ELSEVIER

Surface Science 397 (1998) 179–184

surface science

# The chemistry of methyl iodide on Mo(100): formation and reaction of adsorbed methyl species

Gefei Wu, Hebert Molero, W.T. Tysoe *

*Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin–Milwaukee, Milwaukee, WI 53211, USA*

Received 5 June 1997, accepted for publication 2 September 1997

## Abstract

The adsorption of methyl iodide is studied on Mo(100) where ultraviolet photoelectron spectroscopy shows that the methyl iodide thermally decomposes to form methyl species on warming to ~200 K This self-hydrogenates to yield methane which desorbs at ~230 K and predosing the surface with deuterium forms essentially only $CH_3D$ indicating that the methyl species reacts with adsorbed hydrogen and that there is little H–D exchange This methane desorption temperature is identical to that found when methylene species are grafted on the surface by adsorbing methylene iodide indicating that methyl hydrogenation to methane is the rate-limiting step This temperature is substantially lower than that at which methyl and methylene species yield methane from clean and oxygen-covered Mo(100) when formed by other routes It is proposed that this is due to the effect of relatively large iodine atoms adsorbed in the four-fold hollow site affecting neighboring (either atop or bridge) sites © 1998 Elsevier Science B V

*Keywords* Chemisorption, Low index single crystal surfaces, Methyl iodide, Molybdenum, Synchrotron radiation photoelectron spectroscopy, Thermal desorption spectroscopy

## 1. Introduction

$C_1$ species form the chemical building blocks in many catalytic reactions They, for example, can be formed from CO and hydrogen in Fisher–Tropsch polymerization catalysis [1–5]. Carbene species have been suggested to be the active site in olefin metathesis where these are proposed to react with an alkene to form a metallacycle [6–10] We have recently found that ethylene can adsorb on oxygen-covered Mo(100) and evolve methane in temperature-programmed desorption [11] Similar methane desorption from both Mo(100) and also oxygen-covered Mo(100) has also recently been found following adsorption of propylene and butene on these surfaces [12,13] The reaction pathway to form methane is not yet clear, but clearly involves a reaction of a surface $C_1$ species. Photoelectron spectroscopy data suggest that ethylene dissociatively adsorbs to yield methylene species [11]. It has also been demonstrated by adsorbing methylene iodide on the surface that these can react to form methane both on Mo(100) and oxygen-modified Mo(100) [14] as well as on Mo(110) [15]. This is now a well-established strategy for grafting hydrocarbon species to transition metal surfaces since the C–I bond is relatively weak compared to the C–H bond [16,17] In addition, since the metal iodine bond is relatively strong, there is a kinetic and thermodynamic driving force for the deiodization

---

* Corresponding author Tel. (+1) 414 229-5222, fax (+1) 414 229-5530, e-mail wtt@csd uwm edu

*PII* S0039-6028(97)00730-9

of these species which provides a strategy for easily and conveniently adsorbing hydrocarbon fragment on the surface.

In the case of methane formation, for example from propylene, there is also the possibility that adsorbed methyl groups can react to form methane. We have therefore used a similar strategy to investigate this problem and have studied the adsorption of methyl iodide on metallic molybdenum. Here the idea is similar. This reacts to form adsorbed iodine and a methyl species. Note that there are other strategies for adsorbing methyl species onto transition metals surfaces, for example, by generating methyl radicals directly by thermally decomposing diazomethane in a heated dosing tube [18]. Another impetus for investigating the chemistry of methyl species formed from methyl iodide is that the methane formation kinetics after methylene iodide adsorption are different from those found following ethylene adsorption where in the former case methane desorbs at ~230 K and at ~390 K in the latter. Both are presumably due to the hydrogenation of methylene species, but one reaction takes place in the presence of iodine whereas the other does not. Note that when methyl species are adsorbed on oxygen-covered Mo(100), where the oxygen coverage is >1 monolayer, methane reactively forms by methyl hydrogenation at ~450 K [18] This temperature is similar to, but somewhat higher than that found for the kinetics of methane formation from alkenes on oxygen-covered Mo(100).

