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The electron stimulated chemistry of methyl lactate on Cu(1 1 1)

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ABSTRACT

The electron stimulated chemistry of monolayers of (R)/(S)-methyl lactate ((S)/(R)-MLAc) adsorbed on Cu(1 1 1) has been investigated. Monolayers of MLAc undergo highly efficient electron stimulated processes predominately desorption, but also a significant fraction is converted to an adsorbed alkoxide moiety through the selective cleavage of the O–H bond. The efficiency of the depletion of the adsorbed MLAc state and the absence of significant non-selective fragmentation contrasts with previous studies of the electron beam irradiation of monolayers of oxygen containing organic molecules.

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1. Introduction

Electron beam stimulated chemistry of adsorbed molecular materials is of interest to a broad range of areas, such as materials processing, astrophysical chemistry and the study of radiation induced damage of biological materials. The majority of electron stimulated chemistry studies of organic molecules are concerned with condensed multilayers, often referred to as ices [1–4], with fewer studies focused on organic monolayers adsorbed on well-defined substrates [5–15]. The mechanisms responsible for electron beam induced chemistry in the condensed phase (multilayers and monolayers) are the same as those in the gas phase, namely electron impact excitation/ionisation and electron attachment. However, in the case of monolayers on metallic surfaces, efficient quenching of electronic excitation, with a commensurate decrease in excited state lifetimes, results in a reduction in the overall efficiencies of electron stimulated processes.

In this paper we present a study of the effects of electron irradiation upon monolayers of (R)/(S)-methyl lactate $(HOCH(CH_3)-CO_2CH_3)$ ((S)/(R)-MLAc) on Cu(111). There have been several studies of the effects of electron irradiation on monolayers of oxygen containing organic molecules on metal surfaces [6–12], in all of the cases electron impact ionisation is believed to be the active mechanism. Electron impact ionisation causes molecular fragmentation resulting in non-selective chemistry, with C–H, C–C and C–O cleavage, with the consequent production of a variety of both adsorbed moieties and gas phase products. In contrast the electron induced chemistry observed for monolayers of halocarbons proceeds via dissociative electron attachment, which results in selective C-Hal cleavage, and the production of a narrower range of products [13–15]. In this paper we demonstrate that the electron stimulated dissociation of (S)-MLAc displays a high level of selectivity towards O–H cleavage.

2. Experimental

Experiments were performed in an UHV system that has been described in detail previously [16]. The system was equipped with the usual sample preparation facilities and a retarding field analyzer which was used to perform low energy electron diffraction (LEED) and Auger electron spectroscopy, as well a shielded quadrupole mass spectrometer (QMS) that was used to obtain temperature programmed desorption profiles, which were collected using a heating rate of 0.5 K s⁻¹. The electron gun of the RFA was used to irradiate the samples. The Cu(111) crystal surface (diameter 10 mm) was cleaned by cycles of Ar⁺ bombardment (1 keV, 40 min, ca. 16 µA) followed by annealing to 900 K. Surface cleanliness was monitored by electron beam AES, while LEED was used to monitor surface quality. Methyl lactate (Sigma Aldrich Ltd.) was stored in a glass gas handling line and was purified through freeze pump thaw cycles; adsorption was carried out at crystal temperatures of ca. 110 K. The electron gun of the LEED optics was used to irradiate the sample. The monolayers were irradiated with a defocused beam, with an approximately "top-hat" profile of width 15 mm. The incident beam current was monitored with an electrometer.

3. Results

We will present results of experiments performed with (S)-MLAc, similar results were obtained for (R)-MLAc, which is to be expected for an achiral substrate.



