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Field ionization behavior of cyclohexane on Au tips

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Abstract

Ion formation by field ionization (FI) of molecules also depends on the chemical reactivity of the field anode surface and of the molecules in the neutral and ionized state. Since cyclohexane is known not to chemically interact with Au surfaces and in addition does not form fragment ions by field dissociation its FI behavior on Au tip surfaces was investigated by field ion microscopy (FIM) and FI MS. It is shown that cyclohexane does not react with Au tip surfaces at lower field strengths up to the onset of FI of molecules remote from the surface. However, at higher field strengths the Au tip surface becomes chemically reactive and the electron bombardment of the surface by FI of molecules remote from the surface leads to the dissociation of C–H bonds of adsorbed molecules with a preferential binding of the H atoms to the surface. The cyclohexyl radicals are either field desorbed or chemisorb on the Au surface. The subsequent FI of chemisorbed cyclohexyl molecules forms surface ions at which the FI probability for molecules supplied from the gas phase is enhanced. This is indicated by the appearance of bright spots in the field ion microscope. (Int J Mass Spectrom 185/186/187 (1999) 189–194) © 1999 Elsevier Science B.V.

Keywords: Field ion microscopy; Field ion mass spectrometry; Field induced surface reactions

1. Introduction

Ion formation by field ionization (FI) of molecules does not only depend on the applied electric field, the ionization energy of the molecules and the work function of the field anode surface but also on the chemical reactivity of the surface and of the molecules in the neutral and ionized state exposed to the external field. Accordingly ions are also formed by field induced surface reactions [1]. Products of such surface reactions are frequently abundant in FI mass spectra of polar and unsaturated compounds. If ions are formed with a chemical bond to the surface the ionization conditions change in that the FI probability of molecules is enhanced at these surface ions [2]. In field ion microscopy (FIM) the possible effects of a field induced chemistry on the surface structure and the ionization conditions have to be considered.

For imaging of surfaces by FIM at low field strengths, i.e. low field stress on the surface, cyclohexane has been considered to provide favorable properties as an image gas [3,4]. Its ionization energy of $E_I = 9.9$ eV [5] is low compared to that of the rare gases typically used in FIM, it does not have a polar group nor double bonds and its cyclic structure prevents fragmentation by field dissociation. In a recent study [6] the FI behavior of cyclohexane on Pt-tip surfaces was investigated by FIM and FIMS. Experiments with freshly prepared Pt tips revealed the dependence of the onset of FI of molecules supplied

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Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

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from the gas phase on the formation of surface ions, i.e. the ionization of chemisorbed cyclohexane molecules. At higher field strengths the low partial pressure of water by which cyclohexane is typically contaminated leads to the disappearance of surface ions and the oxidation of the Pt-tip surface by field induced reactions. During the oxidation of the surface hydride ion transfer reactions from cyclohexane to the surface occur which lead to a high intensity ratio of $(M - H)^+/M^+$ ions of about 20%. The onset field strength of FI of cyclohexane on an oxidized Pt surface is determined by the high work function of the surface and is significantly lower than the onset field strength on an unoxidized Pt surface.

These results of the dependence of FI of cyclohexane on the surface chemistry with Pt prompted us to perform similar experiments with Au tips. In contrast to Pt surfaces Au surfaces are hydrophobic and chemically inert towards hydrocarbons. Accordingly the question arises for the appearance of image contrast phenomena in FIM of gold tips with cyclohexane as image gas and for the origin of the observed phenomena. In the experiments a low field strength regime and a high field strength regime had to be distinguished. The low field strength regime is determined by the onset of ion emission from the tip and the high field strength regime by the onset of FI of molecules remote from the surface.

2. Experiment

A field ion microscope equipped with a single micro channel plate image intensifier with the entrance at earth was used. The Au tips were prepared from 125 μm wires (Goodfellow, >99.99%) by electrochemical etching with an aqueous solution of KCN [7]. The tips were spot welded on a 0.1 mm tungsten loop for resistive heating of the tip. Before use in the FIM experiments with the hydrocarbons the surface of the tips was smoothed and cleaned by field evaporation with neon as an image gas at liquid nitrogen temperature. The relation between field strength and tip potential was calibrated by measuring the tip voltage of the onset of field evaporation of metal atoms from a smooth tip surface. The corresponding field strength is about $F \approx 35$ V/nm for Au [7]. In the FIM experiments the accuracy of the field strength calibration was about $+/-1$ V/nm and in the FI MS experiments not better than $+/-2$ V/nm.

