Dimerization and Polymerization of Isoprene at High Pressures

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The high-pressure reactivity of isoprene has been studied at room temperature up to 2.6 GPa by using the diamond anvil cell technique in combination with Fourier transform infrared spectroscopy. Both dimerization and polymerization reactions take place above 1.1 GPa. At this pressure, the two processes are well separated in time, the dimerization being the only one occurring in the first 150 h. Both processes simultaneously occur as the pressure increases. The reaction product is composed of a volatile fraction, identified as sylvestrene, and a transparent rubberlike solid formed by *cis*-1,4- and 3,4-polyisoprene. The activation volume of the dimerization reaction has been obtained from the kinetic data. The photoinduced reaction, studied at room temperature for two different pressures, takes place through a two-photon absorption process, and the threshold pressure is lowered to 0.5 GPa. At this pressure, both the dimerization and polymerization processes occur, but the dimerization is not as selective as in the purely pressure-induced reaction. 4-Ethenyl-2,4-dimethylcyclohexene is obtained in addition to sylvestrene. By increasing the pressure, the photoinduced reaction becomes more selective, and the monomer is quantitatively transformed into the same polymer obtained in the purely pressure-induced reaction.

1. Introduction

The high-pressure instability of molecular systems in condensed phases has recently attracted great interdisciplinary interest for its important implications in chemistry, physics, and geo- and material sciences.[1,2] The structural and electronic changes induced in these highly compressible materials by a pressure increase can be pushed until the redistribution of the electronic densities gives rise to a chemical reaction. The extended covalently bonded solids obtained by compressing N_2[3−5] and CO_2[6−8] are spectacular examples of chemical reactions, fully reversible with the pressure release, requiring rather extreme pressure and temperature conditions to occur. Irreversible transformations have been reported under milder conditions for simple unsaturated hydrocarbons[1,2] in which, as a consequence of the geometrical constraints set by the high density and as a consequence of the relevant changes in the electronic structure, new reaction pathways have been observed or a higher selectivity introduced in comparison to ambient pressure conditions. The activation of chemical reactions in molecular compounds due to the mixing of electronic states tuned by the pressure increase was first suggested by Drickamer et al.[9] On this basis, it can be understood that the same effect can be, in principle, realized at lower pressure through a selective excitation of the particular electronic excited-state involved in the reaction.[10] It has been indeed shown in several high-pressure reactions that an optical activation is extremely efficient in lowering the threshold pressure and increasing the extent of the reaction,[11,12] two relevant features in view of practical synthetic applications. Moreover, irradiation may also select a specific process among alternative reaction paths.[13]

Among the hydrocarbons studied so far, the behavior of the simplest unsaturated molecules, which are the monomeric units of some of the most important commercial polymers, is of particular interest. Ethylene spontaneously polymerizes in the crystal phase above 3 GPa,[14] but the reaction can also be activated by irradiating the liquid at 0.7 GPa by visible or near-ultraviolet laser light.[15] A completely different behavior is exhibited by propene, whose reactivity under pressure was expected to be of interest for the possibility of inducing some selectivity in the position of the methyl groups with respect to the molecular backbone. Their position determines the stereochemistry and then the mechanical properties of the resulting polypropenes. In this case, the polymer formation was never observed at high pressure, despite the different $P-T-h\nu$ conditions explored to trigger the reaction,[16] the product always being composed by a mixture of linear oligomers. The selectivity that can be achieved at high pressure has been nicely demonstrated in the case of butadiene, the simplest conjugated molecule and also the prototype for the Diels−Alder dimerization. In the liquid phase at 0.7 GPa, butadiene quantitatively dimerizes into vinylcyclohexene, but under laser irradiation at 488 nm in the same pressure regime, a conformationally pure *trans*-polybutadiene is the only product.[13]

Isoprene is the last important monomer of this series. It is the basic structural unit of some important natural oligomers, such as the terpenes (essential oils, steroids, carotenoids), and of natural polymers such as caoutchouc (*cis*-1,4) and gutta-percha (*trans*-1,4). Also in the case of isoprene, a competition between dimerization and polymerization exists, but only a few studies on the effect of pressure on the reaction have been performed.[17−19] Furthermore, the presence of a methyl group represents a marker to test the stereochemistry of the reaction and offers the possibility to relate this behavior to the homologous butadiene, as has been done for ethylene and propene.[16] The polymerization of isoprene under pressure, and especially the effect of different catalysts, was studied a very long time ago.[17] Freshly prepared samples were found to partly react, in the absence of any catalyst, only at 1.2 GPa. Neither the polymer

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nor the volatile fraction obtained were characterized. In a more recent study, performed with HI as a catalyst, an increase in the polymerization rate with pressure was reported, but although the amount of *cis*-1,4-polyisoprene decreases, the amounts of both *trans*-1,4 and, to a lesser extent, the 3,4 isomers increase with pressure.[18] The dimerization reaction is also strongly accelerated by compression, and the activation volumes obtained at different temperatures suggest a diradical open chain cyclic transition state.[19] Among the different isomers that can be obtained by the dimerization of isoprene, the main products are those resulting from a $[4\pi + 2\pi]$ cycloaddition: the 1-methyl-4-(1-methylethenyl)-cyclohexene, commonly called limonene or dipentene, and 1-methyl-5-(1-methylethenyl)-cyclohexene, also known as sylvestrene or diprene. Only the latter forms near room temperature, whereas a temperature increase results in a lower selectivity of the reaction and both dimers are obtained.[20,21] A pressure increase seems to have the same effect as a temperature decrease, favoring the formation of sylvestrene,[19] but this result is still controversial. The final product of the dimerization is actually fundamental to understand the structure of the diradical intermediate.