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4. Thermal chemistry

Fig. 1 contains nested TPD profiles showing the desorption of intact parent molecules from a $Cu(1 \ 1 \ 1)$ surface which had been exposed to successively greater amounts of (S)-MLAc at 110 K. The profiles were taken by following the most intense ion fragment in the (S)-MLAc cracking pattern, 45 amu $(C_2H_5O^+)$. At the lowest exposure there is a peak at 220 K (α_2) and desorption over a broad range up to 360 K which we assign to desorption from defect sites. Slightly increasing the exposure saturates the defect desorption state, while a peak at 209 K (α_1) begins to develop and grow concurrently with α_2 . Increasing the dose further saturates α_2 , where after it exists as a shoulder to the dominant α_1 peak. With further exposure a peak at 176 K develops, which both does not saturate and shifts to higher temperature with mounting exposure, indicating desorption from multilayers. Displayed in Fig. 1 are profiles obtained by monitoring the 43 amu fragment, which is the most intense ion in the cracking pattern of methyl pyruvate ((OC(CH₃)-CO₂CH₃)(MP), the reduced analogue of (S)-MLAc, but only a minor component of (S)-MLAc cracking pattern. Profiles showing the desorption of MP, Fig. 1, can be derived using the 43 and 45 amu by first scaling the 45 amu profiles by the relative intensity of 43/45 amu fragments in the cracking pattern of (S)-MLAc, and subsequently subtracting this scaled profile from the 43 amu profile, this removes the contribution that desorbing (S)-MLAc makes to the profile. For the two lowest exposures of (S)-MLAc, the same amount of methyl pyruvate desorption is observed with a $T_{\rm max}$ = 375 K. Further exposure, which also results in the concurrent population of state α_1 , causes an abrupt increase in the amount of MP desorption and an upward shift in T_{max} to 381 K. Subsequent exposure up to (but not beyond) monolayer saturation results in a gradual increase in the amount of MP desorption from the surface and an upward shift in $T_{\rm max}$ to 381 to 385 K. After saturation of the monolayer the MP peak shifts back down in temperature to 372 K. In a previous study [17] we have shown that on Cu(111) MP bonds through its carbonyl group, predominately in a di- σ , η_2 geometry which desorbs at 364 K, with a minority occupying a weakly bound η_1 geometry that desorbs at 230 K. The high temperature at which MP evolves in the current study suggests that its production is reaction limited. By comparison with TPD data from our previous study, we estimate that the amount of MP formed by the decomposition of (S)-MLAc is equivalent to \approx 10% of a saturated MP monolayer. Desorption of H₂, Fig. 1, occurs over a similar temperature range to that of MP. For coverages up to monolayer saturation the H_2 desorption peak has a T_{max} of 371 K with a pronounced shoulder to lower temperatures. Post TPD AES



Fig. 1. (A) (Lower panel) Displayed are a series of nested TPD 45 amu profiles obtained from surfaces which have been exposed to sequentially larger doses of (S)-MLAc. Multilayers and the α_1 , α_2 , defect states have been labelled. (Upper panel) Displayed are nest 43 amu profiles which were collected concurrently with those shown in the lower panel. (B) (Lower panel) Displayed are a series of nested profiles that have been derived from the data in Fig. 1 which represent the desorption of methyl pyruvate. (Upper panel) Displayed are 2 amu profiles, charting the evolution of H₂ from the surface which were collected concurrently with those displayed in Figs. 1 and 2. Inset is a plot of methyl pyruvate peak area as a function of methyl lactate exposure.

spectra revealed the presence of residual C with a C/Cu ratio of 0.005 + 0.002, indicating a small fraction of the (S)-MLAc monolayer undergoes a more complete decomposition, we estimate the amount of C on the surface corresponds to $\leq 10\%$ of a monolayer of (S)-MLAc.

The TPD data, and the thermal chemistry it reflects, are qualitatively similar to that observed in previous studies of higher alcohols on Cu surfaces [18,19]. Monolayers of higher alcohols predominately undergo reversible molecular desorption below room temperature, while a small fraction undergoes H–O cleavage to produce strongly chemisorbed alkoxide moieties and H_{ads}. The alkoxide moieties either undergoes further decomposition resulting in the evolution of the aldehyde/ketone, or recombinative desorption with H_{ads}; desorption of H₂ also occurs; these process are observed between 300 and 380 K.

The α_1 and α_2 states arise from reversible desorption from weakly chemisorbed states associated with the (1 1 1) terraces. The two desorption states can originate from either: two distinct co-existing adsorbed states; or alternatively they arise because of a coverage driven phase transition within the (S)-MLAc layer. The TPD data, specifically the observation that both states develop concurrently at low exposures, is consistent with α_1 and α_2 originating from two distinct co-existing states. In systems that display coverage driven phase transitions two desorption states are observed, but they are populated sequentially with increasing exposure [16].

