Adsorption and reactions of CH$_2$I$_2$ on Ru(001) surface

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Abstract

The adsorption and dissociation of CH$_2$I$_2$ were studied at 110 K with the aim of generating CH$_2$ species on the Ru(001) surface. The methods used included X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), temperature programmed desorption (TPD), Auger electron spectroscopy (AES) and work function measurements. Adsorption of CH$_2$I$_2$ is characterized by a work function decrease (0.96 eV at monolayer), indicating that adsorbed CH$_2$I$_2$ has a positive outward dipole moment. Three adsorption states were distinguished: a multilayer ($T_p$ = 200 K), a weakly bonded state ($T_p$ = 220 K) and an irreversibly adsorbed state. A new feature is the formation of CH$_3$I, which desorbs with $T_p$ = 160 K. The adsorption of CH$_2$I$_2$ at 110 K is dissociative at submonolayer, but molecular at higher coverages. Dissociation of the monolayer to CH$_3$ and I proceeded at 198–230 K, as indicated by a shift in the I(3d$_{5/2}$) binding energy from 620.6 eV to 619.9 eV. A fraction of adsorbed CH$_3$ is self-hydrogenated into CH$_4$ ($T_p$ = 220 K), and another one is coupled to dis-bonded ethylene, which — instead of desorption — is converted to ethylidyne at 220–300 K. Illumination of the adsorbed CH$_2$I$_2$ initiated the dissociation of CH$_2$I$_2$ monolayer even at 110 K, and affected the reaction pathways of CH$_2$. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the last decade considerable progress has been made in establishing the chemistry of different hydrocarbon fragments (CH$_2$, CH$_3$, C$_2$H$_6$, C$_2$H$_5$, etc.) on metal single crystal surfaces [1–6]. By means of several surface science tools our knowledge of the bonding, stability and reaction pathways of these hydrocarbon species has been significantly broadened. As C$_2$H$_4$ fragments are the possible reaction intermediates in most of the catalytic syntheses involving hydrocarbons, the results obtained may help to refine the mechanisms of these catalytic processes and to develop more efficient catalysts.

In this project an important step was the development of methods for the preparation of C$_x$H$_y$ species of a given composition. Halogenated hydrocarbons were thought to be suitable sources for these species. The first studies, however, revealed that chloro compounds (CH$_3$Cl, CH$_2$Cl, etc.) are quite stable on metal surfaces and dissociate to CH$_3$ and Cl only at high temper-
atures, when CH$_x$ undergoes secondary reactions [7–12]. Iodo compounds were found to be more reactive substances as they dissociate at much lower temperatures [1–6,13,14]. An important further step was the pyrolysis of azomethane to produce CH$_3$ [15,16].

In the present work we examine the adsorption and dissociation of CH$_2$I$_2$ on a Ru(001) surface with the aim of obtaining information on the chemistry of the CH$_2$ fragment on this surface. Previous studies revealed that the nature of the metal plays a decisive role in both the adsorption and the reaction pathway of the CH$_2$ formed [17–29]. The chemistry of CH$_2$I$_2$ on Ru surfaces has not been investigated yet, but some measurements on the adsorption of the other CH$_2$ precursor compounds (ketene and diazomethane) were performed [30,31].

2. Experimental

2.1. Methods

The experiments were performed in standard ultrahigh vacuum systems with a background pressure of 5 × 10$^{-10}$ mbar produced by turbomolecular, ion-getter and titanium sublimation pumps. The chamber was equipped with an electrostatic hemispherical analyzer (Leybold-Hereaus LHS-10), a differentially pumped UV photon (HeI, II) source for ultraviolet photoelectron spectroscopy (UPS), an X-ray source with Al anode for X-ray photoelectron spectroscopy (XPS) and an electron gun for Auger electron spectroscopy (AES) measurements. The angles of the UV source and electron analyzer with respect to the surface normal were 70 and 16°, respectively. All binding energies are referred to the Fermi level. Collection times for UPS and XPS were 15 and 30 min, respectively. XP spectra were smoothed by a fast Fourier transform method. For temperature programmed desorption (TPD), the sample was heated at 10 K's from 110 K to a selected temperature. The mass spectrometer was in line of sight. Changes in work function were obtained by measuring the secondary electron cut-off in the Hel UP spectra with the sample at −9 V relative to earth.

