

Effects of Oxygen Coverage on the Partial Oxidation of Methylene: Reactions of Diiodomethane on Oxygen-Covered Rh(111)

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Abstract: The influence of oxygen coverage on the surface chemistry of diiodomethane (CH_2I_2) on oxygen-covered Rh(111) has been investigated, using a combination of temperature programmed reaction and high resolution electron energy loss spectroscopies. Partial oxidation to formaldehyde is favored at high oxygen coverages, while nonselective dehydrogenation and methane formation are prevalent at low and total combustion at intermediate oxygen coverages. Oxygen influences the chemistry of diiodomethane on Rh(111) in four distinct ways: (1) stabilization of carbon–iodide bonds, (2) inhibition of carbon–hydrogen bond cleavage in adsorbed hydrocarbons, (3) scavenging and removing of surface hydrogen, and (4) direct addition to gaseous methylene fragments. At high oxygen coverages, CH_2I_2 dissociation is inhibited, so as to produce transient CH_2 that reacts with surface oxygen to form formaldehyde prior to equilibration with the surface. Equilibration of methylene with the rhodium surface ultimately leads to dehydrogenation and subsequent CO and CO_2 formation. Specifically, there is no evidence for oxygen insertion into the Rh– CH_2 bond.

Introduction

The vast reserves of natural gas are currently severely underutilized as starting material for organic synthesis, because of the absence of affordable routes from methane to valuable starting materials, such as methanol and formaldehyde. High selectivities for partial oxidation of methane to oxygenated hydrocarbons are difficult to achieve because competing complete combustion to CO_2 and H_2O is thermodynamically much more favorable. Recent success in converting methane to syngas (CO and H_2) with high selectivity using rhodium monolith catalysts^{1–3} triggered our study of the fundamental steps of methane oxidation on rhodium. Using iodides as a source of methyl (CH_3I) and methylene (CH_2I_2), we have shown that methylene, not methyl, is partially oxidized to formaldehyde on oxygen-covered Rh(111).⁴ A recent study by Solymosi and Klivenyi showed similar results.⁵ This result is surprising because methyl is generally thought to yield partial oxidation products, while further dehydrogenation to methylene would lead to total combustion. Indeed, we have recently shown that gaseous CH_3 adds directly to chemisorbed oxygen to yield adsorbed methoxy.⁶ However, methoxy does not yield formaldehyde; it decomposes to CO, CO_2 , and H_2O .^{6–8} We have previously shown that formaldehyde is produced via direct addition of methylene to surface oxygen, not by oxygen insertion into the Rh– CH_2 bond.⁴ Similar results have also been reported by Solymosi and Klivenyi.⁵ Recently, the partial oxidation of surface-bound methylene to formaldehyde was reported in the

reaction of ClCH_2I on oxygen-covered Pt(111)⁹ and in the reaction of CH_2I_2 on oxygen-covered Pd(100),¹⁰ indicating that oxidation of CH_2 to formaldehyde on metal surfaces is rather general.

In this study, we investigate the dependence of the product distribution on the coverage of oxygen on Rh(111), in order to better understand the roles of oxygen in oxidation chemistry on this surface. Previously, we have shown that partial oxidation is enhanced at high oxygen coverages in the oxidation of ethyl and 2-propyl iodide on Rh(111).¹¹ We have also reported similar trends in the oxidation of thiolates,¹² olefins,^{13–15} and alcohols¹⁶ on oxygen-covered Rh(111). This is opposite to the trend reported for most metals and supported catalysts, where complete combustion is prevalent at high oxygen coverages, and partial oxidation is favored at low oxygen coverages, as would be expected on the basis of Le Chatelier's law.¹⁷ The behavior of oxygen on Rh(111) is attributed to the fact that oxygen on rhodium does not serve as a Brønsted base. In fact, oxygen on rhodium inhibits nonselective C–H bond cleavage by the surface, leading to more bond-selective chemistry at higher oxygen coverages.

Herein we report that partial oxidation of methylene on oxygen-covered Rh(111) is also favored at high oxygen coverages, demonstrating the generality of this trend; partial oxidation to formaldehyde is the dominant reaction pathway at high oxygen coverages, while H_2 and CH_4 formation is prevalent at low and total combustion at intermediate oxygen coverages. On

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clean $\text{Rh}(111)$, the C–I bonds of CH_2I_2 cleave between 150 and 300 K, affording adsorbed iodine and methylene. Methylene subsequently reacts by hydrogenation to methane or dehydrogenation to surface carbon, with the concomitant evolution of dihydrogen. Formaldehyde is formed by direct addition of gaseous methylene to surface oxygen. Total decomposition, yielding CO, CO_2 , and H_2O , is a competing pathway, even at the highest oxygen coverage. The relative yield of formaldehyde formation increases sharply with increasing oxygen coverage, reaching a selectivity of $72 \pm 18\%$ on $\text{Rh}(111)\text{--p}(2 \times 1)\text{--O}$, while the relative yields of methane and dihydrogen, products from reaction on the clean surface, decrease. On $\text{Rh}(111)\text{--p}(2 \times 1)\text{--O}$ no more evolution of methane and dihydrogen is observed. The relative yields of combustion products, CO, CO_2 , and H_2O , first increase as oxygen becomes available and later decrease with increasing oxygen coverage. Our results qualitatively agree with those recently reported for the thermal and photolytic decomposition of CH_2I_2 and CH_2Cl_2 on oxygen-covered $\text{Rh}(111)$,⁵ although there are some important quantitative differences, especially in the dependence on the oxygen coverage. These differences can be explained by a systematic overestimation of the oxygen coverage by Solymosi and Klivenyi,⁵ possibly due to oxygen removal by background hydrogen or the presence of impurities on the surface, and the larger yield of methylene in the photochemical dissociation.

Experimental Section

All experiments were performed in a stainless steel ultrahigh vacuum chamber with a base pressure below 1×10^{-10} Torr.¹⁸ The chamber is equipped with a cylindrical mirror analyzer (PHI 15–155) for Auger electron spectroscopy, optics for low-energy electron diffraction (PHI 15–120), a computer-controlled quadrupole mass spectrometer (UTI-100C) for temperature programmed reaction spectroscopy,¹⁹ and a computer-controlled LK2000–14-R electron spectrometer for high resolution electron energy loss spectroscopy.

