Reaction of CH₂ with adsorbed O on Ru(001) surface

A. Kis, J. Kiss, F. Solymosi *

Institute of Solid State and Radiochemistry, University of Szeged, and Reaction Kinetics Research Group of the Hungarian Academy of Sciences, P.O. Box 168, H-6701 Szeged, Hungary

Received 15 January 2000; accepted for publication 30 March 2000

Abstract

The reaction pathways of CH₂ in the presence of coadsorbed oxygen atoms on Ru(001) surface were investigated by means of temperature-programmed desorption (TPD), photoelectron spectroscopy (XPS and UPS) and work function measurements. CH₂ species were produced by thermal and photoinduced dissociation of CH₂I₂. Preadsorbed oxygen atoms markedly stabilized C–I bonds, shifted the desorption of CH₂I₂ to higher temperatures and reacted with CH₂ formed to give formaldehyde above 200 K. Adsorbed formate was also detected in the temperature range of 300–450 K. The oxidation of surface species (CH₂O, HCOO, CₓHᵧ) proceeded above 450 K, to produce CO, CO₂, and H₂O. Illumination of the (CH₂I₂ + O) coadsorbed layer initiated the dissociation of CH₂I₂ and induced the reaction of CH₂ with O slightly above 110 K. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Aldehydes; Oxygen; Photochemistry; Ruthenium; Thermal desorption spectroscopy; Ultraviolet photoelectron spectroscopy; Work function measurements; X-ray photoelectron spectroscopy

1. Introduction

The coupling and reactions of hydrocarbon fragments (CH₂, CH₃, CₓHᵧ etc.) with adsorbed oxygen atoms represent important elementary steps in the selective and total oxidation of hydrocarbons and also in the reforming of methane to produce synthesis gas [1]. Previous works showed that CH₂ produced by the thermal and photodissociation of adsorbed CH₂I₂ on Pt(111) [2], Rh(111) [3–7] and Pd(100) [8] surfaces is readily combined with adsorbed oxygen atoms to give CH₂O which is released in the gas phase after its formation. Different results were obtained for Cu(100) [9].

In this case adsorbed O did not alter the dominant pathways of the reaction of CH₂ formed above 200 K, e.g., the coupling of CH₂ into CₓHᵧ. Formaldehyde formation was observed only when CH₂ was produced at 100 K by illumination of CH₂I₂ + O/Cu(100) system.

In a previous paper we gave an account on the chemistry of CH₂I₂ on the Ru(001) surface [10]. The aim of the present work is to elaborate the primary interaction of adsorbed CH₂ with atomically adsorbed O on Ru(001) surface and to determine the routes of subsequent reactions in the coadsorbed layer. Unlike other platinum metals, Ru is an excellent catalyst for the synthesis of higher hydrocarbons, but it is markedly less active and selective in the production of oxygenated hydrocarbons. Therefore, it was interesting to see its effect on the coupling of CH₂ with O.
2. Experimental

2.1. Methods

The experiments were performed in standard ultrahigh vacuum systems with a background pressure of $5 \times 10^{-10}$ mbar produced by turbomolecular and ion-getter pumps. The chamber was equipped with an electrostatic hemispherical analyzer (Leybold-Heraeus LHS-10), a differentially pumped UV photon (He I, II) source for UPS, an X-ray source with Al anode for XPS and an electron gun for AES measurements. The directions 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 with the Ru 3d$_{5/2}$ peak at 280.0 eV. Collection times for UPS and XPS were 15 and 30 min, respectively. XP spectra were smoothed by the fast Fourier transform method. For TPD, the sample was heated at 10 K s$^{-1}$ 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 cutoff in the He I UP spectra with the sample at $-9$ V relative to earth. The UV light source was a focused 40 W Hg lamp. The light passed through a high-purity sapphire window into the vacuum chamber. The incident angle was 30° off the surface normal.
2.2. Materials

