Gas-phase photodissociation of $AuCH_2^+$: the dissociation threshold of jet-cooled and rotationally thermalized ions

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Received 29 November 1999

Abstract

The photofragment spectra of jet-cooled and rotationally thermalized $AuCH_2^+$ are reported. Two channels are observed: loss of H_2 and loss of CH_2 with a branching ratio of 1.4:1 over the region studied. The presence of a threshold at 322 nm for the dissociation of jet-cooled $AuCH_2^+$ to $Au^+ + CH_2$ implies the *upper limit* $D_0^o(Au^+–CH_2) \leq 372 \pm 3$ kJ mol^{-1}. The dissociation threshold of ions rotationally thermalized in an ion trap shifts to lower energy by the amount of parent rotational energy. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Over the past two decades, the acquisition of accurate $M^+–CH_2$ bond energies has been the goal of several ion beam [1–4] and photodissociation studies [5,6]. Metal–carbon bond energies are of particular interest because they provide a means of assessing when reactions with hydrocarbons are energetically feasible. For example, dehydrogenation of methane (reaction (1)) is exothermic and occurs readily for those third-row transition-metal cations which have $D_0^o(M^+–CH_2) \geq 464$ kJ mol^{-1} (M = Ta$^+$, W$^+$, Ir$^+$, Os$^+$ and Pt$^+$) [1]. The reaction is endothermic for first- and second-row transition-

metal cations, which form much weaker $M^+–CH_2$ bonds.

$$M^+ + CH_4 \rightarrow MCH_2^+ + H_2 . \qquad (1)$$

Although complementary experimental and theoretical bond dissociation energies exist for many first- and second-row transition–metal organometallic cations, a similar synergism has not been obtained for third-row transition-metal compounds. This is primarily due to the sparse experimental data available and the expense of computationally treating relativistic effects in late transition-metal atoms [7,8]. Among the third-row transition-metal MCH_2^+ complexes, the closed-shell $AuCH_2^+$ is one of the simplest to treat computationally, and thus serves as a benchmark system for theory. To date, there is reasonable agreement between the calculated [9–11] and experimental [12] values of the $Au^+–CH_2$ dissociation energy. However, to assess the reliability of the theoretical methods, which can be further applied

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to open-shell MCH_2^+ systems, additional experimental data are required. In an attempt to fulfill this requirement, we measure the bond dissociation energy of $AuCH_2^+$.

In a 1996 review [4] Armentrout and Kickel note that the internal energy of the reactants will shift the measured thresholds of endothermic reactions. Therefore, bond strengths measured in guided-ion beam experiments have to be corrected for the parent internal energy. In this Letter, we examine the effect of parent rotational energy on the photodissociation threshold by comparing the photofragmentation of jet-cooled and rotationally thermalized $AuCH_2^+$.

2. Experimental approach

In a typical experimental sequence, ions produced in the source are mass selected, photodissociated at the turning point of a reflectron, and the masses of fragment ions determined by their flight times. The dual time-of-flight (TOF) mass spectrometer used has been described in detail elsewhere [13].

Gold cations are generated by laser ablation of a 6.1 mm dia. brass rod electroplated with 0.13 mm gold (Fountain Plating, Springfield, MA, 99.97% pure). Ablated Au^+ reacts with the reagent gas mixture, 1% ethylene oxide (Merriam-Graves, 99.7% pure) in helium (UHP grade, 99.999% pure), to produce $AuCH_2^+$. Ions produced in the source undergo a supersonic expansion and cool to a rotational temperature of ~ 10 K. After expansion, ions are skimmed, accelerated to 1800 V kinetic energy and then rereferenced to ground potential prior to entering the field-free flight tube. Photoexcitation of the mass-selected $AuCH_2^+$ ions is accomplished at the turning point of the reflectron using the frequency-doubled output of a tunable Nd:YAG-pumped dye laser. The charged dissociation fragments, Au^+ and AuC^+, are identified by their subsequent flight times to a 40 mm dia. microchannel plate detector.

Dissociation channels are monitored by taking the difference of the $AuCH_2^+$ mass spectrum with and without the dissociation laser. Depletion of the parent ions results in a negative-going peak, while the fragment ion peaks appear in the positive direction (Fig. 1). The photofragment spectrum is obtained by monitoring the yield of a specific fragment ion as a
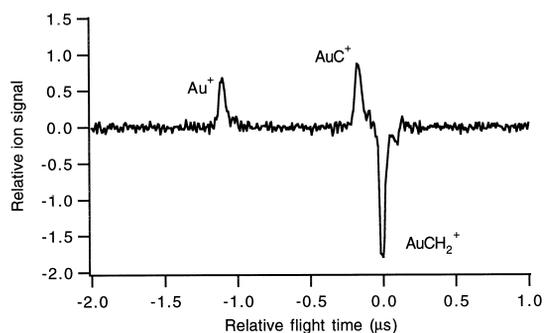
Fig. 1. Photodissociation of jet-cooled $AuCH_2^+$ at 311 nm. Two clearly resolvable channels, loss of H_2 and CH_2, are active at this wavelength.

function of wavelength and normalizing to parent ion signal and laser power. A linear fragmentation response at 292 nm, with laser fluence up to 150 mJ cm^{-2}, indicates a one-photon fragmentation process for both channels.

