Reactions of CH₂ with Adsorbed Oxygen To Produce Oxygenated Compounds on Rh(111)

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The reaction pathways of CH₂ in the presence of coadsorbed oxygen atoms were investigated by means of temperature-programmed desorption and high-resolution electron energy loss spectroscopy. The CH₂ species was produced by the dissociation of CH₂I₂. Adsorbed oxygen atoms reacted with CH₂ above 170 K to give formaldehyde, which desorbed from the surface after its formation. Above 340 K, the oxidation of CH₂ led to the production of CO₂ and H₂O.

Introduction

In previous studies, we examined the interactions of several halogenated hydrocarbons, and particularly iodo compounds, with Pd(100) and Rh(111) surfaces.¹⁻⁵ In all cases, illumination markedly enhanced the extent of dissociation even at 90 K and produced the corresponding hydrocarbon fragments (CH₂, CH₃, and C_2H_5) in relatively high concentration. This permitted establishment of the thermal stabilities and reaction channels of these surface species. Similar studies have been performed on other metal surfaces.^{6,7} A further aspect of this research is to examine the reactions of hydrocarbon species with adsorbed oxygen to produce oxygenated surface complexes which are reaction intermediates in the catalytic synthesis of alcohols at high temperature and pressure. Our early attempt to generate methoxy species in the reaction of adsorbed CH₃ and O did not lead to a positive result.⁸ Now, however, for the first time to our knowledge, we have succeeded in producing CH₂O by the oxidation of a surface CH_2 intermediate on the Rh(111) surface.

Experimental Section

The experiments were carried out in an ultrahigh-vacuum (uhv) chamber with a base pressure of 4×10^{-10} Torr, equipped with facilities for Auger electron spectroscopy (AES), highresolution electron loss spectroscopy (HREELS), and temperature-programmed desorption spectroscopy (TPD). In HREELS, all spectra were taken with a beam energy of 5.0 eV and resolution of 10-12 mV full width at half-maximum. Impact and collection angles were 45° to the surface normal. The absolute intensity was in general $5 \times 10^4 - 1 \times 10^5$ counts/s. The UV light source was a focused 30 W Hg lamp. The light passed through a high-purity silica window into the vacuum chamber. Sample cleaning is achieved by both Ar⁺ sputtering and cycles of oxygen treatments (3 \times 10⁻⁷ Torr of O₂, local pressure, for 10-30 min, with sample at 800-1200 K). The X-ray photoelectron spectroscopic (XPS) measurements were performed in a Kratos XSAM 800 instrument at a base pressure of 10^{-9} Torr using Mg K α primary radiation (14 kV, 15 mA). Gases were dosed through a 0.1 mm diameter capillary that terminated 2 cm from the sample. The pressure around the sample was about 10^{-9} Pa during the dosing. CH₂I₂ and CH₂- Cl_2 were obtained from Fluka; they were further purified by several freeze-pump-thaw cycles.

Results and Discussion

The interaction of CH_2I_2 with a clean Rh(111) surface has been investigated in great detail by means of HREELS, XPS, and TPD measurements.⁹ At monolayer coverage, CH₂I₂, CH₄, H_2 , and C_2H_4 (in traces) were found in the desorbing products. As the TPD spectra presented in Figure 1 show, these compounds were also formed in the presence of adsorbed oxygen, but CH₂O ($T_p = 280$ K), CO₂ ($T_p = 410$ K), and H₂O $(T_{\rm p} = 415 \text{ K})$ were additionally produced. The identity of the CH₂O registered at m/e = 29 was confirmed by comparison of the measured TPD intensities of the species with m/e values of 30 (CH₂O), 29 (CHO), and 28 (CO) with the known fragmentation pattern of CH₂O. Determination of the XPS signal for $I(3d_{5/2})$ at 620.0–620.4 eV suggests that the uptake of CH_2I_2 on an oxygen-dosed Rh(111) surface is not influenced up to $\Theta_0 = 0.3$, but decreases by about 20-25% at higher oxygen coverages.

Variation for the oxygen coverage reveals that the amount of CH₂I₂ desorbing with $T_p = 220$ K from a clean surface decreases, and a more weakly held CH₂I₂ develops even at low oxygen coverages of $\Theta_O = 0.07$. This desorption peak was observed or a clean Rh(111) only at high exposures and was attributed to multilayer formation.⁹ At the same time a new, more stable adsorption state appeared with $T_p = 275$ K. The peak temperature for CH₄ desorption ($T_p = 240$ K), and the area of the CH₄ peak, remained practically unaltered up to Θ_O = 0.3. Above this oxygen coverage, less CH₄ was formed, and its T_p was shifted to the higher temperature of 260 K.

Formation of CH₂O was observed at the lowest oxygen coverage used in this work, $\Theta_0 = 0.07$. Its formation started above 170 K and reached a maximum at 230 K. These values shifted to higher temperature as Θ_0 was increased. The highest peak temperature for CH₂O evolution was 280 K. An increase of the O coverage enhanced the production of H₂O and CO₂. These two compounds desorbed in the same temperature range, with a constant peak temperature of 410–415 K.

Taking into account the areas of TPD peaks for different products, we found that at $\Theta_0 = 0.3$ the ratios for CH₂O/CO₂, CH₂O/CH₄, and CO₂/CH₄ were 0.25, 0.06, and 0.22, respectively. It is interesting that CO was detected only in traces. It may be noted that the formation of CH₂O in the reaction of CH₂ (produced by thermal dissociation of ClCH₂I and CH₂I₂) with adsorbed oxygen was also observed on the Pt(111)¹⁰ and Pd(100)¹¹ surfaces.