The UV light source was a focused full arc 40 W Hg lamp. The maximum photon energy at the sample was not greater than 5.4 eV (the onset of UV intensity from the Hg arc lamp). The light passed through a high-purity sapphire window into the vacuum chamber. The incident angle was 30° from the surface normal.

2.2. Materials

The oriented disk-shaped Ru crystal (purity 99.99%, diameter 8 mm, thickness 1.5 mm) was oriented within 0.5° at the (001) face and mechanically polished with diamond paste. The crystal was spotwelded to two 0.25 mm diameter wires for resistive heating and cooled to 110 K by heat conduction to a liquid nitrogen reservoir. The sample was heated from the rear by radiation from a tungsten filament and resistively with the spotwelded Ta wires. The temperature was measured with a chromel–alumel thermocouple junction, fastened to the side of the crystal. Rigorous sample cleaning was done by Ar$^+$ bombardment to remove oxides and common impurities. Routine cleaning of the surface was accomplished by cycling the crystal temperature between 900 and 1450 K in an O$_2$ pressure of 1 × 10$^{-8}$ mbar, as measured by the system’s ion gauge. This was followed by annealing at 1350 K to remove adsorbed oxygen. CH$_2$I$_2$ was obtained from Fluka and degassed by freeze-pump-thaw cycles prior to use.

3. Results

3.1. Adsorption of CH$_2$I$_2$

Fig. 1 shows the XP spectrum of Ru(001) in the iodine region as a function of CH$_2$I$_2$ exposure at 110 K. The binding energy of I(3d$_{5/2}$) was 619.9 eV, which shifted to higher values, up to 620.6 eV, at high CH$_2$I$_2$ exposures. The area of the XPS signal for I(3d$_{5/2}$) is plotted against exposure in Fig. 2A. It increased continuously as a function of CH$_2$I$_2$ exposure at 110 K; saturation was not attained.

The interaction of CH$_2$I$_2$ with the Ru surface
was also followed by work function measurements. The adsorption of CH$_2$I$_2$ caused a gradual decrease in the work function of Ru(001), as illustrated in Fig. 2B. The maximum decrease, $\Delta \Phi = -0.96$ eV, was attained at an exposure of only 3.0 L.

Hel photoelectron spectra of Ru(001) under the same experimental conditions are displayed in Fig. 3. At a very low exposure (~0.3 L) we obtained only one signal at 5.4–5.7 eV. At higher exposure the positions of the photoemission signals were 4.4, 7.3 and 9.7 eV (Fig. 3A). A summary of observed binding energies of adsorbates is given in Table 1.

Thermal desorption curves following CH$_2$I$_2$ adsorption on the Ru(001) surface are depicted in Fig. 4. No desorption of CH$_2$I$_2$ was seen below an exposure of 1.0–1.5 L. At and above this exposure, a CH$_2$I$_2$ peak appeared with $T_p = 220$ K. This peak is denoted $\beta$. On increasing the CH$_2$I$_2$ exposure, the amount of desorbed CH$_2$I$_2$ increased and finally saturated at 6.0 L of exposure. We assume that the saturation of a monolayer occurred at this exposure. At the same time a new peak developed with $T_p = 200$ K (denoted $\alpha$) which could not be saturated.

3.2. Effects of annealing of adsorbed layer

XP spectra of adsorbed layers annealed to different temperatures are displayed in Fig. 1B. No shift in the binding energy (BE) of I(3d$_{5/2}$) can be observed up to 169 K. The peak became appreciably wider at 198 K when it underwent a significant attenuation. Above this temperature a large shift in the BE of I(3d$_{5/2}$) occurred from 620.6 eV to 619.9 eV. The position and intensity of the
Fig. 2. (A) Area of the iodine XPS signal and (B) changes in the work function ($\Delta \phi$) of Ru(001) as a function of CH$_2$I$_2$ exposures at 110 K and (C, D) annealing temperature.