Cyclohexane (Aldrich: c-$C_6H_{12} > 99.9\%$; $H_2O < 0.01\%$) was introduced via a leak valve. It had been subjected to three freeze-pump-thaw cycles prior to introduction into the vacuum chamber. The background pressure in the microscope was about 5×10^{-9} mbar. If not otherwise stated the image gas pressure was about 1×10^{-4} mbar and the microscope at room temperature, i.e. about 25°C.

A video system with a PC compatible video digitalizer system was used for recording the ion images on tape. The figures shown are single digitalized frames (time resolution 40 ms) of the video.

The FI-mass spectra (FI-MS) were obtained with a modified double-focusing Kratos MS 9 mass spectrometer equipped with an FI source. A direct combination of the field ion microscope with the mass spectrometer was not possible.

3. Results and discussion

3.1. FIM with cyclohexane and Au tips at lower field strengths

In the FIM experiments Au tips were first prepared and cleaned by field evaporation at −150°C with neon as image gas and the relation between tip voltage and field strength calibrated. Then cyclohexane was introduced at zero field strength with the tip at room temperature. Fig. 1 shows the cyclohexane ion emission from an Au tip for two field strengths. The onset field strength of ion emission is about 13 V/nm and 20% higher than the onset field strength observed with freshly prepared Pt tips [6]. Because a layer of chemisorbed cyclohexane is formed on a Pt surface but not on an Au surface the onset field strength of FI observed with Au tips cannot be related to the appearance of surface ions by FI of chemisorbed cyclohexane. This is indicated by the missing of bright spots and the rather low contrast of the ion

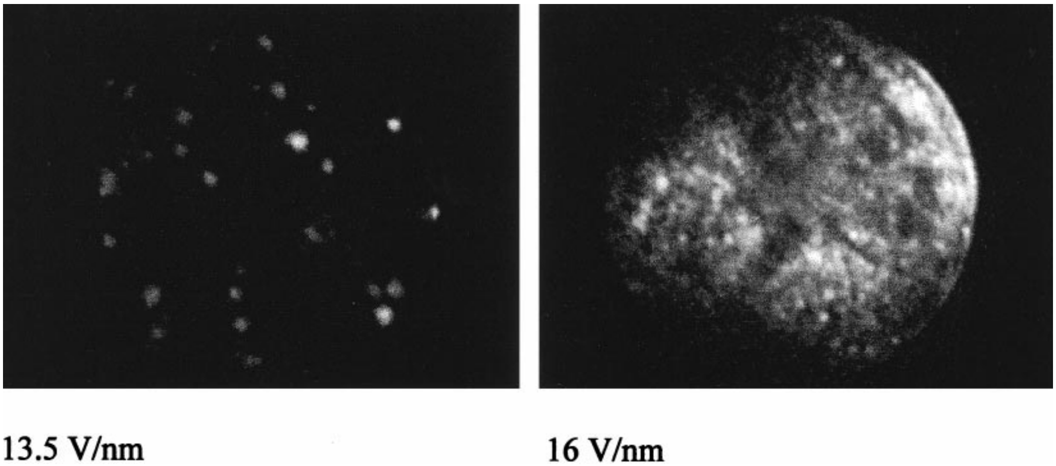

Fig. 1. FIM images of an Au tip with cyclohexane as image gas showing the ion emission with increasing field strength. The diameter of the ion images corresponds to a surface area with a diameter of about 90 nm. The gas pressure of cyclohexane was about 1×10^{-4} mbar, the residual gas pressure of water about 2×10^{-8} mbar and the tip temperature 25°C.

emission areas observed with Au tips at lower field strengths. The image contrast obtained with Au tips and their field strength dependence are in support of FI of molecules from physical adsorption layers and a rough structure of the surface on an atomic scale.

The minimum field strength F required for FI of molecules from an adsorption layer can be estimated by using the simplified condition for FI of molecules at a minimum ionization distance (x_c) [1]:

$$ex_cF \approx E_I - \Phi - e^2/4x_c$$

with E_I the ionization energy of the molecules and Φ the work function of the surface. This condition disregards from polarization effects and activation energies and only considers the energy difference between the initial and final state of the reaction for the electron tunneling process. With the ionization energy $E_I(C_6H_{12}) = 9.9$ eV, the work function Φ(Au) $\approx$ 5.3 eV [5], and a minimum ionization distance of about $x_c \approx 0.25$ nm, a field strength of about $F \approx 13.5$ V/nm is calculated for the formation of the $C_6H_{12}^+$ ions. This estimated threshold field strength agrees with the range of field strengths in which the first spots appear in the FIM images of Au tips. The FI conditions as indicated by the FIM images of the tip were found to be not affected by a partial pressure of water of about 1×10^{-6} mbar added to the image gas pressure of cyclohexane of 1×10^{-4} mbar. At lower field strengths (<15 V/nm) the M^+ molecular ion and the $(M - H)^+$ ion of cyclohexane were detected by mass spectrometry with an intensity ratio $(M - H)^+/M^+$ of less than 0.1%.

