

# Absolute Cross Sections for the Electron-Induced Formation of Unsaturated Hydrocarbons from Solid Cyclopropane

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Electron-stimulated reactions in solid films of cyclopropane, condensed on Ar spacers deposited on a Pt substrate, were induced and monitored simultaneously using a high-resolution electron-energy-loss spectrometer. Absolute cross sections for the formation of propene, including similar unsaturated species, were independently determined as  $\sigma_p = (7.2 \pm 3.9) \times 10^{-17} \text{ cm}^2$  and  $\sigma_p = (9.6 \pm 4.8) \times 10^{-17} \text{ cm}^2$  at an incident electron energy of 15 eV using both characteristic electronic and vibrational energy losses, respectively. The cross section obtained as a function of the film thickness of cyclopropane deposited on a fixed 5-layer spacer of Ar was found to increase above 3-layer coverage. This suggests that intermolecular reactions are not only involved, but also increase the production rate of unsaturated compounds in multilayer films.

## 1. Introduction

Chemical reactions induced by low-energy electrons are not only important as fundamental steps of processes following the production of secondary electrons under the effect of high-energy radiation.<sup>1</sup> They are also interesting as a tool for modifying or patterning surfaces of molecular materials such as ultrathin organic coatings. This concerns not only plasma processes<sup>2</sup> but can also be done on a macroscopic scale by rastering the surface with a focused beam of electrons,<sup>3</sup> exposing it to electrons through a mask,<sup>4</sup> or on a nanometer scale by using the tip of a scanning tunneling microscope as a local electron source.<sup>5</sup> Although examples of such modifications are known, the reaction mechanisms are far from being understood. Therefore fundamental studies are required concerning the products and cross sections of elementary reaction steps taking place at or near the surface of ultrathin molecular films under exposure to low-energy electrons.

Since the cross sections for low-energy electron-induced reactions may vary strongly with electron impact energy ( $E_0$ ), it is of utmost importance to study these reactions at well-defined  $E_0$ . The cross sections and knowledge of the energy distribution of secondary electrons, for instance, would make it possible to assess modifications to a sample upon high-energy irradiation. High-resolution electron-energy-loss (HREEL) spectroscopy can be used both for sample irradiation at a chosen  $E_0$  and analysis of the modifications at the same time. This provides an important advantage over XPS, which is a convenient method to follow modifications in the immediate chemical environment of specific atoms<sup>6</sup> but itself may induce fast and unspecific sample damages due to the use of high-energy radiation. Compared to temperature-programmed desorption (TPD), which is frequently used to investigate electron-induced reactions,<sup>7</sup> but may involve

thermally activated secondary processes, HREEL spectroscopy offers the advantage that temperature changes are not required to monitor the products. In addition, vibrational and electronic excitations can both be detected without modification of the experimental arrangement.<sup>8,9</sup> The former excitations reveal fingerprints of specific molecular subunits, whereas the latter are most valuable for the identification of the type of  $\pi$ -electron system present in the reaction products.

In the present work, we use the combination of vibrational and electronic spectroscopy to study in more detail the electron-induced formation of unsaturated products from cyclopropane. This reaction was identified recently in solid multilayer films of cyclopropane exposed to subnanoampere currents for extended times.<sup>9,10</sup> Propene was identified as the primary product but secondary reactions occur and lead to the formation of dienes and possibly larger oligomers.<sup>9</sup> Interestingly, electron-induced reactions have not been detected at such low incident currents in the case of cyclopropane adsorbed at monolayer coverage on Cu(110).<sup>11</sup> These findings suggest that multilayer films of cyclopropane are more reactive under exposure to low-energy electrons. Therefore the aim of the present study is to quantify the reactivity by measuring the cross section for the production of propene and other unsaturated species. A method for measuring absolute cross sections for electron-induced reactions in the condensed phase by use of HREEL spectra in the range of electronic excitations has been established previously for the case of CO formation from different oxygen-containing molecules.<sup>12,13</sup> To investigate if the same approach can be used to determine the cross section for the formation of unsaturated products from cyclopropane we concentrate in this work on the effect of electrons at  $E_0 = 15 \text{ eV}$ . As an extension to the previous method, characteristic signals in both the vibrational and electronic excitation ranges of the unsaturated hydrocarbons produced under electron exposure are now used to quantify the

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production. This will establish the basis for an upcoming study of the energy dependence of this reaction.