I(3d$_{5/2}$) signal remained unaltered above this temperature up to 900 K, the temperature of the onset of iodine desorption. Changes in the area of I(3d$_{5/2}$) peak are displayed in Fig. 2C.

Annealing the adsorbed layer caused an increase in the work function. A constant value was attained at 200 K. In this case the work function of the sample was about 0.5 eV lower than that
before CH$_2$I$_2$ adsorption. The next increase started at 850 K; the value characteristic of the clean surface was not attained even at 1200 K (Fig. 2D).

The effect of annealing was also registered in the UP spectra of the adsorbed layer. Up to 200 K the spectra remained practically unaltered. At 241 K the dominant photoemission lines were at 5.7 and 4.5 eV, which were seen even after annealing the sample to 715 K, where — according to AES — only iodine and carbon were present on the surface. In order to identify the formation of other adsorbed species produced during annealing, the spectrum taken after heating the sample to 715 K was subtracted from each of the spectra taken at lower temperatures. The magnified difference spectra obtained in this way are displayed in Fig. 3B. For the sample annealed at 241 K, signals appeared at 3.8, 5.4 and 7.4 eV. The 5.4 eV peak disappeared only above 298 K, whereas the other two disappeared at 450–502 K.

By means of TPD we detected the following desorption products: CH$_4$ ($T_p = 220$ K), H$_2$.

### Table 1

<table>
<thead>
<tr>
<th>Species</th>
<th>UPS (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$I$_2$/Pd(100)</td>
<td>4.0, 6.7, 9.2, 13.0</td>
<td>[17]</td>
</tr>
<tr>
<td>CH$_2$I$_2$/Cu(100)</td>
<td>3.9, 6.7, 7.4, 9.1, 13.2</td>
<td>[23]</td>
</tr>
<tr>
<td>CH$_2$I$_2$/Ru(001)</td>
<td>4.3, 6.6, 9.2, 13.0</td>
<td>(present work)</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>5.8–6.2</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td>5.4–5.6</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td>5.5–5.8</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>5.4</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td></td>
</tr>
<tr>
<td>CCH$_3$</td>
<td>7.6</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>7.4</td>
<td>(present work)</td>
</tr>
</tbody>
</table>
Fig. 4. Thermal desorption spectra of CH$_2$I$_2$ (amu 127) as a function of CH$_2$I$_2$ exposures. Adsorption temperature was 110 K. ($T_p$=430–420 K at lower exposures, $T_p$=300 and 430–450 K at higher exposures) and I ($T_p$=1080–1140 K). Note that the H$_2$ adsorbed from the background is released with $T_p$=430 K. Its amount is about one third of that measured after 0.3 L of CH$_2$I$_2$ exposure. In addition, we also found a peak for amu 142, which we identified as CH$_3$I. TPD spectra are presented in Fig. 5. It is important to note that we found no sign of ethylene formation following 27 and 28 amu. The activation energies for the desorption of these compounds were calculated by the Redhead formula assuming a pre-exponential factor of $1 \times 10^{13}$ s$^{-1}$.

Characteristic TPD data are collected in Table 2.

3.3. Effects of illumination

The primary aim of the illumination study was to promote the generation of CH$_2$ at low temperature (~100 K), where its decomposition and secondary reactions are minimal. The effect of illumination was exhibited by changes in the positions of the I(3d$_{5/2}$) in the XP spectra. Fig. 6 shows the effect of illumination time on the position of...
the I(3d_{5/2}) peak at monolayer coverage. The BE value clearly shifted from 620.6 eV to 619.8 eV even after a relatively short (1–5 min) irradiation, which was also accompanied by a decrease of the peak area.

Illumination of the adsorbed layer caused a dramatic alteration in the HeI photoelectron spectrum. After photolysis, photoemission signals characteristic of the adsorbed CH$_2$I$_2$ almost disappeared and a very intense signal appeared at 5.7 eV.

