



Thermal desorption spectrometry for identification of products formed by electron-induced reactions

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ABSTRACT

Thermal desorption spectra of thin films of acetaldehyde and hexamethyldisiloxane were recorded before and after exposure to electrons with an energy of 15 eV to monitor the formation of the products CO, propionaldehyde, and methane. While the identification of the products in previous work reported in literature has relied on a comparison with desorption temperatures of pure multilayer films, it is proposed here to compare with reference samples containing specific amounts of the anticipated product. It is shown that this approach is more accurate because the desorption temperatures can be modified considerably by a molecular matrix or by coadsorbates. Also trapping of the products within a molecular film can occur and lead to a delayed desorption as exemplified by the production of methane in thin films of hexamethyldisiloxane.

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1. Introduction

Low-energy electrons induce chemical reactions not only in gaseous molecules, electron impact ionisation in mass spectrometry being a prominent application, but also in molecules adsorbed or condensed as thin film on surfaces [1–5]. The near-surface layers of materials can thus be modified by interaction with electrons. While the measurement of electron-stimulated desorption (ESD) is a way to monitor the chemical reactions that occur [6–8], it is even more important to investigate the material remaining at the surface after exposure to electrons. Thus, it is essential to (1) identify the non-desorbing reaction products and (2) measure their rates of formation in order to establish reaction mechanisms for electron-induced processes.

Thermal desorption spectrometry (TDS) has been suggested as a suitable method to study reactions induced by low-energy electrons in adsorbates and thin molecular films [9]. In this and subsequent studies on different halocarbons [10] products of reactions induced at energies between 5 eV and 100 eV were identified by simultaneously measuring the TDS curves at various m/z and comparing their relative intensities with known mass spectra. In addition, multilayer desorption temperatures of the so-identified products were used to provide further support for the assignments.

Using a similar approach, we have previously started to investigate electron-induced reactions in thin films of organic molecules

at well-defined energies between 5 eV and 15 eV, i.e., a range of energies where secondary electrons are still not abundant, with the aim of identifying reaction mechanisms and learning to control the modifications within the films. More specifically, we have observed the formation of larger products from simple molecules in both condensed films of acetaldehyde [11,12], in acetonitrile as well as mixtures of acetonitrile with ethane [13], and in hexamethyldisiloxane (HMDSO) [14]. These samples are used as model systems that provide insight in the elementary processes of electron-induced reactions in the condensed phase. Equally, a procedure has been developed to measure cross-sections for the depletion of the initial material and the formation of specific products [12]. On the other hand, these and other results presented here and in a previous study on CCl_4 embedded in amorphous solid water (ASW) [15] show that desorption temperatures critically depend on the environment from which the product desorbs. A similar effect has been observed in ESD experiments on ASW [8]. Comparison with multilayer desorption temperatures can thus be misleading and it is advisable to base the assignment not on single-component multilayer samples but reference mixtures containing the anticipated product to an amount comparable to that found in the reaction mixture. This article presents prototypical examples illustrating this problem.

2. Experimental

The experimental apparatus and procedures were the same as those described recently [13]. Briefly, the apparatus consists of an ultrahigh vacuum (UHV) chamber pumped by a turbomolecular

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pump to a pressure of about 10^{-10} Torr with the residual gas consisting mainly of hydrogen. Additional pumping can be provided by employing a titanium sublimator.

A polycrystalline Au sheet serves as a substrate, which can be cooled to a base temperature of 35 K by a closed-cycle helium refrigerator (Leybold Vacuum) and resistively heated for substrate cleaning and recording of TDS curves. The temperature was measured using a thermocouple type E press-fitted to the Au substrate. Unless otherwise stated, gases or/and vapours introduced via a gas-handling manifold were deposited on the metallic substrates held at 35 K. TDS curves were then acquired at a linear heating rate of 1 K/s using a quadrupole mass spectrometer (QMS) residual gas analyser (Stanford, 200 amu) with electron impact ionisation at 70 eV. The thickness of the deposited films was estimated by recording TDS curves for increasing coverage as quantified by stating the pressure drop in the gas-handling manifold and identifying the monolayer as described previously [13].