It is likely that the majority of (S)-MLAc decomposition is associated with defect sites (steps and kinks). This is supported by the observation that there is a greater amount of MP and residual produced from overlayers on a $Cu(1 \ 1 \ 1)$ surface roughened by ion bombardment and from the highly stepped $Cu(6 \ 4 \ 3)$ [20].

The thermal chemistry of (S)-MLAc is summarised below:

$$(HOCH(CH_3)CO_2CH_3)_{(ads)} \rightarrow (HOCH(CH_3)CO_2CH_3)_{(g)}$$
(1)

$$(HOCH(CH_3)CO_2CH_3)_{(ads)} \rightarrow (-OCH(CH_3)CO_2CH_3)_{(ads)} + H_{(ads)}$$
(2)

$$(-OCH(CH_3)CO_2CH_3)_{(ads)} \rightarrow (OC(CH_3)CO_2CH_3)_g + H_{(ads)}$$
(3)

$$(-OCH(CH_3)CO_2CH_3)_{(ads)} + H_{(ads)} \rightarrow (HOCH(CH_3)CO_2CH_3)_g \qquad (4)$$

 $2H_{(ads)} \rightarrow H_{2(g)} \tag{5}$

 $(-OCH(CH_3)CO_2CH_3)_{(ads)} \rightarrow residue \tag{6}$

5. Electron stimulated chemistry

Electron stimulated experiments were performed on monolayers formed by exposing a Cu(111) surface at 180 K to a quantity of (S)-MLAc sufficient to saturate a monolayer, after exposure the crystal was cooled back down to 110 K and subsequently irradiated with an electron beam. Monolayers have been irradiated with electron beams of the following energies: 10, 25, 40, 50, 65, 85 and 100 eV. The entire sample surface was irradiated and electron beam current densities of between 1 and $4 \,\mathrm{A \, cm^{-2}}$ were used. For each beam energy, monolayers were exposed to at least three different fluences of electrons, and subsequent to irradiation TPD profiles collected. An attempt was made to find desorption products other than (S)-MLAc, MP and H₂ by monitoring a number of masses. We searched for, but found no evidence for any desorption products other than (S)-MLAc, MP and H₂. Specifically we monitored the 60, 44, 32, 29, 28, 18, 16 and 15 amu ion signals, which tracked those of (S)-MLAc and MP as a function of temperature. For illustrative purposes displayed in Fig. 2 are (S)-MLAc and MP TPD profiles (derived from the 45 and 43 amu data) obtained after irradiation with electron beam of 50 eV. For all beam energies used electron irradiation causes a progressive depletion of the reversibly adsorbed (S)-MLAc α states resulting in a reduction in the total amount of (S)-MLAc desorbing from the surface.



Fig. 2. Displayed are a series of nested TPD 45 amu profiles (upper) and methyl pyruvate (lower) profiles obtained subsequent to irradiating a monolayer of (S)-MLAc with increasingly greater fluences of 25 eV electrons at 110 K. No electron irradiation (a). $0.6 \times 10^{15} \, e^- \, cm^{-2}$ (b). $1.25 \times 10^{15} \, e^- \, cm^{-2}$ (c). $2.5 \times 10^{15} \, e^- \, cm^{-2}$ (d). $5 \times 10^{15} \, e^- \, cm^{-2}$ (e). $1 \times 10^{16} \, e^- \, cm^{-2}$ (f). $1.5 \times 10^{16} \, e^- \, cm^{-2}$ (g) and $2.0 \times 10^{16} \, e^- \, cm^{-2}$ (h). The insert is a plot of the amount of MP desorbing from the surface versus electron exposure.