The preparation and routine cleaning procedure of the crystal²⁰ and the preparation of the oxygen overlayers¹² have been described in detail previously. The procedures used in data collection have also been described in detail elsewhere.¹² In short, in a temperature-programmed reaction experiment, the reactants are introduced to the crystal at 100 K, after which the crystal is radiatively heated to 700 K in line-of-sight to an apertured mass spectrometer. The heating rate decreases monotonically from 9 K/s at 100 K to 6 K/s at 700 K and is highly reproducible. During heating, the crystal is biased at -60 V to preclude electron-induced chemistry. Electron bombardment is used for heating in the range of 700 to 1500 K, in order to desorb iodine and oxygen. All gaseous products are identified on the basis of quantitative analysis of mass spectrometer fragmentation patterns, as described previously.^{4,11}

In a high-resolution electron energy loss experiment, the reactants are introduced to the crystal at 100 K. The crystal is heated to the specified temperature at the same rate as used in temperature-programmed reaction experiments and allowed to cool down before recording a spectrum. The spectrometer operates at a primary beam energy of ≈ 3 eV, with a resolution of ≈ 55 cm^{-1} at a count rate of more than 1×10^6 counts per second for the elastic peak. All spectra shown are obtained for specular detection angles.

Diiodomethane (Aldrich, 99%) and diiodomethane- d_2 (Cambridge Isotope, 98%) were stored over molecular sieves and subjected to several freeze–pump–thaw cycles before each day of experiments. $^{16}\text{O}_2$ (Matheson, 99.99%) and $^{18}\text{O}_2$ (Cambridge Isotopes) were used as received. The purity of all reagents was regularly confirmed by mass spectrometry. Reactants are directly dosed onto the crystal, with the crystal face ≈ 5 mm from the aperture of the doser. The pressure rise during dosing is typically on the order of 2×10^{-11} Torr.

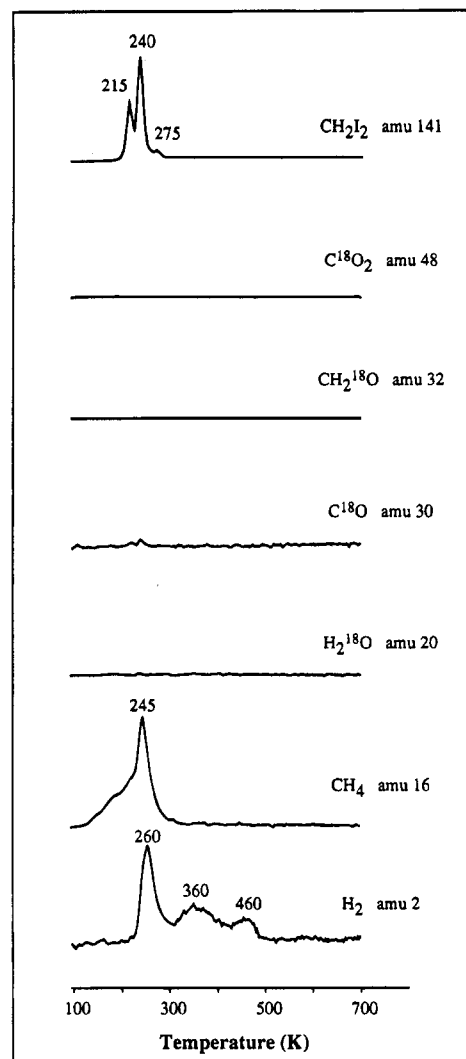


Figure 1. Temperature-programmed reaction of CH_2I_2 on clean $\text{Rh}(111)$. All signals have been corrected for contribution of higher masses. The evolution of CH_2I_2 is monitored at 141 amu because the parent ion at 268 amu falls outside the range of our mass spectrometer.

Results

Temperature-Programmed Reaction Studies. Methane and dihydrogen are the only products evolved during temperature programmed reaction of a saturation coverage of CH_2I_2 on clean $\text{Rh}(111)$ between 100 and 700 K (Figure 1). Iodine and carbon are deposited on the surface. No methylene recombination to C_2 or higher hydrocarbons is observed.

Methane evolves in a broad feature between 150 and 300 K, with a peak temperature of 245 K. The rate of methane evolution is reaction-rate limited; molecular methane is expected to desorb well below 100 K on clean $\text{Rh}(111)$, based on the temperature of methane desorption from $\text{Pt}(111)$.²¹ Hydrogen evolves in three overlapping peaks at 260, 360, and 460 K. The lower temperature peak is due to the recombination of surface hydrogen,²² while the higher temperature peaks are attributed to dehydrogenation of CH_x species on the surface.

Molecular desorption of CH_2I_2 leads to peaks at 215, 240, and 275 K. The peak at 215 K, attributed to the sublimation of condensed multilayers, increases indefinitely in intensity with increasing CH_2I_2 exposure. Upon further heating iodine desorbs around 850 K.

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Rapid, reversible C–H bond activation occurs below 220 K based on the extensive deuterium incorporation into methane when CH_2I_2 reacts on Rh(111) previously exposed to deuterium. All isomers of methane (d_0 through d_4) are formed. For instance, the measured yields of methane- d_0 , d_1 , d_2 , d_3 , and d_4 are 33%, 22%, 27%, 11%, and 7% of the total methane yield, respectively, when the ratio of the total amounts of hydrogen and deuterium on the surface during reaction is approximately 1.0:0.8. Similar results are obtained when CD_2I_2 reacts on Rh(111) exposed to hydrogen, and for methane formation from CH_3I and CD_3I on deuterated and hydrogenated Rh(111).²³ The amount of isotopic exchange in the methane product decreases as a function of oxygen coverage. For example, methane- d_3 and - d_4 only account for respectively 6% and 3% of the methane produced, in the reaction of CH_2I_2 on Rh(111)- $\text{p}(2\times 2)\text{-O}$, preexposed to deuterium, when the ratio of the total amounts of hydrogen to deuterium present on the surface during reaction is approximately 1.0:0.6.

