Electron-Induced Reactions in Methanol Ultrathin Films Studied by Temperature-Programmed Desorption: A Useful Method To Study Radiation Chemistry

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The exposure of multilayers of an adsorbate to low energy (\leq 55 eV) electrons under ultrahigh vacuum (UHV) conditions followed by temperature-programmed desorption (TPD) is shown to be an effective method to identify radiolysis products. In conjunction with isothermal experiments, postirradiation TPD experiments were used to identify eight previously known radiolysis products of methanol. The utility of the method is demonstrated by the identification of a previously unknown methanol radiolysis product: methoxymethanol (CH₃OCH₂OH). Moreover, this technique allows study of the dependence on initial electron energy, providing additional insight into the physical processes underlying radiation chemistry.

1. Introduction

Electron-induced processes on surfaces have come under increased scrutiny as evidenced by over 1000 research publications since 1960 in the field of electron-stimulated desorption alone.¹ Studies of surface reactions induced by electrons enhance understanding of electron beam lithography,² photochemistry on surfaces,³ electron damage to adsorbates,⁴ and orientation of adsorbate bonds.¹ In addition, bond-specific electron-induced dissociation of adsorbates can be used to synthesize catalytically interesting surface intermediates in significant quantities.⁵ We report the use of temperatureprogrammed desorption (TPD),⁶ a well-established surface science technique, to study the interactions of electrons with *multilayer* adsorbed films to identify reaction products of radiation chemistry.

Radiation chemistry involves the study of how high-energy particles (e.g., electrons, protons, alpha particles) and highenergy photons (X-rays and γ -rays) interact with matter, inevitably causing ionization.⁷ Radiation chemistry has applications in modifying physical properties of polymers, curing surface coatings and adhesives, sterilizing food and disposable medical supplies, treating sewage sludge and exhaust gases, synthesizing organic molecules, and treating cancer.⁷ Typical radiation sources employed in such applications include: (1) natural or synthetic radioactive isotopes, (2) X-ray generators, (3) accelerators, (4) Van de Graaff generators, and (5) nuclear reactors.⁸ Although the above sources produce radiation with energies in excess of thousands of electronvolts, the primary result from the interaction of such high-energy radiation with matter involves the massive production of low-energy secondary electrons.⁹ Electrons with energies as low as 10 eV may have sufficient energy to cause ionization and may provide better insight into the initial events of radiation chemistry.⁷

During the past decade, low-energy electrons have been utilized to study elastic scattering, vibrational and electronic excitation, dissociative electron attachment (DEA), and dissociative ionization in multilayer films deposited on metallic substrates under ultrahigh vacuum (UHV) conditions (base pressure $\sim 10^{-10}$ Torr).¹⁰ Film thicknesses were sufficiently large to preclude the influence of the metal on the outermost adsorbate layers. The UHV environment offers well-defined

conditions and is easily controlled, providing for the reduction of electron scavengers such as oxygen which may profoundly affect radiation chemical events. These elegant isothermal studies, involving the state-resolved detection of products desorbing during electron irradiation, have provided detailed information regarding the dynamics of electron-induced condensed phase reactions relevant to radiation chemistry. For example, recent studies have delineated the role of dissociative electron attachment, ionization, Frenkel-type exciton decay, and electron-hole pair recombination events during the electronstimulated desorption of D_2 from amorphous D_2O^{11} . In this paper we show that analysis of the chemical products following irradiation can give additional information of importance in understanding electron-induced reactions in thin films. Specifically, we demonstrate that postirradiation TPD is a valuable technique in identifying radiolysis products not detected with isothermal experiments. Although a similar experimental procedure was recently used, the focus of this study was the synthesis of complex hydrocarbon intermediates of catalytic importance.12

In the study described herein, TPD and isothermal desorption experiments have been employed successfully to probe the molecular fragmentation caused by low-energy electrons (\leq 55 eV) incident on thin multilayer films of methanol molecules adsorbed on a Mo(110) single crystal under UHV conditions. During TPD experiments, following electron irradiation of methanol multilayers, ethylene glycol (HOCH₂CH₂OH), ethanol (CH₃CH₂OH), dimethyl ether (CH₃OCH₃), and formaldehyde (H_2CO) are observed to desorb. Isothermal experiments reveal the formation and desorption of hydrogen (H₂), carbon monoxide (CO), methyl radicals (°CH₃), and methane (CH₄) during electron impact on methanol multilayers at \sim 85 K. All of the above eight reaction products have been previously identified during radiolysis of methanol.¹³ However, our identification of methoxymethanol (CH₃OCH₂OH), a highly labile species, as a reaction product of electron-induced dissociation of methanol is a new finding.