The 99.99% purity, disk-shaped Ru crystal (diameter 8 mm, thickness 1.5 mm) was oriented within 0.5° at the (001) face and was mechanically polished with diamond paste. The surface orientation was checked by XRD and LEED before mounting the sample. The crystal was spotwelded as a function of CH$_2$I$_2$ exposure were plotted in Fig. 1A. At saturation O coverage ($\theta_O=0.5$), a very low CH$_2$I$_2$ exposure produced an I 3d$_{5/2}$ peak at 619.9 eV which shifted to higher values, up to 620.3 eV, at high exposures. Fig. 1C indicates that the uptake of CH$_2$I$_2$ on oxygen-dosed Ru(001), $\theta_O=0.5$, at different CH$_2$I$_2$ exposures is practically the same as that for the clean surface. Adsorption of CH$_2$I$_2$ did not exert an observable alteration in the position of O 1s peak at 530.2 eV.

XPS spectra of coadsorbed layers annealed to different temperatures are displayed in Fig. 2B. A broadening of the I peak, indicating the onset of the dissociation of CH$_2$I$_2$, occurred at 298 K. Above this temperature the position of the peak clearly moved to lower energy. As shown in Fig. 1D, this temperature is much higher as compared with the clean surface, where a shift in the I 3d$_{5/2}$ signal was detected even at 198 K [10]. A $^{18}$O$_2$ was obtained from CIL Cambridge Isotope Laboratories and it was 95–98% purity with respect to $^{16}$O$_2$. The oxygen coverage was determined by O 1s XPS signal which is calibrated against the ideal O coverage of p(1 x 2)-O (assumed to be 0.5 ML) [11].

3. Results

3.1. Thermal measurements

The adsorption of O$_2$ on Ru(001) at 110 K caused a linear increase in the work function; the maximum enhancement amounted to 1.0 eV. Exposure of O-dosed Ru to CH$_2$I$_2$ at 110 K led to a decrease of the work function by more than 1.0 eV. The final value, which was somewhat less than that of the clean Ru was attained at approximately 3.6 L of CH$_2$I$_2$ exposure (Fig. 1A). On heating the adsorbed layer, an increase in $\Delta\phi$ was observed at 200 and 300 K. The next increase could be detected above 750 K in harmony with I desorption. Above 1000 K there was no change in $\Delta\phi$ until the O$_2$ desorption set in. The value ($\sim$0.4 eV) between 1000 and 1250 K was lower than that of the original O-dosed surface. Results obtained are plotted in Fig. 1B.

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 surface was accomplished by cycling the crystal temperature between 900 and 1450 K with an O$_2$ flux to 1 x 10$^{-8}$ mbar pressure. This was followed by annealing at 1550 K to remove adsorbed oxygen. CH$_2$I$_2$ was obtained from Fluka; it was degassed by freeze–pump–thaw cycles prior to use. The O$_2$ was obtained from Messer-Griesheim. $^{18}$O$_2$ isotope was used in TPD measurements in order to assist the identification of different oxygenated products. $^{18}$O$_2$ was obtained from CIL Cambridge Isotope Laboratories and it was 95–98% purity with respect to $^{16}$O$_2$. The oxygen coverage was determined by O 1s XPS signal which is calibrated against the ideal O coverage of p(1 x 2)-O (assumed to be 0.5 ML) [11].