While formaldehyde, CO, CO_2 , and H_2O are formed, as well as CH_4 , H_2 , and adsorbed C, during temperature-programmed reaction of CH_2I_2 on oxygen-covered surfaces at all oxygen coverages studied, 0.15–0.5 monolayer, the yields of the various products depend strongly on the initial oxygen coverage (Figures 1–4).^{24,25} In addition, the maximum amount of CH_2I_2 that reacts decreases with increasing oxygen coverage, from 0.44 ± 0.02 ²⁴ on clean Rh(111), to 0.37 ± 0.02 on Rh(111)- $\text{p}(2\times 2)\text{-O}$, to 0.10 ± 0.01 on Rh(111)- $\text{p}(2\times 1)\text{-O}$. The total amount of CH_2I_2 reacting on Rh(111)- $\text{p}(2\times 1)\text{-O}$ is determined at 0.10 ± 0.01 molecules per rhodium atom based on the combined yields of CH_2O , CO, and CO_2 , the only carbon-containing products on this surface.⁴ The total amount of CH_2I_2 reacting at lower oxygen coverages is determined by comparing the integrated signal intensity in the iodine evolution around 850 K to that for the reaction on the full $\text{p}(2\times 1)\text{-O}$ overlayer.

The relative yield²⁵ of formaldehyde increases monotonically with increasing oxygen coverage, reaching a maximum at the maximum attainable oxygen coverage, 0.5 monolayer (Figure 4). The temperature of formaldehyde evolution also shifts, from 255 K on Rh(111) with 0.15 monolayer of oxygen, to 300 K on Rh(111)- $\text{p}(2\times 2)\text{-O}$ ($\theta_0 = 0.25$) (Figure 2), and ultimately to 335 K on Rh(111)- $\text{p}(2\times 1)\text{-O}$ ($\theta_0 = 0.5$) (Figure 3). The rate of formaldehyde evolution is reaction-rate limited, since molecular formaldehyde desorbs from Rh(111)- $\text{p}(2\times 1)\text{-O}$ at 310 K²³ and at 280 K from Rh(111)- $\text{p}(2\times 2)\text{-O}$,²⁶ for example. We ascribe the differences in the temperatures for formaldehyde production to the inhibition of C–I bond scission by surface oxygen. There is no C–H bond activation along the pathway to evolve gaseous formaldehyde on either Rh(111)- $\text{p}(2\times 1)\text{-O}$ or Rh(111)- $\text{p}(2\times 2)\text{-O}$. Only CH_2O and CD_2O are formed when a mixture of CH_2I_2 and CD_2I_2 reacts on these surfaces; no CHDO is detected.

The relative yields²⁵ of H_2O , CO, and CO_2 all first increase and later decrease as a function of oxygen coverage, reaching their maxima at an oxygen coverage of 0.4 monolayer of oxygen. The temperatures of CO and CO_2 evolution are essentially independent of the oxygen coverage (Figures 1–3).

The normalized yield of methane first increases and later decreases with increasing oxygen coverage, reaching a maximum at an oxygen coverage of 0.15 monolayer. On Rh(111)-

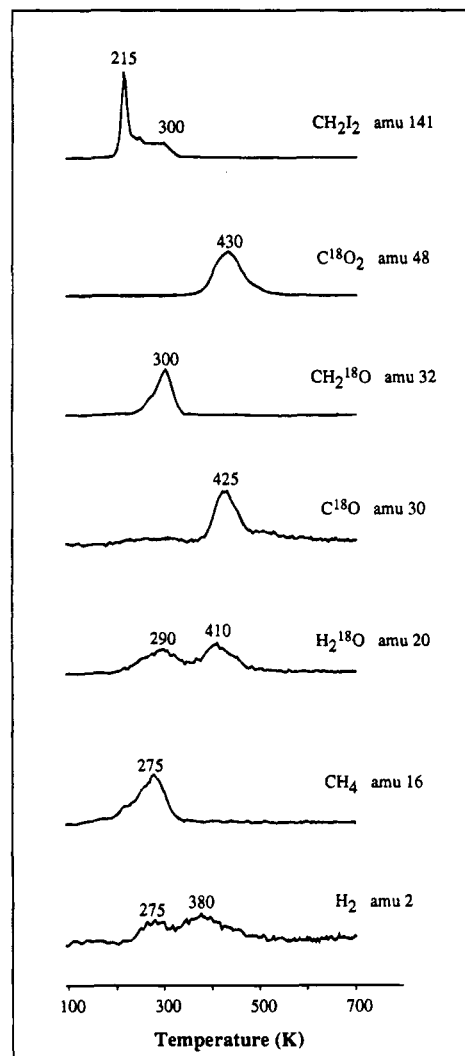


Figure 2. Temperature-programmed reaction of CH_2I_2 on Rh(111)- $\text{p}(2\times 2)\text{-}^{18}\text{O}$. All signals have been corrected for contribution of higher masses. The evolution of CH_2I_2 is monitored at 141 amu because the parent ion at 268 amu falls outside the range of our mass spectrometer. All oxygen-containing products are ^{18}O substituted.

$\text{p}(2\times 1)\text{-O}$ no more methane evolution is observed. The temperature of methane evolution increases from 245 K on the clean surface to 275 K on Rh(111)- $\text{p}(2\times 2)\text{-O}$ (Figure 2) and 300 K on Rh(111) with 0.4 monolayer of oxygen. Notably, methane is always evolved at a temperature below CH_2O formation (Figures 2 and 3).

Water evolves in two peaks; the low-temperature-evolution peak increases from 255 K on Rh(111) with 0.15 monolayer of oxygen to 290 K on Rh(111)- $\text{p}(2\times 2)\text{-O}$ (Figure 2), and finally to 335 K on Rh(111)- $\text{p}(2\times 1)\text{-O}$ (Figure 3), while the highest temperature peak remains constant at ~ 415 K. The normalized yield of dihydrogen monotonically decreases with increasing oxygen coverage, reaching zero at Rh(111)- $\text{p}(2\times 1)\text{-O}$. The temperature of dihydrogen evolution is independent of the oxygen coverage and all three hydrogen evolution peaks decrease equally.

Molecular desorption competes with CH_2I_2 reaction, leading to peaks at 265 and 335 K on Rh(111)- $\text{p}(2\times 1)\text{-O}$, and a broad feature peaking at 300 K on Rh(111)- $\text{p}(2\times 2)\text{-O}$. Condensed multilayers sublime around 215 K on all surfaces.

At the highest oxygen coverage formaldehyde formation is the dominant pathway. On Rh(111)- $\text{p}(2\times 1)\text{-O}$ a total of 0.10 ± 0.01 molecule of CH_2I_2 reacts per rhodium atom at the surface, 72% forming formaldehyde. The remainder nonselec-

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(24) The errors are based on the standard deviation in sets of five experiments. Although the experimental values are highly reproducible, quoted errors are sometimes relatively large, due to the propagation of errors in calculations.