In order to study the effect of parent rotational energy on the photofragment spectrum, the source was modified to allow ions to be trapped after formation and supersonic expansion. Ions were trapped for 1.5 ms in a R.F. quadrupole ion trap (R.M. Jordan) operating at 400 V_{pp} and 1 MHz with ~ 1 mTorr He buffer gas. Following the decay of the R.F. voltage, typically after a 2 μs delay, the ions are injected into the TOF mass spectrometer by applying a 80 V pulse to the front cap of the ion trap [14]. During its residence in the trap, an ion will collide ~ 30 times with the helium buffer gas, assuming a Langevin collision rate of 5.4×10^{-10} cm^3 s^{-1} $molecule^{-1}$ [15]. As a result ions are rotationally thermalized (~ 298 K), which was confirmed by measuring the photofragment spectrum of the $^6\Sigma-^6\Sigma$ band [13] of FeO^+ near 349 nm at several trapping times. Spectra obtained at trapping times greater than 1.0 ms are insensitive to trapping time and are consistent with simulations at a rotational temperature of ~ 298 K. The vibrational distribution should not be significantly affected by only tens of collisions with helium.

3. Results and discussion

Photodissociation of jet-cooled $AuCH_2^+$ yields Au^+ and AuC^+ (reactions (2) and (3)) which appear

as positive peaks in Fig. 1. Although generation of $AuCH^+$ (reaction (4)) is not observed, our mass resolution precludes us from ruling out this channel.

$$AuCH_2^+ + h\nu \rightarrow Au^+ + CH_2, \qquad (2)$$

$$AuCH_2^+ + h\nu \rightarrow AuC^+ + H_2, \qquad (3)$$

$$AuCH_2^+ + h\nu \rightarrow AuCH^+ + H. \qquad (4)$$
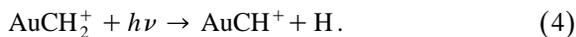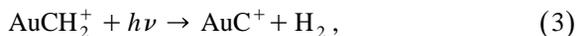
Fig. 2 shows the yield of Au^+ and AuC^+ as a function of laser wavelength. In both photofragment spectra, there is a threshold at 322 nm, with signal increasing to shorter wavelength, reaching a plateau near 302 nm. Other than the threshold, these spectra, and spectra taken over several regions using ~ 0.3 cm^{-1} steps, are featureless and the branching ratio $AuC^+:Au^+ = 1.4:1$ is observed at all wavelengths studied. The threshold at 322 nm in Fig. 2 for the photoappearance of Au^+ and AuC^+ implies the *upper limits* $D_0^o(Au^+ - CH_2) = D_0^o(AuC^+ - H_2) \leq 372 \pm 3$ kJ mol^{-1}. These values also imply an $Au^+ - C$ dissociation energy of 324 ± 4 kJ mol^{-1} if one assumes that photodissociation of $AuCH_2^+$ occurs *at* the thermodynamic threshold. By including the full energy distribution of vibrational [10] and rotational states in both parent and photofragment products, we obtain the *upper limit* $D_{298}^o(Au^+ - CH_2) \leq 377 \pm 3$ kJ mol^{-1}.
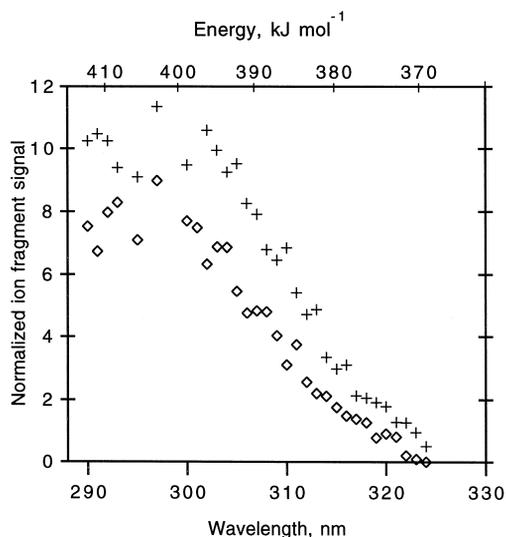
Fig. 2. Photoappearance spectra of Au^+ ($\diamond$) and AuC^+ ($+$) from dissociation of jet-cooled $AuCH_2^+$ as a function of wavelength. Au^+ and AuC^+ photosignals have been normalized to the parent ion intensity and the laser power.
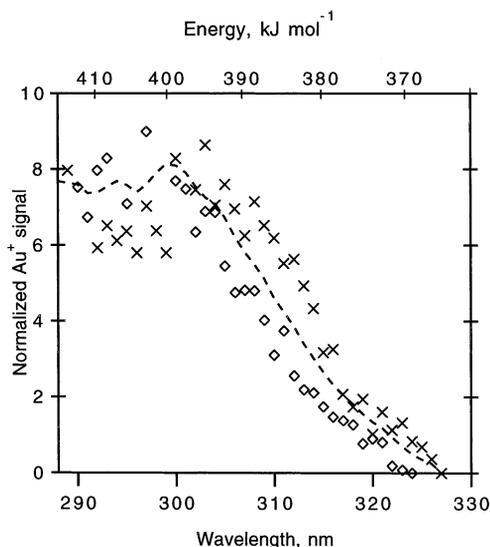
Fig. 3. Photoappearance spectra of Au^+ as a function of wavelength obtained by monitoring the fragmentation of jet-cooled ($\diamond$) and rotationally thermalized ($\times$) $AuCH_2^+$ ions. The dashed line is the spectrum obtained by convoluting the photoappearance spectrum of internally cold Au^+ with the calculated rotational energy distribution of $AuCH_2^+$ at 298 K.