## 2. Experimental

The apparatus used for the temperature-programmed desorption experiments has been described in detail elsewhere [14]. Briefly it consists of a 12″ diameter, stainless-steel chamber which operates at a base pressure of $\sim 8 \times 10^{-11}$ Torr following bakeout. It is equipped with a multiplexed quadrupole mass analyzer which can sequentially collect up to five masses The sample can either be resistively heated to collect temperature-programmed desorption data at a heating rate of 10 K $s^{-1}$ or electron-beam heated to anneal the sample to above 2000 K to remove contaminants (primarily oxygen). The sample can also be cooled to 80 K by thermal contact to a liquid-nitrogen filled reservoir. The chamber is also equipped with a double-pass, cylindrical mirror analyzer for collecting Auger data.

Photoelectron spectra were collected using the Mk. V Grasshopper monochromator at the Wisconsin Synchrotron Radiation Center in Madison, Wisconsin. These were measured using a photon energy of ~60 eV which optimized the scattering cross-section of the shallow carbon 2s core levels [19], and by using a double-pass, cylindrical-mirror analyzer operating at a pass energy of 25 eV. This, combined with the linewidth of the incident radiation yielded an overall spectral resolution of 0.15 eV.

The Mo(100) sample was cleaned using a standard protocol and adjudged clean when no signals due to impurities were detected in Auger spectroscopy. The methyl iodide (Aldrich, 99.5%) was transferred to a darkened glass bulb and further purified by repeated freeze–pump–thaw cycles and was introduced to the chamber via a capillary dosing source to minimize background contamination.

## 3. Results

Fig. 1 displays a series of ultraviolet photoemission spectra collected as a function of temperature after exposing a clean Mo(100) surface to 8 L ($1\ L = 1 \times 10^{-6}$ Torr $s^{-1}$) of methyl iodide Annealing temperatures are displayed adjacent to each spectrum which were collected by heating to the indicated temperature for a period of 5 s following which the sample was allowed to cool to 80 K to prevent any further chemical changes from taking place. The spectrum was then recorded. Shown for comparison is the gas-phase photoelectron spectrum of methyl iodide [20] which has been rigidly shifted so that the gas-phase and surface peaks align to correct for differences in reference levels used for the different spectra. This allows the peak at ~13 eV binding energy (BE) to be assigned to photoemission from $a_1$ level of methyl iodide which consists primarily of the C 2s level. The feature at ~8.5 eV BE is

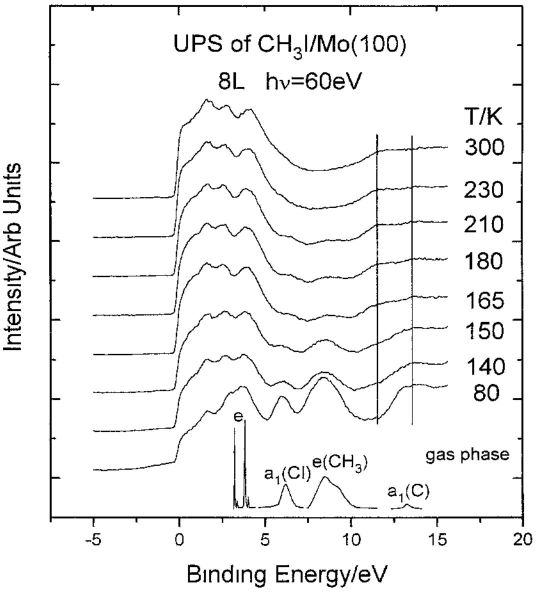


Fig 1 Ultraviolet photoelectron spectrum of methyl iodide ($CH_3I$) adsorbed on a clean Mo(100) following an exposure of 8 L collected using 60 eV photons as a function of annealing temperature Annealing temperatures are marked adjacent to the corresponding spectrum

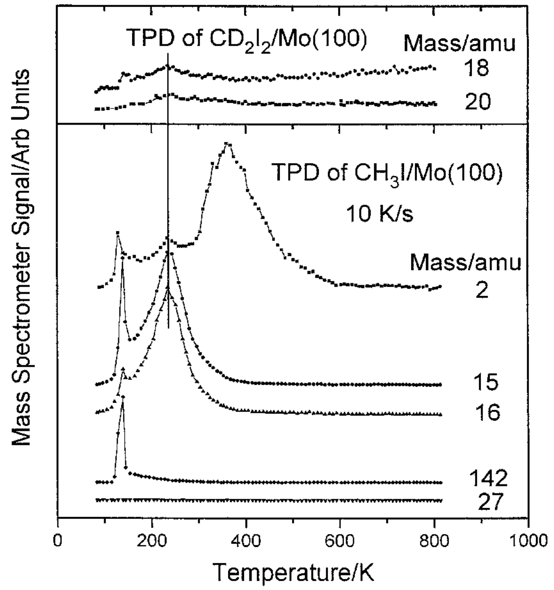


Fig 2 Temperature-programmed desorption spectra collected at various masses at a heating rate of 10 K s$^{-1}$ after saturating Mo(100) with methyl iodide ($CH_3I$) The detected mass is marked adjacent to each spectrum Shown for comparison are the 18 and 20 amu temperature-programmed desorption spectra collected after exposing clean Mo(100) to methylene iodide ($CH_2I_2$)