This estimate was verified by comparing with measurements on a number of other, smaller molecules and taking into account the different sizes of the molecules as deduced from the densities of their liquids.

Acetaldehyde (CH_3CHO , stated purity of 99.95%) was purchased from Fluka and propionaldehyde ($\text{CH}_3\text{CH}_2\text{CHO}$, 99+%) was obtained from Acros Organics. Hexamethyldisiloxane ($(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$, 99.9%) was purchased from ABCR, methane (CH_4 , 99.995%) from Messer Griesheim, and CO (2.0 quality) from Linde. All compounds were used without further purification. Liquid samples were degassed by repeated freeze-pump-thaw cycles under vacuum.

3. Results and discussion

Similar to the approach suggested in the literature [9,10] we have previously started to identify the products of electron-induced reactions in condensed molecular films by (1) measuring TDS curves after irradiation at m/z ratios characteristic of the anticipated products and (2) comparing their desorption temperatures to those observed in pure films of the products [13] or reported in the literature [11]. It was observed that significant deviations to desorption temperatures from literature can occur [11] but also the actual desorption temperature of a specific product depends on the composition of the molecular film into which it is embedded [13].

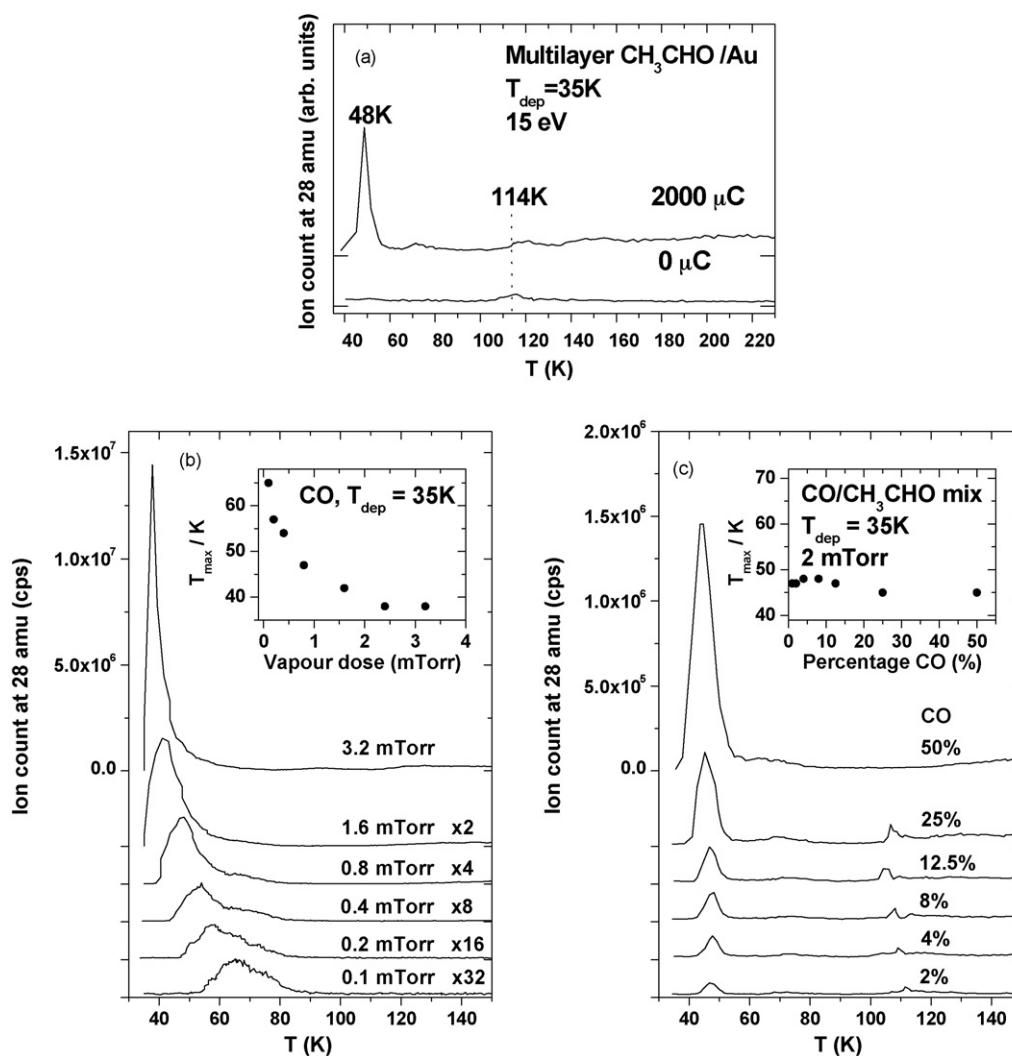


Fig. 1. (a) Thermal desorption spectra recorded at 28 amu for multilayer films of acetaldehyde deposited at 35 K before and after electron exposure of 2000 μC at 15 eV. The 114-K signal relates to desorption of acetaldehyde. (b) Thermal desorption spectra recorded at 28 amu for films of CO deposited at 35 K from increasing amounts of gas. The inset shows the position of the desorption peak maximum as function of deposited CO vapour. (c) Thermal desorption spectra recorded at 28 amu for reference samples produced from 2 mTorr of acetaldehyde mixed with the stated amounts of CO. The inset shows the position of the desorption peak maximum as function of CO content.

In consequence, to identify a product on the basis of its desorption temperature, we suggest to rather compare with reference mixtures produced by admixing to the original films a certain percentage of the anticipated product. The necessity of this approach is demonstrated here for several prototypical examples by recording TDS curves for such mixtures and comparing them to those obtained from pure films of the products and to desorption peaks observed in