To study the effect of parent rotational energy on photofragmentation, we monitored the $Au^+ + CH_2$ photofragment channel of rotationally thermalized $AuCH_2^+$ ions (Fig. 3). The observed red-shifted threshold at 327 nm implies an $Au^+ - CH_2$ dissociation energy of 366 ± 3 kJ mol^{-1} which is slightly smaller than the value derived from jet-cooled ions. Since this decrease is due to the additional rotational energy in the parent ions, we calculated the rotational energy distribution of the $AuCH_2^+$ ions at 298 K. The simulated spectrum, shown by the dashed line in Fig. 3, was generated by convolution of the photofragment spectrum of jet-cooled ions with the calculated rotational energy distribution of $AuCH_2^+$ ions. The excellent agreement between the simulated and the rotationally thermalized thresholds demonstrates that the rotational energy of the parent ions is applied to bond cleavage. This result is the spectroscopic counterpart of the coupling between the internal energies of reactant ions and the reaction coordinate in ion-beam studies of bimolecular reactions [4].

In 1987, Chowdhury and Wilkins studied the reactions of Au^+ with several organic molecules in an ion cyclotron resonance spectrometer [12]. They

observed that the dominant reaction of Au^+ with CH_3Cl and CH_3Br is formation of $AuCH_2^+$ (94% and 70%, respectively), with the $Au(CH_3X)^+$ adduct as the secondary product. In contrast, $AuCH_2^+$ is the least abundant (6%) of the five products generated in the reaction of Au^+ with CH_3I, and it is not observed in the reaction with cyclopropane. Straightforward calculations based on recent $\Delta_f H^o_{298}$ values [16], give the estimated Au^+–CH_2 bond energy limits > 380 and > 390 kJ mol^{-1} for the exothermic reaction of Au^+ with CH_3Cl and CH_3Br, respectively. Exothermic reaction with CH_3I and cyclopropane requires $D^o_{298}(Au^+–CH_2) > 403$ and > 390 kJ mol^{-1}, respectively. Chowdhury and Wilkins suggested an Au^+–CH_2 dissociation energy of > 399 kJ mol^{-1} (original value from Ref. [12]), based on the reaction with CH_3I. However, this assignment has been questioned [9,17], as even a small amount of electronically excited Au^+ could form the $AuCH_2^+$ product observed in the $Au^+ + CH_3I$ reaction. Our observed *upper limit* $D^o_{298}(Au^+–CH_2) \leq 377 \pm 3$ kJ mol^{-1}, implies that reaction of Au^+ with CH_3Cl is thermoneutral, slightly endothermic with CH_3Br and cyclopropane and significantly endothermic with CH_3I. These results are in reasonable agreement with the reactions observed by Chowdhury and Wilkins.