In this work, we have studied the pressure-induced reaction in pure isoprene without using any stabilizer or inhibitor. The kinetics of the dimerization reaction has been investigated at room temperature for four different pressures between 1.1 (the reaction threshold pressure) and 2.6 GPa. We have also employed a photochemical activation to trigger the reaction at lower pressure, succeeding in inducing a selective polymerization.

2. Experimental

A membrane diamond anvil cell equipped with IIa type diamonds was employed to pressurize the pure isoprene samples. The sample was contained by a stainless steel gasket, and its initial dimensions were on the order of 150 μm in diameter and 45 μm in thickness. The liquid isoprene (purity >99% from Aldrich) employed for the experiment contained ~0.02% of *p-tert*-butylcatechol to prevent polymerization. In order to avoid the loading of this inhibitor and exploiting the high volatility of isoprene, we fluxed helium, which acted as gas carrier, through the isoprene vapor to get the condensation of the latter onto the diamonds well below its melting point (131 K) in a nitrogen atmosphere. After closing the cell, care was taken to maintain liquid isoprene at an initial pressure not exceeding 0.5 GPa. The pressure was measured by the ruby fluorescence method using the second harmonic emission line (532 nm) of a diode-pumped Nd:YAG laser as the excitation source. The laser power was reduced to 0.2 mW to avoid unintended photochemical effects. FTIR absorption measurements, with an instrumental resolution of 1 cm^{-1}, were performed with a Bruker-IFS 120 HR spectrometer specifically modified for high-pressure measurements.[22,23] The laser-assisted high-pressure reactions were triggered by using the blue lines of an Ar ion laser with power ranging from 50 to 610 mW. The laser beam was focused onto the sample by using a 200 mm focal length, and the sample was displaced by the exact focal point in order to homogeneously irradiate the whole sample.

3. Pressure-Induced Reaction

The samples loaded in the cell did not show any transformation, even after 2−3 days when kept at ambient temperature and pressures below 1 GPa. Neither *p-tert*-butylcatechol nor any other chemical was detected in our loaded isoprene samples. Pressure was raised in steps of ~0.1 GPa, and for each step,
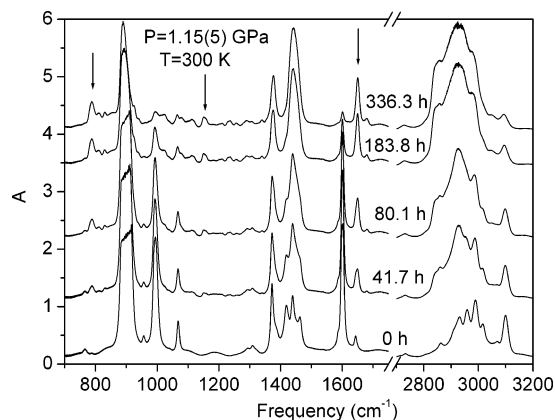

Figure 1. IR spectra recorded during the room temperature reaction of isoprene at 1.15 GPa. The first spectrum (0 h) of the kinetics is entirely due to the monomer and is measured just after the pressure of the experiment has been set. The arrows indicate the absorption bands of the product that do not overlap with monomer peaks.

the IR spectrum was monitored over a time interval ranging from 10 to 24 h. The first spectral changes, indicating the occurrence of a chemical transformation, were detected at ~1.1 GPa, in agreement with previous reports in which a threshold of 1.2 GPa was reported.[17,18] At the onset of the reaction, we detected a drop in the sample pressure that was compensated by increasing the helium pressure in the membrane. The pressure was equilibrated in a few tens of seconds, and its oscillation did not exceed 0.05 GPa. This behavior clearly indicates that a denser material than isoprene is formed, thus suggesting that oligomerization, polymerization, or both processes take place. In Figure 1 the evolution of the IR spectrum with time at 1.15 GPa is shown. The best evidence of the reaction is provided by the weakening with time of the strong absorption peaks of the monomer at about 900 ($=CH_2$ wagging and twisting), 1000 ($-CH$ wagging), and 1600 ($C=C$ a-stretching) cm^{-1}. In all the other spectral regions, such as around 1400 ($-CH_3$ bending and $=CH_2$ scissoring) and 3000 ($-C-H$; $=C-H$ stretching) cm^{-1}, the bands of the monomer and the products overlap, thus making it difficult to extract qualitative information on the reaction evolution. The almost complete disappearance of the two monomer bands at 1000 and 1600 cm^{-1} indicates that the reaction is almost quantitative, and only a minimal amount of monomer remains once the equilibrium for the reaction is reached (after more than 300 h at 1.1 GPa). We studied the pressure-induced reaction at four different pressures: 1.15 (5), 1.47 (3), 1.91 (9) and 2.60 (8) GPa. The pressure values of the four kinetics have been obtained by averaging all the pressure measurements performed during the entire experiment; the standard deviations are also reported in parentheses. The four experiments have been performed in a quite narrow pressure range because of the strong increase in the reaction rate with rising pressure. As will be shown in the following, the equilibrium is reached in 2−3 h at 2.6 GPa, and a good sampling of the propagation step is mandatory to provide reliable kinetic data. Our FTIR measurements were typically separated by ~10 min, which was the time necessary to measure the spectrum with a good signal-to-noise ratio and to check and adjust the sample pressure.