The depletion of reversibly adsorbed α states must result from either (or some combination of) electron stimulated desorption or dissociation. If electron stimulated dissociation was a major contributor to the depletion of the α states, then one would expect compared to the thermal behaviour, a significant increase in the amount of MP and recombinative (S)-MLAc desorption; as well as an increase in the amount of residual C retained after irradiation



Fig. 3. Displayed are a series of nested TPD 43 amu profiles obtained subsequent to irradiating a monolayer of MP with increasingly greater fluences of 100 eV electrons at 110 K. No electron irradiation (a), $0.2 \times 10^{15} e^- cm^{-2}$ (b), $0.5 \times 10^{15} e^- cm^{-2}$ (c), $1.0 \times 10^{15} e^- cm^{-2}$ (d), $2 \times 10^{15} e^- cm^{-2}$ (e), $5 \times 10^{16} e^- cm^{-2}$ (g). The desorption peaks associated with the η_1 and η_2 bonded states are labelled, the assignments are taken from Ref. [17]. In the insert is a semi-logarithmic plot of the depletion of the η_2 state versus electron exposure.

The effects of electron irradiation upon MP desorption is the similar for all beam energies, irradiation leads to an initial increase in the amount of MP desorption, which reaches a maximum and then subsequently decreases. At its maximum the amount of MP evolved is $\approx 2 \times s$ that produced thermally. The electron dose at which maximum MP desorption occurs, decreases with increasing electron energy, which correlates with the increase in the cross for the depletion of the reversibly adsorbed state. At all beam energies and fluences used the T_{max} of MP desorption is shifted to lower temperature, ≈ 24 K, than that observed for the non-radiated monolayer. The T_{max} is consistent with desorption limited evolution of MP, with the shoulder to higher temperature seen at low electron exposures arising from reaction limited production of MP. For large electron doses desorption of small amounts of MP are observed at 275 K, which we believe is a stabilised η_1 bonded MP. From the current data we are unable to determine whether electron irradiation can cause (S)-MLAc to directly decompose to MP, or if it undergoes sequential decomposition via adsorbed alkoxide. However, we believe that sequential decomposition is more likely. The depletion of the MP state with increasing electron exposure can be attributed to the electron stimulated desorption. To illustrate this we irradiated a monolayer of MP on Cu(111) with a 100 eV electron beam. In Fig. 3 are TPD data that shows the effects of progressive electron irradiation, beam energy 100 eV, on monolayers of MP. Electron irradiation causes the electron stimulated desorption of MP, with no observable electron stimulated dissociation, as evidenced by both the absence of residual C after post irradiation AES and other desorbing species apart from MP.

The H₂ desorption peak shifts to lower temperature, $\Delta T \approx 23$ K, upon irradiation. Concurrent with the decrease in MP desorption with extended electron beam exposure, there is an increase in the amount recombinative (S)-MLAc desorption over the 300–370 K temperature range.

Finally, the amount of residual C remaining after an electron irradiation and thermal desorption cycle was measured using the following procedure. A (S)-MLAc monolayer was irradiated with

an electron flux (1 keV beam and a fluence of 4.5×10^{16} cm⁻²) sufficient to drive any electron processes to completion. A thermal desorption cycle was performed and AES spectra subsequently collected. AES data gave a C/Cu ratio of 0.006 + 0.002, which is within experimental error of the value obtained after thermal reaction (0.005 + 0.002), thus irradiation does not significantly increase the amount of MLAc which undergo more complete decomposition.

It is clear from the data that some electron stimulated dissociation of (S)-MLAc occurs, with TPD providing evidence for the presence of adsorbed alkoxide, MP and H_{ads}. The amount of MP and recombinative MLAc desorbing from the surface after irradiation cannot account for all MLAc which is lost from the α states. The maximum amount of MP evolved from the surface corresponds to $\approx 20\%$ of saturated MP overlayer, which when the amount of residual *C* is taken into account implies that $\leq 30\%$ of the (S)-MLAc layer undergoes electron stimulated dissociation, consequently the majority of (S)-MLAc undergoes electron stimulated desorption.