New high temperature peaks appeared for CH$_2$I$_2$ and its decomposition products registered for a clean surface. Results obtained at $\theta_O=0.25$ are shown in Fig. 3. CH$_2$I detected in the products desorbing from the clean surface, was completely missing. New high temperature peaks appeared for CH$_2$I$_2$ with $T_P=260$ K $\pm 298$ K. The peak temperature of methane desorption also shifted from 220–230 K (clean surface) to 270 K (O-dosed surface) accompanied by a decrease in the amount of CH$_3$O to a low level. Smaller amounts of H$_2$ desorbed in several not well-resolved peaks. The most intense peaks were $T_P=270$ K and $T_P=490$ K. The most interesting feature is the release of new products, CH$_2$I$^{18}$O ($T_P=298$ K).
Fig. 5 illustrates the effect of CH$_2$I$_2$ exposure on the desorption of CH$_2$I$_2$ and CH$_2$O formed at $\theta_O=0.5$. At low exposure, CH$_2$I$_2$ desorbed in one peak at 260 K, which shifted to lower temperature with increasing CH$_2$I$_2$ exposure. At the same time new peaks developed at 330 and 200 K. A significant change also occurred in the formation of CH$_2$O: its amount increased with the CH$_2$I$_2$ exposure, which was accompanied by a shift in TP from 267 to 340 K (Fig. 5B). Some characteristic desorption data are collected in Table 1. Taking into account the sensitivity of the mass spectrometer to the desorbing products, we calculated that about 70% of CH$_2$ formed at $\theta_O=0.5$ was oxidized to CH$_2$O, and the rest was converted into a stable hydrocarbon species. As regards the product ratios we obtained, the CH$_2$O/CO and CH$_2$O/CO$_2$ ratios increased monotonically as a function of O coverage.

The UP spectrum at monolayer coverage of CH$_2$I$_2$ on oxygen-dosed Ru(001) was very similar to that measured for the clean surface (Fig. 6). Photoemission lines slightly shifted to lower energies, to 4.0, 6.2, 8.7 and 11.0 eV. Significant spectral changes were experienced when the coadsorbed layer was flashed to higher temperatures. At 219 K, peaks were registered at 3.5, 5.7, 8.8 and 11.0 eV, at 298 K signals were seen at 5.0, 5.7, 8.5, 9.0 and 10.7 eV, whereas at 450 K they were at 5.4, 8.4 and 10.9 eV. Further annealing to 640 K eliminated these signals and only very weak peaks remained in the spectrum at 4.3 and 5.7 eV. Above 900 K the only detected signal was at 5.7 eV besides the characteristic photoemission lines of bare Ru metal.

3.2. Effect of illumination

The effects of photolysis of coadsorbed layer was first followed by XPS measurements. As shown in Fig. 7, a shift in the binding energy of the I 3d$_{5/2}$ signal occurred at 110 K even after a short illumination time, 1–3 min, which was independent of the O coverage. After 60 min of illumination the binding energy was at 619.7 eV, which is near the value of atomically adsorbed iodine.
The effect of photolysis at 110 K was examined with UPS method at high and low coverages of adsorbed CH\textsubscript{2}I\textsubscript{2}. The He I spectra taken after illumination did not reveal the generation of CH\textsubscript{2}I\textsubscript{2}. The signals of CH\textsubscript{2}I\textsubscript{2} shifted to lower binding energies. Post-irradiation TPD spectra are displayed in Fig. 8. The illumination at 110 K eliminated the low temperature peak for CH\textsubscript{2}I\textsubscript{2}, and considerably decreased the amount of CH\textsubscript{2}I\textsubscript{2} desorbed at higher temperature. Desorption of CH\textsubscript{2}I\textsubscript{2} however, did not cease even after 60 min of irradiation in contrast with the clean surface. Photolysis of the coadsorbed layer exerted a dramatic influence on the formation of CH\textsubscript{18}O. Its evolution started slightly above the temperature of illumination, and after 60 min the peak temperature of its desorption was 250 K. In contrast, the temperature range of the desorption of the other products of the oxidation hardly changed (Fig. 8). A noteworthy effect is the development of a new high temperature peak for C\textsuperscript{18}O at 740 K, and that after 60 min of illumination C\textsuperscript{18}O desorbed mainly in a peak with a \(T_p = 535\) K.

4. Discussion

4.1. Adsorption and dissociation of CH\textsubscript{2}I\textsubscript{2} on O-dosed Ru(001)

Previous LEED and STM measurements revealed that O atoms form islands on Ru(001) surface occupying threefold hollow sites [11]. The islands below saturation coverage are in thermodynamic equilibrium with fluctuations because of the relatively high hopping rate (14 \(\pm 3\) s\(^{-1}\)) of individual O atoms at room temperature. At \(\theta_O = 0.25\) the (2 \(\times\) 2) structure and at saturation coverage, \(\theta_O = 0.5\), the p(1 \(\times\) 2) structure were found.