Post-irradiation TPD measurements for monolayer coverage showed that the amount of CH$_2$I$_2$ desorbed (β peak) decreased with increasing irradi-
with photoemission line at 5.5–5.8 eV was also detected for Cu(100) surface [23]. With photoemission line at 5.5–5.8 eV was also detected for Cu(100) surface [23].

$2$-alkyl halides, it is very likely that $\text{CH}_2$ bonds were increased continuously with the rise of the binding energy of I(3d$^{5/2}$) for atomically adsorbed I. It is always lower, 618.5–619.7 eV, than that for molecularly adsorbed iodo compounds, ≥620.5 eV [1–6]. From Fig. 1 the position of the I(3d$^{5/2}$) peak at very low exposure was 619.9 eV, and at higher exposures 620.6 eV. This latter value is characteristic of the molecularly adsorbed CH$_2$I$_2$.

The lower value of binding energy for I(3d$^{5/2}$) suggests the occurrence of dissociation of CH$_2$I$_2$ at submonolayer at 110 K. From Fig. 1A we calculated that no more than 5% of a monolayer dissociates at 100 K.

Adsorption of CH$_2$I$_2$ on Ru(001) gave very weak photoemission signals in HeI photoelectron spectra at low coverage. At monolayer coverage (at an exposure of 6.0 L), when the position of the binding energy of I(3d$^{5/2}$) in the XPS suggested the presence of molecularly bonded CH$_2$I$_2$, photoemission peaks emerged at 4.4, 6.6, 9.2 and 13 eV. The position of these signals shifted to higher energies at multilayer coverage. If the gas-phase molecular photoelectron spectrum of CH$_2$I$_2$ and the gas-phase ionization potentials are considered [32], the above peaks can be assigned to the (2b$^1$, 3b$^1$, 1a$^1$, 4a$^1$), (2b$^1$, 3a$^1$), 1b$^1$ and 2a$^1$ orbitals. The differences in binding energies in the adsorbed layer on Ru(001) approximate well to the values measured for gaseous CH$_2$I$_2$ [32]. From this finding, it may be concluded that the bonding of CH$_2$I$_2$ to Ru(001) did not result in a strong distortion of its molecular electronic structure.

As the analysis of XP spectra suggested the dissociation of CH$_2$I$_2$ at submonolayer coverage, great attention was paid to the UP spectra of these adsorbed layers. In the magnified difference spectra we observed a new photoemission line at 5.7 eV. In the UP spectra of polycrystalline Ni and Co, following the dissociative adsorption of CH$_2$I$_2$, a photoemission line at 5.5–5.8 eV was also detected [33]. This signal was also seen in the HeII photoelectron spectrum of adsorbed CH$_2$I$_2$ at submonolayer coverage on Pd(100) and Cu(100) surfaces [17,23]. In all these cases, this signal was attributed to adsorbed CH$_2$ species: this assignment is very likely valid in the present case, too.

### Table 2

Some characteristic data for TPD. Data refer to monolayer coverage of CH$_2$I$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Desorption peak temperature $T_p$ (K)</th>
<th>Activation energy $E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$I$_2$</td>
<td>220</td>
<td>63</td>
</tr>
<tr>
<td>CH$_2$I</td>
<td>160</td>
<td>46</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>220</td>
<td>63</td>
</tr>
<tr>
<td>H$_2$</td>
<td>300, 450, &gt;600</td>
<td>–</td>
</tr>
</tbody>
</table>

