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CO_2 laser-induced photolysis of spirohexane: time resolved observation of vibrationally excited 1,3-butadiene

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Abstract—Vibrationally excited spirohexane (SHX) generated in CO_2 laser irradiation undergoes photolysis producing ethylene, 1,3-butadiene and a C_4 compound as major products. Collisional energy pooling plays a major role in the multiphoton excitation process. Time-resolved formation of 1,3-butadiene is monitored by UV absorption from which the unimolecular rate constant for SHX dissociation is found to be $5.6 \times 10^5\ s^{-1}$. A red shift of 40 nm observed in the transient UV absorption spectrum has been assigned to nascent 1,3-butadiene, which suggests that vibrationally hot 1,3-butadiene molecules are formed. The effects of laser energy fluence and pressure of SF_6 as a sensitizer on dissociation yield are also investigated.

1. INTRODUCTION

HIGHLY STRAINED molecules are especially suitable for revealing relationships between structure and reactivity. An important class of strained organic molecules is spiroalkanes, which are topics of current research [1–3]. The first member of this series, spiropentane, has been very well studied. Pyrolysis experiments [4] showed that spiropentane derivatives cleave via diradicals into propenes and methylenecyclobutanes without any expulsion of ethylene. However, photolysis [5] of spiropentane at 147 nm is reported to proceed mostly by elimination of ethylene. In the case of spirohexane (SHX), the next member of the spiroalkane series, few studies have been reported. Laser driven thermolysis [6] of SHX has been shown to occur via expulsion of ethylene and intermediary formation of cyclic carbene.

It is well known for spirocompounds that the driving force for any chemical transformation is clearly the relief of angle strain. In unimolecular reactions, the large strain energy so released is available as excess energy to the nascent products. A fraction of excess energy which is channelled into the vibrational modes of the product can bring about a red shift in the electronic absorption spectra of the nascent products. To our knowledge the photochemistry of SHX has not been studied under purely vibrational excitation conditions. In this paper we report pulsed TEA CO_2 laser-induced dissociation of SHX by direct excitation as well as in the presence of the energy transfer agent SF_6. The real time formation of the product butadiene and its UV absorption spectrum are reported. The nascent butadiene spectrum is found to be red shifted by about 40 nm.

2. EXPERIMENTAL

Direct dissociation of SHX was studied in an SS cell 10 cm long with a total volume of 50 cm^3 SHX (0.9 Torr) was taken and irradiated at the 10R(36) laser line at a fluence of 1.5 J cm^{-2} for 3000 pulses. For sensitized experiments a cell 4.7 cm long with a total volume of 32 cm^3 was used. Both cells were fitted with two polished KCl windows. SHX (0.9 Torr) was taken and different amounts of SF_6 were added to find the optimum conditions for maximum dissociation yield. The mixture was irradiated for a total of 150 pulses at a fluence of 0.7 J cm^{-2}. For fluence dependence studies a 1:3 mixture of SHX–SF_6 was made in a stock bulb and known amounts of sample were transferred to the irradiation cell through a vacuum line. At each fluence the mixture was irradiated for 400 pulses. All sensitized experiments were carried out at the 10P(20) line of the CO_2 laser. Depletion of SHX was monitored by gas chromatography. The products were separated on a 2 ft column of silicone grease and detected using a flame ionization detector.

Time resolved experiments were carried out in a specially designed SS cell (volume = 263 cm^3) fitted with a pair of KCl windows orthogonal to another pair of quartz windows in an IR/UV crossed beam configuration. SF_6-sensitized photolysis was studied using the 10P(20) laser line. The laser beam was partially focussed in the centre of the cell by a BaF_2 lens ($f = 25$ cm). A cw spectroscopic UV probe beam from a pulsed mode operated Xe lamp (150 W) with associated optics, monochromator ($\phi = 3.5$), fast PMT (IP28) and signal processing system (Gould Biomation 4500, 10 ns resolution), as discussed in our earlier paper [7], was used for detection of transient/stable products in CO_2 laser irradiation. The CO_2 laser is triggered at a time when the pulsed lamp intensity reaches the maximum and remains steady over a period of 200 μs. The complete operation from firing of the CO_2 laser to data collection is computer controlled. Signals were averaged for 16 shots and data were transferred to computer/plotter for further processing. The post-irradiated sample was transferred to a quartz cell (vol. 15 cm^3) of 1 cm path length and was analysed on a Hitachi 330 UV–vis spectrophotometer.