3.1. The Reaction Product. The products recovered from all the experiments show the same IR absorption spectrum, indicating that the same materials form in the whole pressure range investigated. Before opening the cell, the product appears homogeneous and transparent because a residual pressure is still applied to the sample, but when the cell is opened, most of the
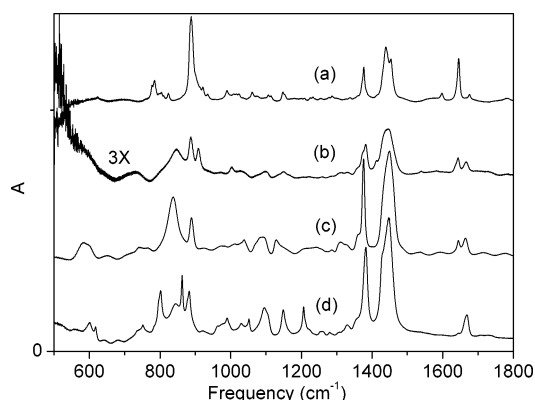
Figure 2. IR spectra of the products recovered from the reaction at 1.15 GPa. From the top: (a) spectrum measured on the closed cell (both volatile and solid fractions contribute), (b) recovered solid product (the absorbance values have been multiplied by a factor of 3), (c) commercial 1,4-*cis*-polyisoprene, and (d) commercial 1,4-*trans*-polyisoprene.
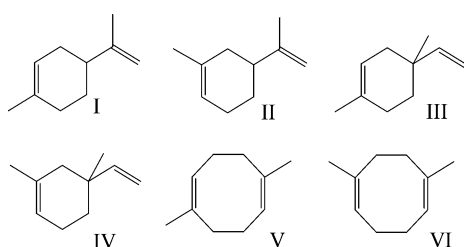

Figure 3. Dimerization products attainable from a $[4\pi + 2\pi]$ (I−IV) and $[4\pi + 4\pi]$ (V and VI) cycloaddition of two isoprene molecules.[24] I, limonene; II, sylvestrene; III, 4-ethenyl-1,4-dimethylcyclohexene; IV, 4-ethenyl-2,4-dimethylcyclohexene; V, 1,5-dimethylcycloocta-1,5-diene; and VI, 1,6-dimethylcyclooocta-1,5-diene.

sample is lost, and a rubberlike transparent solid remains on the diamonds. In Figure 2, the spectra of the products obtained in the 1.15 GPa reaction before and after opening the cell are shown along with the spectra of two commercial polyisoprenes. The spectrum labeled as (a) in Figure 2 is the superposition of the volatile and the solid fractions; spectrum (b) is due to the solid product only. The relative amount of volatile and solid products cannot be exactly determined, but the comparison of the two spectra clearly reveals that the former is dominant. The spectrum of the volatile fraction indicates the presence of a negligible amount of unreacted isoprene. Therefore, according to the literature data,[20] it is reasonable to assume that this part of the product is mainly composed of a mixture of dimers. Among the more abundant and stable dimers (see Figure 3), previous high-pressure studies showed that only limonene (I) and sylvestrene (II) form at high pressure, the latter being progressively favored by a pressure increase,[19] even though another study reports that limonene formation is favored by compression.[18] The comparison among the IR spectra of the volatile product and the possible dimers allows one to rule out the presence of linear as well as four- ($[2\pi + 2\pi]$ addition) and eight-membered (V and VI) cyclic dimers. Our analysis is, therefore, restricted to six-membered cyclic dimers whose IR spectra are qualitatively very similar to one another and to the spectra of the volatile fractions recovered in all our high-pressure experiments. In the upper panel of Figure 4, we report as an example the comparison between the IR spectrum of the volatile compound and those of commercial limonene (from Fluka >98%) and sylvestrene.[24] Despite the close resemblance among the three spectra, some insight about the nature of the dimer formed in the DAC can be gained by analyzing in more detail
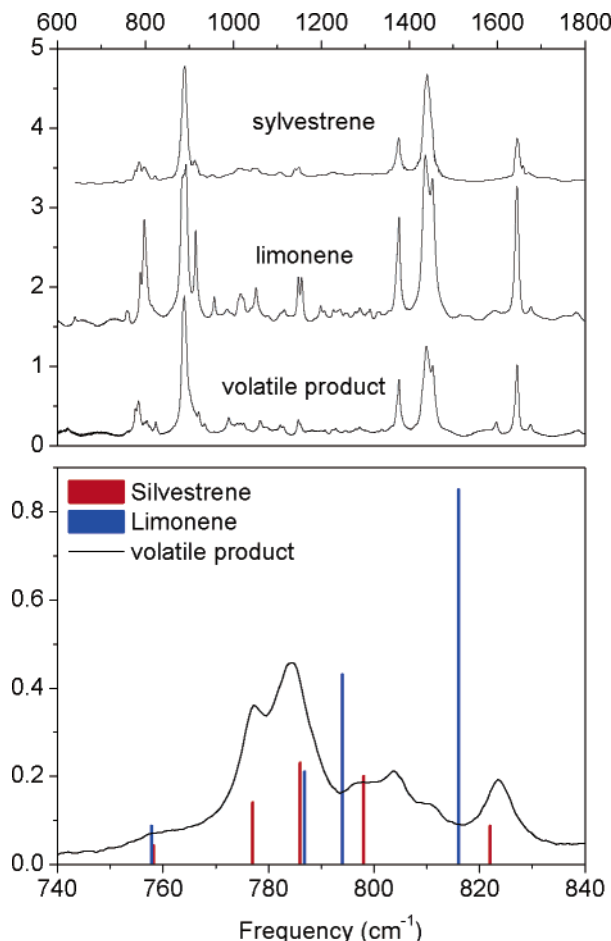

