

Bond Formation in Reactions of Solid Cyclopropane Induced by Low-Energy Electrons

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Reactions of cyclopropane and propene in the condensed phase have been induced and monitored simultaneously using a conventional high-resolution electron energy loss spectrometer. Reaction products are identified from both the vibrational and the electronic spectra of the irradiated solid samples. Propene is identified as the major initial reaction product from its characteristic vibrational bands. Subsequent reactions are shown to lead to the formation of longer chains. Some of these chains contain conjugated diene units. This latter product cannot be the result of standard oligomerization reaction steps following the formation of primary radicals by dissociative processes alone. Subsequent collision processes leading to additional H abstraction must be invoked to explain the formation of the diene units.

1. Introduction

Bond rupture following low-energy electron impact is frequently investigated by the detection of neutral and charged fragments emerging from a sample.^{1,2} From these experiments, it is obvious that breaking of certain types of bonds takes place at specific electron energies. The outcome of an electron-induced reaction may thus be controlled by using an appropriate impact energy. On the other hand, experiments whose goal is the detection of reaction products remaining within a solid sample and especially of bond formation are more demanding. As the electron-induced reactions typically take place within the first few uppermost layers of a molecular solid,³ very sensitive analytic techniques are needed. Furthermore, as the reactions often yield a mixture of products, a combination of several spectroscopic techniques is required.

High-resolution electron energy loss (HREEL) spectroscopy provides a source of low-energy electrons with well-defined energy and an analytic technique at the same time. Compared to temperature programmed desorption (TPD) which is frequently used to investigate electron-induced reactions, a spectroscopic method like HREELS offers the advantage that temperature changes are not required to monitor the products. Therefore, subsequent thermally activated processes are avoided. In addition, a wide range of spectroscopic processes such as vibrational and electronic excitations can both be detected without modification of the experimental arrangement.⁴ This represents a particularly simple way of combining two different analytic techniques for the study of electron-induced reactions. The interest in vibrational spectroscopy lies in its capacity to reveal characteristic molecular fingerprints, whereas its electronic counterpart often provides specific information on the type of π -electron system present in the reaction products. The latter is for example evident from a systematic red-shift of the lowest excitations with increasing conjugation length.^{5–8}

In the present study, we use the combination of vibrational and electronic spectroscopy to investigate in more detail the

products of electron-induced reactions in solid cyclopropane. As shown previously using only vibrational HREEL spectroscopy, low-energy electrons produce primarily propene which is easily observed when multilayer films are exposed to subnanoampere currents for extended intervals of time.⁹ Although preliminary evidence for the formation of oligomers was found, these secondary products could not be identified unequivocally. Here, the additional electronic HREEL spectra allow us to establish the formation of oligomers by showing that conjugated diene units are created. With this finding and in contrast to previous work on electron-induced chemistry of cyclopropane at monolayer coverages on Pt(111) and Cu(110),^{10,11} we provide direct evidence for the formation of molecular bonds under low-energy electron impact at very low temperatures. Such reactions are assumed to play an important role in resist patterning in electron beam lithography.¹² Possible reaction mechanisms known from polymerization chemistry are examined, and their relevance to electron-induced reactions of cyclopropane is evaluated.

2. Experimental Section

The experiments were performed with an electrostatic HREEL spectrometer described in detail previously.¹³ 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 ± 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 with a current of 0.45 nA incident on the sample. The apparatus is housed in a μ -metal UHV chamber maintained at a base pressure of 1×10^{-10} Torr by the combined action of a 400 L/s ion pump and a liquid-N₂ cooled titanium sublimation pump.