The previous finding that not only propene but also oligomers are produced when cyclopropane is exposed to low-energy electrons<sup>9</sup> suggests that intermolecular reactions contribute to the product formation. Such reactions, on the other hand, should be favored at multilayer coverage given the larger number of immediate neighbors as compared to monolayer experiments. To evaluate the importance of this effect, we have investigated the production of unsaturated species as a function of the thickness of the cyclopropane film on top of a spacer film of Ar. The spacer layer is used to suppress possible effects of the underlying Pt(111) substrate. At the same time, this allows us to compare the reactions occurring in solid cyclopropane, where only intermolecular effects should occur, to those observed on Cu(110), where the metal is presumed to play a significant role.<sup>11,14</sup>

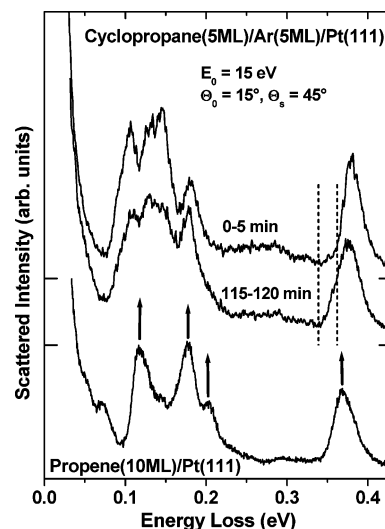
## 2. Experimental Section

The experiments were performed with an electrostatic HREEL spectrometer described in detail previously.<sup>15</sup> Briefly, the spectrometer consists of a monochromator and an analyzer both having hemispherical deflectors with rectangular entrance and exit slits. Double zoom lenses at the exit of the monochromator and at the entrance of the analyzer allow a nearly constant beam focusing and beam size over the electron energy range 2–25 eV. The monochromator, which can be rotated from 8° to 80° with respect to the normal of the sample, was set at 15° and the analyzer fixed at 45° at the opposite azimuth. The incident energy scale ( $E_0$ ) was calibrated to  $\pm 0.1$  eV, using the onset of the current transmitted through the sample. The combined resolution of the spectrometer was set at 16 meV full width at half-maximum for a current  $I_0 = 0.18$  nA incident on the sample surface. The apparatus is housed in a  $\mu$ -metal UHV chamber that is maintained at a base pressure of  $10^{-10}$  Torr by the combined action of a 400 L/s ion pump and a liquid-N<sub>2</sub> cooled titanium sublimation pump.

The samples are initially prepared from the gas phase by using a gas-handling manifold. Known amounts of gas, measured from the differential pressure drop in a calibrated volume, are leaked via a stainless steel capillary having an opening located just in front of a Pt(111) single crystal (Johnson and Matthey). The crystal is mounted on a low-temperature sample manipulator that allows cooling to 18 K, precise translations in the X, Y, and Z directions, as well as azimuthal and flip rotations, as described in detail previously.<sup>16</sup> This device enables a determination of the incident beam profile via measurement of the spatial distribution of the products formed when the sample is exposed to electrons. The surface of the crystal was cleaned by resistive heating. Cyclopropane was purchased from Aldrich at a stated purity of 99+% and propene from Matheson at a stated purity of 99.6%. The molecular films were condensed on spacer films of argon (99.9995%, Matheson of Canada Ltd.) to avoid effects of the Pt surface. The number of layers in a condensed film was estimated to  $\pm 10\%$  from the calibrated amount of gas needed to deposit a monolayer, assuming no change in sticking coefficient and growth mode for the adlayers, as described elsewhere.<sup>17</sup> The reliability of this estimate was further verified by monitoring the transmitted current before and after each film deposition.

## 3. Results

**(a) Electron Energy Loss Spectra and Quantification of Reaction Rate.** Vibrational HREEL spectra of a 5-layer film

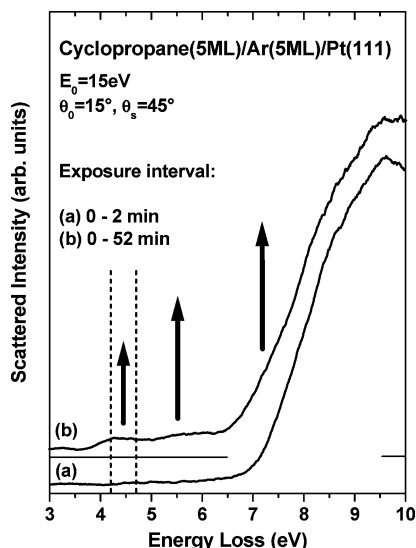


**Figure 1.** Vibrational electron-energy-loss spectra of a 5-layer cyclopropane film on a 5-layer spacer of Ar recorded at  $E_0 = 15$  eV for the first 5-min interval of electron exposure and for a 5-min interval after about 2 h of exposure. For comparison, the spectrum of a 10-layer film of propene recorded for the first 5-min interval of electron exposure at the same  $E_0$  is included. Vertical dashed lines indicate the range over which the spectra are integrated for the quantitative measurement of propene formation. ML = monolayer equivalent. The short horizontal bars indicate the zero baseline of the vertically shifted spectra.

of cyclopropane deposited on a 5-layer spacer of Ar after a brief and after a 2-h exposure to 15-eV electrons are shown in Figure 1. At this energy the production of unsaturated hydrocarbons is obvious from characteristic changes in the vibrational spectrum during exposure to the electron beam. Briefly, the intensity between 170 and 180 meV increases and a shoulder appears around 200 meV. This latter signal stems from the excitation of the C=C stretching vibration as supported by the comparison with the spectrum of a pure propene film (Figure 1 and ref 10). Similarly, the CH stretching peak (380 meV) broadens considerably and decreases in height during exposure, implying that a part of the original intensity is shifted toward lower energy loss. This is consistent with the formation of an open-chain species as evident from a comparison with the spectrum of propene, which is dominated by a typical saturated CH stretching band at lower energy loss ( $\approx 360$  meV).<sup>9,10</sup>

To measure the production rate, several vibrational spectra were recorded in sequence with the electron beam focused at the same location on a film. The probed part of the film was thus exposed to electrons having a constant incident energy during the entire experiment. As a result, each spectrum contains information that is averaged over its acquisition time, which is reported in Figure 1. Among the new vibrational signals, the shoulder appearing on the low-energy side of the CH stretching band, upon formation of the product, is the easiest to quantify. The evolution of the integral intensity in the range between 339 and 362 meV (marked by vertical dashed lines in Figure 1) will therefore be used to determine the production rate.