3. RESULTS

Irradiation of neat SHX by a pulsed TEA CO_2 laser at a fluence of 1.5 J cm^{-2} gives ethylene, 1,3-butadiene and two incomplete identified products which are suggested by GC-MS to be four and six carbon atom containing compounds. As no hydrogen is obtained among the products, C_6 product is an isomer of SHX. The dissociation yield is very low (even after irradiating for 3000 pulses) because of poor IR absorption of this compound in the CO_2 laser region. Irradiation in the presence of SF_6 at the 10P(20) laser line increased the dissociation yield by more than two orders of magnitude, maintaining the nature and relative yield of the products.

3.1. *SF_6 pressure dependence*

SHX (0.9 Torr) was taken and irradiated in the presence of different pressures of SF_6 at a fixed fluence of 0.7 J cm^{-2} for a total of 150 pulses using the 10P(20) line. The dissociation yield was found to increase linearly with the pressure of SF_6 (Fig. 1). To investigate the nature of collisional effects affecting the dissociation yield of SHX, argon was added in some experiments during irradiation. It was observed that the presence of argon decreased the dissociation yield significantly.

3.2. *Fluence dependence*

A mixture of 0.9 Torr of SHX and 2.5 Torr of SF_6 was irradiated for a total of 400 pulses at different fluences. The dissociation yield increased linearly with the fluence (Fig. 2), starting from 15% at 0.5 J cm^{-2} to 53% at 1.2 J cm^{-2}.

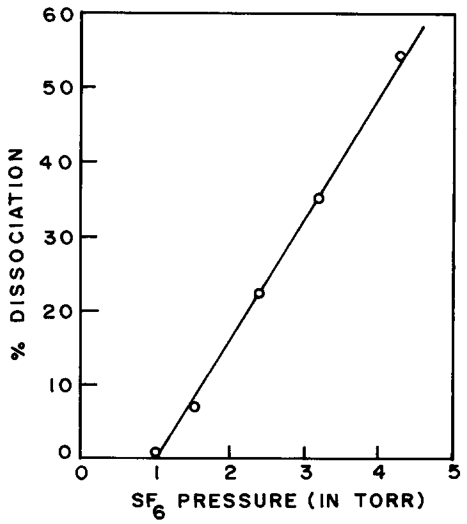


Fig. 1. Dissociation yield of spirohexane vs SF_6 pressure.

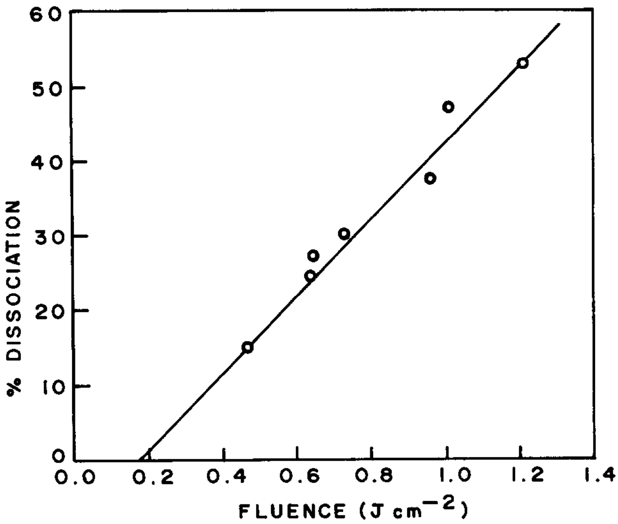


Fig. 2. Effect of laser energy fluence on the dissociation yield of spirohexane.