The samples are initially prepared from the gas phase using a gas-handling manifold. Known amounts of gas, measured from the differential pressure drop in the calibrated volume, are leaked via a stainless steel capillary having an opening located just in

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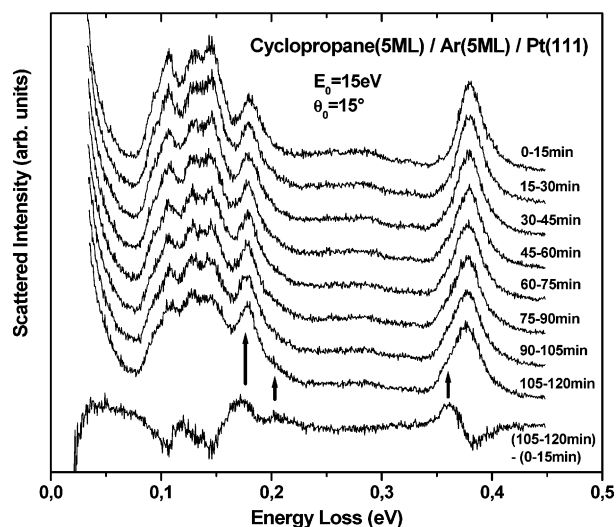


Figure 1. Vibrational electron energy loss spectra of a 5-layer cyclopropane film on a 5-layer Ar spacer recorded at an incident energy of 15 eV. Each spectrum is accumulated during subsequent 15-min intervals of electron exposure up to 120 min. Also shown is the difference between the first and the last spectrum of the investigated exposure interval.

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 X, Y, and Z translations, as well as azimuthal and flip rotations, as described in detail previously.¹⁴ This device proved to be decisive in obtaining electronic HREEL spectra of compounds that decompose rapidly under electron impact as it allowed us to acquire data at different new locations on the same sample. Crystal cleaning was achieved by resistive heating at 1100 K. Cyclopropane was purchased from Aldrich at a stated purity of 99+%, and propene was purchased from Matheson at a stated purity of 99.6%. In the present study, all molecular films were condensed on a 5-layer spacer of Ar, supplied by Matheson with a stated purity of 99.9995%, to prevent any effects from the Pt surface. The number of condensed layers in a 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.¹⁵

3. Results

The changes occurring within the vibrational HREEL spectrum of an initially pure 5-layer film of cyclopropane upon exposure to 15 eV electrons are shown in Figure 1. This energy was chosen because it has previously been shown to lead to an easily detectable production of propene, whereas the reaction rate is negligible at incident energies of 7.5 eV and lower.^{9,16} At the same time, an energy of 15 eV is high enough to record the electronic spectrum of cyclopropane and propene in the range of the lowest excited states. This energy range is relevant for the detection of possible additional products. As illustrated in Figure 1, following the deposition of cyclopropane, several vibrational spectra are recorded in sequence with the electron beam being kept at the same location. The probed part on the sample is 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.

The changes within the vibrational spectra of condensed cyclopropane under exposure to 15 eV electrons are the same as those which have been found previously using a different spectrometer.⁹ However, here the spectral changes appear more

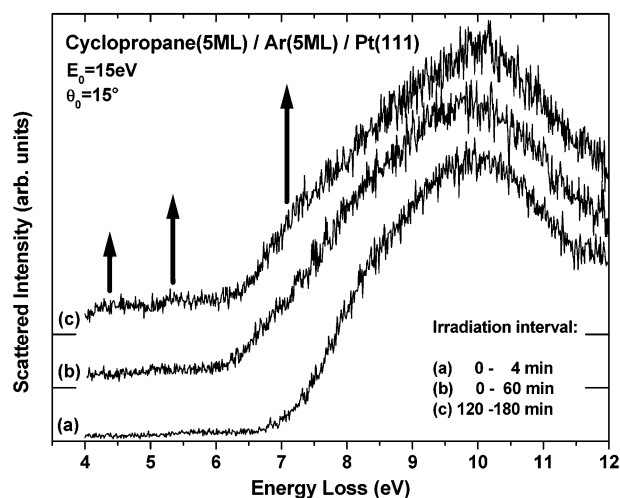


Figure 2. Electron energy loss spectra of a 5-layer film of cyclopropane on a 5-layer Ar spacer recorded at an incident energy of 15 eV. (a) Sum of 26 spectra each obtained for 4-min exposure time either on a fresh sample or at a new beam location on the same sample, (b) spectrum obtained on the same sample and location during an exposure interval from 0 to 60 min, (c) same as (b) but during the exposure interval from 120 to 180 min.