* $E_a$ was calculated by assuming first order kinetics ($k = 10^9$ s$^{-1}$).
TPD measurements indicated two adsorption states denoted by \( \beta \) (\( T_p = 220 \) K) and \( \gamma \) (\( T_p = 200 \) K). The \( \beta \) peak, which saturated at 6.0 L of CH\(_2\)I\(_2\) exposure, represents the weakly adsorbed CH\(_2\)I\(_2\). As we could not obtain saturation of the \( \gamma \) peak even at very high exposures, we may conclude that this peak corresponds to desorption of a monolayer. The value of \( T_p \) is nearly the same as determined for Rh(111) (\( T_p = 205 \) K) and Cu(100) (\( T_p = 210 \)–219 K). The surface coverage at monolayer calculated from TPD and XPS results is \( 8 \times 10^{14} \) CH\(_2\)I\(_2\) molecules/cm\(^2\). The calculation was based on the comparison of the I(3d\(_{5/2}\)) signal obtained for monolayer CH\(_2\)I\(_2\) at 100 K with the XPS signal registered at saturation coverage of atomic iodine. Adsorbed iodine occupies one third of surface Ru atoms at saturation [34].
4.2. Annealing of adsorbed CH$_2$I$_2$

Spectroscopic results clearly showed that, in addition to the weakly adsorbed CH$_2$I$_2$, a strongly bonded CH$_2$I$_2$ also exists on the surface, which dissociates at higher temperatures. According to the XPS measurements (Fig. 1B), this occurred by 198 K, where the I(3d$_{5/2}$) peak broadened and a shoulder could be distinguished at lower binding energy. The presence of this shoulder suggests that a fraction of the molecularly adsorbed CH$_2$I$_2$ underwent dissociation even at this temperature. At 239 K this shoulder became the dominant peak for I(3d$_{5/2}$), suggesting the completeness of the dissociation process CH$_2$I$_2$\(\rightarrow\)CH$_2$ + 2I.

In the desorption products we found CH$_4$ (\(T_p = 220\) K) and H$_2$ (\(T_p = 300\) K and 430–450 K), but could not detect ethylene, the product of the dimerization of adsorbed CH$_2$. The formation of CH$_4$ suggests that the self-hydrogenation of CH$_2$ 4CH$_2$\(\rightarrow\)2CH$_4$ + 2C proceeds on Ru(001). The emission at 4.5 eV in UP spectra above 200 K clearly shows the presence of C$_{ads}$ \([33]\). This process may consist of the following steps

CH$_2$\(\rightarrow\)C + 2H$_{ads}$
CH$_2$ + H$_{ads}$\(\rightarrow\)CH$_3$
CH$_3$ + H$_{ads}$\(\rightarrow\)CH$_4$g.

We cannot exclude the possible assistance of hydrogen from the background to the above reactions.

The absence of ethylene in the desorbing gases is a somewhat surprising result as Ru is a good
catalyst for hydrocarbon synthesis. This behavior of Ru(001) resembles that of Rh(111) [18,19]. On Pd(100) we found a larger amount of C$_2$H$_4$ besides CH$_3$ [17], while on Cu surfaces only C$_2$H$_4$ was produced without CH$_3$ [23]. Careful examination of UP spectra revealed that after the desorption of weakly bonded CH$_3$I$_2$ at 205–210 K, weak photoemission signals at 5.7 and 7.4 eV remained in the magnified difference spectrum (Fig. 3B). The first is no doubt attributed to adsorbed CH$_3$ species. On the basis of previous study [35], the 7.4 eV signal can be ascribed to adsorbed ethylidyne, CCH. Accordingly, adsorbed CH$_3$ formed in the dissociation of CH$_3$I$_2$ above 173 K is coupled into ethylene, very likely in the di-sigma-bonded form, which is converted into ethylidyne in a fast process

\[
C_2H_{2s}\rightarrow CCH_{2s} + H_{2g}.
\]

As has been demonstrated on several metal surfaces, the di-sigma-bonded ethylene readily transforms into this species at 150–300 K [36–39].