an actual reaction mixture. The selected examples relate to previous work on electron-induced reactions in thin films of acetaldehyde [11] and hexamethyldisiloxane [14]. To summarize briefly, irradiation of acetaldehyde films with electrons at 15 eV leads to production of CO, methane and propionaldehyde, the latter being ascribed to recombination of CH_3 and CH_2CHO radicals produced through fragmentation of acetaldehyde under electron exposure [11,12]. Exposure of HMDSO films equally produces methane [14] but also small amounts of ethane and tetramethylsilane as well as larger siloxanes [16]. The identification of CO and propionaldehyde produced from acetaldehyde and of methane produced in HMDSO films will be discussed in the following.

3.1. Production of CO in acetaldehyde

The formation of CO in thin films of acetaldehyde upon an exposure to 15 eV electrons of $2000 \mu\text{C}$ is inferred by a desorption peak at 48 K in a TDS curve recorded at $m/z = 28$ while this peak is absent in a non-irradiated sample (Fig. 1a). The desorption signal maintains its position as the electron dose is increased. Only at the highest dose level used in the present experiments ($16000 \mu\text{C}$; data not shown), the peak position is shifted to 50 K. Acetaldehyde desorption [11,12] starts around 96 K and continues with small intensity up to 160–165 K, the major peak between 96 K and 125 K reaching a maximum at about 114 K seen as a small signal in the $m/z = 28$ TDS curve for the non-irradiated sample.

To verify that the observed desorption signal indeed relates to CO, TDS curves of pure CO films produced from increasing amounts of gas as well as mixed films of CO and acetaldehyde with CO content varying between 1% and 50% (reference mixtures) were recorded (Fig. 1b and c). In the case of pure CO films, the maximum of the desorption signal shifts from 65 K to below 40 K as the coverage increases (Fig. 1b). At submonolayer coverage the molecules are more tightly bound by the substrate while intermolecular interactions in higher layers are weaker and molecules desorb at lower temperature characteristic of the molecular solid. The continuous shift observed here suggests a gradual transition between these extremes. CO embedded in acetaldehyde, on the other hand, has a nearly constant desorption temperature over a wide range of CO percentage within the film (Fig. 1c). This temperature agrees closely with that observed for CO formed after electron exposure. The interaction with acetaldehyde thus dominates the desorption behaviour of CO.