Figure 4. Upper panel: IR spectrum of the volatile fraction (difference spectrum between spectra (a) and (b) of Figure 2) recovered from the reaction at 1.15 GPa as compared to those of sylvestrene (from ref 24) and of commercial limonene. Lower panel: detail of the more diagnostic spectral region as compared to the lines of limonene and sylvestrene.

the region below 850 cm^{-1}. In the lower panel of Figure 4, together with the spectrum of the volatile product, the position of the lines of limonene and sylvestrene[24] are reported with their experimental intensities as vertical bars. A much better agreement between the spectrum of the volatile product and that of sylvestrene, rather than with the limonene one, is noticed, allowing the identification of sylvestrene as the main volatile product of the reaction.

The comparison among the IR spectra of the solid fraction and commercial polyisoprenes (see Figure 2) reveals strong similarities between the spectra of the high-pressure-synthesized solid material and that of 1,4-*cis*-polyisoprene, especially in the fingerprint region. In this spectral region, the differences from the 1,4-*trans*-polyisoprene spectrum are quite pronounced, allowing one to rule out a massive presence of this latter polymer in our recovered sample. Nevertheless, two clear and systematic differences between our recovered solid samples and 1,4-*cis*-polyisoprene occur in all the spectra: the band measured at 909 cm^{-1} is missing in the 1,4-*cis*-polyisoprene spectra, and the 1650 cm^{-1} doublet has reversed relative intensities. The latter of these two differences can be explained by the presence of 3,4-polyisoprene in the recovered polymer synthesized at high pressure. In fact, the spectral peculiarity of 3,4-polyisoprene is the single band at ∼1644 cm^{-1}[25] that overlaps with the low-frequency component of the 1,4-*cis*-polyisoprene doublet. The superposition of the two contributions can give rise to the observed intensity ratio. The relative intensity of this doublet
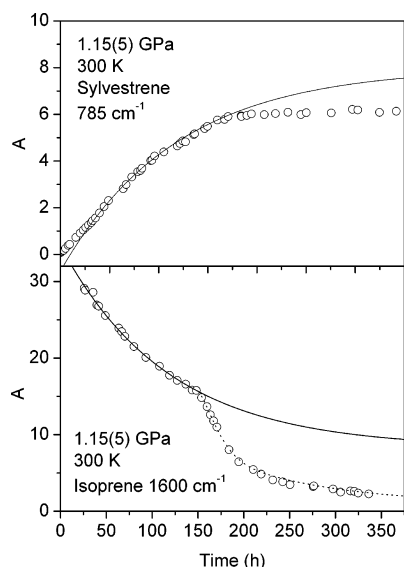
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Figure 5. Upper panel: time evolution of the integrated absorbance of the 785 cm^{-1} band of sylvestrene at 1.15 GPa. The full line is drawn according to a second-order kinetic law (eq 1). Lower panel: time evolution of the integrated intensity of the C=C stretching mode of isoprene at 1600 cm^{-1}. The full line is drawn according to a second-order kinetic law (eq 1) by using the rate constant obtained from the fit of the 785 cm^{-1} line of sylvestrene (see upper panel). The dashed line is drawn by summing the contributions due to the dimerization and polymerization processes simultaneously occurring for $t > 150$ h. We used the Avrami law to describe the polymerization: $A_p(t) = B(1 - e^{-k_p t^n})$, where k_p is the rate constant of the polymerization and n is a parameter depending on the nucleation law and growth geometry.[26]

further supports the absence of 1,4-*trans*-polyisoprene that exhibits a doublet with most of the intensity on the high-frequency component. The band observed at 909 cm^{-1} in the recovered sample spectrum is a characteristic band due to the =CH$_2$ wagging mode of the vinyl group that can be present as a chain substituent as a consequence of a 1,2 addition. Finally, the spectra of the polymeric products from all our experiments are identical, indicating the obtainment of the same material at all the probed pressures. This latter result is in contrast with a previous report[18] in which the amount of *cis*-1,4 polymer was observed to decrease with rising pressure in favor of a larger amount of *trans*-1,4 and, to a lesser extent, 3,4-polyisoprene.