3.2. FIM with cyclohexane and Au tips at higher field strengths

The field strength at which cyclohexane molecules are ionized remote from the surface in free space with a similar probability as H_2 at 30 V/nm [8] is estimated to be about 15 V/nm [9]. Above about 16 V/nm bright spots appear in the FIM images of Au tips with cyclohexane as image gas. This is shown in Fig. 2 for a freshly prepared Au tip and field strengths of 18 V/nm and 19 V/nm. The ion images flicker because spots randomly appear and disappear at a high frequency. This frequency increases with the cyclohexane gas pressure and decreases with the tip temperature below room temperature. At field strengths of about 20 V/nm the image contrast disappear. At these field strengths spots from surface ions are still detectable in FIM with Pt tips [6] which indicates that molecules supplied from the gas phase can reach the surface. Experiments with a partial pressure of water of up to 1×10^{-6} mbar did not change the FIM

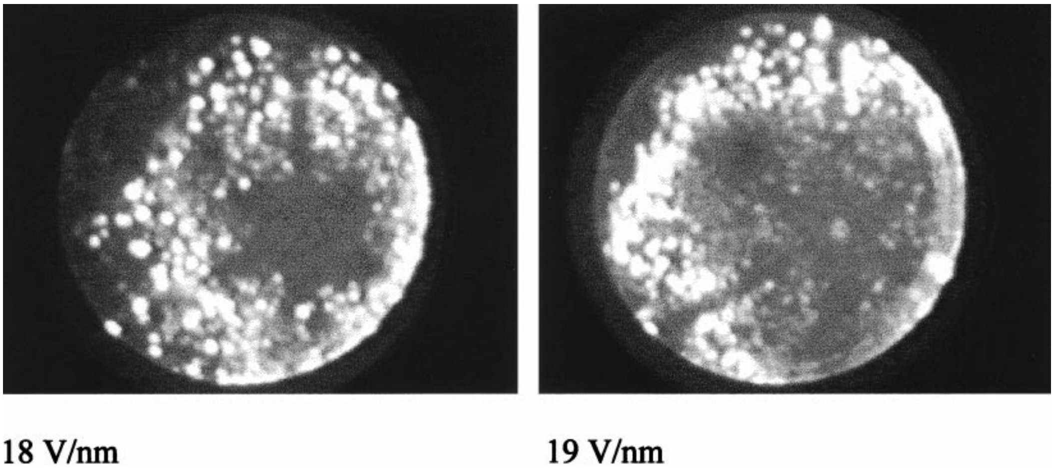

Fig. 2. FIM images of an Au tip with cyclohexane as image gas showing the appearance of bright spots at higher field strengths. The diameter of the ion images corresponds to a surface area with a diameter of about 90 nm. The gas pressure of cyclohexane was about 1×10^{-4} mbar, the residual gas pressure of water about 1×10^{-8} mbar and the tip temperature 25°C.

phenomenology. Only at higher partial pressures of water ($>10^{-5}$ mbar) the field induced oxidation of the Au tip surface by water could be observed by the appearance and growth of bright islands in FIM with cyclohexane.

Mass spectrometry experiments showed that with the appearance of the flickering spots in FIM the $(M - H)^+/M^+$ intensity ratio of cyclohexane strongly increases. Accordingly an intensity ratio of about 0.1% was measured at a field strength of about 14 V/nm and an intensity ratio of about 23% at 18 V/nm at which the ion emitting flickering spots are observed by FIM. At higher field strength the intensity ratio decreases again. The intensity ratio also increases with the gas pressure of cyclohexane and with the gas pressure of Xe added to cyclohexane (Table 1). In the same way as done with cyclohexane [9] the field strength at which Xe ($E_I = 12.1$ eV) is ionized remote from the surface in free space with a similar probability as H_2 at 30 V/nm is estimated to be about $F \approx 20$ V/nm. The use of a double focusing mass spectrometer relates the measured intensity ratios to ions formed near the surface of the Au tip only, i.e. with an energy loss of probably less than about 50 eV.

These MS results clearly reveal a relation between the appearance of the flickering spots, the formation of $(M - H)^+$ ions and FI of molecules remote from the surface, i.e. electron bombardment of the surface from FI processes in free space.