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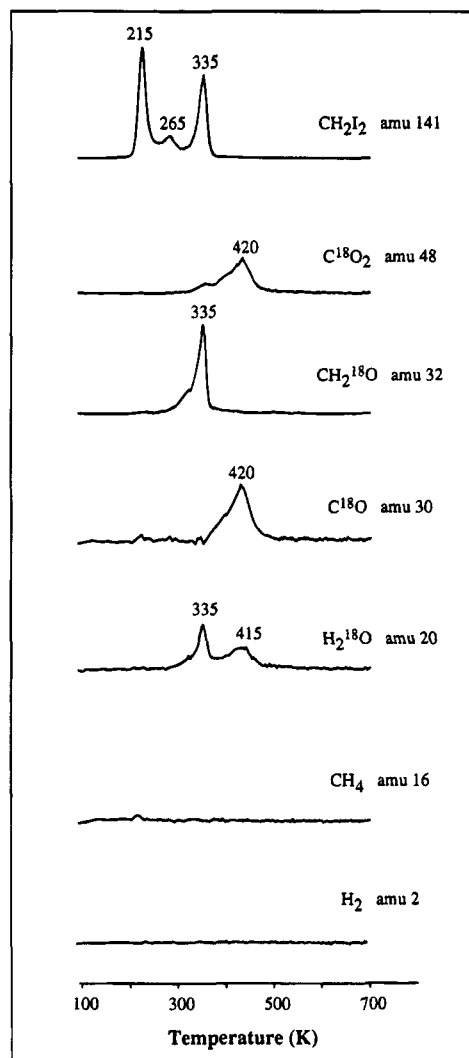


Figure 3. Temperature-programmed reaction of CH_2I_2 on $\text{Rh}(111)\text{-p}(2\times 1)\text{-}^{18}\text{O}$. All signals have been corrected for contribution of higher masses. The evolution of CH_2I_2 is monitored at 141 amu because the parent ion at 268 amu falls outside the range of our mass spectrometer. All oxygen-containing products are ^{18}O substituted.

tively decomposes to form CO , CO_2 , and H_2O . At slightly lower oxygen coverages formaldehyde formation, methane formation and total combustion all occur with similar selectivities. On $\text{Rh}(111)$ with 0.4 monolayer of oxygen, for instance, 0.14 ± 0.01 molecule of CH_2I_2 reacts per rhodium atom, $\sim 34\%$ of which form formaldehyde, $\sim 34\%$ methane, and $\sim 32\%$ CO , CO_2 , H_2 , and H_2O . At low oxygen coverage methane formation is the prevalent product of CH_2I_2 reaction. On $\text{Rh}(111)$ with 0.15 monolayer of oxygen, for instance, 0.39 ± 0.02 molecule of CH_2I_2 reacts per rhodium atom, $\approx 0.8\%$ forming formaldehyde and $\sim 46\%$ methane, while the remaining 54% decomposes to form surface carbon, CO , CO_2 , H_2 , and H_2O . On clean $\text{Rh}(111)$ 0.44 ± 0.02 molecule of CH_2I_2 reacts per rhodium atom, $\sim 31\%$ forming methane, while the remainder decomposes to gaseous dihydrogen and adsorbed carbon.

No formaldehyde is formed in the reaction of surface-bound methylene and atomic oxygen, suggesting that formaldehyde is formed immediately following C-I bond cleavage. Vibrational data show that adsorbed CH_2 is formed on clean $\text{Rh}(111)$ when CH_2I_2 is heated to 220 K. No formaldehyde evolution is observed during temperature-programmed reaction up to 700 K, for any combination of methylene (0.0–0.4 monolayer) and oxygen (0.0–0.25 monolayer) coverages studied, when CH_2I_2 is dosed on clean $\text{Rh}(111)$ at 100 K and annealed to 220 K

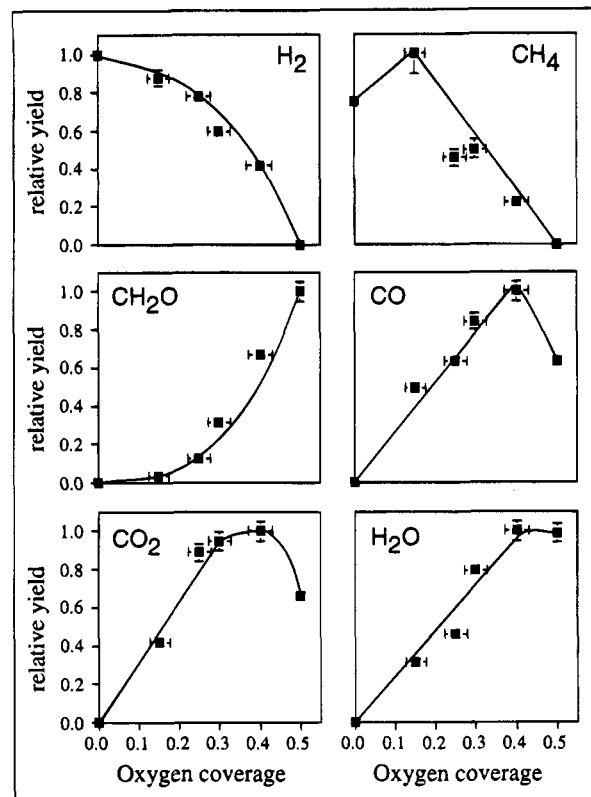


Figure 4. Relative yields²⁵ of H_2 , CH_4 , CH_2O , CO , CO_2 , and H_2O as a function of the oxygen coverage in the reaction of CH_2I_2 on oxygen-covered $\text{Rh}(111)$. The relative yields are determined by measuring the integrated signal intensity in temperature programmed reaction experiments and normalizing for the total amount of CH_2I_2 reacting. The evolution of H_2 , CH_4 , CH_2O , CO , CO_2 and H_2O is monitored at 2, 16, 32, 30, 48, and 20 amu, respectively. All oxygen-containing products are ^{18}O substituted. All signals have been corrected for contributions from higher masses.

followed by adsorption of O_2 at 100 K. CH_4 , H_2 , H_2O , CO , and CO_2 are the only products. Although at least part of the oxygen will remain in the molecular state after exposure of a methylene-covered $\text{Rh}(111)$ surface to dioxygen at 100 K, only $\text{O}_{(a)}$ remains at 200 K; O_2 desorbs between 120 and 160 K upon heating. High resolution electron energy loss spectroscopy shows that only $\text{O}_{(a)}$ is present after heating to 200 K (Figure 6C). The spectrum collected after heating a surface, prepared as described above, to 200 K shows a strong loss at 560 cm^{-1} , assigned to the Rh-O stretch in adsorbed atomic oxygen and no significant intensity at 650 cm^{-1} , the frequency expected for $\nu(\text{O-O})$ in O_2 . Importantly, the losses characteristic of $\text{O}_{2(a)}$ and $\text{O}_{(a)}$ are readily resolved in spectra obtained at 100 K. Furthermore, the production of H_2O , CO , and CO_2 is clearly the result of the reaction with atomic oxygen, based on independent studies of $\text{C}_{(a)}$ and $\text{O}_{(a)}$.