$AuCH_2^+$ has by far the highest bond dissociation energy of the coinage metal metallocarbenes ($CuCH_2^+$, 259 ± 7 kJ mol^{-1}; $AgCH_2^+$, 107 ± 7 kJ mol^{-1}) [3,18]. This tendency of gold, and the third-row transition metals in general, to form much stronger chemical bonds than first- and second-row transition metals has been attributed to two main relativistic effects: the stabilization of the 6s shell and the destabilization of the 5d shell [7,8,19]. In this way, the singlet ground state in $AuCH_2^+(^1A_1)$ is generated by a dative bond between ground state $Au^+(d^{10}s^0, {}^1S_0)$ and $CH_2(\tilde{a}, {}^1A_1)$, rather than a covalent bond between excited $Au^+(d^9s^1, {}^3D)$ and $CH_2(\tilde{X}, {}^3B_1)$, as in $CuCH_2^+$ and $AgCH_2^+$ [10]. The strong Au^+–CH_2 bond is produced by interaction of the σ^2 lone pair of the singlet methylene with the empty 6s orbital of $Au^+(^1S_0)$, and overlap of the doubly-occupied $5d_{xz}$ orbital with the empty p_x orbital of carbon to produce a π bond [9]. A quasirelativistic LDA + B density-functional calculation performed by Heinemann et al. [11] indicates that the

relativistic contribution accounts for more than 70% of the total bond energy in $AuCH_2^+$. The experimental value presented in this Letter, $D^o_0(Au^+–CH_2) = 372 \pm 3$ kJ mol^{-1}, is in good agreement with their dissociation energy of 363 kJ mol^{-1}, in excellent agreement with the CCSD(T)-QR value of 378 kJ mol^{-1} reported by Hrušák [10] and in reasonable agreement with the 393 ± 9 kJ mol^{-1} value recommended by Irikura and Goddard [9] (for comparison purposes, calculated D_e values were converted to D_0 values using $AuCH_2^+$ vibrational frequencies reported by Hrušák [10]). Although the bond dissociation energy of AuC^+ has not been measured yet, our derived value of 324 ± 4 kJ mol^{-1} agrees with the CCSD(T) value of 335 kJ mol^{-1} calculated by Barysz and Pyykkö [20] and is comparable to the dissociation energy of 352 kJ mol^{-1} of the isoelectronic AuB neutral [21].

In addition to increasing the bond energy, relativistic effects account for the breakdown of the spin selection rules. We observe the spin-forbidden dissociation $AuCH_2^+(^1A_1) + h\nu \rightarrow Au^+(^1S_0) + CH_2(\tilde{X}, {}^3B_1)$ rather than the spin-allowed dissociation $AuCH_2^+(^1A_1) + h\nu \rightarrow Au^+(^1S_0) + CH_2(\tilde{a}, {}^1A_1)$. If dissociation occurred on the singlet surface, an *upper limit* of 339 ± 3 kJ mol^{-1} is obtained by subtraction of the experimental excitation energy of $CH_2(\tilde{a}, {}^1A_1)$ [22] from our $D^o_{298}(Au^+–CH_2)$ value. This result is significantly lower than the available experimental and theoretical data. The high yield of Au^+, close to the yield of AuC^+ in the spin-allowed dissociation $AuCH_2^+(^1A_1) + h\nu \rightarrow AuC^+(X, {}^1\Sigma) + H_2(X, {}^1\Sigma)$, is further evidence of the breakdown of the spin selection rules. Although relativistic effects cause Au^+ to bind more strongly to CH_2 than most first- and second-row transition-metal cations, it binds more weakly than the remaining third-row transition-metal ions [1]. Thus, while Ta^+, W^+, Os^+, Ir^+ and Pt^+ dehydrogenate methane, implying $D^o_{298}(M^+–CH_2) = 464$ kJ mol^{-1}, the reaction of Au^+ with methane is ~ 87 kJ mol^{-1} endothermic and is not observed [12].

4. Conclusions

Photofragmentation of $AuCH_2^+$ from 285 to 322 nm yields $AuC^+ + H_2$ and $Au^+ + CH_2$ at a branch-

ing ratio of 1.4:1, irrespective of wavelength. From the observed dissociation threshold we obtain the *upper limits* $D_0^o(Au^+-CH_2) = D_0^o(AuC^+-H_2) \leq 372 \pm 3$ kJ mol^{-1}, and $D_{298}^o(Au^+-CH_2) \leq 377 \pm 3$ kJ mol^{-1}. The photofragment spectrum of rotationally thermalized $AuCH_2^+$ is red-shifted from that of jet-cooled ions, demonstrating that the rotational energy of the parent ions contributes to the fragmentation of $AuCH_2^+$ near the dissociation threshold. The strong Au^+-CH_2 bond and high yield of Au^+ in the spin-forbidden dissociation $AuCH_2^+(^1A_1) + h\nu \rightarrow Au^+(^1S_0) + CH_2(\tilde{X}, ^3B_1)$ show the influence of relativistic effects on the chemistry of gold.

Acknowledgements

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