rapidly owing to the higher current density on the sample as compared to the previous experiment.^{9,17} Briefly and as seen more clearly in a difference spectrum (Figure 1, bottom), the intensity between 170 and 180 meV increases and a shoulder appears around 200 meV. The behavior of the CH stretching peak (380 meV), which broadens considerably and decreases in height, implies that a part of the original intensity is shifted toward lower energy loss. The initial spectral changes are related to the appearance of a CC double bond stretching vibration typically located around 200 meV and a saturated CH stretching signal (≈ 360 meV) that has a lower energy than the CH stretching modes of the strained cyclopropane unit. These observations show essentially that an isomerization of cyclopropane to propene, which is an important photochemical reaction product of cyclopropane,¹⁸ is taking place. The same conclusion has been drawn previously from a detailed analysis of difference spectra and a comparison with reference spectra of propene.⁹ On the other hand, our inability to mathematically reproduce the spectrum of irradiated cyclopropane by a weighted sum of the pure cyclopropane and propene spectra recorded at the same E_0 implied that secondary products appear as well after a certain electron exposure.⁹ Changes in the spectra of propene and especially the formation of a small shoulder at 92 meV upon irradiation suggested that a solid-phase oligomerization leading to the formation of longer alkyl chains may also be occurring, but evidence was too weak to lead an unequivocal identification of the products.⁹

To establish the nature of these secondary products, we show in Figure 2 the electronic HREEL spectra for different time intervals during electron exposure at the same incident energy. Curve a results from a sum of 26 spectra of 4.3-min acquisition time. Each spectrum was recorded on a fresh sample or at a new (X,Y) position on a locally damaged sample. Because such a sum of recordings is representative of a short time interval, it is largely free of reaction products and compares closely to the very broad and structureless optical spectrum of solid cyclopropane.¹⁹ Extending the acquisition time over 60 min at the same location on a sample produces noticeable changes in the spectrum (Figure 2b). The most important one, besides an overall intensity increase below 6 eV, is the appearance of a

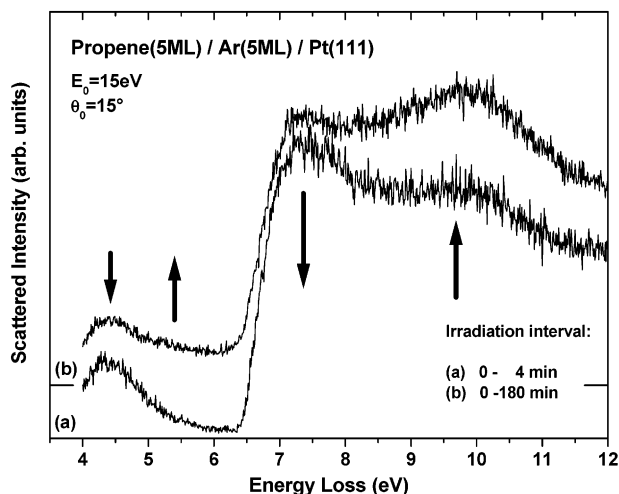


Figure 3. Electron energy loss spectra of a 5-layer film of propene on a 5-layer Ar spacer recorded at an incident energy of 15 eV. (a) Sum of 26 spectra each obtained during a 4-min exposure time either on a fresh sample or at a new beam location on the same sample, (b) spectrum obtained on the same sample and location during an exposure interval from 0 to 180 min.