XPS measurements indicate that the uptake of CH\textsubscript{2}I\textsubscript{2} on oxygen-saturated Ru(001) is only slightly altered as compared with the clean surface.
Fig. 5. Thermal desorption spectra for CH$_2$I$_2$ (A) and CH$_2$O$^{18}$O (B) at $\theta_O=0.5$ as a function of CH$_2$I$_2$ exposure at 100 K.

<table>
<thead>
<tr>
<th>Desorption products</th>
<th>Desorption peak temperature (K) $\theta_O=0.25$</th>
<th>Desorption peak temperature (K) $\theta_O=0.5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$I$_2$</td>
<td>200, 260, 298</td>
<td>200, 250, 340</td>
</tr>
<tr>
<td>CH$_2$I</td>
<td>270</td>
<td>270</td>
</tr>
<tr>
<td>H$_2$I</td>
<td>270, 490</td>
<td>270, 490</td>
</tr>
<tr>
<td>I$^+$</td>
<td>950</td>
<td>800</td>
</tr>
<tr>
<td>CH$_2$O$^{18}$O</td>
<td>298</td>
<td>340</td>
</tr>
<tr>
<td>CO</td>
<td>535, 615</td>
<td>535, 615</td>
</tr>
<tr>
<td>CO$^{18}$O</td>
<td>505, 600</td>
<td>520, 600</td>
</tr>
<tr>
<td>H$_2$O$^{18}$O</td>
<td>510</td>
<td>510</td>
</tr>
</tbody>
</table>

(Fig. 1C). The position of the I 3d$_{5/2}$ peak shifted from 620.6 to 620.3 eV with increasing O coverage at approximately 1 ML coverage of CH$_2$I$_2$ indicating (i) the difference in bonding state of the molecules as compared with clean Ru(001) surface and (ii) the enhanced final state effect caused by the presence of adsorbed O atoms. The marked decrease of the work function following the adsorption of CH$_2$I$_2$ suggests that CH$_2$I$_2$ molecules – as on the clean surface – bond to the surface via their negatively charged iodine atoms (Fig. 1A). The bonding of CH$_2$I$_2$, however, is strongly influenced by preadsorbed oxygen. The formation of a multilayer ($\alpha$ peak $T_P=200$ K) occurred at much lower CH$_2$I$_2$ exposure than on the clean surface (Fig. 5A), as O presumably occupies some of the bonding sites of CH$_2$I$_2$. Its desorption temperature, however, remained unaltered. The desorption from the monolayer (designated the $\beta$ peak) observed for the clean surface at $T_P=220$ K is shifted to 250 K and a new
high temperature peak (γ) appeared at $T_p = 300$–$350$ K. This feature indicates that CH$_2$I$_2$ is bonded close to island edges of adsorbed O, or forms (CH$_2$I$_2$ + O) mixed island especially at high CH$_2$I$_2$ concentration. The Coulomb interaction forces between positively charged C atoms of CH$_2$I$_2$ and the negatively charged O atoms may also stabilize the CH$_2$I$_2$ molecule.

The stabilization of adsorbed CH$_2$I$_2$ is reflected in its dissociation. In the XP spectra, a shift in the binding energy of I 3d$_{5/2}$, corresponding to the dissociation of adsorbed CH$_2$I$_2$ at monolayer, occurred at higher temperatures than on a clean surface: the difference amounts to 100 K at saturation O coverage (Fig. 1D). In the explanation of these features we cannot rule out that preadsorbed oxygen atoms, by occupying the adsorption sites, prevent the dissociation of CH$_2$I$_2$, and hence force a fraction of adsorbed molecules to desorb instead of dissociating. We may also assume that the strong interaction between adsorbed CH$_2$I$_2$ and O also contributes to the stabilization of C–I bonds by decreasing the electron density of Ru d$\pi$ bands, from where electrons are donated to C–I antibonding orbitals. Interestingly, preadsorbed O atoms also affect the desorption of iodine: it lowers the peak temperature by almost 200 K (Fig. 4C), which we attribute to the repulsive interaction between O and I in the adsorbed layer.