The electron stimulated chemistry of (S)-MLAc is summarised below:

$$(\text{HOCH}(\text{CH}_3)\text{CO}_2\text{CH}_3)_{(\text{ads})} + e \rightarrow \left((\text{HOCH}(\text{CH}_3)\text{CO}_2\text{CH}_3)_{(\text{ads})} \right)^* \sigma_{\text{ex}}$$
(7)

$$(\text{HOCH}(\text{CH}_3)\text{CO}_2\text{CH}_3)_{(\text{ads})^*} \rightarrow (\text{HOCH}(\text{CH}_3)\text{CO}_2\text{CH}_3)_{(\text{ads})} \quad k_q \qquad (8)$$

$$\left((\text{HOCH}(\text{CH}_3)\text{CO}_2\text{CH}_3)_{(\text{ads})} \right)^* \to (\text{HOCH}(\text{CH}_3)\text{CO}_2\text{CH}_3)_{(\text{g})} \quad k_{\text{des}} \quad (9)$$

$$\begin{pmatrix} (\text{HOCH}(\text{CH}_3)\text{CO}_2\text{CH}_3)_{(ads)} \end{pmatrix}^* \to (-\text{OCH}(\text{CH}_3)\text{CO}_2\text{CH}_3)_{(ads)} \\ + H_{(ads)} \quad k_{\text{OH}}$$
(10)

$$\begin{split} (-OCH(CH_3)CO_2CH_3)_{(ads)} + e &\rightarrow (OC(CH_3)CO_2CH_3)_{(ads)} \\ &\qquad + H_{(ads)s} \end{split} \tag{11}$$

$$(\mathsf{OC}(\mathsf{CH}_3)\mathsf{CO}_2\mathsf{CH}_3)_{(\mathsf{ads})} + e \to (\mathsf{OC}(\mathsf{CH}_3)\mathsf{CO}_2\mathsf{CH}_3)_{(\mathsf{g})}$$
(12)

 $((HOCH(CH_3)CO_2CH_3)_{(ads)})^*$ is the transient excited state generated by electron excitation, while σ_{ex} is the electron energy dependent electron excitation cross-section, and k_{OH} , k_{des} and k_q are the, the electron beam energy independent, rate constants for O–H cleavage, desorption and quenching respectively.

6. Kinetics of electron stimulated depletion of the α_1 and α_2 states

The amount of (S)-MLAc in the α states was quantified by determining the area under the desorption peak. The initial depletion of the α states is first order following:

$$Ln\frac{I_0}{I_f} = \sigma f$$

where I_0 and I_f are the initial and post irradiation populations of the combined α states, f is the fluence (cm⁻²) of electrons, and σ (cm²) is the cross-section for the electron stimulated depletion of the reversibly adsorbed states, where

$$\sigma = rac{k_{
m des} + k_{
m OH}}{k_q + k_{
m des} + k_{
m OH}} \sigma_{
m ex}$$

The kinetics of the depletion of the α states deviates from 1st order with increasing electron exposure. This behaviour is commonly observed in electron stimulated surface chemistry and is attributed to the build up of moieties on the surface formed by electron stimulated decomposition. The values of σ versus incident electron beam energy are plotted in Fig. 4.

The cross-section for the electron stimulated depletion of the di- σ bonded MP state can be determined from the data in Fig. 3 using the same procedure as used for ML state. The initial cross-section for the depletion of the di- σ MP state is $5.7 \pm 0.17 \times 10^{-16}$ cm⁻², which is a factor of \approx 3 times smaller than the value obtained for the depletion of the reversible adsorbed ML state.

7. Discussion

The primary focus of this discussion is the electron stimulated processes, which leads to the depletion of the α states. The observed behaviour can be rationalised in terms of the known electron stimulated chemistry of alcohols in the gas phase. To facilitate further discussion of the electron stimulated chemistry it is necessary to comment on the likely nature of the adsorption structure of (S)-MLAc. Although the current data provides no insight into the nature of the α_1 and α_2 states we speculate that they are associated with conformations of (S)-MLAc. DFT calculations [21] have determined that there are four possible stable conformations. Two conformers, (S)-MLAc1 and (S)-MLAc2, enable the formation of an intramolecular hydrogen bond between the hydroxyl group hydrogen and the carbonyl and alkoxy oxygens respectively; while intramolecular hydrogen bonding is not possible for other two possible non-hydrogen bonded configurations. Calculations show that in the gas phase, water and methanol solutions (S)-MLAc1 > (S)-MLAc2 are both significantly more stable than the other non-hydrogen bonded conformer. These theoretical predictions are validated by experimental evidence, studies of gas phase (S)-MLAc observed only the (S)-MLAc1 conformation, while in a matrix isolation study performed at ca. 10 K both (S)-MLAc1 and (S)-MLAc2 were observed [22-28]. Based in particular on the results of the cryogenic matrix isolation study it is tempting to suggest that the two states observed in the TPD originate from the two intramolecular hydrogen bonded conformers, clearly further work is required to clarify this issue.