new band at the low-energy side of the original cyclopropane transition with an onset at about 6.4 eV. Within a time interval of electron exposure from 120 to 180 min, two additional bands located around 4.3 and 5.3 eV become obvious (Figure 2c). These bands represent an additional fingerprint of the reaction products and help to identify their nature. A spectrum representative of a more specific interval during irradiation may be obtained by acquiring data within a few minutes similar to the case of the nonirradiated sample. This is the usual procedure for the determination of reaction cross sections from a signal within a restricted spectral range.^{17,20} As the irradiated and probed area of the sample in the present instrument are of comparable size, the experiment would have to be repeated in order to obtain a signal-to-noise ratio similar to Figure 2a in a wide-range survey spectrum. The identification of a product that is formed over a long time interval, on the other hand, does not require a good time resolution. Therefore, a spectrum integrated over a certain exposure interval is sufficient for this purpose.

For comparison, electronic HREEL spectra of a 5-layer film of propene on Ar were recorded (Figure 3). Again, curve a shows a spectrum of the sample exposed to the electron beam for only 4.3 min. This is important because propene undergoes electron-induced reactions as well.⁹ The genuine propene spectrum shows a band with an onset close to 6.3 eV and a maximum around 7.3 eV and therefore coincides closely with the band occurring in cyclopropane during electron exposure (Figure 2). This band is identified as the $^1\pi\pi^*$ transition of propene while that appearing at 4.3 eV after prolonged electron exposure is assigned to the corresponding $^3\pi\pi^*$ transition.²¹ Propene alone cannot account for the new band appearing at 5.3 eV in the cyclopropane spectra (Figure 2c). However, exposure of propene to prolonged irradiation with 15 eV electrons also results in an increase of the intensity around 5.3 eV. The unidentified reaction product can thus be formed from both cyclopropane, possibly via the production of propene, and propene itself.

Considering the exclusive presence of C and H atoms in the sample, the unidentified product must clearly be a compound with unsaturated bonds. A literature search for possible hydrocarbons having an intense excitation band around 5.3 eV yielded only two reasonably simple π -electron systems, namely fulvene and a diene (Figure 4).⁵⁻⁷ As representatives of these classes

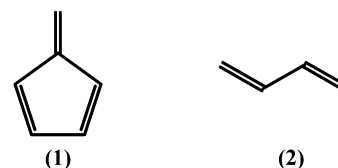


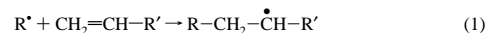
Figure 4. Structure of π -electron systems of possible candidates responsible for the 5.3 eV excitation band.

of compounds, butadiene, and dimethylfulvene have been investigated previously by HREEL spectroscopy in the condensed phase.^{22,23} Compared to the more structured gas-phase spectrum,²⁴ the maximum of the intense second singlet band of dimethylfulvene undergoes a small shift from 4.74 to 4.9 eV in the condensed phase.²³ Assuming that the shift is similarly small for fulvene, whose band maximum in the gas phase is located at 5.3 eV,²⁴ this compound would appear to be a possible candidate. On the other hand, the formation of fulvene, C_6H_6 , from two cyclopropane or propene units, C_3H_6 , requires an enormous loss of six H atoms. Hence, the identification of the product as being fulvene appears unlikely. The maximum of the most intense band in the HREEL spectrum of solid butadiene, which is located at 5.8 eV,²² is clearly too high in energy. However, solid-phase optical spectra show that the band shifts considerably upon methyl substitution with a maximum at about 5.3 eV for 2,3-dimethyl butadiene.⁶ A dimethyl-substituted butadiene, C_6H_{10} , therefore appears to be the simplest candidate for the so far unidentified reaction product. Besides, the fact that it can be produced by much fewer H abstractions than fulvene makes it a more likely candidate.