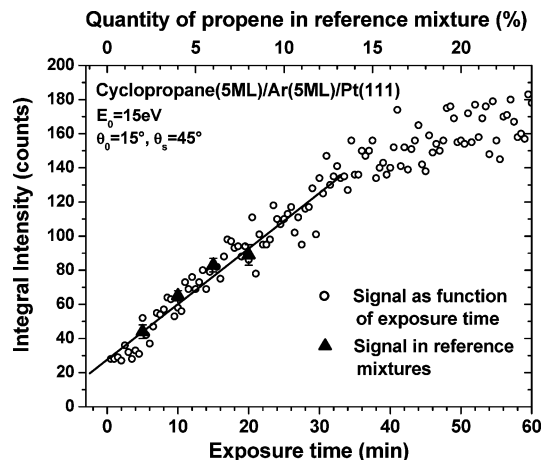
Electronic HREEL spectra recorded for different time intervals during electron exposure of a 5-layer film of cyclopropane deposited on a 5-layer spacer of Ar at  $E_0 = 15$  eV are shown in Figure 2. Curve a results from a sum of 26 recordings of 2-min acquisition time, each of which was taken on a fresh sample or at a new (X,Y) position on a locally exposed sample. Such a sum of data is representative of a spectrum in the limit of a short irradiation time. It is therefore largely free of reaction products and compares closely to the very broad and structureless optical spectrum of solid cyclopropane.<sup>18</sup> For a longer



**Figure 2.** Representative electronic electron-energy-loss spectra of a 5-layer film of cyclopropane on a 5-layer spacer of Ar recorded at  $E_0 = 15$  eV. (a) Sum of 26 spectra each obtained for 2-min exposure time either on a fresh sample or at a new beam location on the same sample, and (b) spectrum obtained on the same sample and location during an exposure interval from 0 to 52 min. Vertical dashed lines indicate the range over which the spectra are integrated during the experiments aiming at the quantitative measurement of propene formation. ML = monolayer equivalent. The short horizontal bars indicate the zero baseline of the vertically shifted spectrum.

acquisition time noticeable changes appear in the spectrum, as one can see in Figure 2b. The most important one, besides an overall intensity increase below 6 eV, is the appearance of a new excitation on the low-energy side of the original cyclopropane band with an onset at about 6.4 eV. As shown previously by comparison with a spectrum of pure propene, this band is attributed to the  $^1\pi\pi^*$  transition of a nonconjugated unsaturated hydrocarbon.<sup>9</sup> In addition, two bands located around 4.3 and 5.3 eV become obvious. The lowest energy one is assigned to the  $^3\pi\pi^*$  transition of a nonconjugated unsaturated hydrocarbon,<sup>9,19</sup> while the higher one is due to a reaction product containing a conjugated diene unit.<sup>9</sup> In this work, a second and independent quantification of the formation of unsaturated hydrocarbons relies on the evolution of the  $^3\pi\pi^*$  transition in the range marked by vertical dashed lines in Figure 2 of the HREEL spectrum recorded at  $E_0 = 15$  eV during exposure to 15-eV electrons.

It was previously shown that the vibrational HREEL spectrum of a cyclopropane film damaged by a sufficiently small exposure to 15-eV electrons can be reproduced by a weighted sum of spectra of pure cyclopropane and propene films.<sup>10</sup> For a larger exposure, additional spectral contributions became obvious. For example, an electronic transition characteristic of a conjugated diene gave evidence of the formation of oligomers.<sup>9</sup> Besides, the CH stretching band could no longer be reproduced by a weighted sum of the spectra of cyclopropane and propene. For the present determination of the production rates, we will use only data acquired during sufficiently small exposure time, i.e., a time during which only a few percent of the molecules have experienced reactive electron collisions. Still during this exposure time, oligomers having spectral properties (i.e., double bond stretch, saturated CH stretching bands, and, in the case of nonconjugated oligomers, the triplet states) very similar to those of propene may contribute to the spectrum of the damaged film. We therefore interpret the reaction rates to be determined in