This example represents a particularly favorable case where the product can be identified accurately based on its desorption temperature. Such a behaviour can be expected for a product whose quantity is small enough so that its environment essentially consists of the initially deposited molecules. The surprising finding that the range of constant desorption temperature extends up to 50% CO may suggest that CO–acetaldehyde dimers are formed upon film deposition.

3.2. Production of propionaldehyde in acetaldehyde

Propionaldehyde is formed as a minor product upon exposure of acetaldehyde films to 15 eV electrons. The assignment of this product has been discussed extensively before [11]. Fig. 2a shows representative TDS curves recorded at $m/z = 58$ before and after

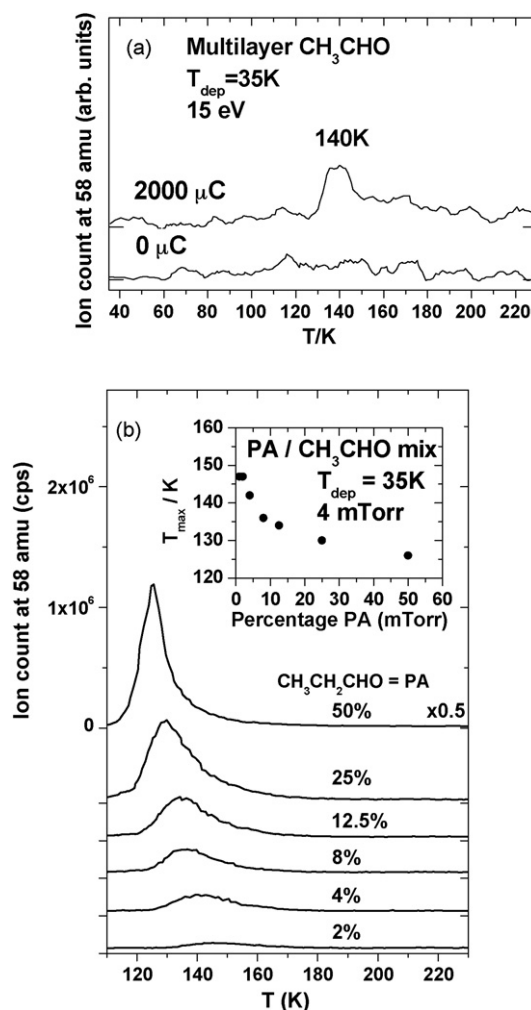


Fig. 2. (a) Thermal desorption spectra recorded at 58 amu for multilayer films of acetaldehyde deposited at 35 K before and after electron exposure of $2000 \mu\text{C}$ at 15 eV. (b) Thermal desorption spectra recorded at 58 amu for reference samples produced from 4 mTorr of acetaldehyde mixed with the stated amounts of propionaldehyde. The inset shows the position of the desorption peak maximum as function of propionaldehyde content.

electron exposure of $2000 \mu\text{C}$. Results obtained at different exposures (not included) show that the desorption peak position of propionaldehyde remains constant at around 140 K with increasing propionaldehyde production.

In the reference mixtures, the peak position shifts to lower temperatures with increasing propionaldehyde percentage (Fig. 2b). This is not surprising taking into account that acetaldehyde desorption is nearly complete before desorption of propionaldehyde occurs. Propionaldehyde thus desorbs essentially from a pure film produced from increasing amounts of vapour and the desorption temperature thus shifts to lower temperature upon transition from the submonolayer to the multilayer coverage.