3.2. Kinetic Analysis. The two bands at 778 and 785 cm^{-1}, reported in the lower panel of Figure 4 and assigned to sylvestrene, are the only bands of the dimer not overlapping with the polymer absorptions. The high-frequency peak is the only one detectable since the beginning of the reaction. The time evolution of its integrated absorption was used to study the kinetics of the dimerization process at the different pressures. The intensity decrease of the C=C stretching band of isoprene at 1600 cm^{-1} can also be followed up to the end of the reaction, but in this case, both the dimer and the polymer formation contribute to its evolution. In addition, the data at the very beginning of the reaction are missing because the band saturates the absorption. However, its analysis provides some interesting insight in the reaction dynamics. In the upper panel of Figure 5, the time evolution of the integrated intensity of the sylvestrene band at 785 cm^{-1} is reported for the reaction at 1.15 GPa, whereas in the lower panel, we present the intensity decrease with time of the monomer peak at 1600 cm^{-1} measured in the same experiment. In this latter Figure, it can be observed that 150 h after the onset of the reaction, the decrease of the monomer concentration exhibits a sudden acceleration that does not have a counterpart in the amount of formed dimer. This
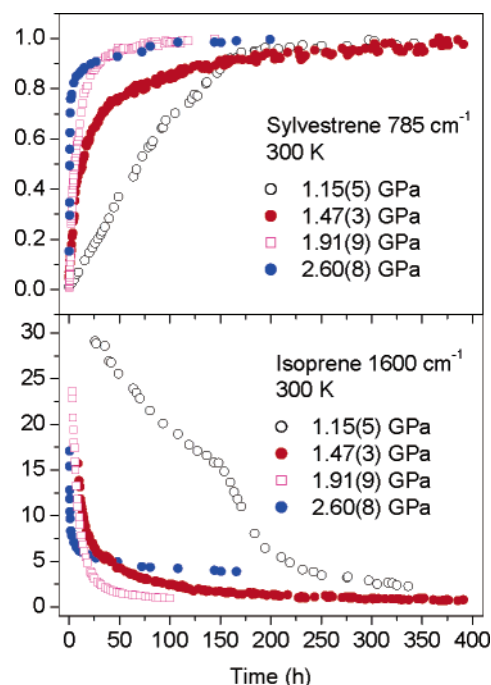

Figure 6. Upper panel: room temperature time evolution of the normalized integrated absorbance of the 785 cm^{-1} mode of sylvestrene at all the pressures investigated in the present work. Lower panel: corresponding data for the isoprene band at 1600 cm^{-1}.

result can only be explained by the opening of a new reaction channel giving rise to the polymer formation, the only other identified product. This behavior is interpreted on the basis of a temporal separation between the dimerization and the polymerization processes. It is worth commenting that the separation of the two processes could be achieved in ambient pressure experiments only through the employment of picric acid as a partial inhibitor of the polymerization process.[27] When the reaction kinetics is probed at pressures higher than 1.15 GPa, the time evolution of the monomer absorption (see lower panel of Figure 6) does not show the slope change observed at 1.15 GPa, revealing the overlapping in time of the dimerization and polymerization processes. According to the kinetic curves reported in the upper panel of Figure 6, an acceleration of the dimerization on rising pressure is evident, a qualitative indication of a negative activation volume.

To extract quantitative information about the mechanism of the dimerization reaction, a fit of the kinetic curve has to be performed. The fit of the data measured at 1.15 GPa is extremely difficult due to the presence of a nucleation step responsible for the observed sigmoidal shape at short reaction times and the activation of the polymerization reaction that stops the dimerization at 150 h (see Figure 5). We therefore first reproduced the curves measured at higher pressures using both a first- and a second-order kinetic laws. A much better agreement is obtained by using a second-order kinetics (see Figure 7) according to the relation

$$A(t) = \frac{2k_d A_{inf}^2 t}{1 + 2k_d A_{inf} t} \qquad (1)$$

where k_d is the rate constant of the dimerization process and $A(t)$ and A_{inf} are the integrated absorbance at time t and at the equilibrium, respectively. A second-order kinetics was also reported in previous studies performed at higher temperature up to 0.8 GPa.[19] A first-order process is absolutely unsuitable

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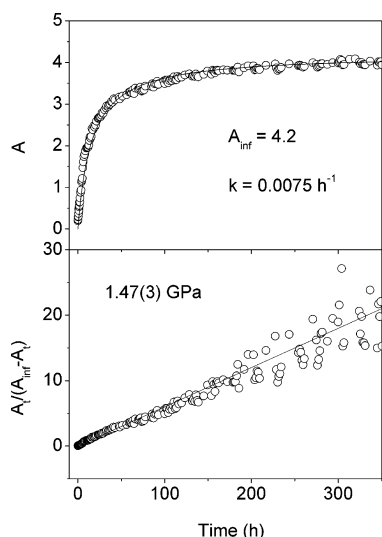
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Figure 7. Upper panel: time evolution of the integrated absorbance of the 785 cm^{-1} mode of sylvestrene at 1.47 GPa. The full line is the best fit to a second-order kinetic law (eq 1). The rate constant, k, and the asymptotic ($t = \infty$) absorption value (A_{inf}) obtained from the fit are also reported. Lower panel: linear fit of the time evolution of (A_t/A_{inf} − A_t) according to a second-order kinetics (A_{inf} is obtained from the fit shown in the upper panel).
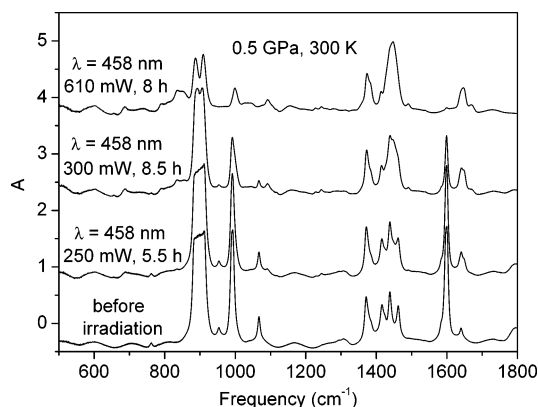

Figure 8. Evolution of the IR spectra upon successive irradiation cycles (from bottom to top) performed on the same sample by using the 458 nm Ar$^+$ laser line at room temperature and 0.5 GPa.

at 1.47 GPa, but it gives an increasingly better agreement with increasing pressure, thus suggesting a lowering of the reaction order on compression. A second-order law was finally employed to fit also the 1.15 GPa kinetics. A satisfactory fit up to 150 h (see Figure 5) could be obtained with different sets of k_d and A_{inf} values; therefore, we extracted from the fit the minimum and maximum rate constant values to be employed to calculate the activation volume of the reaction.