3.3. *Time-resolved studies*

When 4.0 Torr of SHX were irradiated in focussed conditions no UV absorption signal was obtained. This is in accordance with GC results on irradiation of neat SHX, where very low yield/pulse was observed. Subsequently, the laser line was changed to 10P(20) and an equal amount of SF_6 was added and still no signal was observed. Increasing the pressure of SF_6 to 9 Torr resulted in detection of an absorption signal at 250 nm. A further increase in SF_6 pressure up to 12 Torr proved to be slightly helpful in raising the signal level. After reaching the maxima in 6 μs (Fig. 4), the decay of signal is slow, which indicates that absorption may be due to some long-lived transient or a stable product. To verify this we added 5 Torr of NO to the mixture during irradiation. It was found that neither the signal level nor the nature of the signal were affected, thus confirming that UV absorption is due to some stable product. However, on a longer time scale there was a gradual decay of the signal due to the combined effects of cooling down of hot molecules and their diffusion from the zone of probe. For kinetic studies a mixture of 9 Torr of SF_6 and 4.5 Torr of SHX was taken. The UV absorption spectrum with λ_{max} of 250 nm of nascent product (Fig. 3) was recorded at 6 μs delay. On recording the UV spectra of the post-irradiated sample on the spectrophotometer, a typical gas phase UV structured spectrum [8, 9] of 1,3-butadiene with λ_{max} at 210 nm and no absorption at 250 nm was obtained. This observation suggests that the time-resolved UV spectrum with λ_{max} at 250 nm at 6 μs is due to nascent 1,3-butadiene product. The red-shifted broad

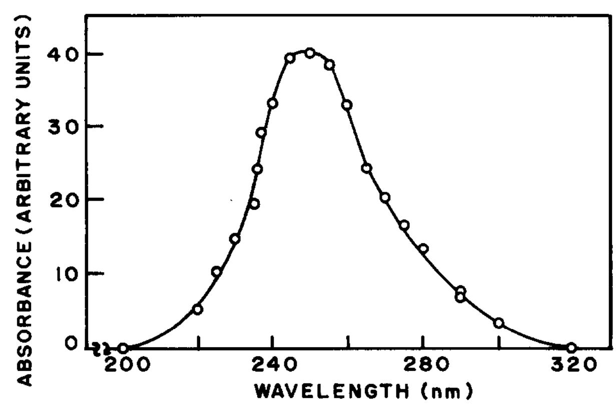


Fig. 3. Transient UV absorption spectrum of nascent 1,3-butadiene.

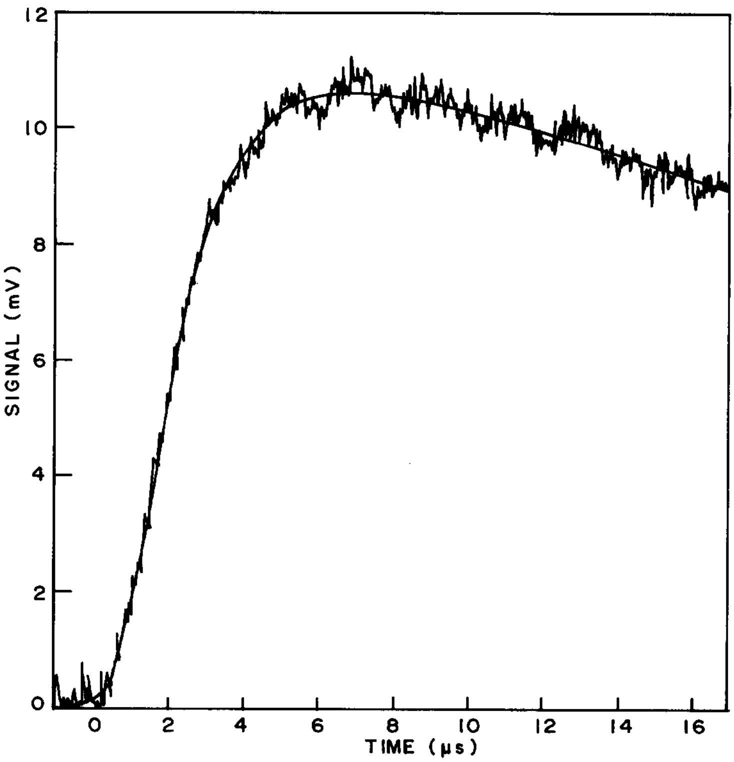


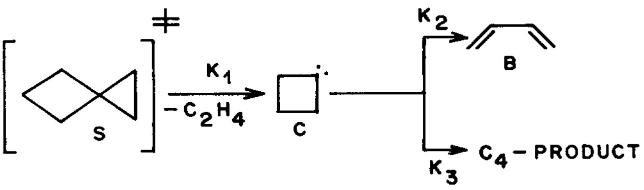
Fig. 4. Temporal growth of 1,3-butadiene.