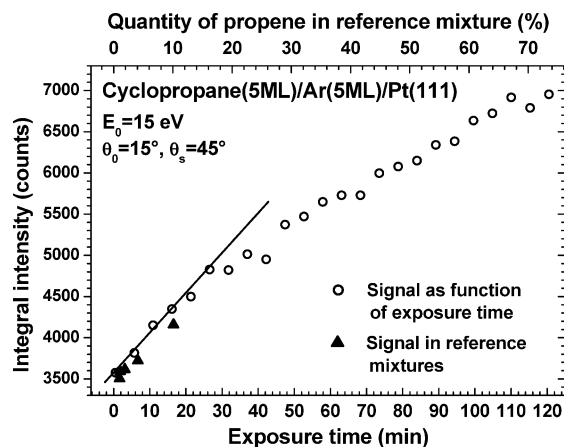
**Figure 3.** Integral intensity ( $\circ$ ) between 4.2 and 4.7 eV, (i.e., in the range of the lowest triplet band of propene as indicated in Figure 2), during exposure of a 5-layer film of cyclopropane deposited on a 5-layer spacer of Ar to 15-eV electrons. Integral intensity ( $\blacktriangle$ ) in the same spectral range recorded at  $E_0 = 15$  eV on 5-layer films of reference mixtures containing 2%, 4%, 6%, and 8% propene deposited on 5-layer spacers of Ar plotted as a function of propene content as given on the top scale. The solid line represents a linear fit to the data of the exposure experiment during the initial 20 min of exposure. ML = monolayer equivalent.

the next section as being representative of the formation of propene including certain contributions from oligomers.

**(b) Dependence of the Spectra on the Electron Exposure and Cross Section Calibration.** The progress of the reaction is quantified independently from the intensities in the range of the CH stretching band and the  $^3\pi\pi^*$  band of propene. By using integral quantities, a satisfactory signal-to-noise ratio in the plot of the intensities as a function of exposure time is achieved even for relatively short recording times. The production rates are determined during the initial stages of exposure to the electron beam where the amount of the product increases linearly with time. Within this linear reaction regime, the slope of a straight line passing through the experimental data represents, within a constant factor, the production rate (in counts per minute) of only those molecules that can be detected by the probing electron beam. Here and in the following, we will refer to this quantity as an *apparent* production rate as opposed to the *actual* amount of molecules produced per unit time. To determine the constant factor and thus quantify the production rate, we compared the integral intensities to those obtained for fresh cyclopropane films containing up to about 8% of propene (i.e. reference mixtures) and having identical thicknesses on the Ar spacer as those for the bombardment experiments.

The amount of unsaturated hydrocarbons produced by 15-eV electrons incident on the cyclopropane film deposited on a 5-layer spacer of Ar, as probed from the integral intensity of the  $^3\pi\pi^*$  excitation of propene between energy losses of 4.2 and 4.7 eV (vertical dashed lines in Figure 2), is shown as a function of the exposure time in Figure 3. During at least the first 20 min of bombardment the intensity of the signal increases linearly. This indicates that during the initial stages of the product formation the reaction rate is practically constant and charging effects are minimal. The solid triangles in Figure 3 correspond to the integral intensity of the  $^3\pi\pi^*$  transition of propene in the reference mixtures for several propene concentrations, which are given in percent on the top scale. They exhibit an almost linear increase with propene concentration. By aligning the reference mixture data to the straight line obtained from a fit to the electron exposure data (open circles and bottom





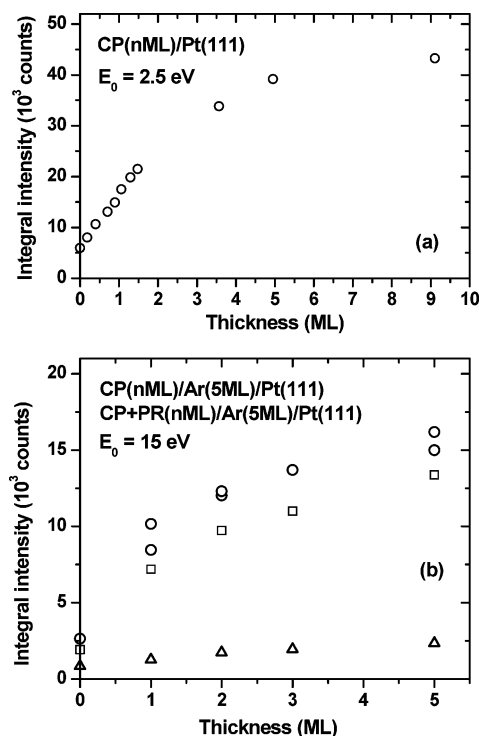
**Figure 4.** Integral intensity (○) between 0.339 and 0.362 eV (i.e., in the range of the CH stretching band of propene as indicated in Figure 1), during exposure of a 5-layer film of cyclopropane deposited on a 5-layer spacer of Ar to 15-eV electrons. Integral intensity (▲) in the same spectral range recorded at  $E_0 = 15$  eV on 5-layer films of reference mixtures containing 1%, 1.1%, 1.9%, 4.1%, and 10.1% propene deposited on 5-layer spacers of Ar as a function of propene content as given on the top scale. The solid line represents a linear fit to the data of the exposure experiment during the initial 20 min of exposure. ML = monolayer equivalent.