4. Laser-Assisted High-Pressure Reaction

The effect of laser irradiation on the threshold pressure of the reaction and a comparison between the purely pressure-induced and the laser-assisted reactions have been pursued to verify if a greater selectivity could be introduced by a photochemical activation of the reaction. Two room-temperature experiments have been performed at 0.5 and 1.1 GPa. In Figure 8, the IR spectra measured after different irradiation cycles at 0.5 GPa are reported. At this pressure, the sample is stable at least on a scale of several days. An irradiation of several hours with some tens of milliwatts of the 488 nm line does not cause any change in the IR absorption spectrum, allowing one to rule
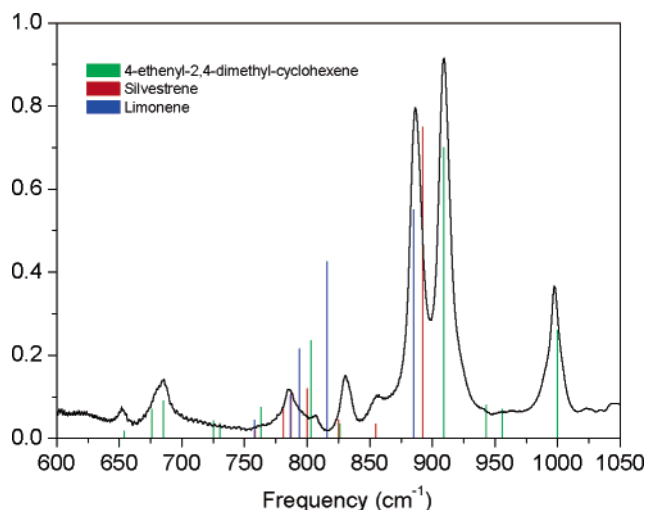

Figure 9. Comparison between the IR spectrum of the volatile fraction obtained in the photoinduced reaction at 0.5 GPa and the bands position and intensity for limonene, sylvestrene, and 4-ethenyl-2,4-dimethyl-cyclohexene (from ref 24).

out any sample transformation. If the 458 nm line is employed, minimal changes are observed in the spectrum, even after quite long irradiation cycles and a laser power set to 250 mW. When the irradiation power is raised to 300 mW, a sudden intensity decrease of the monomer bands and the formation of new bands are observed. The absorption at 458 nm likely takes place through at least a two-photon process, since the electronic origin of the $S_0 \rightarrow S_1$ transition is located around 240 nm at ambient conditions.[28] Once the laser power on the sample is raised to 610 mW, the reaction is completed in a few hours (almost complete disappearance of the monomer bands), but 340 h is necessary at 1.1 GPa in the purely pressure-induced reaction to reach the reaction equilibrium at which the strongest bands of the monomer are still clearly detected. This result is quite general, since the lowering of the threshold pressure and an overall acceleration of the reaction have been reported for all the unsaturated organic molecules whose reactivity under pressure and laser irradiation have been studied so far.[2] Particularly important is the comparison of the products obtained from the two laser-assisted experiments with those recovered from the purely pressure-induced reaction. The macroscopic result is that under irradiation at 0.5 GPa, a volatile and a solid fraction are recovered, as in the purely pressure-induced reaction, but at 1.1 GPa, only the solid polymer is obtained. The comparison between the IR spectra of the volatile fractions obtained with and without laser activation reveals important differences. In Figure 9, we compare the IR spectrum of the volatile fraction in the region below 1050 cm^{-1}, the more diagnostic to identify the dimer formed, with the experimental absorption frequencies and intensities[24] of the dimers I, II, and IV (see Figure 3). The IR spectrum of dimer III was not available in the literature; therefore, it was calculated[29] but not reported here because it was not distinguishable from that of dimer IV. The result of this analysis shows that the volatile product is mainly composed of 4-ethenyl-2,4-dimethylcyclo-hexene (or 4-ethenyl-1,4-dimethylcyclohexene), even though the presence of sylvestrene, to which the low-frequency peak of the main doublet at 900 cm^{-1} is assigned, is still consistent. At 1.1 GPa, in the same irradiation conditions, we observe the quasicomplete polymerization of isoprene without evidence of a volatile fraction. Contrary to what was observed for the volatile fraction, the polymers obtained in all the reactions studied in
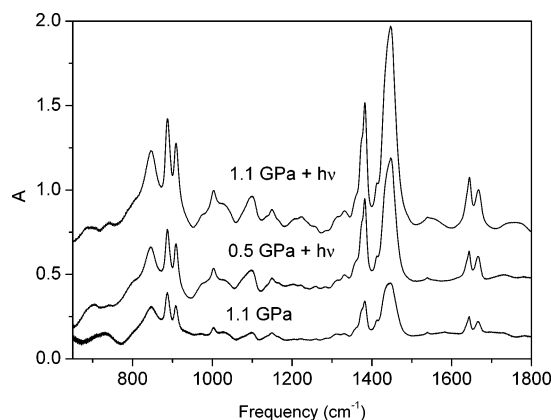
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Figure 10. Comparison among the IR spectra measured at ambient conditions of the polymers recovered from the photoinduced reactions (0.5 and 1.1 GPa) and from the purely pressure-induced reaction at 1.1 GPa. Since the starting amount of monomer is approximately the same in all the experiments, the higher intensity of the IR spectrum of the solid recovered from the photoassisted reaction at 1.1 GPa is uniquely related to a larger polymerization yield.

this work, by pure compression or in combination with laser activation, are always the same, as shown in Figure 10.

