listed in table 1.

4. Discussion

Normally, except for a small correction which is usually on the order of 1/2 kcal/mol, the value of the enthalpy change is nearly equal to the bond energy, D_0 , of the formed complex [15]. Hence, the bond energies of $Ag^+(C_2H_4)$ and $Ag^+(C_2H_4)_2$ are determined to be ≈ 33.7 kcal/mol, and 32.4 kcal/ mol, respectively. Before making any comparisons, we need to discuss the uncertainty of the bond energies reported in this Letter. The bond energy of $Ag^+(C_2H_4)_2$ is deduced directly from the van 't Hoff plot; the statistical error (standard deviation) for the fit to the van 't Hoff plot shown in fig. 1 is about 0.2 kcal/mol. However, because of possible sources of systematic errors [22], the overall uncertainty of the reported value is expected to be less than 1.5 kcal/ mol.

The bond energy of Ag⁺ (C₂H₄) is not determined directly from the van 't Hoff plot. Its accuracy depends on the accuracy of the calculated entropy change. We estimate the uncertainty of the calculated entropy change resulting from the error of the calculated constants of Ag⁺ (C₂H₄), to be less than 3.0 cal/mol K ^{#2}. Considering the possible error of the measured ΔG^0 , the overall uncertainty of the bonding strength for Ag⁺ (C₂H₄) is expected to be also less than about 3.0 kcal/mol.

Next, we consider the implications of the experimental findings reported herein by first comparing the bonding strength of $Ag^+(C_2H_4)$ with some of the calculated values. According to his ab initio calcu-

^{#2} For footnote see next page.

	Rotation (cm^{-1})		σ	Vibration $d^{(1)}$ (cm ⁻¹)			
	A	В	C		vib1	vib2	vib3
$\overline{C_2H_4}$	4.86 ^{b)}	1.00 ^{b)}	0.83 ^{b)}	4			
$Ag^+(C_2H_4)$ ΔS (cal/mol K)	0.10 °)	0.11 °) 7.4	0.81 ^{c)}	2	184.2 ^{c)}	191.3 °) 10.3	488.1 ^{c)}

Table 2

The calculated entropy changes a) along with the molecular constants of C2H4 and Ag+(C2H4) used in the calculation

^{a)} The calculated entropy change from translational motion is $-\Delta S = 39.8$ cal/mol K.

^{b)} From ref. [19]. ^{c)} See ref. [20], and footnote 1.

^{d)} Since the frequencies of the normal modes of C_2H_4 are nearly the same before and after the association, and the frequencies are very large, only the contribution from those three newly formed vibrational modes are taken into account in computing the vibrational entropy changes.

³¹ The program we used is GAUSSIAN 88 (Gaussian Inc., Pittsburgh, PA). The basis set for Ag⁺ is the LANDZ1 [21]. For C and H are D95V. The full geometry optimization has been conducted at SCF level and the rotational and vibrational constants are determined with the optimized geometry.

lation, Basch [3] predicted that the bonding of $Ag^+(C_2H_4)$ is purely electrostatic, and the bond energy would be just under 1 eV (≈ 23 kcal/mol). Obviously, the calculated result is much smaller than the bond energy obtained from the present work. Such a disagreement might result from the inaccuracy of the Basch calculation, because he used a SCF level ab initio calculation with a fixed structure; sometimes, SCF level calculations result in a much weaker bonding energy as indicated by the findings of Rosi and Bauschlicher [9].

It is very interesting to compare the bonding of C_2H_4 to Ag⁺, with that to alkali ions such as Na⁺, because the alkali ion complexes are expected to display pure electrostatic bonding due to the noble gaslike electronic configurations involved. We have attempted to measure the bonding energy of Na⁺ to C_2H_4 . Unfortunately, because of the very weak bonding, once $Na^+(C_2H_4)$ is formed, C_2H_4 is immediately replaced by the trace impurities in the C_2H_4 sample to form other more stable Na⁺ complexes. Hence, such an attempt was not successful. Therefore, in order to estimate the bond energy of $Na^+(C_2H_4)$, we performed ab initio calculations. The GAUSSIAN 86 program [23] is used in the calculation employing a 6-31*G basis set. The structure of $Na^+(C_2H_4)$ is optimized at the SCF level, and the bond energy is determined at the MP4 level with the SCF optimized geometry. Our calculation indicates that the bonding of Na^+ to C_2H_4 is indeed electrostatic in origin, and that the bond energy is only about 14.5 kcal/mol. (The failure to detect the complex experimentally is consistent with the bonding being