In a search for new surface compounds, HREELS measurements were carried out under similar conditions. The adsorption

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Figure 1. (A) TPD spectra following CH_2I_2 adsorption on a clean and oxygen-dosed Rh(111) ($\Theta_0 = 0.3$) at 90 K. (B) Effects of oxygen coverage on the formation of CH_2O following CH_2I_2 exposure on clean and oxygen-dosed Rh(111) at 90 K. Exposure time of CH_2I_2 was 20 min for (A) and (B). The adsorption of oxygen was performed at 300 K, while that of CH_2I_2 was at 90 K.

TABLE 1: Characteristic Losses of Adsorbed CH_2I_2 and CH_2 on the Rh(111) Surface

vibration modes	CH ₂ I ₂ /Rh(111)	CH _{2(a)} /Rh(111)
$\nu_{\rm as}(\rm CH_2)$	3030	2940
$\nu_{\rm s}({\rm CH_2})$	2940	
$\delta(CH_2)$	1350	
$\omega(CH_2)$		
$\gamma(CH_2)$	1080	1190
$\varrho(CH_2)$	720	780
$\nu_{\rm as}({\rm CI}_2$	560	
$\nu_{\rm s}({\rm CI}_2)$		
$\nu(MC)$		650

of CH₂I₂ on oxygen-dosed Rh(111) at 90 K yielded very similar spectra as those obtained for the clean surface (Figure 2A). The characteristic losses of molecularly adsorbed CH₂I₂ for Rh(111) and their assignments are listed in Table 1. Independently of the oxygen coverage, there was no spectral indication of the presence of adsorbed CH₂O at 90 K; its characteristic losses are at 2960 cm⁻¹, ν (CH₂); 1430–1450 cm⁻¹, δ (CH₂); 1100–1120 cm⁻¹, ν_a (OCO); 960–965 cm⁻¹, ν_s (OCO); and 620 cm⁻¹, δ (OCO).¹² No other new surface compounds were observed either.

Figure 2 displays some selected spectra for the annealed system. On a clean surface, spectral changes indicative of the dissociation of molecularly adsorbed CH₂I₂ started at 173 K, when losses appeared due to CH₂, the primary product of the dissociation. This process was almost complete at 219 K. In the presence of preadsorbed oxygen ($\Theta_0 = 0.3$) these features were shifted to higher temperatures. This is well illustrated by the presence of the losses δ (CH₂) (1350 cm⁻¹) and γ (CH₂) (1100 cm⁻¹) of CH₂I₂ even at 240 K. New loss features corresponding to oxygenated compounds did not appear at high temperature either.

In light of these features, we can state that at low oxygen coverages the main reaction channel for CH₂ is still its self-hydrogenation (with the possible participation of background hydrogen), as indicated by the unaltered production of CH₄. Parallel with this, a fraction of CH₂ formed in the dissociation of CH₂I₂ and interacted with adjacent adsorbed oxygen atoms to give CH₂O, which desorbs promptly after its formation, without appreciable oxidation. Its formation is undoubtedly a reaction-limited process. It this assumption is correct, then illumination of the adsorbed layer at 90 K may produce CH₂O around this temperature, as the illumination of adsorbed CH₂I₂ on the Pd(100) and Rh(111) surfaces induces the production of CH₂ through the dissociation of CH₂O was identified above 110 K by means of the postirradiation TPD measurements.

The total oxidation of CH₂ proceeds at much higher temperatures (above 340 K) to give gaseous CO₂ and H₂O. We found no indications of the presence of these compounds in the HREEL spectra, which is not surprising, as CO₂ desorbs from carefully cleaned Rh(111) with $T_p = 250$ K¹³ and H₂O does so with $T_p = 158$ and 183 K.¹⁴ As regards the formation of these products, there are several possible reaction channels. Most probable is that the oxidation occurs through the formation of formate species, HCOO, which decomposes to CO₂ and H₂. Formate can exist only transitorily on the surface, as the HREEL spectra did not indicate its presence at all. This is consistent with the finding that formate decomposes on Rh(111) between 230 and 280 K.¹⁵ An alternative route involves the oxidation of CH formed in the decomposition of adsorbed CH₂ above 350-400 K.

In order to prove further that CH_2 is a key species in the formation of CH_2O and in the complete oxidation reactions,





we examined the effects of adsorbed oxygen on the CH₂Cl₂/ Rh(111) system. In contrast with the iodo compound, CH₂Cl₂ adsorbs molecularly at 90 K and undergoes only a limited dissociation (less than 15%) during annealing. By means of TPD we detected the formation of a small amount of CH₄ with $T_p = 200$ K. In the HREELS spectrum, we could identify only the characteristic losses of the molecularly adsorbed compound. The same features were observed following adsorption and annealing on an oxygen-dosed Rh(111) surface. We found no traces of CH₂O in the temperature range 90–300 K. However, when the coadsorbed layer had been illuminated for 60 min at 90 K, which induced the dissociation of CH₂Cl₂, the evolution of CH₂O occurred in the postirradiation TPD at around 230 K.

Conclusions. (i) Coadsorbed oxygen atoms slightly increase the temperature of dissociation of CH_2I_2 . (ii) They react with CH_2 to give CH_2O above 170 K and with CO_2 and H_2O above 340 K. (iii) On unperturbed sites, the main reaction channel for CH_2 is still its self-hydrogenation to CH_4 .

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