High-Resolution Electron Energy Loss Studies. CH_2I_2 adsorbs intact on clean $\text{Rh}(111)$ at 100 K, but decomposes by carbon-iodine bond breakage below 300 K, based on high resolution electron energy loss spectroscopy. All losses in the spectrum collected following a monolayer exposure of CH_2I_2 to clean $\text{Rh}(111)$ at 100 K (Figure 5A) can readily be assigned to intact CH_2I_2 , based on comparison to the spectrum for multilayers of CH_2I_2 and reference gas phase infrared data (Table 1).²⁷ The observed spectrum also agrees well with a previous study of CH_2I_2 on $\text{Rh}(111)$.⁵ Specifically, the presence

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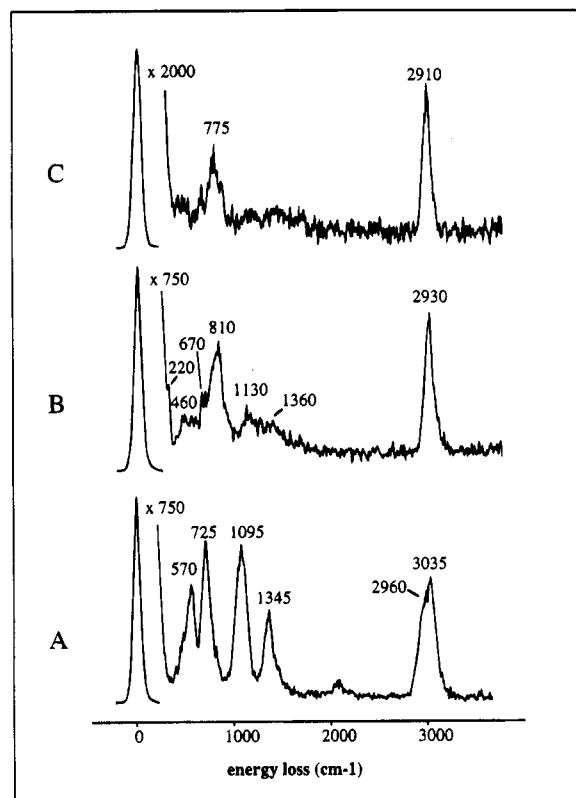


Figure 5. High-resolution electron energy loss spectra corresponding to (A) saturation coverage of CH_2I_2 on clean $\text{Rh}(111)$ at 100 K, (B) 50% of saturation coverage of CH_2I_2 on clean $\text{Rh}(111)$, heated to 220 K, and (C) saturation coverage of CH_2I_2 on clean $\text{Rh}(111)$, heated to 300 K.

of the strong loss at 570 cm^{-1} , assigned to the carbon–iodide stretch, is indicative of intact C–I bonds. Also, the absence of losses due to Rh-I and Rh-CH_2 stretching modes, expected around 220 and $400\text{--}700\text{ cm}^{-1}$, respectively, indicates that the C–I bonds remain intact at 100 K. At 150 K a loss at 220 cm^{-1} appears, assigned to the Rh-I stretch, signifying the onset of C–I bond breakage on clean $\text{Rh}(111)$. This temperature corresponds to the onset of methane evolution in temperature programmed reaction of CH_2I_2 on clean $\text{Rh}(111)$. At 300 K, all losses due to intact CH_2I_2 are absent for all initial CH_2I_2 coverages studied. The spectrum collected after annealing CH_2I_2 multilayers on clean $\text{Rh}(111)$ to 300 K indicates that adsorbed iodine and methylidyne are present (Figure 5C). The three losses at 450, 775, and 2910 cm^{-1} , assigned to $\nu(\text{Rh-CH})$, $\delta(\text{C-H})$, and $\nu(\text{C-H})$, respectively (Table 1), correspond well with infrared data of transition metal complexes²⁸ and previous studies of adsorbed methylidyne.^{29,30} A mixture of iodine, methylene, methylidyne, and intact CH_2I_2 is present on the clean surface between 150 and 300 K (Figure 5B). The exact ratio of surface species at any given temperature is determined by the initial CH_2I_2 coverage, where lower coverages show more complete decomposition at lower temperature. For instance, the spectrum collected after exposing clean $\text{Rh}(111)$ to 50% of a saturation exposure of CH_2I_2 and annealing to 220 K (Figure 5B) consists of a combination of modes attributed to adsorbed iodine, methylene, and methylidyne (Table 1). The observed frequencies are in good agreement with those previously