The lack of a shift of the propionaldehyde desorption signal upon increasing electron exposure and thus increasing propionaldehyde content of the irradiated acetaldehyde film seems to contradict the result obtained from the reference mixtures. On the other hand, a further product with desorption temperature of 156 K, i.e., above that of propionaldehyde, and identified as an alcoholic species from the $m/z = 31$ signal has also been observed previously [11]. The constant temperature of propionaldehyde desorption from the reaction mixture thus indicates that this product desorbs from a matrix formed by other products rather than from the substrate itself. This

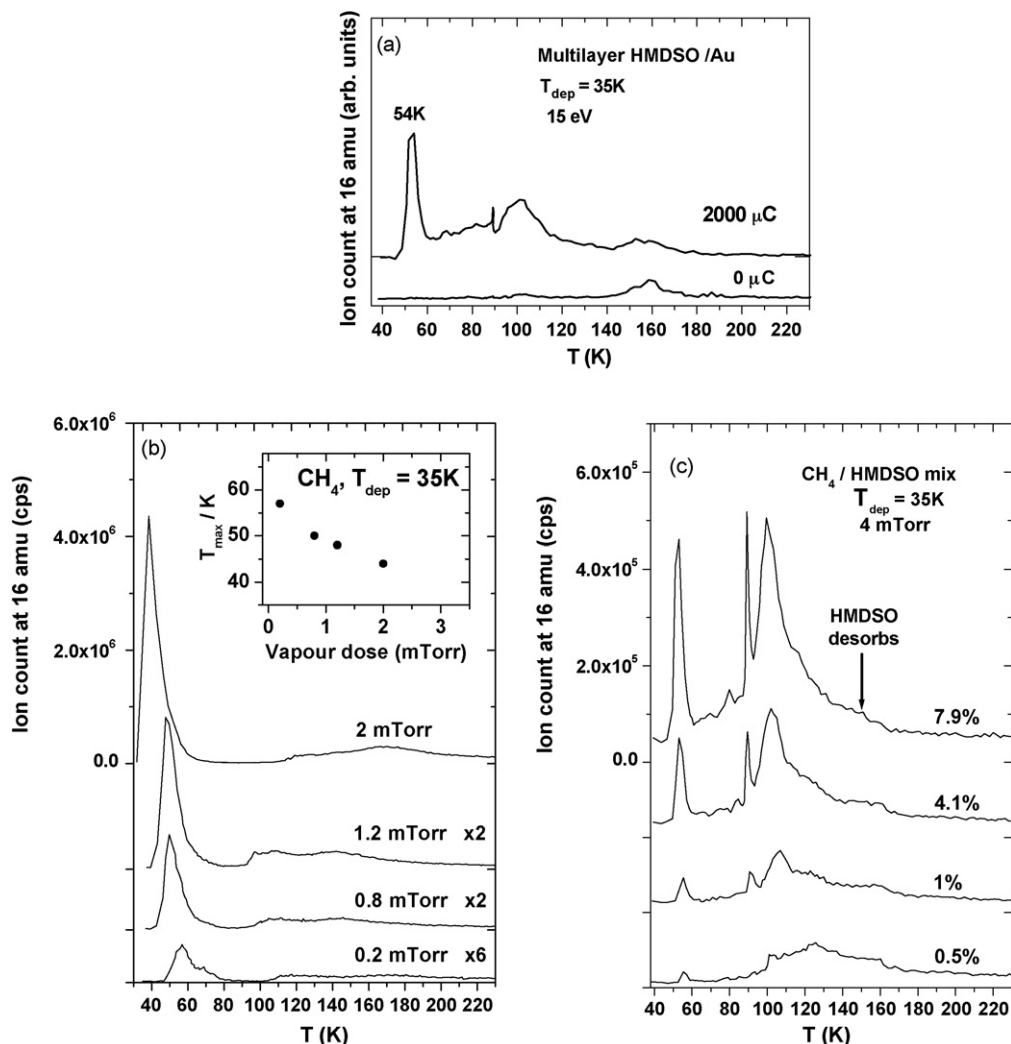


Fig. 3. (a) Thermal desorption spectra recorded at 16 amu for multilayer films of HMDSO deposited at 35 K before and after electron exposure of 2000 μC at 15 eV. The 160 K signal relates to desorption of HMDSO. (b) Thermal desorption spectra recorded at 16 amu for films of CH_4 deposited at 35 K from increasing amounts of gas. The inset shows the position of the desorption peak maximum as function of deposited CH_4 vapour. (c) Thermal desorption spectra recorded at 16 amu for reference samples produced from 4 mTorr of HMDSO mixed with the stated amounts of CH_4 .

case is similar to the one described in the last section but the exact reproduction of the desorption temperature by reference mixtures is more difficult now because the other products equally have to be identified.