UV absorption indicates that the 1,3-butadiene formed is vibrationally hot. The energy content in a vibrationally excited molecule can be obtained from its UV absorption spectrum by using Franck–Condon factors and the population of various levels involved in vibronic transitions. However, an approximate excess energy content in the hot butadiene molecule can be evaluated by taking the difference in energy at two different λ_{max} values corresponding to the vibrationally excited and ground state electronic absorption spectra of butadiene. Using this method the excess energy is calculated to be 22 kcal/mol^{-1}.

4. DISCUSSION

4.1. *Major dissociation channels*

Ethylene is produced in the major dissociation channel of SHX either by molecular elimination in a concerted pathway or by a radical mechanism. Our experimental results are not sufficient to unambiguously explain the mechanism of ethylene expulsion. However, the existence of a minor isomerization channel suggests the possibility of a radical mechanism (via a biradical). This possibilty does not exclude the existence of a molecular elimination channel. The relative yields of 1,3-butadiene and other C_4 products are independent of laser fluence and SF_6 pressure. This suggests that these photoproducts do not compete with each other and are formed from a common precursor whose formation alone is the rate determining step in the photolysis of SHX. After ethylene elimination, the cyclobutylidene formed is probably the precursor for both C_4 products. The conversion of the carbene precursor to C_4 products is very fast, evidence for which comes from the fact that the expected intermediate cyclobutene in the formation of 1,3-butadiene is not stabilized by high SF_6/Ar pressure (6 Torr). The following dissociation scheme is proposed to account for the major products:



4.2. *Kinetic treatment*

From kinetic treatment of the above dissociation scheme, the time-dependent concentration of 1,3-butadiene, $B(t)$, is found to be

$$B(t)=A_1[1-\exp(-k_1t)]-A_2[1-\exp(-k't)] \tag{1}$$

where A_1 and A_2 are two constants defined as

$$A_1=k_2[S_0]/(k'-k_1),\ A_2=k_1K_2[S_0]/k'(k'-k_1),$$

$k'=k_2+k_3$ and $[S_0]$ is the initial concentration of excited SHX. As discussed earlier, the rate constants k_2 and k_3 are much faster as compared to k_1 and the formation of the intermediate is the rate determining step. Therefore, effectively the first exponential term of Eqn (1) determines the time evolution of the product butadiene. Hence $B(t)$ is given by

$$B(t)=A_1[1-\exp(-k_1t)]. \tag{2}$$

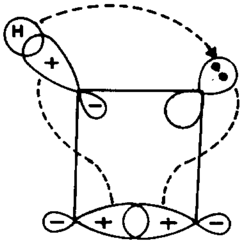
The rising part of the absorption signal is fitted to Eqn (2) with A_1 as the maximum butadiene signal and the unimolecular rate constant of dissociation, k_1, under sensitized conditions is found to be $5.6\times10^5\,s^{-1}$.

4.3. *Symmetry allowed isomerization of cyclobutylidene*

In IR multiphoton dissociation, the products formed with excess vibrational energy can undergo secondary reactions. Addition of inert gases during irradiation brings about fast V-T relaxation and stabilizes the excited product before it undergoes further reactions. In laser driven thermolysis of SHX, Pola *et al.* [6] explained the formation of butadiene from cyclobutylidene via a cyclobutene intermediate. However, they could not find any evidence for this intermediate. In our experiments we could not stabilize this possible intermediate by adding Ar or SF_6, whereas perfluoro butadiene, an intermediate in IRMPD of perfluoro cyclohexene, has been stabilized by the addition of Ar [10]. This observation suggests that the rearrangement of cyclobutylidene to butadiene is possibly a single step concerted process without involving cyclobutene. A symmetry allowed pathway, based on Woodward–Hofmann rules [11] for conversion of cyclobutylidene to butadiene classified as $[\sigma^2s+\sigma^2s+\omega^2s]$ (where σ and ω refer to the types of electrons involved), is proposed in Fig. 5.