scale in Figure 3), we obtain the calibrated production rate of propene as being  $(0.40 \pm 0.08)\% \cdot \text{min}^{-1}$  at  $E_0 = 15$  eV. From this value an *absolute* electron scattering cross section  $\sigma_p$  for the formation of propene can be determined with the method described previously.<sup>12,13</sup> Assuming for simplicity an incident electron beam characterized by a constant current density  $i_0 = I_0/S_0$  within the beam area  $S_0$  and  $i_0 = 0$  outside, we obtain the cross section from the relation

$$\sigma_p \cong \frac{n_{\text{propene}} S_0}{n_0 I_0 t} \quad (1)$$

In this expression,  $n_0$  represents the number density of molecules in the film prior to bombardment (i.e., the number density of cyclopropane in the fresh film) and  $n_{\text{propene}}$  the number density of propene molecules formed after a bombardment time  $t$ . The calibrated production rate corresponds to the combined factor  $n_{\text{propene}}/n_0 \cdot t$ , that derives from the relation between the propene signal intensity and the concentration of propene in a mixture film (Figure 3).  $S_0$  was determined in a different bombardment experiment from the profiles in the  $X$  and  $Y$  directions of the intensity of the CH stretching signal of propene integrated over the range specified in Figure 1. The resulting triangular intensity profiles in both directions, which are similar to those obtained in ref 12, indicate a practically constant current density over the irradiated area  $S_0 = (1.2 \pm 0.2) \times 10^{-3} \text{ cm}^2$ . Finally, taking  $I_0 = (0.18 \pm 0.04) \text{ nA}$ , we find a cross section  $\sigma_p = (7.2 \pm 3.9) \times 10^{-17} \text{ cm}^2$  at  $E_0 = 15$  eV.

Alternatively, the cross section for the formation of propene from cyclopropane can also be determined from an analysis of vibrational energy losses. Here, using the CH stretching signal of propene integrated over the range indicated in Figure 1, we determine this cross section from a 5-layer film of cyclopropane deposited onto a 5-layer spacer of Ar at  $E_0 = 15$  eV. Again, as one can see in Figure 4, the intensity of this signal increases linearly during at least the first 20 min. As for the case of the  $^3\pi\pi^*$  excitation, the slope of the straight line resulting from a fit within the linear regime yields an apparent production rate. Comparing this production rate from two exposure experiments to the dependence of the integral CH signal on the propene



**Figure 5.** (a) Integral CH stretching intensities in the range between 348 and 421 meV as a function of film thickness at  $E_0 = 2.5$  eV for cyclopropane (CP) deposited on Pt(111). (b) Integral CH stretching intensities at  $E_0 = 15$  eV as a function of film thickness for both cyclopropane (○, 348–421 meV) and a reference mixture containing 90% cyclopropane and 10% propene (CP+PR) (□, 370–420 meV; △, 340–362 meV) deposited on a 5-layer spacer of Ar (b). Electrons were incident at an angle of  $15^\circ$  and detected at  $45^\circ$ . ML = monolayer equivalent.

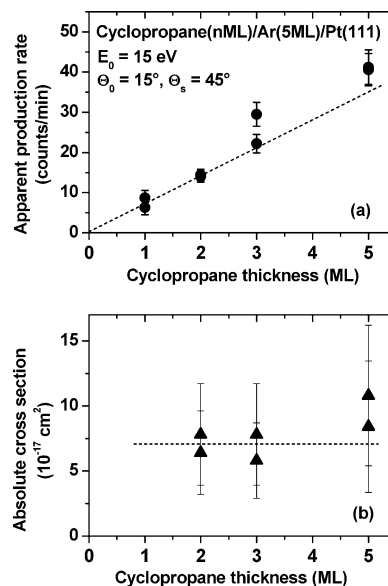
concentration in several reference mixtures, we deduce an average calibrated production rate of  $(0.59 \pm 0.15)\% \cdot \text{min}^{-1}$ . Owing to intensity fluctuations among the vibrational spectra, this comparison is based on intensities relative to the height of the cyclopropane CH stretching band. Taking this calibrated production rate, the average value of the measured irradiated area for the two experiments  $S_0 = (1.1 \pm 0.2) \times 10^{-3} \text{ cm}^2$ , and the incident current  $I_0 = (0.18 \pm 0.04) \text{ nA}$ , we obtain a cross section of  $\sigma_p = (9.6 \pm 4.8) \times 10^{-17} \text{ cm}^2$  at  $E_0 = 15$  eV.

**(c) Dependence of the Propene Production on Cyclopropane Coverage.** Changes in the vibrational HREEL spectra were recorded for different cyclopropane film thicknesses on the spacer of Ar. Here the measurement of reaction rates under the effect of exposure to low-energy electrons must take into account the attenuation of the probing electron beam within the solid (i.e., probed depth). For electrons that enter a film at a given energy, scatter once on specific molecules, and then leave the film at a final energy, thus generating a backscattered signal, the *probed depth* corresponds to the effective mean free path of the electron. This quantity results as the inverse sum of the inverse electron mean free path before and after the scattering event.<sup>15</sup> In principle, the beam attenuation should limit the thickness of a film within which the newly formed molecules can be probed or detected efficiently. To illustrate this effect, the integral of the energy-loss intensities of the CH stretching signal for 2.5-eV electrons incident on a cyclopropane film is shown as a function of the film thickness in Figure 5a. The signal follows a linear behavior up to an estimated coverage of roughly two layers and then tends progressively to a saturation level at higher coverages.