The effect of preadsorbed oxygen is manifested in the reactions of CH$_2$I observed for the clean surface: its self-hydrogenation into methane occurred at higher temperature than on the oxygen-free surface, in accord with the higher dissociation temperature. In addition, a large fraction of CH$_2$ formed undergoes oxidation in the adsorbed layer, which led to the decrease in the amount of CH$_4$ formed. At $\theta_0 = 0.5$, CH$_4$ was no
Fig. 8. Post-irradiation TPD spectra for adsorbed CH$_2$I$_2$. (A) CH$_2$I$_2$; (B) CH$_2$O, (C) C$^{18}$O$_2$, (D) C$^{18}$O. $\Theta_0 = 0.5$. CH$_2$I$_2$ exposure was 6 L.
longer detectable in the desorbing gases. The products detected are CH$_3^{18}$O, H$_2^{18}$O, C$_2^{18}$O and C$_3^{18}$O. An interesting feature of the CH$_3^{18}$O formation is that its peak temperature sensitively depends on the oxygen coverage (Fig. 4B). At the lowest coverage, $\theta_0=0.06$, CH$_3^{18}$O was released at $T_p=245$ K, while at saturation oxygen coverage, $\theta_0=0.5$, this value was 340 K with a tail extending below 200 K in both cases. This behavior is no doubt in connection with the inhibition of the dissociation of CH$_3$J$_2$ with increasing oxygen coverage, as indicated by the XPS results (Fig. 2). Accordingly, we may assume that the dissociation of CH$_3$J$_2$ is the prerequisite for the formation of the CH$_3^{18}$O, in this temperature regime. A similar conclusion was reached for the Rh(111) and Pd(100) surface [4,8]. This conclusion was confirmed by the study of the reaction of CH$_3$Cl$_2$ on O-dosed Pd(100) [8]. This compound adsorbs molecularly on Pd(100) and desorbs below 250–300 K with detectable dissociation. Following the adsorption of CH$_3$Cl$_2$ on oxygen-dosed Pd(100), we found no traces of CH$_2$O and detected only very small amounts of H$_2$O and CO$_2$. However, when the adsorbed layer was illuminated which promoted the dissociation of the C–Cl bond on Pd(100) [8] – the formation of CH$_3$O occurred easily.

We cannot rule out, however, that the formation of CH$_3^{18}$O, particularly above 300 K, proceeds as a result of a rearrangement between the strongly stabilized CH$_3$J$_2$ ($T_p=340$ K) and $^{18}$O, as described in the scheme below:

The small FWHM value for CH$_3^{18}$O desorption and the coincidence of the desorption peaks of CH$_3^{18}$O and CH$_3$J$_2$ suggest that the formation and desorption of CH$_3^{18}$O in this temperature regime is controlled by the amount of strongly stabilized CH$_3$J$_2$. Concomitant desorption requires that the activation energy of this reaction must be higher than the energy necessary for the desorption of CH$_3^{18}$O.