4.4. *Pressure and fluence effects*

With increasing partial pressure of SF_6, the dissociation yield of SHX increases linearly, which can be explained by rotational hole filling [12] and collisional energy pooling. That the former effect does not play a role here has been found by performing experiments in the presence of argon. Instead of an increase in dissociation yield by rotational hole filling due to Ar, a decrease is observed due to Ar-induced collisional de-excitation of energized SF_6 and SHX molecules.



$$[\sigma^{2}s + \sigma^{2}s + w^{2}s]$$

Fig. 5. Symmetry allowed pathway for cyclobutylidene→butadiene conversion.

The sensitized dissociation of SHX is found to show a linear dependence on laser energy fluence. From this linear plot the dissociation threshold of SHX in the sensitized condition is found to be about $0.2\,\mathrm{J\,cm^{-2}}$. The increase in dissociation yield with increasing fluence is due to an increase in average number, $\langle n \rangle$, of photons absorbed per SF_6 molecule.

4.5. *UV spectrum of nascent* 1,3-*butadiene*

Band shape and λ_{max} are two important characteristic features of an electronic absorption spectrum. The shape of a band results from convolution of the fine structure contribution from the various vibrational modes, and λ_{max} is determined from the product of the Franck–Condon factor and the population of the corresponding level. The number of vibrational modes in mid-sized and big molecules being large, consequently the number of fine structure lines is also very large. The latter exhibits a rapid increase with increasing energy of the molecules, resulting in broadening of the absorption band. In the case of 1,3-butadiene, the excess energy of about 22 kcal/mol^{-1} may be sufficient enough to smear out all fine structures, giving a broad UV spectrum.

Of the two isomers of 1,3-butadiene, the *trans* form is thermodynamically more stable by about 2.8 kcal mol^{-1}, with an activation barrier of 6.6 kcal mol^{-1} [13] for its isomerization to the *cis* form. The *trans* form has a structured UV absorption spectrum [8, 9] with λ_{max} at 210 nm, whereas the *cis*-isomer at 20 K [13] has a broad absorption band with λ_{max} at 226 nm. With increasing temperature the fraction of the *cis* form increases and hence at 621 K appreciable absorption is observed, even at 249 nm [13, 15], where the *trans* form has negligible absorption. Apparently, this spectral information suggests that the 40 nm red-shifted nascent 1,3-butadiene spectrum seen in the IRMPD of SHX is mainly due to its *cis*-isomer. Hot butadiene molecules are formed with an excess energy of about 22 kcal mol^{-1}, which is more than the activation barrier between the two isomers. Therefore, at such a high excess energy there is no identity of individual isomers. Hence, the broad structureless UV absorption obtained with λ_{max} at 250 nm is due to vibrationally hot 1,3-butadiene, which is devoid of any specific isomeric structure. Hot molecules gradually cool down to the thermodynamically more stable *trans* form, which is detected by UV absorption in the post-irradiated mixture.

4.6. *Energetics of SHX dissociation*

From the unimolecular rate constant, k, of SHX dissociation, the average internal energy, E, contained in the energized SHX molecules is computed to be 88 kcal mol^{-1} by the RRK expression:

$$k = A(1 - D/E)^{s-1} \tag{3}$$

taking the Arrehnius frequncy factor, A and the dissociation energy, D, of SHX to be $10^{15.1}\,\mathrm{s^{-1}}$ and 58.1 kcal mol^{-1} respectively [6]. s is taken to be 21 (50% of the total vibrational degrees of freedom for SHX). The total energy available for partitioning among the various degrees of freedom of products is about 75 kcal mol^{-1}, obtained by subtracting the enthalpy of reaction [16] (about 12.8 kcal mol^{-1}) from the average internal energy in the energized SHX molecules. A part of this energy is transferred as vibrational energy to 1,3-butadiene and, hence, its nascent UV absorption spectrum is red-shifted by 40 nm, which corresponds to about 22 kcal mol^{-1}.

5. CONCLUSION

The IR multiphoton excitation of spirohexane (SHX) opens up two primary dissociation channels from its ground electronic state. The major channel is elimination of ethylene producing 1,3-butadiene and its isomer. The temporal evolution of 1,3-butadiene as a photoproduct is monitored. From its real time formation, a unimolecular dissociation rate constant for SHX has been found to be $5.6 \times 10^5\, s^{-1}$. The average internal energy contained in energized SHX molecules is computed to be 88 kcal mol^{-1}. The UV absorption spectrum of 1,3-butadiene reveals a red shift of 40 nm, suggesting the formation of vibrationally hot moleclues.

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