5. Discussion

Sylvestrene is by far the most abundant product of the dimerization of isoprene when the reaction takes place at close to ambient conditions. With an increase in the temperature, the reaction becomes less selective, and the amount of limonene, and to a lesser extent also of the other dimers, increases.[20] On the other hand, experiments performed above 330 K show an increasing selectivity with an increase in the pressure in favor of sylvestrene formation with respect to all the other isomers.[19] Under all the conditions described above, limonene is always the main byproduct of the reaction. In this work, we have studied the pressure-induced reaction at ambient temperature, and no indication of the presence of limonene among the recovered product is gained by the IR spectra. According to Figure 4, the presence of limonene should be revealed by a strong absorption peak just above 800 cm^{-1}. Dimers III and IV were also not detected. In a previous study, the abundance of limonene was reported to decrease with increasing pressure, but it was still on the order of 8% at 0.8 GPa,[19] an amount that should be perfectly detectable in our spectra. This relevant difference with our results can only be ascribed to the lower temperature of our experiment.

The dependence of the rate constant, k, upon pressure at constant temperature is given by

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^{\neq}}{RT} \qquad (2)$$

where, according to the transition state theory, $\Delta V^{\neq}$ is the activation volume of the process. In Figure 11, we have reported the evolution of the ln k values for the dimerization reaction as a function of pressure. The nonlinear evolution of the ln k values with pressure was reproduced by a parabolic law[16,30],

$$\ln k = a + bP + cP^2$$

with $a = -15$ (2), $b = 7.7$ (9) GPa^{-1}, and $c = -1.3$ (6) GPa^{-2}. By using this quadratic dependence of ln k on P, the activation volume at any pressure is obtained.
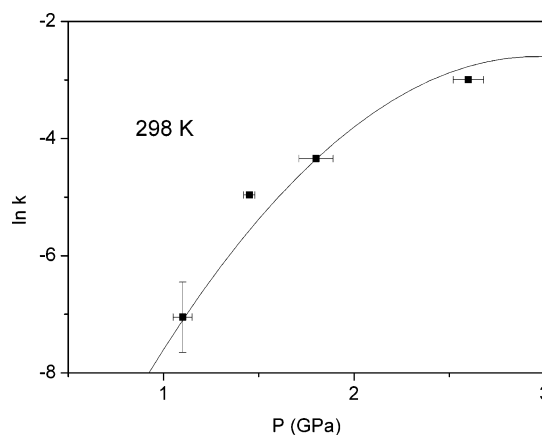
$$\Delta V^{\neq} = -(b + 2cP)RT$$

Figure 11. Quadratic fit of the values of ln k as a function of pressure at ambient temperature. The bar reported with the ln k value at 1.15 GPa represents the range in which the rate constant can be varied to obtain a satisfactory fit of the experimental data (see text).

$\Delta V^{\neq}$ is found to be -24.3 cm^3 mol^{-1} at atmospheric pressure, in remarkable agreement with the values obtained at 60 and 75 °C up to 0.5 GPa, where the evolution of ln k was found to be linear with pressure.[19] The $\Delta V^{\neq}$ value decreases to -16.1 cm^3 mol^{-1} at 1 GPa, -7.9 cm^3 mol^{-1} at 2 GPa, vanishing at ∼3 GPa, and then becoming positive at higher pressures. The reaction is, therefore, strongly accelerated by compression at relatively low pressures, but this effect reduces when the pressure is increased until the process is retarded by further compression above 3 GPa. This result, deriving from an interplay between the effects of the increased density on the reactants and on the transition state, is extremely useful to understand the reaction mechanism. The ambient pressure value of $\Delta V^{\neq}$, about one-half of the over-all volume change, was taken as evidence for an open-chain diradical intermediate.[19] The mechanism should, therefore, be composed of two steps: the formation of the open-chain intermediate, which according to the second-order kinetics is the rate-limiting step, and its closure. The decrease in the $\Delta V^{\neq}$ value with an increase in the pressure indicates that this mechanism is still valid when the pressure is increased, ruling out the possibility that a cyclic transition state is favored at high pressure. In addition, this conclusion is also supported by the lowering of the reaction order with increasing pressure. This latter result is worth being discussed in further detail, taking into account the different effects played by the high density on the two reaction steps.