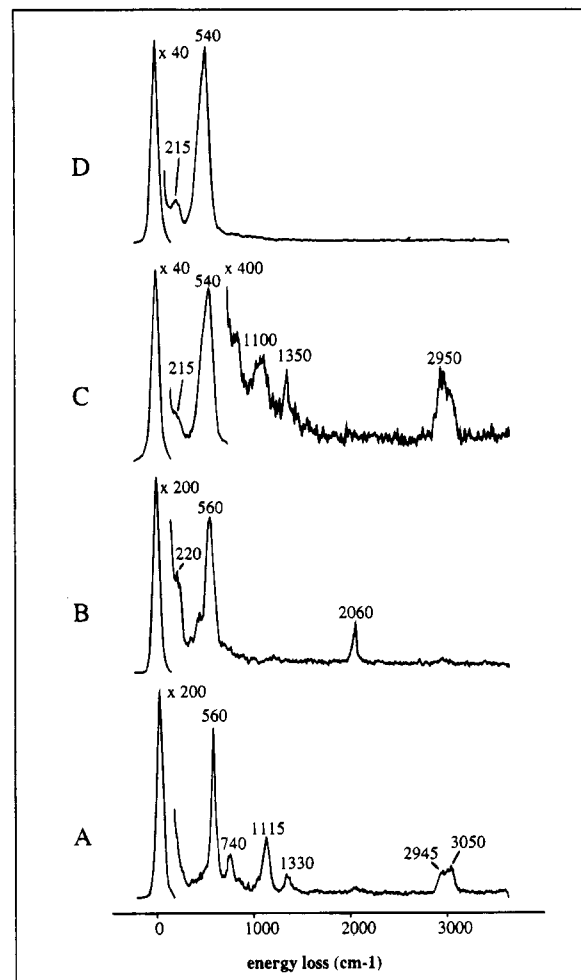


Figure 6. High-resolution electron energy loss spectra for the following: (A) saturation coverage of CH_2I_2 on $\text{Rh}(111)\text{-p}(2\times 1)\text{-}^{16}\text{O}$, heated to 300 K, corresponding to molecular CH_2I_2 ; (B) saturation coverage of CH_2I_2 on $\text{Rh}(111)\text{-p}(2\times 1)\text{-}^{16}\text{O}$, heated to 400 K, showing $\text{CO}_{(a)}$ ($\nu(\text{C=O}) = 2060\text{ cm}^{-1}$); (C) coadsorbed CH_2 , I, and oxygen synthesized from 75% of saturation coverage of CH_2I_2 on clean $\text{Rh}(111)$, heated to 220 K, followed by adsorption of $^{16}\text{O}_2$ at 100 K, and subsequently heating to 200 K; and (D) adsorbed I and O remaining after heating $\text{CH}_{2(a)}$, $\text{I}_{(a)}$, and $\text{O}_{(a)}$, prepared as in part C, to 400 K.

Table 1. Vibrational Assignments for Products of CH_2I_2 on Clean $\text{Rh}(111)$

| intact CH_2I_2 on clean $\text{Rh}(111)$ at 100 K | $\text{CH}_{(a)} + \text{CH}_{2(a)}$ from CH_2I_2 on $\text{Rh}(111)$ at 220 K | $\text{CH}_{(a)}$ from CH_2I_2 on $\text{Rh}(111)$ at 300 K | assign |
|---|--|---|---------------------------------|
| | 220 | n.r. | $\nu(\text{Rh-I})$ |
| | 460 | 450 | $\nu(\text{Rh-CH})$ |
| 570 | | | $\nu(\text{C-I})$ |
| | 670 | | $\nu(\text{Rh-CH}_2)$ |
| 725 | 810 | 775 | $\rho(\text{CH}_2)$ |
| | | | $\delta(\text{CH})$ |
| 1095 | | | $\omega(\text{CH}_2\text{I}_2)$ |
| | 1130 | | $\omega(\text{CH}_2)$ |
| 1345 | | | $\delta(\text{CH}_2\text{I}_2)$ |
| | 1360 | | $\delta(\text{CH}_2)$ |
| | 2930 | | $\nu(\text{CH}_2)$ |
| | | 2910 | $\nu(\text{CH})$ |
| 2960 | | | $\nu_s(\text{CH}_2\text{I}_2)$ |
| 3035 | | | $\nu_a(\text{CH}_2\text{I}_2)$ |

reported for adsorbed methylene.^{5,29,31,32} However, the relatively high intensities of the losses at 810 and 2930 cm^{-1} probably

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Table 2. Vibrational Assignments for CH₂I₂ on Rh(111)-p(2×1)-¹⁶O and for CH₂ on Rh(111) plus ¹⁶O₂

| monolayer CH ₂ I ₂ on Rh(111)-p(2×1)- ¹⁶ O | | CH ₂ on Rh(111) + ¹⁶ O ₂ | | assign |
|--|----------|---|----------|---------------------------------|
| at 300 K | at 400 K | at 200 K | at 400 K | |
| | 220 | 215 | 215 | $\nu(\text{Rh}-\text{I})$ |
| | 445 | | | $\nu(\text{Rh}-\text{CO})$ |
| 560 | 560 | 540 | 540 | $\nu(\text{Rh}-\text{O})$ |
| n.r. | | | | $\nu(\text{C}-\text{I})$ |
| | | n.r. | | $\nu(\text{Rh}-\text{CH}_2)$ |
| 740 | | | | $\rho(\text{CH}_2\text{I}_2)$ |
| 1115 | | | | $\omega(\text{CH}_2\text{I}_2)$ |
| | | 1100 | | $\omega(\text{CH}_2)$ |
| 1330 | | | | $\delta(\text{CH}_2\text{I}_2)$ |
| | | 1350 | | $\delta(\text{CH}_2)$ |
| | 2060 | | | $\nu(\text{CO})$ |
| 2945 | | | | $\nu_s(\text{CH}_2\text{I}_2)$ |
| | | 2950 | | $\nu(\text{CH}_2)$ |
| 3050 | | | | $\nu_a(\text{CH}_2\text{I}_2)$ |

indicate the coexistence of methylidyne (CH) on the surface. These are similar to the frequencies assigned to CH adsorbed on Ni(111).³³ Importantly, no methyl is detected at any temperature or coverage. Adsorbed methyl would be indicated by losses around 1195 and 2620 cm⁻¹.^{6,34} After heating to 500 K, past the temperature of hydrogen evolution in temperature programmed reaction, the spectrum consists of losses due to surface iodine and carbon, at 220 and 500 cm⁻¹, respectively.

The addition of oxygen increases the minimum temperature necessary for C-I bond breakage from 150 K on the clean surface, to 200 K on Rh(111)-p(2×2)-O, and to 300 K on Rh(111)-p(2×1)-O. The spectrum collected after annealing a monolayer of CH₂I₂ on Rh(111)-p(2×1)-O to 300 K is indicative of intact CH₂I₂; all modes attributed to intact CH₂I₂ are present (Figure 6A, Table 2). The C-I stretch, expected around 570 cm⁻¹, is obscured by the intense Rh-O stretch at 560 cm⁻¹. However, no losses due to Rh-I (~220 cm⁻¹) or Rh-molecule stretching modes are observed. No modes associated with adsorbed formaldehyde are observed either. Upon further heating all modes associated with CH₂I₂ decrease in intensity. At 400 K, only losses due to adsorbed oxygen, iodine, and CO ($\nu(\text{CO}) = 2060$ cm⁻¹) are observed (Figure 6B). Only modes at 560 and 220 cm⁻¹, due to adsorbed oxygen and iodine, remain after heating to 550 K, past the temperature of CO₂ evolution in temperature-programmed reaction. Importantly, at no temperature is there any indication of a surface-bound hydrocarbon species, such as CH, CH₂, or CH₃.