3.3. Production of methane in hexamethyldisiloxane

Methane is an important product formed in multilayer films of HMDSO upon exposure to electrons at 15 eV. Fig. 3a shows TDS curves recorded at 16 amu before and after an electron exposure of 2000 μC . HMDSO has a complex desorption behaviour with two maxima at 149 K and at 158 K, the first one saturating after a certain vapour dose while the second starts to grow upon saturation of the first [14]. Unlike the case of CO in acetaldehyde (Section 3.1) formation of methane in HMDSO manifests itself not only through a sharp desorption peak near 54 K but also leads to a broad signal around 100 K. A very sharp peak at 90 K might be an artifact related to nonlinearity in the temperature ramp at this point.

A set of TDS spectra of pure methane recorded over a range of deposited gas amounts is shown in Fig. 3b. The signal at 57 K is assigned to methane at or near monolayer coverage. As in the case of pure CO, a plot of desorption temperature of this peak ver-

sus gas exposure indicates a shift towards lower temperature with increasing gas dose.

The methane desorption from the irradiated HMDSO film occurring around 100 K cannot be ascribed to a thermally activated reaction of fragments formed during electron exposure at low temperature because the same desorption features are observed in the reference mixtures (Fig. 3c). In general, methane desorption is completed when the temperature reaches 160 K, i.e., when HMDSO desorbs. This indicates that the higher temperature desorption feature stems from methane trapped within the HMDSO film. A reorganisation of this film probably induces delayed desorption of methane near 100 K. Interestingly, the sharp peak at 90 K is reminiscent of results reported previously for CCl_4 embedded in ASW films [15]. In this case, a very sharp desorption peak of CCl_4 occurs upon crystallisation of ASW. Methane desorption from HMDSO at 90 K might be due to a similar effect providing an alternative explanation for this feature. This, nonetheless, remains to be investigated more closely.

On the other hand, the relative intensities of the 54-K peak and the 100-K desorption signal are different in the sample exposed to electron and in the reference mixtures. This must be due to a different distributions of methane in these two samples. While

due to a limited electron mean free path methane is preferably produced near the film–vacuum interface upon electron exposure, methane is either evenly distributed in the reference films or even concentrated near the substrate–film interface because of a higher mobility of gaseous methane as compared to HMDSO. Methane thus tends to be trapped to a smaller extent in the irradiated samples in accord with the higher intensity of the 54-K peak.

This example demonstrates that trapping of the product molecules in a molecular film may occur but can be detected by recording TDS curves for reference mixtures. Quantification of the production rates then requires to integrate the desorption signals over the full temperature range in which the specific product desorbs.

4. Conclusions

The results demonstrate that the products formed in electron-induced reactions can be identified with higher accuracy when TDS experiments on similarly composed reference samples are performed. The following aspects have to be taken into account when the results obtained from irradiated samples are compared to those from reference mixtures:

- The desorption temperature of a reaction product formed within a molecular film upon electron exposure strongly depends on the actual environment from which the product desorbs.
- Products desorbing during a TDS experiment before the initial compound do not significantly change their peak position with increasing irradiation and thus product yields. The reaction products formed in the film may be trapped and desorb only when their local environment becomes mobile.
- The desorption temperature of products desorbing after the initial compound is comparable to that of the pure product, but depends, as in the pure film, on the amount of product desorbing from the surface. The presence of other products formed simul-

taneously during electron irradiation, and whose desorption temperature is higher than that of the product under consideration, may still influence the desorption temperature of the latter.

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