Figure 5b shows the thickness dependence of the energy-loss integral of the CH stretching signal for 15-eV electrons incident on a pure cyclopropane film and on reference mixture films containing 10% propene. In the mixture case, the energy-loss integrals are included for both the propene CH signal between 340 and 362 meV (i.e., in a range similar to that used for the determination of production rates) and the cyclopropane CH signal between 370 and 420 meV. In the cyclopropane case, the energy-loss integral was extended over the whole CH stretching signal (i.e. 348–421 meV). Corresponding values for the integrated signals at zero coverage in Figure 5b were obtained simply from the line passing across the base of the CH stretching peak for the monolayer coverage. Similar to Figure 5a, the data in Figure 5b also show a deviation from a linear intensity increase with thickness that hints toward a trend to saturation at higher coverage. As a consequence of the nonlinear behavior of the CH stretching signal at coverages above an estimated two layers, the apparent production rate would indeed underestimate the total amount of propene within the film owing to the corresponding limited *probed depth* for vibrations. In other words, as mostly the outer layers of the cyclopropane film are effectively probed, the observed intensity increase upon electron exposure reflects essentially the amount of propene formed within these layers. A comparison of apparent production rates for different film thicknesses, therefore, has to take into account the limited *probed depth* within the cyclopropane film. The direct way to do this is to determine absolute cross sections from a comparison with films of reference mixtures having the same thickness. The effect of the limited *probed depth* cancels out when the apparent production rate in a given film is divided by the slope of the straight line passing through the intensities of the reference mixtures plotted as a function of propene percentage in a film of the same thickness because both measurements probe the same number of layers. It is therefore essential to calibrate independently the cross section at each film thickness. This is a tedious procedure. Therefore the cross section measurements were limited to one specific  $E_0$  in the present work. Also, because of a relatively large scatter in the intensity data of the reference mixture films at monolayer coverage the cross section was determined only for multilayer films of cyclopropane.

In Figure 6a we show the apparent production rate in terms of the CH stretching signal ascribed to propene (Figure 1) as a function of the cyclopropane coverage on a 5-layer spacer of Ar. In Figure 6b, we show the corresponding cross section for propene production as obtained from comparing to the multilayer reference mixtures and using eq 1. This result should give information more specifically on the importance of possible intermolecular reaction steps.

Assuming small electron exposures, negligible electron beam attenuation within a film, and single electron–molecule collisions with no further reaction of the initial molecular product with its neighbors, the production rate should be constant with time and directly proportional to the number of irradiated molecules.<sup>12,13</sup> This has been found to be the case for the production rate of CO in acetone films over the thickness range of 0–5 layers<sup>12</sup> and in methanol films over the range of 0–12 layers<sup>13</sup> from probing the  $a^3\Pi$  electronic excitation of CO in those films. However, in Figure 6a the apparent production rate at large film thicknesses seems to deviate slightly toward higher values from the linear extrapolation (dashed line) based on the values at one and two layer thickness. This would suggest that the reaction proceeds at a faster pace in the multilayer regime and would explain a previous qualitative work where the spectral



**Figure 6.** (a) Apparent production rate of propene in cyclopropane films of variable thicknesses deposited on a 5-layer spacer of Ar upon exposure to 15-eV electrons. The amount of propene in a cyclopropane film is monitored in terms of its integrated CH stretching signal in the range defined in Figure 1. The dashed line represents an approximate linear fit to the data points at low thickness as discussed in the text. (b) Absolute cross section for propene formation in cyclopropane films of variable thicknesses. The dashed line serves as guide to the eye. ML = monolayer equivalent.

changes have been found to be more prominent in a multilayer film of cyclopropane than at monolayer coverage.<sup>8</sup> If the percentage of propene formed in the cyclopropane film during a given electron exposure would have been independent of the film thickness then the relative intensities of propene and cyclopropane signals would have been the same irrespective of thickness. A larger probability of propene formation in the multilayer film can be better corroborated by the plot of the corresponding cross section values in Figure 6b. Under the assumption of single electron–molecule collisions these values should be independent of the film thickness even in the presence of electron-beam attenuation. This is found to be the case at 2 and 3 layers of cyclopropane but not at 5 layers where the cross section increases by roughly 30%.

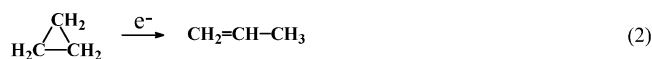
Although a calibration of the cross section could not be achieved in the case of a monolayer film of cyclopropane on the spacer of Ar, it is instructive to note the result of experiments performed for monolayer cyclopropane on Ar spacers of varying thickness. The apparent production rates observed for 2, 5, and 8 layers of Ar were found to be about the same with no obvious dependence on the thickness of the spacer.