No CO_(a) is formed by the oxidation of adsorbed CH₂. No losses indicative of adsorbed CO are observed at any temperature if CH₂I₂ is dosed on the surface first and heated to 220 K to break the C-I bonds to form adsorbed CH₂, followed by the adsorption of oxygen at 100 K (Figure 6D, Table 2). This is consistent with the notion that surface-bound CH₂ dehydrogenates to surface carbon, which is subsequently oxidized to gaseous CO and CO₂, and strongly argues against insertion of oxygen into the Rh-CH₂ bond.

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(34) The loss at loss at 2620 cm⁻¹ is assigned to a softened C-H stretching mode, similar to those observed on other surfaces.³⁸⁻⁴¹ This mode was not observed in a study of adsorbed methyl, formed from methyl iodide, on Rh(111) by Solymosi and Klivenyi,⁴² perhaps because of limited signal-to-noise ratio or the presence of impurities. We have shown that mode softening is absent in adsorbed methyl on Rh(111) with coadsorbed oxygen.⁶ It is unlikely that the presence of coadsorbed iodine is the reason for the absence of mode softening, since other studies using methyl halides as a source of methyl have reported extensive mode softening on other metals.³⁸⁻⁴¹

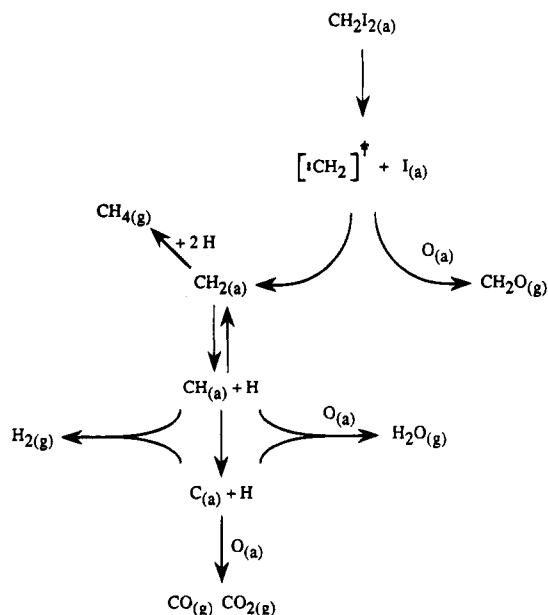


Figure 7. Proposed mechanism for the reaction of CH₂I₂ on oxygen-covered and clean Rh(111). The relative importance of the different pathways and the reaction temperature for the different steps depend on the oxygen coverage.

Discussion

The addition of oxygen dramatically alters the observed product distribution in the reaction of CH₂I₂ on Rh(111). Oxygen influences the chemistry of CH₂I₂ on Rh(111) in four distinct ways: oxygen inhibits carbon-iodide bond scission, retards C-H bond breakage by the surface, scavenges surface hydrogen and removes it as water, and adds to methylene and other carbon-containing fragments formed in the thermal decomposition of CH₂I₂. The branching ratios for CH₂I₂ reaction on Rh(111) are influenced by oxygen coverage as shown in the general mechanism formulated on the basis of our data (Figure 7).

On clean Rh(111), CH₂I₂ reacts by carbon-iodide bond breakage, affording adsorbed iodine and methylene, between 150 and 300 K, based on high-resolution electron energy loss spectra (Figure 7). Methylene undergoes competing reversible dehydrogenation to methylidyne and hydrogenation to methane, leading to methane evolution between 150 and 300 K and hydrogen desorption at 260 K in temperature programmed reaction spectroscopy. Molecular desorption of intact CH₂I₂ is a competing process. Between 150 and 300 K, methylene, methylidyne, and intact CH₂I₂ coexist on the surface. No evidence for the presence of methyl was found, suggesting that it is not a long-lived surface species, although it is probably a transient intermediate leading to methane. Hydrogenation and dehydrogenation reactions are facile on Rh(111), resulting in the formation of all possible isotopes of methane from the reaction of CH₂I₂ on the deuterium-covered surface. The recombination of surface hydrogen around 260 K effectively shuts down the hydrogenation pathway. No more methane formation is observed above 300 K. Above 300 K, methylidyne dehydrogenates to surface carbon with concomitant evolution of dihydrogen at 360 and 460 K. No recombination of surface methylene to gaseous ethylene is observed.

While on clean Rh(111) all C-I bonds in CH₂I₂ are cleaved below 300 K, all CH₂I₂ remains intact up to this temperature on Rh(111)-p(2×1)-O, based on vibrational data. The minimum temperature required for C-I bond breakage increases from 150 K on the clean surface, to 200 K on Rh(111)-

$p(2 \times 2)$ -O, and 300 K on Rh(111)- $p(2 \times 1)$ -O. As a consequence, the competing molecular desorption of CH_2I_2 also increases, leading to a decrease in the amount of CH_2I_2 reaction, as a function of increasing oxygen coverage, decreasing from 0.44 ± 0.02 on the clean surface, to 0.37 ± 0.02 on Rh(111)- $p(2 \times 2)$ -O, and 0.10 ± 0.01 on Rh(111)- $p(2 \times 1)$ -O. We have previously reported a similar effect in the reactions of ethyl and 2-propyl iodide on oxygen-covered Rh(111).¹¹ Site-blocking of Rh sites by oxygen is most certainly important in inhibiting C-I bond cleavage, although electronic effects cannot be ruled out. The Rh(111)- $p(2 \times 1)$ -O surface, e.g., is densely packed with oxygen. Indeed, it is possible that CH_2I_2 dissociation occurs primarily at vacancies in the oxygen layer.