The ethene desorption observed during postirradiation TPD of methanol is attributed to the dissociation of ethylene glycol on the Mo(110) surface. Ethene is not a radiolysis product of methanol.

2. Experimental Section

Experiments were performed in a custom-designed stainless steel UHV chamber with a base pressure of 5×10^{-11} Torr. A

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UTI Model 100C quadrupole mass spectrometer (QMS) was used to perform TPD and isothermal experiments using an ionization energy of 70 eV. A shield with a small (0.125 in. diameter) aperture was used to optimize the detection of molecules desorbing from the center of the crystal during these experiments. The Mo(110) single crystal sample was mounted on a precision sample manipulator capable of x, y, and z translations. A differentially pumped rotary feedthrough provided for polar rotation. The crystal could be cooled to 85 K with liquid nitrogen and heated to 800 K radiatively or to 2200 K by electron bombardment. The temperature was measured by a tungsten-rhenium, W-5% Re vs W-26% Re, thermocouple spot-welded to the edge of the crystal.

Surface cleanliness of the Mo(110) crystal was verified with Auger electron spectroscopy (AES), and the surface structure was verified with low-energy electron diffraction (LEED) in a UHV chamber at Harvard University. In the UHV chamber at Wellesley College, the Mo(110) crystal was cleaned routinely by oxidation in oxygen (2×10^{-9} Torr at a surface temperature of 1200 K for 5 min) followed by heating briefly to 2200 K, exceeding the desorption temperature of oxygen and sulfur. Using TPD experiments to quantify the desorption of CO following oxygen adsorption, the carbon coverage on the surface after the cleaning procedure described above was estimated to be 0.002 ML (1 monolayer (ML) = 1.4×10^{15} atoms/cm²), an order of magnitude below the Auger detection limit.

All methanol samples, CH₃OH (Aldrich, 99.9+%), ¹³CH₃OH (Cambridge Isotope, 99 atom % ¹³C), and CD₃OD (Cambridge Isotope, 99.8 atom % D) were stored over baked molecular sieves and degassed by three freeze-pump-thaw cycles before use each day. Oxygen (Wesco, 99.994%) was used without further purification. The purity of the gases introduced into the UHV chamber was checked by mass spectrometry.

Direct dosers with precision leak valves allowed for controlled deposition of the methanol onto the clean Mo(110) crystal surface at 85 K to obtain multilayer coverages of either 4 layers (TPD experiments) or 10 layers (isothermal experiments). Layer-by-layer growth (Frank-van der Merwe type growth) has been observed during methanol multilayer adsorption on Pd(100),¹⁴ and three-dimensional island formation has been ruled out during methanol condensation on Cu(100).¹⁵ The methanol multilayers at 85 K constitute an amorphous solid sample (glass) because crystallization of methanol occurs only above 128 K.¹⁶

Irradiation of the methanol multilayers was accomplished using electrons thermionically emitted from the OMS filament with the Mo(110) crystal grounded. The QMS without modification provides an electron flux of $\sim 6 \times 10^{13}$ cm⁻² s⁻¹ (lower limit because scattered electrons are not counted) with an energy of 55 eV at the sample surface. Previous measurements with a cylindrical mirror analyzer (CMA) indicate that the fwhm of the electron energy distribution of a UTI mass spectrometer filament is 1.5 eV.17 The electron energy was varied (5 to 55 eV) by changing the QMS filament bias voltage. After electron irradiation, TPD experiments were conducted to identify radiolysis products. Since the crystal is close to the OMS filament during TPD experiments, the crystal was negatively biased (-100 V) prior to each TPD experiment to prevent further electron-induced reactions. As the surface was heated from 85 to 700 K via radiative heating at \sim 7 K/s, TPD data were collected with the QMS and the thermocouple both of which were interfaced to an IBM PC. Although up to 100 masses could be monitored under a multiplexing arrangement, typically only 10 masses were sampled during a single experiment. Fragments up to m/e = 150 were monitored systematically to verify product identifications.