Analysis of H$_2$ desorption curves is difficult due to the presence of hydrogen in the background. Although the extent of the adsorption of this hydrogen is certainly decreased at higher coverage of CH$_3$I$_2$, its contribution cannot be completely excluded, particularly at low CH$_3$I$_2$ coverage. The peak temperature for H$_2$ desorption following H$_2$ adsorption on clean Ru(001) is 430 K at low coverage, which is shifted to lower temperatures with increasing coverage [40,41]. This shift was also observed in our experiment (Fig. 5). In addition, a new H$_2$ peak developed with $T_p$ = 300 K at higher surface concentration of CH$_3$I$_2$, very likely due to the influence of adsorbed iodine. It is known that coadsorbed species, like CO, forming a compressed overlayer shift the desorption temperature of H$_2$ to lower temperature [40]. The other peak for H$_2$ appeared at 440–450 K, which may correspond to the decomposition of ethylidyne

\[
CCH_{2s}\rightarrow CCH_{2s} + H_{2g}.
\]

Although CCH$_3$ decomposes on Ru(001) surface at 300–350 K, the adsorbed species, in the present case the adsorbed iodine, can increase this temperature value by blocking the sites required for the surface decomposition. The CCH formed in the above reaction is quite stable, it releases hydrogen only at 750 K (Fig. 5C).

An interesting feature of the CH$_3$I$_2$/Ru(001) system is the formation of CH$_3$I in the desorbing products with $T_p$ = 160 K. This peak temperature agrees well with that registered following CH$_3$I adsorption on Ru(001) [42]. The production of this compound from adsorbed CH$_3$I is rather unusual, it has been reported only on Al(111) surface [43]. The formation of methyl iodide, CH$_3$I$_2$, was also observed following the adsorption of CH$_2$I$_2$ on Pt(111), where the strength of the C–halogen bonds is obviously different [20].

As the formation of CH$_3$I occurred at higher CH$_3$I$_2$ coverages, when most of the active sites of the Ru surface are blocked, we may assume that it causes the adsorbed CH$_3$I$_2$ molecules to be tilted away from the surface normal as shown in Fig. 8. The CH$_3$I bonds to the surface through the I atoms, but the structure of the (001) hcp plane does not fit perfectly. This "mismatching" means that one of the iodine atoms of CH$_3$I cannot occupy a site (presumably three-fold hollow sites) with the same binding energy. This is also reflected in the change of the work function, as $\Delta \phi$ reaches its minimum before the saturation of the first layer, approximately at 2.4 L, when CH$_3$I appeared in the desorption products. This is in harmony with the tilting mechanism, as the macroscopic dipole moment, and $\Delta \phi$, depend on cos $\alpha$, e.g. on the angle between the C$_3$ axis of the molecule and the surface normal [34]. The more molecules are on the surface, the larger is the tilting angle, with the results that (i) bonding I atoms are not equivalent and the CH$_3$I$_2$ molecule is in a stretched configuration, and (ii) the partially positive C atoms of CH$_3$I become more open to nucleophilic reactants, such as surface H.

4.3. Photolysis of adsorbed CH$_3$I$_2$

Illumination of the adsorbed layer at 110 K caused a gradual shift in the position of I(3d$_{z^2}$) binding energy in XPS. After 10 min illumination time the peak attained a value of 619.65 eV, which is considered as a sign of the dissociation of CH$_3$I$_2$ to a great extent. At the same time the area
of the I(3d_{5/2}) signal decreased by 40%, indicating that a significant fraction of adsorbed CH$_2$I$_2$ underwent a photo-induced desorption (Fig. 6A). This conclusion is supported by the TPD results. The amount of CH$_2$I$_2$ desorbed around 220 K decreased and completely ceased after 60 min of illumination. A similar feature was observed for CH$_3$I desorption. In contrast, the formation of methane and iodine did not change, indicating that the extent of CH$_2$I$_2$ dissociation remained practically the same.

5. Conclusions

1. CH$_2$I$_2$ adsorbs dissociatively at submonolayer coverage on Ru(001) surface at 110 K, and molecularly at higher coverages.
2. The primary products of the dissociation are adsorbed CH$_2$ and I.
3. The majority of CH$_2$ is self-hydrogenated to CH$_4$, a small fraction coupled into strongly bonded C$_2$H$_4$, very likely di-s-bonded form, which is converted immediately to ethylidyne. This compound decomposed above 400 K.
4. Illumination of adsorbed CH$_2$I$_2$ with a Hg arc lamp enhanced the extent of dissociation even at 110 K, but did not change the reaction pathway of adsorbed CH$_2$.

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