assigned to emission from a level with e symmetry due to the methyl species and the slightly smaller feature at 6 5 eV BE is an $a_1$ level assigned to a C–I orbital. The broad feature at 3–4 eV BE are due to e levels. The structure below ~3 eV binding energy is due to emission from the substrate d-orbitals.

The shallow 2s core levels have proven particularly useful in following chemical changes on surfaces first, since their chemical shifts are rather sensitive to small chemical changes and second, the energies of the molecular orbitals formed by these species can be simply calculated using Hückel theory [19,21]. The single C(2s) peak at ~13 eV indicates the adsorption of a $C_1$ species on the surface. Furthermore, the intensity of the 13 eV peak decreases as the temperature increases and shifts to ~11 5 eV. This is proposed to be due to the thermal decomposition of methyl iodide into iodine and an adsorbed methyl group. This effect is emphasized by the vertical lines superimposed on the spectra

Fig. 2 displays the temperature-programmed desorption data for a saturated methyl iodide overlayer. A sharp feature is detected at ~130 K with intensity at 142 amu with fragments at 16, 15 and 2 amu. This is assigned to the presence of a small amount of condensed methyl iodide since this state continues to grow without saturation with increasing exposure. No other methyl iodide desorption states were detected. Another relatively broad symmetric state is detected at ~230 K with intensity at 15 and 16 amu. A careful measurement of its fragmentation pattern confirms that this is due to methane desorption. Finally, a broad feature is detected at ~380 K due to hydrogen from the thermal decomposition of the adsorbed hydrocarbons. Shown for comparison in an upper panel is the temperature-programmed desorption spectrum taken at 20 and 18 amu following adsorption of $d_2$-methylene iodide on Mo(100) [14]. Since the methane yield was rather low in this case, deuterated species were used to avoid any possible complications due to $H_2$ adsorption from the background. Methylenes have been shown to form methane by reaction with surface hydrogen and it is striking that methane is formed from both methylene diiodide and methyl iodide at the same temperature although significantly less methane is formed from methylene diiodide than from methyl iodide.

It has been shown in reactions performed at high pressures that, in addition to forming methane, the adsorbed $C_1$ species can polymerize to form higher hydrocarbons [22]. In order to investigate whether a similar pathway could be detected in ultrahigh vacuum, we searched for higher hydrocarbons. The lack of signal at 27 amu (Fig. 2) indicates a complete absence of ethylene formation. Note that no dimerization products were found on Mo(100) or oxygencovered Mo(100) following either ethylene [11] or methylene iodide [14] adsorption

In order to determine the origin of the additional hydrogen required to form methane, the surface was predosed with 0.5 L of deuterium and then dosed with 2 L of methyl iodide. The resulting temperature-programmed desorption spectra are displayed in Fig 3 which shows a single, intense state at ~230 K with intensity at 16 and 17 amu, but with relatively little intensity at 18 amu suggesting the formation of predominantly $CH_3D$.

## 4. Discussion

Both the photoelectron spectra (Fig 1) and temperature-programmed desorption data (Fig. 2) indicate that methyl iodide adsorbed on Mo(100) thermally decomposes to form an adsorbed methyl group and deposit atomic iodine on the surface. The photoelectron spectrum of Fig. 1 confirms that methyl iodide adsorbs onto the surface and the chemical shift in the C 2s peak connotes thermal decomposition of the adsorbed methyl iodide as the sample is heated to above 200 K. The formation of predominantly $CH_3D$ when the surface is precovered with deuterium (Fig. 3) confirms this chemistry and this also indicates that the adsorbed methyl group does not undergo an additional dehydrogenation to yield a methylene species and hydrogen since this, although it has