In the study of the behavior of CH$_3$O on clean Ru(001), it appeared that the CH$_3$O desorbs from the clean Ru(001) surface in three peaks, $T_p=130$, 150 and 275 K [12]. The decomposition of adsorbed CH$_3$O occurred at 250–300 K to give H$_2$ and CO. On oxygen-dosed Ru(001), $\theta_0=0.25$, the formation of formate species was detected by HREELS which decomposed in the temperature range of 400–450 K [12]. The peak temperatures for CH$_3$O decomposition and the products of CH$_3$O decomposition remained practically unaltered: neither H$_2$O nor CO$_2$ were detected in the desorbing gases. As a result of the effect of preadsorbed O, the peak temperature for CO slightly shifted to lower temperature, to 450 K [12] which is consistent with the previous results obtained for CO + O/Ru(001) system [13]. In the present case these products are released at much higher temperature, $T_p=505–615$ K in two distinct peaks (Fig. 3). As H$_2$O and CO$_2$ desorb from Ru(001) below room temperature [14,15], we can conclude that the evolution of these compounds is a reaction-limited process. As the peak temperature for CO desorption from Ru(001) is 450–500 K [16], the release of a certain fraction of CO in the present case is also a reaction-limited process. As neither CH$_3$ nor CH$_2$O are stable above 600 K it seems likely that CH$_3$ fragments produced by reaction of CH$_2$ are oxidized to the above compounds with $T_p=600–615$ K. This assumption is supported by our results obtained in the oxidation of CCH$_3$ on clean Ru(001) where C$_2^{18}$O and C$_2$O$_2^{18}$ peak appeared above 600 K. The oxidation of C$_2^{16}$O formed in the decomposition of CH$_3^{18}$O may also contribute to the production of C$_2^{18}$O. We note here that the decomposition of
Table 2

<table>
<thead>
<tr>
<th>Species</th>
<th>Surface</th>
<th>Photoemission signals (eV)</th>
<th>Reference</th>
<th>Signals observed in the present work (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>Cu(100)</td>
<td>5.7–6.0</td>
<td>[8,9]</td>
<td>5.4</td>
</tr>
<tr>
<td>CH₂I₂</td>
<td>Pd(100)</td>
<td>4.3, 6.8, 9.0, 13.0</td>
<td>[8,9]</td>
<td>4.0, 6.2, 8.7, 13.0</td>
</tr>
<tr>
<td>CH₂I₂</td>
<td>Pd(100)</td>
<td>5.9–6.1</td>
<td>[8,9]</td>
<td>5.7</td>
</tr>
<tr>
<td>I</td>
<td>Cu(100)</td>
<td>5.5</td>
<td>[9]</td>
<td>5.7</td>
</tr>
<tr>
<td>CH₂O</td>
<td>Cu(110)</td>
<td>5.7, 9.3, 11.2, 16.0</td>
<td>[19]</td>
<td>5.7, 8.8, 11.0</td>
</tr>
<tr>
<td>HCOO⁠</td>
<td>K(Pd(100))</td>
<td>5.1–5.3, 8.6–8.9, 10.3–10.7, 13.7–13.8</td>
<td>[20]</td>
<td>5.6, 8.5, 9.0, 10.7</td>
</tr>
<tr>
<td>H₂O</td>
<td>Pd(100)</td>
<td>6.2, 8.5, 12.3</td>
<td>[8]</td>
<td>--</td>
</tr>
<tr>
<td>CO</td>
<td>Pd(100)</td>
<td>8.2, 10.8</td>
<td>[21]</td>
<td>8.4, 10.9</td>
</tr>
</tbody>
</table>

formate species on Ru(001) produced H₂, H₂O, CO and CO₂ [17,18], which is in contradiction with the previous results of the same school [12]. Accepting this finding we can also count with the occurrence of this process below 600 K.

In a search for new adsorbed compounds, UPS measurements were carried out under similar conditions. In order to assist assignment, in Table 2 we list the photoemission signals of all surface compounds possibly formed in the coadsorbed layer. On annealing the sample to 219 K (Fig. 6), new photoemission signals were seen at 5.7, 8.8 and 11.0 eV which can be attributed to adsorbed CH₂O [19]. This means that CH₂O could remain in the adsorbed layer after its formation, which was not experienced for Pd(100) and Rh(111) surfaces [4,8]. At 298 K, other new lines appeared at 5.0, 8.5, 9.0 and 10.7 eV, which can be assigned to the adsorbed HCOO species [20]. Above 450 K, the dominant photoemission peaks were at 8.4 and 10.9 eV, which are characteristic of the adsorbed CO [21].