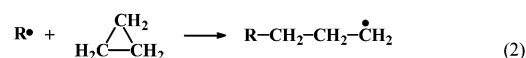
4. Discussion

Possible secondary products of the isomerization of cyclopropane to propene were recently discussed on the basis of known photochemical reactions.⁹ This approach is reasonable because, among the wide range of possible excitations, low-energy electrons can induce electronic transitions that are also responsible for photochemistry. When performed under matrix isolation conditions, photochemical reactions lead to the production of allyl (**IV**) and cyclopropyl (**V**) as intermediate radicals and to allene (**VI**) and propyne (**VII**) as final products (Figure 5).^{18,25} In addition, a biradical (**II**) was postulated as intermediate in the initial isomerization step.¹⁸

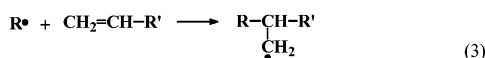
The present HREEL spectra in the range of the electronic excitations show that an oligomer with conjugated double bonds is formed under exposure to 15 eV electrons. Below, we examine several possible reaction mechanisms. Intermediate radicals that can be formed by electron impact are reactive species that may initiate oligomerization reactions through addition to an olefin with the position of the attack being determined by steric effects:²⁶



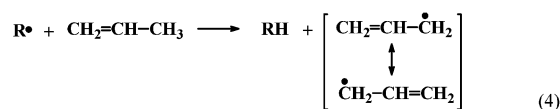
Similar addition reactions leading to ring-opening have been reported for cyclopropane.²⁷ A possible initial step can be formulated as



In the solid phase, the relative orientation of the reaction partners is largely fixed. The reaction probability thus depends on local structure. This may prevent the reaction from taking place or may enable a sterically less favorable reaction such as

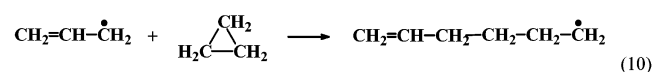
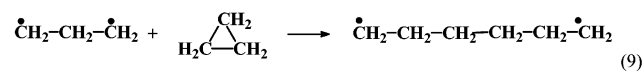
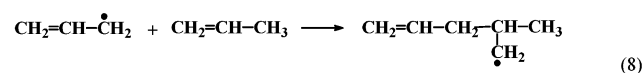
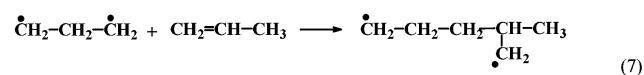
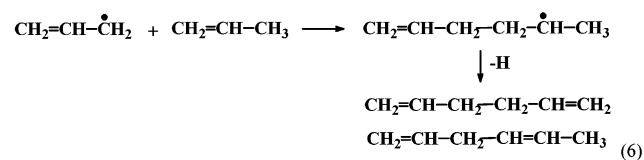
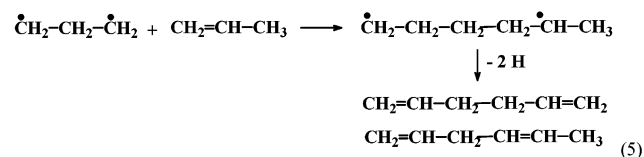


Transfer of a H atom from propene to a radical may, on the other hand, lead to the formation of the allyl radical, which is stabilized by the mesomeric effect:

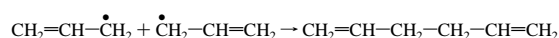


Because of this reaction, the radical-initiated polymerization of propene is known to be very slow.²⁶

According to the photochemical reaction scheme (Figure 5) the biradical (II) and the allyl radical (IV) are the most immediate products of cyclopropane (I) and propene (III). Assuming that they are also formed in the solid phase, following an excitation induced by electron impact, these radicals could attack adjacent molecules, which are most likely cyclopropane or propene, according to one of the reactions (1)–(3). Double bonds could then be formed by subsequent hydrogen abstraction. As the sample initially contains only C₃ units, the smallest compound capable of containing two double bonds must be C₆ units, (i.e., a dimer). Such a dimer can be formed according to the following addition reactions:



Hydrogen abstraction steps following reactions (7)–(10) are analogous to the sequences (5) and (6) and are therefore not explicitly included. In addition, the dimerization of two of the initial radicals is possible. For example, the allyl radical (IV) can directly form a diene:



Under the present reaction conditions, such a step is rather

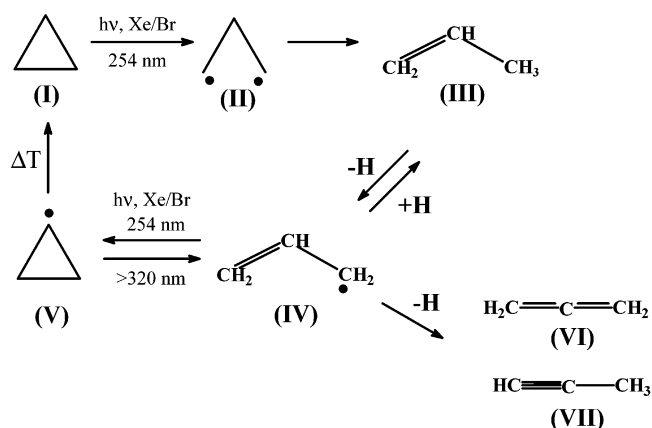


Figure 5. Schematic of photochemical reactions of matrix-isolated cyclopropane according to refs 18 and 25.

unlikely because the allyl concentration within the solid sample presumably remains small during electron irradiation.⁹

The schemes listed above have been selected to illustrate all possible products of reactions that may occur in a mixture of cyclopropane and propene after formation of an initial radical. In general, energetic considerations may be used to discriminate between more or less likely reactions. On the other hand, such arguments are difficult to apply here because of the conditions under which the reactions take place. Thermochemical data are only available for temperatures considerably above that of the present experiment and depend strongly on the molecular environment.²⁸ They are therefore not representative of the condensed phase at cryogenic temperatures. One may also try to apply threshold arguments to comment on the overall likelihood of the above-mentioned reaction schemes. Rupture of a C–H or C–C bond requires an energy between 4.0 and 4.5 eV.²⁹ Therefore, at $E_0 = 15$ eV, enough energy should be available to produce the initial radical and to overcome activation barriers for additional reactions as exemplified by the activation energy of propagation in free radical polymerization of 23.4 kJ/mol (0.24 eV) for gaseous propene.²⁸ On the other hand, simple threshold arguments may not be valid because the electron does not necessarily transfer all of its energy to the sample. Also, the probability that an electron–molecule encounter indeed leads to bond rupture depends strongly on E_0 . For example, C–H rupture becomes noticeable only around 10 eV as evidenced by the formation of H[−] from solid hydrocarbons.³⁰ These considerations, together with the fact that kinetic factors arising from the fixed orientation of the reaction partners in the solid must strongly influence the reaction rates, show that it is difficult to accurately judge the relative likelihood of the reactions (1)–(10) from energetic arguments. These reactions nevertheless provide a valid basis for discussing the mechanism of conjugated diene formation under electron exposure.

None of the reaction schemes above can explain the formation of two conjugated double bonds in the dimer. If the same reaction mechanisms apply, this conclusion is equally valid for larger oligomers where the radical sites or double bonds are even further apart. Oligomerization has also been observed in high-energy radiolysis experiments, but the products contained only one unsaturated bond.³¹ In this case, ionization is thought to lead to a cationic addition reaction. However, because high-energy radiation produces copious amounts of secondary low-energy electrons, radical reactions are also likely to occur under high-energy particle radiolysis. On the other hand, as electrons with an energy of 15 eV can already ionize the sample to some extent, cationic species may also be involved in the reactions

observed in the present experiments. An analysis similar to the one performed above for the radical reactions nevertheless shows that production of a conjugated diene unit via a cationic mechanism is also not expected.