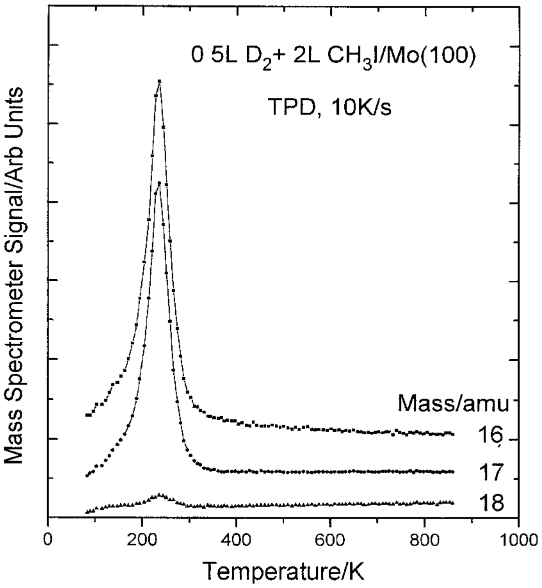


Fig 3 Temperature-programmed desorption spectra collected at various masses using a heating rate of 10 K $s^{-1}$ after exposing a deuterium-covered Mo(100) surface (0 5 L) to 2 L of methyl iodide ($CH_3I$)

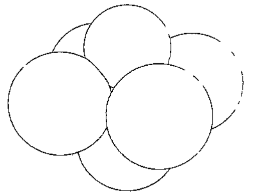
been demonstrated that methylenes can hydrogenate to yield methane, would lead to a substantial yield of $CH_2D_2$ at 18 amu. The small signal evident at this mass in Fig. 3 is probably due to this effect, but its relatively small size compared to both the 16 and 17 amu signal indicates that the probability for this process is low. Methyl group dehydrogenation is clearly responsible both for the methane that is formed from adsorbed methyl species in the absence of hydrogen (Fig. 2) as well as the substantial amount of hydrogen desorption found in this experiment Methane desorbs at ~230 K in the absence of pre-adsorbed hydrogen and this temperature is not substantially affected by pre-covering the surface with hydrogen. It is striking that the peak temperature for the formation of methane from methylene iodide is identical to that for the formation of methane from an adsorbed methyl iodide. Clearly, methane must be formed from methylene hydrogenation via the following reaction sequence:

$$CH_{2(ads)}+2H_{(ads)}\rightarrow CH_{3(ads)}+H_{(ads)}\rightarrow CH_{4(g)}.$$

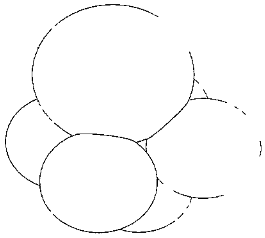
Since both adsorbed methylene and methyl species yield methane in temperature-programmed desorption with identical peak temperatures, the second step in this reaction must be rate limiting so that the formation of methyl species from methylene species must be fast compared to subsequent hydrogenation.

Note also that the methane formation kinetics, in particular on metallic molybdenum, are different when the hydrocarbon is formed from an iodine-containing precursor or from an alkene. For example, both methylene and methyl species formed from methylene diiodide and methyl iodide, respectively, desorb at ~230 K (Fig 2) and this desorption temperature is unaffected by predosing the surface with hydrogen (Fig. 3). In contrast, methane formed by methylene hydrogenation, where the methylene species are formed by ethylene dissociation on oxygen-covered Mo(100) for oxygen coverages less than unity, desorbs at ~390 K [11] Propylene yields methane following adsorption on both clean and oxygen-covered Mo(100) also at ~390 K, presumably also due to either methyl or methylene hydrogenation [12]. Methyl radicals adsorbed directly on oxygen-covered Mo(100) for oxygen coverages greater than unity desorb at ~450 K.

These results suggest that the chemistry of both methyl and methylene species are affected by adsorbed iodine, but in a way that is distinct from the effect of oxygen. It has been demonstrated that co-adsorbed iodine has little effect on the chemistry of hydrocarbon fragments grafted to low-index planes of group VIII transition metals [17]. Oxygen occupies the four-fold hollow sites on Mo(100) [23]. These are presumably also the iodine adsorption sites although this remains to be verified. The four-fold hollow sites are more reactive than either the atop or bridge sites so that, for example, it has been shown that alkenes adsorbed on four-fold sites completely thermally decompose to form carbon and hydrogen [11–13] which suggests that methane is synthesized either at atop or bridge sites These sites are rather close to the four-fold hollow site and may therefore be strongly affected by an adsorbate located in the four-fold site. This is illustrated in Fig. 4 where oxygen and iodine are shown adsorbed in the four-fold site where the oxygen and iodine are taken to be ionic [24,25]. Note, however, that the ionic and van der Waals' radii are similar [25] This clearly reveals that the atop and bridge sites are not strongly sterically hindered by oxygen, but *are* drastically affected by iodine This will likely decrease the heat of adsorption of $CH_x$ species, either $CH_2$ or $CH_3$, adsorbed on either bridge or atop sites facilitating their hydrogenation and substantially lowering their desorption activation energies as found experimentally.