The first step is probably not much affected by the higher density that on one hand causes a minor diffusivity, which implies a reduction in the reaction rate, but this effect is balanced by a progressive reduction in the intermolecular distances. As a consequence, the lowering of the reaction order is probably more closely related to the increased difficulty in the reorientation of the intermediate to give rise to the ring closure. Another important result supporting the open-chain intermediate mechanism is represented by the product of the dimerization reaction. Some of the possible paths leading to the four main products reported in the literature are sketched in Figure 12 under the assumption that the isoprene molecules are in the trans conformation (at ambient conditions, the cis conformer is ∼10% of the population[31]). Moreover, a [4 + 2] interaction geometry is assumed because this is the most effective to give rise to six-membered ring products. Only the formation of sylvestrene has an intermediate in which both charges are delocalized on tertiary carbon atoms, thus making this intermediate more stable with respect to the others. On the other hand, the limonene
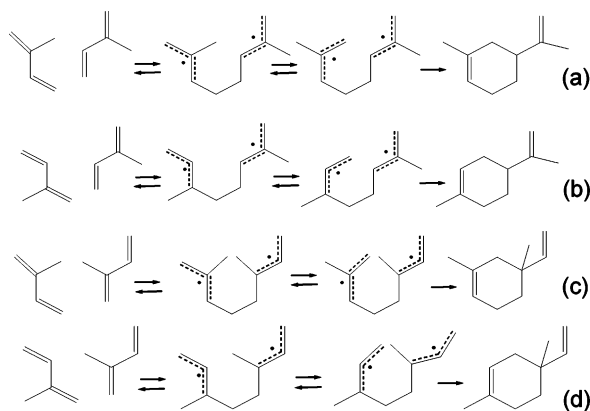
Figure 12. Possible dimerization paths leading, from top to bottom, to sylvestrene (a), limonene (b), 4-ethenyl-2,4-dimethylcyclohexene (c), and 4-ethenyl-1,4-dimethylcyclohexene (d).

formation should be favored from the steric point of view in a concerted mechanism or if the diffusion of the reactants to the reaction site is the rate-limiting step.

Each of the four dimers reported in Figure 12 may exist as an *R,S* mixture due to the presence of the chiral carbon where the vinyl groups are bounded. The stereochemistry of these reaction products also involves the axial/equatorial position of the two substituents at the chiral carbon with respect to the ring conformation. Despite that we are not able to distinguish among these isomers on the basis of the IR and Raman spectra, it can be reasonably argued that the high density of the reaction environment likely performs a selection among different molecular conformations and configurations.

Finally, the competition between the polymer and the dimer formation, which increases with pressure, can be related either to a higher negative value of the activation volume for the polymerization or to the higher energetic barrier to be overcome for the rearrangement of the dimerization intermediate at higher densities. Since this latter step anticipates the ring closure, the chain lengthening becomes competitive with the rearrangement. In addition, this behavior is further evidence of the open-chain intermediate.

The results obtained in the photoassisted reaction are more difficult to rationalize, even though they confirm general results reported for the reactivity of other simple hydrocarbons.[10] First, the threshold pressure for the reaction is lowered, since dimerization and polymerization processes are induced at ambient temperature and 0.5 GPa where the system is otherwise stable. Second, an increased selectivity in favor of the polymerization reaction, already reported for butadiene and ethylene, is also observed for isoprene. The dimerization, observed only at 0.5 GPa, where no reaction occurs without laser activation, is less selective, giving rise to a volatile fraction mainly composed of the dimers III and IV not observed in the purely pressure-induced reaction. It has been reported that irradiation of isoprene containing different sensitizers leads to the formation of seven dimers: three cyclobutane derivatives, the two cyclooctadienes (V and VI) reported in Figure 3, limonene (I), and 4-ethenyl-1,4-dimethylcyclohexene (III).[32,33] The composition of the product mixture changes depending on the reaction conditions or the employed sensitizer. In particular, when the yield of cyclobutanes and cyclooctadienes increases, the amount of the two cyclohexene derivatives accordingly decreases. It was therefore concluded that two different intermediates are responsible for the two groups of products. This conclusion seems to fit nicely with the results presented here, where the obtainment of the dimers III and IV is the most remarkable

novelty with respect to the purely pressure-induced reaction. It is worth emphasizing that neither cyclobutanes nor cyclooctadienes are revealed in our recovered product, thus revealing an increased selectivity with respect to the employment of sensitizers.

The parallel between isoprene and butadiene as the effects of laser excitation are concerned is particularly straightforward. The distortion of the isoprene molecule in the excited states is obviously similar to that reported for butadiene.[34] In the present case, a relevant lengthening of the molecule seems to occur in the $2A_g$ state that is populated through a diabatic transition from the state ($1B_u$) reached by the optical excitation.[28] However, the nonradiative fast decay of the ^2A_g to the ground state suggests that the majority of the photochemical processes likely occur in the ground state, where the characteristic times of the structural rearrangements are much slower, since they are of the vibrational type. The same conclusion was also proposed for the photoinduced polymerization of ethylene in the fluid phase.[15]

6. Summary and Conclusions

The pressure-induced reactivity of isoprene has been studied at room temperature up to 2.6 GPa. The tuning of the pressure in a wide range turned out to be extremely important to understand the reaction mechanism and to gain an insight into the competition between the dimerization and the polymerization processes. An increased selectivity of the reaction has been obtained at high pressure for both processes. First, dimerization and polymerization can be temporarily separated by operating at the pressure threshold of 1.1 GPa. Second, in the purely pressure-induced reaction, the dimerization process appears extremely selective, since sylvestrene is the only dimer detected in the volatile fraction. In this respect also, the role of temperature, lower than in previous studies, is likely decisive. Finally, as already observed in the case of butadiene, the employment of laser light lowers the threshold pressure of the reaction and opens new reaction channels, as demonstrated by the large amount of 4-ethenyl-1,4-dimethylcyclohexene obtained at 0.5 GPa and by the extreme selectivity obtained above 1 GPa when the almost quantitative formation of the polymer is observed. As already observed for other simple unsaturated hydrocarbons, the high-pressure reactivity exhibits peculiarities that are fundamental to understand, especially in connection with photoinduced studies, the role and the relative weight of density, steric hindrance, stability of intermediates, and excited electronic states in selecting specific reactive paths.

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