Figure 1. TPD data showing the reactions of ${}^{12}CH_3OH$ on Mo(110) in the absence of electrons. CO, H₂, and methanol multilayers desorb at 425, 420, and 135 K, respectively.

Under suitable conditions, results of low-energy electron beam studies of thin films grown on metal substrates can be extrapolated to bulk radiolysis studies. Both quenching and image charge effects of the metal substrate must be minimized by utilizing films of sufficient thickness. Our results (see below) indicate that quenching effects are present for the first two layers but are negligible for thicker films. The image force associated with an adsorbate-covered metal substrate initially decreases with distance from the substrate but shows little dependence on film thickness beyond three layers.¹⁸ Hence, we have used four-layer-thick methanol films in our postirradiation TPD experiments.

3. Results and Discussion

A. Methanol Chemistry on Mo(110). TPD data (Figure 1) of methanol obtained on a clean Mo(110) crystal surface without exposure to electrons indicate that ~96% of the chemisorbed monolayer undergoes nonselective decomposition to form atomic carbon, oxygen, and hydrogen, ~3% produces CO (425 K), and ~1% yields CH₄ (450 K) (data not shown). Dihydrogen evolution, due to the recombination of atomic H on the surface, begins at 360 K and peaks at 420 K. Recombination of atomic C and O yields a second CO desorption feature at ~1100 K (data not shown). Multilayers of methanol desorb molecularly with a peak maximum at ~135 K. The above data agree very well with TPD data obtained in a another study in which methoxy (CH₃O) was identified as the sole surface intermediate at a surface temperature of 300 K.¹⁹

B. Ethene Production following Electron Irradiation of Methanol Films. After exposure of methanol multilayers (≥ 3 layers) at 85 K to an electron fluence (electron flux multiplied by exposure time in seconds) as low as 3×10^{14} cm⁻² at an energy of 55 eV, TPD experiments indicate the desorption of a new product: ethene (C₂H₄) at ~355 K. Identification of ethene was verified by the agreement between the observed and the tabulated m/e = 28:27:26 ratio.²⁰ The ethene yield increases with increasing electron fluence, reaching a maximum of ~0.03 ML for a four-layer methanol film. Thermal effects during electron bombardment in the production of ethene can be excluded since exposure of the crystal to electrons for an hour produced a temperature rise of only 0.5 K. In control experi-





Figure 2. TPD data showing the exclusive desorption of ${}^{12}C_2D_4$ (~355 K) following 55 eV electron exposure (fluence = 4×10^{15} cm⁻²) of ${}^{12}CH_3OH$ monolayer and ${}^{12}CD_3OD$ multilayers (three layers) at 85 K. ments to determine the possible role of the Mo(110) surface, the observed lack of ethene production following exposure of a *monolayer* of methanol at 85 K to an electron fluence of 4×10^{15} cm⁻² is attributed to the role of the surface in quenching electronic excitations.²¹ The above results show conclusively that ethene formation is the result of electron-induced reactions (EIR) of methanol multilayers.

Experiments involving isotopic labeling reveal that all of the carbon and hydrogen atoms of the ethene originate exclusively in the methanol multilayers upon electron irradiation. Figure 2 shows TPD data obtained following electron exposure of three layers of ¹²CD₃OD on top of a monolayer of ¹²CH₃O (methoxy). The peak at ~ 420 K for m/e = 28 is due to CO, a product of monolayer methanol dissociation on clean Mo(110) as described previously. The absence of peaks at 355 K for m/e = 27, 29, and 31 indicates that C2D3H, C2D2H2, C2DH3, and C2H4 are not formed, while the presence of peaks for m/e = 28, 30, and 32 shows that C_2D_4 is being formed. This experiment demonstrates that the H atoms in the ethene originate exclusively in the multilayers of methanol. Similar experiments (data not shown) with ¹³CH₃OH multilayers and a ¹²CH₃O monolayer show that both C atoms in the ethene also come exclusively from the multilayer methanol film.