#### 4. Discussion

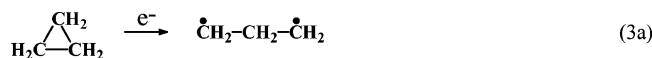
**(a) Increase of the Rates of Product Formation with Cyclopropane Coverage.** The production of unsaturated hydrocarbons, as probed by using the characteristic CH stretching bands, from cyclopropane under exposure to 15-eV electrons is observed to proceed at a faster rate in a multilayer film. As can be seen in Figure 6a, the apparent production rate for the 5-layer film is about six times larger than that for the monolayer. This increase of the reaction rate at larger coverage is reflected more clearly by the absolute cross section (Figure 6b), which accounts for the effects of the *probed depth* by calibrating the production rate against equally thick films of reference mixtures. To understand the increase of the reaction cross section for the

production of unsaturated hydrocarbons from cyclopropane, the different reaction pathways must be discussed in more detail.

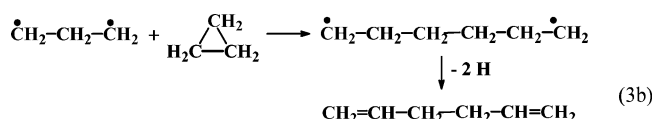
As evidenced by the spectral changes during the initial stages of the reaction, exposure of cyclopropane to low-energy electrons yields propene as the major product formed after a single electron collision in a unimolecular reaction:



This reaction is most likely initiated by a CC bond cleavage:



The oligomers can, in principle, be formed via different reaction pathways of which we only elaborate on the radical mechanism here because ionic reaction steps are expected to lead essentially to the same products. One has to consider that instead of undergoing isomerization to propene, the intermediate biradical may also attack adjacent molecules thus initiating oligomerization:



A single electron collision may therefore also lead to the formation of a nonconjugated oligomer. An isomerization of the intermediate radical of reaction 3b by H migration may produce a conjugated diene. Secondary reaction pathways, i.e., reactions occurring under subsequent reactive electron collisions, include the formation of oligomers from the primary product propene<sup>9,10</sup> and the introduction of additional unsaturated centers in already existing oligomers through further H abstraction.

Considering that with the given approach the production of propene cannot be quantitatively separated from that of the oligomers, the increase of the cross section in thicker films may be attributed to a larger probability for oligomer formation. While secondary reactions, such as those involving already existing propene, can be excluded because cross sections are derived from data that have been obtained under conditions of single reactive electron collisions, reaction 3b can contribute to oligomer formation as long as a sufficient number of close enough neighbors is present. This is more likely the case for a thickness of 5 layers than below. This assumption is based on a previous study modeling organic film growth at low temperatures.<sup>20</sup> Assuming random film growth, this study has shown that the film exhibits a certain roughness under these conditions. Consequently, the first layer of the deposited film is expected to be covered completely by higher layers only after deposition of an amount of material corresponding to 5 layers. Molecules at locations that are not covered by higher layers, on the other hand, have a lower number of nearest neighbors. This population only vanishes at an average 5-layer coverage. A scenario involving the two parallel reactions 2 and 3 therefore gives a reasonable explanation for the increased production rate of species with isolated double bonds at multilayer coverage.

One may also expect that a different probability of long-range quenching of excited states involved in the reaction by the metallic substrate can be responsible for the difference of the reaction cross section at different film thickness. A significant dependence of the cross section has been observed previously for the electron-induced dehydrogenation of alkanethiol self-assembled monolayer (SAM) films on gold.<sup>21</sup> In those experi-

ments, dehydrogenation at electron energies around 10 eV has been found to be strongly localized near the methyl terminations of the film and its associated cross sections to increase rapidly with chain length, i.e., distance from the metal (e.g.,  $1.2 \times 10^{-16}$ ,  $2.8 \times 10^{-16}$ , and  $5.3 \times 10^{-16}$  cm<sup>2</sup> for the C<sub>8</sub>, C<sub>12</sub>, and C<sub>16</sub> SAM at  $E_0 = 10$  eV). Assuming a thickness of 3.4 Å for each layer of Ar<sup>22</sup> and estimating the thickness of a cyclopropane layer at roughly 3 Å from the liquid density<sup>23</sup> would lead to a distance of the upper layer from the metal of 24 Å for a 3-layer film of cyclopropane on 5 layers of Ar versus 30 Å for the 5-layer film of cyclopropane on the same Ar spacer. The ratio of these thicknesses is similar to the one between a C<sub>12</sub> and a C<sub>16</sub> SAM where an increase of the cross section of nearly a factor of 2 has been observed.<sup>21</sup> This would support the assumption that a long-range quenching may affect the cross sections measured at different cyclopropane coverage. On the other hand, the observation from the present experiments that the apparent production rate in monolayer cyclopropane on an Ar spacer does not clearly depend on the thickness of the Ar suggests that the observed change in absolute cross section with cyclopropane film thickness must rather be ascribed to intermolecular interactions as described above. This is possibly due to the different electronic states involved in the reaction. The decomposition of the SAMs at  $E_0 = 10$  eV has been shown to be dominated by a resonant mechanism and thus by a relatively long-lived intermediate state.<sup>21</sup> This is not necessarily the case for the present cyclopropane experiments. Excited states that can be involved at the higher  $E_0$  chosen for the present experiments may have a much shorter lifetime and therefore be less susceptible to long-range quenching effects.