Taking into account the above characteristics we can infer the occurrence of the following elementary steps in the oxidation of CH₂ fragments:

\[
\text{CH}_2\text{I}_2(a) \rightarrow \text{CH}_2(a) + 2\text{I}(a)
\]

\[
\text{CH}_2(a) + \text{O}(a) \rightarrow \text{CH}_2\text{O}(a)
\]

\[
\text{CH}_2\text{I}_2(a) + \text{O}(a) \rightarrow \text{CH}_2\text{O}(a) + 2\text{I}(a)
\]

\[
\text{CH}_2\text{O}(a) \rightarrow \text{CO}(a) + 2\text{H}(a)
\]

\[
\text{HCOO}(a) \rightarrow \text{H}_2\text{O}(g) + \text{CO}(g) + \text{CO}_2(g)
\]

\[
\text{CO}(a) \rightarrow \text{CO}(g)
\]

\[
\text{C}_3\text{H}_7(a) + \text{O}(a) \rightarrow \text{CO}(g) + \text{CO}_2(g) + \text{H}_2(g)
\]

HCOO(a)→H₂O(g)+CO(g)+CO₂(g)
CO(a)→CO(g)
C₃H₇(a)+O(a)→CO(g)+CO₂(g)+H₂(g)

4.2. Photoinduced reactions in the coadsorbed layer

Post-irradiation TPD measurements clearly showed that illumination eliminated the condensed CH₂I₂ characterised with a peak temperature of 200 K (Fig. 8A). As was indicated by the XPS results, illumination of the CH₂I₂+O coadsorbed layer markedly enhanced the dissociation of CH₂I₂ even at 110 K. A complete dissociation, however, was not achieved even after 60 min of illumination. As a result of the enhanced dissociation, a relatively large amount of adsorbed CH₂ formed at 110 K, which underwent reaction with adsorbed O atoms after its formation. This is indicated by the beginning of the release of a fraction of CH₂O slightly above the temperature of the illumination (Fig. 8B). By mean of UPS we could not detect CH₂O at 110 K, but we observed its photoemission signs above 200 K. The desorption of the other products of the oxidation, CO, CO₂ and H₂O, still occurred in the same temperature range as in the dark experiments confirming our previous conclusion that the evolution of these compounds are reaction-limited processes. A new desorption peak for C₃O desorption appeared at \( T_p = 740 \) K (Fig. 8D), which is characteristic of oxidation of surface carbon coming from the ther-
mal decomposition of \( \text{CCH}_3 \). This feature indicates that as a result of the larger amount of \( \text{CH}_2 \) groups produced by illumination, a fraction of \( \text{CH}_2 \) is directly decomposed to carbonaceous species, and/or transformed into \( \text{C}_x\text{H}_y \) through the formation of ethylene and ethylidyne.

5. Conclusion

1. The uptake of \( \text{CH}_3\text{I}_2 \) at 110 K was not influenced by adsorbed O atoms.
2. Preadsorbed O atoms significantly stabilize the C–I bond, shift its dissociation temperature by 100 K to higher temperature and caused the formation of a new adsorbed state.
3. Oxygen atoms coupled with \( \text{CH}_2 \), the dissociation product of \( \text{CH}_3\text{I}_2 \) above 200 K to give \( \text{CH}_2\text{O} \). At higher temperature the formation of formate species also occurred.
4. The oxidation of \( \text{C}_x\text{H}_y \) fragments and decomposition products of formaldehyde and formate proceeded above 450 K to yield \( \text{H}_2\text{O} \), \( \text{CO} \) and \( \text{CO}_2 \).
5. Illumination enhanced the extent of dissociation of \( \text{CH}_3\text{I}_2 \) and even at 110 K caused the formation of formaldehyde slightly above this temperature.

Acknowledgement

This work was supported by the Hungarian Academy of Sciences and Grants OTKA T23023.

References