Oxygen also inhibits nonselective C-H bond scission by the Rh(111) surface, as has previously been shown for longer chain alkyls.¹¹ A similar effect is seen in the reaction of alcohols on oxygen-covered Rh(111), where selective β -dehydrogenation in alkoxides leads to aldehydes and ketones at high oxygen coverages, while only nonselective decomposition is seen on clean Rh(111).^{16,23} The inhibition of nonselective C-H bond dissociation by oxygen is reflected in the initial increase and subsequent fall in CH_4 production, as well as the increase in CH_2O yield as the oxygen coverage increases. Methane production requires both hydrogenation and dehydrogenation of CH_2 . Dehydrogenation provides a source of hydrogen for the hydrogenation reaction. However, intact CH_x fragments are also necessary for methane production. Our data indicate that dehydrogenation and hydrogenation are optimally balanced for methane production at ~ 0.15 monolayer of oxygen.

The scavenging of hydrogen by surface oxygen is also important in determining product yields. Scavenging of hydrogen also contributes to the sharp decrease in the methane yield at higher oxygen coverage, since it depletes the surface of hydrogen. A similar decreasing yield with increasing oxygen coverage is seen for alkane formation from alkyl iodides on oxygen-covered Rh(111).¹¹ The water formation may also serve to decrease the surface oxygen coverage, which opens sites for CH_2I_2 dissociation.

We propose that the addition of oxygen to nascent $:\text{CH}_2$ is the pivotal step in the formation of formaldehyde (Figure 7). We have previously shown facile addition of oxygen to alkyl radicals, yielding alkoxides,^{6,11} and to carbon-carbon double bonds in terminal olefins,¹³⁻¹⁵ yielding ketones, in analogous processes. In this case, we propose that formaldehyde is formed by direct addition of CH_2 to surface oxygen immediately upon its formation by C-I bond cleavage in CH_2I_2 (Figure 7). Equilibrated surface-bound methylene specifically does *not* react with adsorbed oxygen on Rh(111). Temperature-programmed reaction following annealing a 75% of saturation coverage of CH_2I_2 to 220 K, followed by formation of $\text{O}_{(a)}$, does *not* yield any formaldehyde. Adsorbed CO is not formed either. Furthermore, high-resolution electron energy loss data show that CH_2I_2 remains intact up to the temperature of formaldehyde evolution, and surface-bound CH_2 was not detected on Rh(111)- $p(2 \times 1)$ -O. The absence of hydrogen-deuterium exchange in the reaction of a mixture of CH_2I_2 and CD_2I_2 also argues against adsorbed CH_2 as an intermediate in the formation of formaldehyde. Our isotopic exchange experiments with CH_2I_2 and deuterium show that reversible C-H bond scission is rapid for CH_2 adsorbed on Rh(111); however, no reversible C-H bond activation is detected in the production of gaseous formaldehyde. All these data support the proposed mechanism of direct addition of CH_2 to surface oxygen, although a mechanism in which CH_2I adds to oxygen cannot be excluded on the basis of our data. However, the mechanism in which CH_2 adds to oxygen is

supported by previous studies of formaldehyde production from azomethane reaction via CH_2 .^{4,35} We are also currently developing a source of gas-phase methylene to further test for direct addition. The observation of formaldehyde formation at lower temperatures by photochemically induced C-I bond breakage in the reaction of CH_2I_2 on oxygen-covered Rh(111) by Solymosi and Klivenyi⁵ is also consistent with direct addition of gaseous methylene to surface oxygen.

Our results are quantitatively different than those reported for the thermal reactions of CH_2I_2 on oxygen-covered Rh(111) by Solymosi and Klivenyi.⁵ However, all differences can be accounted for by a systematic overestimation of the oxygen coverage by these authors, possibly due to oxygen removal by background hydrogen or the presence of impurities on the surface. For instance, Solymosi and Klivenyi report methane evolution even at the highest oxygen coverage, while we observe the methane yield to drop to zero for reaction on Rh(111)- $p(2 \times 1)$ -O. Also the reported temperatures for methane and formaldehyde evolution on Rh(111) with the highest oxygen coverage, 260 and 280 K, respectively,⁵ are indicative of actual oxygen coverage well below 0.5 monolayer, based on our measurements.

Recently, formaldehyde formation was also reported in the reaction of ClCH_2I on oxygen-covered Pt(111), indicating that this reaction is somewhat general. Formaldehyde was proposed to be formed by the reaction of $\text{CH}_2(a)$ or $\text{ClCH}_2(a)$ with surface oxygen on Pt(111),⁹ although a mechanism involving direct addition to surface oxygen was not considered. Unfortunately, no temperature-programmed reaction of a surface prepared by dosing ClCH_2I first and annealing to form surface methylene, followed by oxygen adsorption, was performed to further investigate the mechanism.

In the formation of formaldehyde from ClCH_2I reaction on oxygen-covered Pt(111), a key promotion role was attributed to coadsorbed halogens. This conclusion was based on the absence of formaldehyde formation in the reaction of diazomethane (CH_2N_2) on this surface.⁴³ This would correspond well with the observed promotion role of alkyl halides on the selectivity for partial oxidation in supported catalysts.³⁶ However, Berlowitz et al.⁴³ attributed the absence of formaldehyde formation in the reaction of diazomethane on oxygen-covered Pt(111) to islanding of the adsorbed oxygen on this surface. Furthermore, the role of coadsorbed iodine appears minimal on oxygen-covered Rh(111), based on the similarity of formaldehyde formation from CH_2 formed in the thermal decomposition of azomethane (CH_3NNCH_3).⁴ Similarly, Bent et al. did not observe any substantial influence from the presence of coadsorbed iodine in the reactions of methyl on Cu(111).³⁷ Experiments in which CH_2 is introduced to the surface without the concomitant formation of adsorbed iodine, currently underway in our laboratory, will address the influence of coadsorbed halogens in more detail.

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Conclusion

Formaldehyde is formed in the oxidation of CH_2I_2 on oxygen-covered $\text{Rh}(111)$. Formaldehyde formation proceeds through the direct addition of methylene to surface oxygen, upon its formation by C–I bond cleavage in CH_2I_2 . Formaldehyde is not formed by the reaction of surface-bound methylene and oxygen. Partial oxidation of CH_2I_2 to formaldehyde is favored at high oxygen coverage, while nonselective decomposition and methane formation and total combustion prevail at respectively

low and intermediate oxygen coverage. Oxygen influences the chemistry of CH_2I_2 on $\text{Rh}(111)$ in four distinct ways; it stabilizes C–I bonds, inhibits nonselective dehydrogenation, scavenges surface hydrogen, and adds directly to methylene fragments.

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