Although all of the atoms which constitute ethene originate in the multilayer, ethene formation does not occur in the multilayer because the evolution of ethene at 355 K is ratelimited by reaction rather than desorption (molecular ethene desorbs from Mo(110) below 300 K²²). For approximately a 50-fold change in surface ethene coverage, the ethene peak temperature remained constant to within 6 K, suggesting that ethene is produced in a first-order *surface* reaction. Hence, we suggest that ethene formation is due to the unimolecular decomposition of a surface intermediate formed as a result of electron-induced reactions of methanol multilayers followed by heating of the crystal (see below).

C. Production of Ethylene Glycol. At higher electron exposures of the methanol multilayers, ethylene glycol (HOCH₂-

Identification of Ethylene Glycol



Figure 3. (a) TPD data obtained following 55 eV electron exposure (fluence = 7×10^{15} cm⁻²) of 12 CH₃OH multilayers (four layers). Ethylene glycol desorption is observed at ~205 K (m/e = 26, 27, 33, and 62). The desorption feature at ~135 K for m/e = 33 is due to methanol desorption (~1% natural abundance of 13 C). (b) TPD of ethylene glycol on a methoxy-covered Mo(110) surface. Multilayers of ethylene glycol are seen to desorb at ~205 K. Ethene desorption occurs at ~350 K.

CH₂OH) is observed to desorb at \sim 205 K as shown in Figure 3a. The desorption feature at ~135 K for m/e = 33 is due to methanol desorption (~1% natural abundance of 13 C). The identification of ethylene glycol as a product of EIR of methanol multilayers was confirmed by independent TPD experiments (data not shown) of ethylene glycol on clean Mo(110); multilayers of ethylene glycol desorb at \sim 210 K, while the monolayer dissociates to form dihydrogen at \sim 380 K and gaseous ethene at \sim 340 and \sim 380 K. Therefore, the ethene formation observed following EIR of methanol is attributed to the decomposition of ethylene glycol on Mo(110). This conclusion was further verified by separate TPD experiments of ethylene glycol on a saturation methoxy-covered Mo(110) demonstrating ethene formation at \sim 350 K as shown in Figure 3b. Ethylene glycol has been previously identified as a product in numerous radiolysis studies of methanol,¹³ and its formation is attributed to the dimerization of hydroxy methyl radicals (*CH₂OH) (see below).

D. Identification of a Previously Unknown Radiolysis Product: Methoxymethanol. Figure 4 shows a desorption feature at 170 K (peak 4) for m/e = 61 but not for m/e = 62, indicating the formation of a radiolysis product (~0.003 ML) of methanol distinct from ethylene glycol. No match was found between the observed masses at 170 K and the fragmentation



Figure 4. Postirradiation (55 eV electrons at a fluence of 1×10^{16} cm⁻²) TPD data of ¹²CH₃OH multilayers (four layers) showing several desorption features labeled by numbers: (1) dimethyl ether (~95 K), (2) methanol (~140 K), (3) ethanol (~160 K), (4) methoxymethanol (~170 K), and (5) ethylene glycol (~205 K).

patterns found in a mass spectral data base.20 The 170 K desorption feature for m/e = 61 occurred instead at m/e = 66and 63 when experiments were conducted with ¹²CD₃OD and ¹³CH₃OH, respectively, indicating that the ion with the highest observed m/e contains five H atoms and two C atoms. Experiments with ¹³CH₃OH also produced a small peak at 170 K for m/e = 65 due to the presence of $\sim 10\%$ ¹³CH₃¹⁸OH in our sample, as verified by mass spectrometry. Statistical analysis of this ¹⁸O data indicates the presence of two O atoms.²³ Hence, the formula of this m/e = 61 ion is C₂H₅O₂. A radical was considered unlikely because postirradiation dosing with oxygen did not eliminate or reduce the 170 K desorption feature. A recently published mass spectrum of methoxymethanol (CH₃OCH₂OH) shows an intense peak at m/e = 61 but only a peak at or below the noise level for the parent ion, $m/e = 62.^{24}$ Moreover, the six most intense fragments (m/e = 29, 30, 31, 33, 45, and 61) in the published mass spectrum are also observed at 170 K in our TPD experiments, providing additional evidence for the first identification of methoxymethanol as a radiolysis product of methanol.