Fig. 4. A plot of the σ for the depletion of the α state, derived from the plots in Fig. 2, versus kinetic energy of the incident electron beam. (up triangle are values for (S)-MLAc, down triangle are values for (R)-MLAc).

From previous extensive gas phase electron scattering studies [29] it has been established that there are two mechanisms, which can lead to O-H dissociation. At very low electron kinetic energies, <10 eV, dissociation of the O-H bond is driven by the transient occupation of the $\sigma_{\rm 0-H}^{*}$, and subsequent O–H vibrational excitation. The cross-section for O-H dissociation from this electron attachment excitation process increases when the group is able to form an intramolecular O-H-O bond [30]. At electron energies above the ionisation threshold, dissociative ionisation is the dominant fragmentation mechanism. The dependence of dissociative ionisation upon incident electron energy has been studied in the gas phase for a series of simple alcohols, the cross-section for R-O⁻ ion formation, formed by O-H cleavage, is qualitatively similar for all alcohols showing a maximum at an electron energy of \approx 60 eV. It is important to point out that in contrast to the gas phase, adsorbed molecules are exposed not only to the primary beam but also a flux of inelastically scattered secondary electrons. Consequently, for electron beam energies above the ionisation threshold both electron attachment and dissociative ionisation mechanisms can be active. Unfortunately, with the current σ data it is not possible to unambiguously determine the relative contributions that DEA and electron impact ionisation make to the depletion of the adsorbed MLAc. However the large σ we observe at 10 eV, an energy close to the threshold for impact ionisation, would suggest that DEA make a significant contribution at low energies. In previous work, it has been shown that with increasing incident beam energy electron impact ionisation makes a greater contribution.

Finally, we should comment of the absence of significant nonselective fragmentation displayed by MLAc, and indeed MP, during electron irradiation. In previous studies of irradiation of monolayers simple alcohols ketones and esters (methanol, acetone, biacetyl and methyl formate [7,10–12]) adsorbed on Ag(1 1 1) induces significant non-selective fragmentation, with the resultant observation in post irradiation analysis of large amounts of residual C. We believe that the absence of non-selective fragmentation is the result of the stronger bonding interaction between MLAc (and MP) with the Cu(1 1 1) compared to the previously reported work in Ag(1 1 1). Methanol, acetone, biacetyl and methyl formate interact very weakly with Ag(1 1 1) desorbing at 146, 146, 185 and 167 K respectively, temperatures which are significantly less than the desorption temperature of adsorbed MLAc (and MP). The stronger interaction of MLAc towards Cu(1 1 1) means that the lifetime of its excited state would be significantly reduced due to more efficient of coupling of its electronic states to the substrate. This relative decrease in the excited state lifetime has two consequences: there is a reduction in the amount of energy imparted to the molecular species: and it limits the likelihood of intramolecular energy transfer. Both of these effects will decrease the probability of non-selective multiple bond cleavage.

The preference of MLAc to undergo O–H cleavage may suggest that DEA make a significant contribution to electron stimulated depletion of the adsorbed MLAc state. A previous gas phase study [30] has shown that O–H groups, which can form intramolecular hydrogen bonds are more susceptible to dissociative electron attachment; in effect the weakening of the O–H by hydrogen bonding facilitate the process. The greater level of O– H cleavage observed in this study could be rationalized by this mechanism.

To summarize, we have observed that the (S)-MLAc undergoes highly efficient electron stimulated chemistry, predominately desorption. The observed behaviour of (S)-MLAc is notably different to that observed in previous studies of related systems, specifically significantly greater cross-section for electron induced processes are observed, and there is absence of significant nonselective fragmentation of the molecule.

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