3.3. Field induced chemistry of cyclohexane on Au

At lower field strengths cyclohexane is ionized from physical adsorption layers. There is no indication of a chemical interaction of cyclohexane with the Au surface. However, the appearance of bright spots at higher field strengths under conditions of electron bombardment of the surface by FI of molecules remote from the surface indicate the formation of surface ions. Considering that the chemical reactivity of a metal anode tip surface exposed to a high field is enhanced [10] the formation of surface ions on Au

Table 1
Dependence of the $(M - H)^+/M^+$ intensity ratio of cyclohexane on gas pressure during FI on an Au tip

$F \approx 18$ V/nm $p(c\text{-hex.})$/mbar	$(M - H)^+/M^+$
2×10^{-5}	0.6%
2×10^{-4}	23%
$F \approx 21$ V/nm, $p(c\text{-hex.}) \approx 2 \times 10^{-5}$ mbar	
p(Xe)/mbar	$(M - H)^+/M^+$
0	0.5%
2×10^{-4}	16%

with cyclohexane can be explained by the following reactions:

$$C_6H_{12} + e^- \rightarrow C_6H_{11}^{\cdot} + {}^*H + e^-(Au) \quad (1)$$

$$C_6H_{11}^{\cdot} \rightarrow {}^*C_6H_{11} \quad (2a)$$

$$C_6H_{11}^{\cdot} \rightarrow C_6H_{11}^{+} + e^-(Au) \quad (2b)$$

$$^*C_6H_{11} \rightarrow {}^*C_6H_{11}^{+} + e^-(Au) \quad (3)$$

In the first step a hydrogen atom transfer from adsorbed molecules to the surface is induced by electron impact (1). The reaction is favoured for hydrogen atoms already in contact with the Au surface and a low activation energy of the reaction. The remaining $C_6H_{11}^{\cdot}$ radicals can also form a chemical bond to the Au surface (2a) or are field desorbed (2b) and detected as $(M - H)^+$ ions. The latter reaction is more probable because the applied field is high and the ionization energy of the cyclohexyl radical is low ($E_I \approx 7.7$ eV [11]). The subsequent FI of the chemisorbed molecules forms surface ions (3) at which the FI probability for molecules supplied from the gas phase is strongly enhanced as is observed in FIM of Pt-tip surfaces covered with chemisorbed cyclohexane [6]. The bright spots in the FIM images provide strong indirect evidence of the reaction sequence (2a) to (3).

The missing of bright spots in the central part of the FIM image of Fig. 2(b), i.e. in surface areas exposed to higher field strengths can be attributed to a low probability for molecules supplied from the gas phase to reach the surface and to a vanishing probability for reaction (2a) in competition with reaction (2b). At higher field strengths the following hydrid ion transfer reaction (4) is also favoured.

$$C_6H_{12} \rightarrow {}^*H + C_6H_{11}^{+} + e^-(Au) \quad (4)$$

The coverage of the surface with atomic hydrogen from reactions (1) and (4) remains low because the mobility of the hydrogen atoms on the surface should be relatively high and the recombination reactions (5) and (6) are exothermic.

$$^*H + {}^*H \rightarrow H_2 \quad (5)$$

$$^*C_6H_{11} + {}^*H \rightarrow C_6H_{12} \quad (6)$$

Reaction (6) explains the disappearance of surface ions and reaction (6) in combination with the reactions (1), (2a), and (3), leading to the formation of surface ions, the observed flickering of the spots and its dependence on surface temperature and gas pressure.

This electron bombardment induced surface chemistry is not observed with cyclohexane and Pt tips because a Pt surface is quickly saturated by chemisorbed cyclohexane and oxidized at higher field strengths by the water introduced with cyclohexane. So far there is no indication of other chemical reactions induced by electron bombardment. The cross sections for breaking other than C–H bonds of cyclohexane by electron impact are very low [12].

4. Conclusions

FI of cyclohexane on Au tips significantly differ from FI on Pt tips. At lower field strengths the Au-tip surface is chemically inert and accordingly molecules are ionized from physical adsorption layers. This is in contrast to FI of cyclohexane on Pt tips where the formation of surface ions by FI of chemisorbed cyclohexane determines the onset of field ion emission. At higher field strengths at which electron bombardment of a surface from FI of molecules remote from the surface occurs an Au surface becomes chemically reactive. The enhanced formation of cyclohexyl ions and the observation of a locally enhanced FI probability by the appearance of bright spots in FIM of Au tips with cyclohexane indicates the formation of surface ions by FI of chemisorbed cyclohexyl molecules. Under these conditions of higher field strengths a Pt-tip surface exposed to cyclohexane becomes oxidized by field induced reactions with water by which cyclohexane is typically contaminated and the surface ions formed at lower field strengths disappear. With Pt tips no effect of electron bombardment of the surface was observed [6].

These results indicate the significance of a field induced surface and ion chemistry to be considered in applications of FIM and show limitations of the use of cyclohexane as image gas in FIM of chemically reactive surfaces.

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