E. Identification of Other Radiolysis Products by TPD. TPD experiments (Figure 4) show that electron-induced dissociation of methanol also yields dimethyl ether (CH₃OCH₃), formaldehyde (H₂CO) (data not shown), and ethanol (CH₃CH₂-OH) which desorb at approximately 95 (peak 1), 95, and 160 K (peak 3), respectively. Separate TPD experiments were conducted with H₂CO (obtained from paraformaldehyde) to confirm that formaldehyde multilayers desorb at 95 K from Mo(110). Multilayers of dimethyl ether and ethanol desorb from Pt(111) at 100 and 155 K, respectively²⁵ (multilayer desorption temperatures are expected to be relatively independent of the substrate). In addition to comparing observed masses with tabulated fragmentation patterns,²⁰ results of postirradiation TPD experiments with ¹²CD₃OD and ¹³CH₃OH were used in the identification of the above products. Formaldehyde, dimethyl

Electron-Induced Formation of Methyl Radicals



Figure 5. Isothermal experiment depicting the desorption of methyl radicals when 55 eV electron irradiation of ¹²CH₃OH (10 layers) is initiated at $t \sim 15$ s.

ether, and ethanol have been previously observed during γ radiolysis of methanol.¹³

F. Isothermal Experiments. In addition to TPD experiments, isothermal experiments were also conducted to investigate the desorption of electron-induced reaction products during electron irradiation. These experiments were conducted as follows. While the surface temperature was kept constant at \sim 85 K, the mass spectrometer signal was monitored as a function of time as the methanol-covered crystal was rotated to face the mass spectrometer. As shown in Figure 5, desorption of methyl radicals ($^{\circ}CH_3$) due to EIR of methanol occurs at ~ 15 s when the crystal comes into alignment with the mass spectrometer filament. This desorption feature cannot be attributed to methane alone since the m/e = 15 signal is larger than the m/e = 16 signal.²⁰ The m/e = 16 signal could be due to methyl radicals abstracting H atoms on the mass spectrometer shield.²⁶ However, isothermal experiments conducted with CD₃OD show a desorption feature for m/e = 20, indicating that methane is also formed. Isothermal experiments also reveal the formation and desorption of hydrogen (H₂) and carbon monoxide (CO) during electron impact of methanol multilayers. All of the above mentioned species (*CH₃, CH₄, H₂, and CO) have been previously observed during methanol radiolysis.^{8,13}

G. Radiolysis Yield as a Function of Electron Energy. The reaction cross section's dependence on initial electron energy was investigated to obtain additional information regarding the dynamics of electron-induced dissociation of methanol. At low electron energies, the electron attenuation length (mean free path if elastic scatting is ignored) in condensed methanol shows little dependence on electron energy¹⁵ and hence should not influence the results reported below. At a constant electron fluence of 1.5×10^{15} cm⁻², the yield of ethene increases monotonically with initial electron energy with a threshold close to 10 eV. During the above electron irradiation, charging of the ultrathin methanol film (four layers) deposited on the conducting Mo(110) substrate is not expected to be significant and should not affect the value of the threshold. However, the difference in work function between the surface and the filament causes an error in the electron energy measurement. Taking into account the 0.4 eV difference in work function between Mo(110) and polycrystalline W,²⁷ and the average 1.5 eV reduction in the work function associated with methanol adsorption on single crystal surfaces,¹⁴ we estimate that the threshold for the radiolysis of methanol to produce ethylene glycol is approximately 11 eV. Since the ionization potential of methanol is 10.8 eV, our results suggest that the radiolysis of methanol is dominated by electron impact ionization rather than dissociative electron attachment (DEA).

Very recent *isothermal* electron-stimulated desorption studies of H⁻ ions emanating from a five-layer-thick methanol film deposited on a platinum substrate have demonstrated that both dissociative electron attachment and electron impact ionization take place at low electron energies (0-20 eV).²⁸ The H⁻ ion yield evinces a maximum at an electron energy of 9.3 eV (attributed to DEA) and a monotonic increase above ~12 eV (attributed to electron impact ionization). A different reaction channel (ethene from ethylene glycol vs H⁻ ion) or the limited resolution of our electron beam source at low electron energies may explain our inability to detect DEA of methanol. Importantly, the H⁻ ion yield at 20 eV is significantly higher than that at 9.3 eV,²⁸ clearly demonstrating the dominance of electron impact ionization over dissociative electron attachment in the radiolysis of methanol.