^{#2} In order to study the effect of the error of the calculated rotational constants of $Ag^+(C_2H_4)$ on the rotational entropy change, we have intentionally changed all the optimized bonding lengths by ± 0.2 Å which is expected to be much larger than the possible error of the geometry optimization. With ± 0.2 Å variation in the bonding length, the change of the calculated rotational entropy change is less than 0.8 cal/mol K. The vibrational constant is obtained from the second derivatives of the energy with respect to the optimized geometry. From our similar calculation on C₂H₄, which gives less than 20% error of the calculated vibration frequencies, we expect error of the calculated vibrational frequencies of $Ag^+(C_2H_4)$ to be less than 30%. This leads to errors in the calculated vibrational entropy change to be less than 2.1 cal/mol K. Therefore, the overall uncertainty of the calculated entropy change is expected to be less than 3.0 cal/mol K.

at least this small, and probably even smaller.) If the bonding of C_2H_4 to Ag^+ were purely electrostatic in nature, the bonding should be very weak just like $Na^+(C_2H_4)$, because Ag^+ has even larger radius [13] than Na^+ . In actual fact the bonding of C_2H_4 to Ag^+ is much stronger than with Na^+ . Therefore, the simple electrostatic interaction model [24] cannot account for the strong bonding found for $Ag^+(C_2H_4)$.

One may argue that the open shell electron configuration of Ag⁺ could lead to an enhancement of the electrostatic interaction in the Ag⁺ complex as found in other open shell metal ion complex systems [25,26]. In order to obtain additional evidence as to whether the bonding of $Ag^+(C_2H_4)$ is primarily electrostatic in origin, but merely enhanced by the rearrangement of the valent orbitals of Ag⁺, it is very instructive to compare the bonding of Ag^+ to C_2H_4 with that of the silver ion to water. Water has a very large dipole moment [13], while ethylene is an unpolar molecule. From the view point of electrostatic interactions, it is expected that the bonding of Ag⁺ to water should be much stronger than to ethylene. But, the bond energy determined in this work indicates that the bonding of Ag⁺ to the first two C₂H₄ molecules is even stronger than to waters [15], which clearly suggests that the strong bonding of Ag⁺ to C_2H_4 does not result from the enhancement of the electrostatic interaction by the orbital rearrangement of Ag^+ . In fact, the bonding of Ag^+ to the first two ethylenes is so strong that it is very difficult to interpret such strong bonding by any other reasonable enhancements of the electrostatic interaction as found in alkali ion complex systems [14].

Based on the above considerations, we believe that Ag^+ and ethylenes are not bound together by pure electrostatic forces (at least, electrostatic forces are not the dominant factors in the complexes), and there must be other stronger interactions involved. The interaction which greatly enhances the bonding of Ag^+ to the first two C_2H_4 might be a covalent interaction or the two-way donor-acceptor interaction as suggested by Dewar [2]. In fact, from the high level ab initio calculations, the strong bonding of C_2H_4 to other transition metal ions has also been attributed to covalent interactions [9].

Finally, it should be pointed out that the thermochemical data provide only the bonding strength, but not information on the nature of the bonding. Hence, more extensive theoretical treatments would be very valuable in furthering an understanding of bonding nature of Ag^+ to C_2H_4 . At present, high level ab initio calculations on the complexes formed by Ag^+ and C_2H_4 are in progress in our laboratory.

5. Conclusions

The bonding strength of $Ag^+(C_2H_4)$ and $Ag^+(C_2H_4)_2$ is determined in the present study. The bonding in $Ag^+(C_2H_4)$ is much larger than that calculated from low level ab initio calculations, and also the bonding in both complexes is stronger than that expected on the basis of a consideration of solely electrostatic interactions. The strong bonding suggests that covalent forces might be involved in the complexes. Extensive ab initio calculation with geometry optimization at CI level is needed to correctly interpret the bonding in the group 11 mono-ion–unsaturated hydrocarbon complexes.

Acknowledgement

Financial support by the US Department of Energy, Grant No. DE-FG02-88-60668, is gratefully acknowledged.

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