**(b) Comparison with Other Cross Section Data.** The cross sections for electron-induced production of propene in cyclopropane at an incident energy of  $E_0 = 15$  eV as obtained independently from the electronic and vibrational spectra agree reasonably well. It is interesting to compare the present values with other data from literature. The cross sections reported so far all refer to experiments performed at monolayer coverage on single crystal metal surfaces. In the present study we exclude short-range interactions with the metal by using a sufficiently thick Ar spacer layer. The values obtained represent a molecular solid, a situation that is rather akin to that encountered in self-assembled monolayers where steric factors prevent an interaction with the metal. Nonetheless, it is instructive to compare the two situations because electron-induced reactions of a number of molecules have been studied near metal surfaces<sup>7,11,14,24–26</sup> but applications, i.e. in lithography, often call for results on thin molecular solids.<sup>3,4,6</sup>

A previous study reported electron-induced reactions of cyclopropane adsorbed at monolayer coverage on Cu(110) cooled at 90 K.<sup>14,26</sup> In that work a much higher current has been used to observe changes in composition of the sample<sup>11</sup> and the chemisorbed cyclopropyl radical and a metallacyclobutane have been identified as products at  $E_0 = 10$  eV.<sup>11,14</sup> A cross section of  $\sigma_p = 8 \times 10^{-18}$  cm<sup>2</sup> has been reported for this reaction.<sup>14</sup> A closer examination of the data reported in the same paper suggests that the cross section has been obtained from an analysis of a decreasing cyclopropane signal and should more exactly be considered as a total depletion cross section. Also, the sample has been exposed to about  $10^{17}$  e<sup>−</sup>·cm<sup>−2</sup> before the analysis of the products.<sup>14</sup> This is 2 orders of magnitude larger than the present electron exposure during the first 20 min, which leads to the formation of about 10% of the product. As the sample is continuously irradiated, subsequent collisions between the incident electrons and the products can still be neglected



only in this linear regime. Considering the cross section for formation of the radical species on Cu(110) as given above, and assuming that secondary reactions of the radical species are not taking place, the overall production must have approached more than 50% in that experiment. The present experiment avoids such large overall productions because of apparent secondary reactions of the immediate products, which are not included in the simple linear treatment of the reaction kinetics.

Assuming that secondary reactions did not take place on Cu(110) so that the only products of the reaction are the two radical species that have been proposed, the depletion cross section may also be interpreted as a cross section for the formation of these species. The mere fact that the reaction was less obvious at  $E_0 = 15$  and 18 eV suggested the presence of a resonant mechanism.<sup>14</sup> The finding from TPD experiments that the amount of cyclopropyl was four times that of metallacyclobutane<sup>14</sup> would imply a cross section of  $\sigma_p = 6.4 \times 10^{-18} \text{ cm}^2$  for the formation of the former. This is an order of magnitude smaller than the present values for formation of propene. This explains why the product on Cu(110) was so difficult to detect at typical subnanoampere current.<sup>11</sup> Another factor that contributes to this problem is the area irradiated by the incident electron beam. In the monolayer study on Cu(110) this area was  $0.02 \text{ cm}^2$ , which is more than an order of magnitude larger than the present one. As a result, the rate of product formation must have been accordingly slower owing essentially to the smaller incident current density. On the other hand, production of the above mentioned radical species on Cu(110) was below the detection limit at  $E_0 = 15 \text{ eV}$ , implying that the cross section for formation of the radicals at this energy is considerably smaller than  $6.4 \times 10^{-18} \text{ cm}^2$ . Quenching of resonances or electronically excited states involved in the initial step of the electron-induced reaction is most probably responsible for the lower cross section of cyclopropane near the metal surface as compared to the present multilayer result.

## 5. Conclusions

Absolute reaction cross sections for the electron-induced isomerization of cyclopropane to propene in the condensed phase were determined by HREEL spectroscopy by monitoring both vibrational and electronic excitations of propene. The cross sections include the formation of similar unsaturated products with isolated double bonds whose spectral signature cannot be distinguished from propene under the present experimental conditions. The independent measurements of the absolute cross sections obtained for a 5-layer film of cyclopropane at an incident energy of 15 eV from the lowest triplet band and the saturated CH stretching signal of propene agree within the present experimental uncertainty. The present values are larger than those obtained from a previous study on cyclopropane adsorbed onto Cu(110) at monolayer coverage<sup>14</sup> but are comparable to a total depletion cross section for monolayer cyclopropane on Pt(111) at 50 eV.<sup>25</sup>

A comparison of cross sections for the electron-induced production of propene in cyclopropane films of varying thickness confirms that the reaction rate increases slightly at larger film thickness. This is explained by additional contributions from a second reaction channel that becomes accessible as the number of nearest neighbors increases in the film. This channel leads to the formation of dimers with two isolated double bonds that have a spectroscopic pattern very similar to that of propene.

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