H. Postulated Mechanisms for Methanol Radiolysis. Our identification of electron impact ionization as the primary route to the radiolysis of methanol is consistent with previously postulated mechanisms.⁸ The observed reaction products suggest a rich array of mechanistic steps and transient species, a few of which are delineated below. The first step involving ionization produces a radical cation (eq 1).

$$CH_3OH \rightarrow [CH_3OH]^+ + e^-$$
(1)

The subsequent ion-molecule reactions involve proton transfer to produce hydroxymethyl ($^{\circ}CH_2OH$) (eq 2) and methoxy radicals (CH₃O[•]) (eq 3).²⁹

$$[CH_3OH]^+ + CH_3OH \rightarrow {}^{\bullet}CH_2OH + [CH_3OH_2]^+$$
(2)

$$\rightarrow CH_3O^{\bullet} + [CH_3OH_2]^+$$
(3)

Both radicals have been identified in several radiolysis studies of methanol using electron spin resonance (ESR) spectroscopy following spin trapping.⁸ Dimerization (eq 4) and disproportionation (eq 5) of the hydroxymethyl radical yields ethylene glycol and formaldehyde, respectively.²⁹

$$CH_2OH + CH_2OH \rightarrow HOCH_2CH_2OH$$
(4)

$$\rightarrow H_2 CO + CH_3 OH$$
 (5)

Ethylene glycol is postulated to dissociate via the surface intermediate 1,2-ethanedioxy ($-OCH_2CH_2O-$) on Mo(110) to form gaseous ethene. Three mechanisms may be postulated for the formation of methoxymethanol. The first mechanism involves the combination of methoxy and hydroxymethyl radicals (eq 6).

$$CH_3O' + CH_2OH \rightarrow CH_3OCH_2OH$$
 (6)

The second mechanism involves a nucleophilic attack of $[CH_2OH]^+$, the dominant positive ion formed during electron impact of methanol,³⁰ by methanol (eq 7), followed by loss of a proton (eq 8).

$$[CH_2OH]^+ + CH_3OH \rightarrow [CH_3OHCH_2OH]^+$$
(7)

 $[CH_3OHCH_2OH]^+ + CH_3OH \rightarrow$

$$CH_3OCH_2OH + [CH_3OH_2]^+$$
 (8)

The third possibility, direct reaction between methanol and formaldehyde, is considered unlikely because mixed multilayers of methanol and formaldehyde on Mo(110) failed to produce methoxymethanol. Nucleophilic attack of protonated methanol by methanol would result in the formation of protonated dimethyl ether (eq 9) whose neutral product would result from the loss of a proton (eq 10).

$$CH_{3}OH + [CH_{3}OH_{2}]^{+} \rightarrow [CH_{3}OHCH_{3}]^{+} + H_{2}O \quad (9)$$
$$[CH_{3}OHCH_{3}]^{+} + CH_{3}OH \rightarrow CH_{3}OCH_{3} + [CH_{3}OH_{2}]^{+}$$
(10)

The steps postulated above should by no means be considered comprehensive.

Additional experiments to probe the dependence on electron energy, electron fluence, and methanol film thickness are currently underway. Postirradiation TPD experiments with CD_3OH are also planned to investigate the possible scrambling of H atoms.

4. Conclusions

In summary, we have demonstrated that irradiation with lowenergy electrons of organic thin films grown under UHV conditions, followed by temperature-programmed desorption, provides an effective method to identify radiolysis products. In conjunction with isothermal desorption experiments, nine radiolysis products of methanol were identified. The method is particularly useful in identifying labile radiolysis products as shown by the first identification of methoxymethanol as a reaction product of methanol radiolysis. The technique can be used to study radiolysis as a function of initial electron energy; our results suggest that electron-induced reaction of methanol is due primarily to electron impact ionization.

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(23) If the fragment contains one O atom, the m/e = 63:65 ratio would be 0.90/0.10 = 9.0. If the fragment contains two O atoms, the m/e = 63:65 ratio would be $(0.90)^2/2(0.90)(0.10) = 4.5$. If the fragment contains three O atoms, the m/e = 63:65 ratio would be $(0.90)^3/3(0.90)^2(0.10) = 3.0$. When the 170 K TPD peak for m/e = 65 is multiplied by 4.5, it overlays on the 170 K TPD peak for m/e = 63, indicating the presence of two O atoms in the fragment.

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