A reasonable explanation for the appearance of doubly unsaturated molecules with conjugated double bonds requires at least a two-step mechanism. The formation of dimers or larger oligomers proceeding through one of the reaction steps (5)–(10) is followed by one or two subsequent H-abstraction steps as the sample is continuously under the effects of electrons. In fact, the importance of such subsequent reaction steps within a molecular sample can be recognized as follows. Suppose that a target, composed of a total number of molecular sites (M), has been exposed to a given total number of electrons (N). The average number of electrons per site is given by $\langle n \rangle = N/M$, where both N and M are large numbers (i.e., $\sim 10^{10}$ – 10^{15}). The probability that a site is hit by one individual electron is thus defined as $1/M = \langle n \rangle/N$. Now we assume that each electron is lost or may escape from the sample after a hit event that reactively modifies the site with the probability $x = p/M = p\langle n \rangle/N$, where $p \ll 1$ represents a branching ratio. Similarly, the probability that the site is not modified is $y = 1 - x$. Considering further that the individual probabilities x for different electrons are independent of each other, the combined probability that a site is modified by 1, 2, 3, ..., or n electrons after the whole target has been exposed to N electrons is given simply by the Poisson distribution

$$P(n) = e^{-p\langle n \rangle} (p\langle n \rangle)^n / n!$$

which applies to infrequent events. For instance, consider an electron beam of $\sim 5 \times 10^{-10}$ A impinging uniformly within an area of ~ 0.0025 cm² onto a 5-layer molecular film ($\sim 2 \times 10^{15}$ molecules/cm²) for 180 min (i.e., $\langle n \rangle = 5$). Taking the sum of cross sections of all possible events occurring at a site for a given incident energy as $Q_T = 5 \times 10^{-16}$ cm² $\sim 1/(2 \times 10^{15}$ molecules/cm²) along with the relatively smaller branching ratios p for a transformation given by $p = Q_p/Q_T \sim 0.02$, with Q_p typically $\sim 1 \times 10^{-17}$ cm²,^{2,17,20} we have for $P(2) \sim 0.005$. In other word, after 180 min electron exposure, the number of molecular sites that have been modified by two electrons amounts to about 0.5% of the total number of molecular sites M , which is a significant percentage in the context of the present experiment. Considering the additional contributions originating from 3, 4, and more electrons hitting a site (i.e., $P(3)$, $P(4)$, ...) can only increase the yield. Besides, multiple scattering is expected to increase the yield as well, because each electron does not necessarily lose all of its energy after a single hit event.

The above considerations underline that at least a two-step mechanism is required for the formation of the final product and likely under the present experimental conditions. Rupture of CH bonds, which can occur statistically within the molecule, may thus introduce additional unsaturated bonds at different locations including the bonds in conjugation with the original double bond. A similar effect can be produced if hydrogen migration occurs so that the radical or unsaturated sites move closer to each other. The present results do not allow differentiating between these possibilities. Nevertheless, the comparison with known radical chemistry allows us to deduce that at least a two-step mechanism is required to produce the conjugated diene observed in the present electronic HREEL spectra.

5. Conclusions

The electron-induced isomerization of cyclopropane to propene in the condensed phase was monitored by HREEL

spectroscopy in the range of both vibrational and electronic excitations. Although propene is the primary product of this reaction, it is shown unequivocally here that longer chains are also formed. This oligomerization, which produces doubly unsaturated species as obvious from the observation of an electronic band characteristic of a conjugated diene unit, possibly proceeds via intermolecular reactions of intermediate radical species with their immediate surroundings. This study not only provides a more comprehensive picture of the reactions that occur in solid films of cyclopropane but also gives a direct proof of the formation of bonds under low-energy electron irradiation at very low temperature. More generally, this shows that electron-induced reactions in solid cyclopropane do not only lead to the fragmentation of molecules but also can be used to produce longer chains and networks of molecules within a solid.

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