**Oxygen adsorbed on the four-fold hollow site on Mo(100)**



**Iodine adsorbed on the four-fold hollow site on Mo(100)**

Fig 4 Schematic diagram showing oxygen and iodine adsorbed in the four-fold site on Mo(100) where the oxygen and iodine are represented by their ionic radii

## 5. Conclusions

Methyl species formed by the thermal decomposition of methyl iodide on Mo(100) react to produce methane with identical kinetics as do methylene species formed by the thermal decomposition of methylene iodide, although the methane yield is larger for methyl hydrogenation than methylene hydrogenation. Isotope labeling experiments confirm that methane is formed by methyl hydrogenation. Adsorbed $CH_2$ species formed by $CH_2I_2$ decomposition form methane at the same temperature (230 K), indicating that the final addition of hydrogen in the reaction of methylenes to methane is rate limiting. No higher hydrocarbons are detected in temperature-programmed desorption and any remaining adsorbed methyl groups thermally decompose to yield hydrogen at ~380 K and to leave carbon on the surface. Methane formed from iodine-containing precursors desorbs at lower temperatures than when no iodine is present. This is proposed to be due to the steric effect that the relatively large iodine, which is proposed to be adsorbed in four-fold hollow sites, has on atop or bridge sites.

## Acknowledgements

We gratefully acknowledge support of this work by the US Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences, under grant no. DE-FGO292ER14289. This work is based upon research conducted at the Synchrotron Radiation Center, University of Wisconsin–Madison, which is supported by the NSF under award no. DMR-95-31009.

## References

[1] D.W Goodman, R.D Kelly, T E Madey, J T Yates, Jr., J Catal. 63 (1980) 226
[2] C B Young, G N Whiteside, J Am Chem Soc 100 (1978) 5808
[3] R C. Brady, R J Pettit, J Am Chem Soc 103 (1981) 1287
[4] T M Duncan, P Winslow, A.T Bell, J Catal. 93 (1985) 1
[5] D W Goodman, J.T Yates, Jr , J Catal 82 (1983) 255
[6] J L Herison, Y Chauvin, Makromol Chem 141 (1970) 161
[7] E O Fischer, K H Dotz, Chem Ber 105 (1972) 3966.
[8] R R Schrock, J Am Chem Soc 98 (1976) 5399
[9] F N Tebbe, G W Parshall, D W Ovenall, J Am Chem Soc 101 (1979) 5074
[10] T R Howard, J B Lee, R H Grubbs, J Am Chem Soc 102 (1980) 6878
[11] G. Wu, B Bartlett, W T Tysoe, Surf Sci 383 (1997) 57
[12] G Wu, W T Tysoe, Surf Sci (in press)
[13] G Wu, W T Tysoe, Surf Sci (in press)
[14] G Wu, B Bartlett, W T Tysoe, Surf Sci 373 (1997) 129
[15] M K Weldon, C M Friend, Surf Sci 321 (1994) L202
[16] F Zaera, Acc Chem Res 25 (1992) 260
[17] F Zaera, Chem Rev 95 (1995) 2651
[18] G H Smudde, Jr , M Yu, P C Stair, J Am Chem Soc 115 (1993) 1988
[19] L P Wang, R Hinkelman, W T Tysoe, J. Electron Spec Rel Phenom 56 (1991) 341
[20] J W Robinson (Ed ), Handbook of Spectroscopy, Vol 1, Chemical Rubber Co , Cleveland, OH, 1974
[21] A W Potts, H J Lempka, D G Streets, W G Price, Phil Trans Roy Soc Lond A268 (1970) 95
[22] B F Bartlett, W T Tysoe, Cat Letts 44 (1997) 37
[23] S H Overbury, P C Stair, J Vac Sci Technol A1 (1983) 1055
[24] R W G. Wykoff, Crystal Structures, Vol 1, Wiley, New York, 1963
[25] D R Lide, (Ed ), CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, FL, 1993