

INFRARED MULTIPHOTON ISOMERIZATION AND FRAGMENTATION REACTIONS OF ORGANIC MOLECULES

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Abstract - The tunability of the CO₂ molecular gas laser permits selective multiphoton infrared excitation of one isomer in a mixture of isomers. This capability can be exploited to drive isomerization reactions in a contra-thermodynamic direction. Examples of such reactions are the trans → cis isomerization of alkenes and the electrocyclic isomerization of butadienes to cyclobutenes. It is also possible to achieve some selectivity in consecutive isomerization reactions (A → B → C) and in competing reactions (A → B + C) via multiphoton infrared excitation. For example, consecutive reactions can be stopped at the intermediate product B in cases where the activation energy for B → C is lower than that for A → B. The product ratio B/C in competing reactions is, in some cases, dependent upon the average vibrational temperature of the reactant A and hence can be altered by changing laser fluence or collisional frequency. In addition, pulsed infrared lasers can be used to create high concentrations of vibrationally excited fragmentation products. We are currently seeking to correlate product vibrational energy distributions with reactant structure and decomposition mechanism.

INTRODUCTION

Reactions of electronically excited polyatomic organic molecules have occurred on earth since the prebiotic era and have been the subject of scholarly publications since the emergence of the modern chemical literature. All photochemists are familiar with the Stark-Einstein law: electronic excitation occurs upon absorption of a single quantum of light. Under the best of circumstances, the electronically excited molecule can undergo chemical transformation with unit efficiency. Absorption of a single infrared photon produces a vibrationally excited molecule with insufficient energy to undergo chemical transformation. With the advent of high powered infrared lasers, it has become possible to effect chemical reactions via multiphoton absorption in an intense laser field (1-4). Thus laser technology has spawned a new field of chemistry, infrared photochemistry. From a historical perspective it is interesting to note that the initial investigations of photochemical mechanisms were conducted in the vapor phase (5). Chemical applications of infrared lasers have thus far been limited almost exclusively to the vapor phase.

THE CO₂ LASER

The commonly used source for infrared laser chemistry is the pulsed CO₂ molecular gas laser. The important characteristics of the CO₂ laser are (a) high power (ca. 10²⁰ photons/pulse or several gigawatts/cm² in a focused beam), (b) moderately short pulse duration (< 1 μs), and (c) limited tunability from ca. 907 to 992 cm⁻¹ and from 1016 to 1092 cm⁻¹. Its high power makes the CO₂ laser well suited for many technological (welding, cutting, etc.) as well as chemical applications. The simplest chemical application of CO₂ lasers is the uniform heating of the irradiated volume either by direct absorption

or by collisional energy transfer from a stable, strongly absorbing molecule ("sensitizer") such as SiF_4 or SF_6 (1). Laser heating or laser-powered pyrolysis (6) differs from vacuum pyrolysis in that the reactor walls are not heated, but normally yields comparable results. The moderately short pulse duration of the CO_2 laser is well suited for the study of the reaction dynamics of vibrationally excited reactants and products. One such application is described in the final section of this lecture. The tunability of the CO_2 laser in some cases permits selective excitation of a single component of a gaseous mixture. The finite vibrational frequency shifts observed for isotopic substitution allow selective fragmentation of the absorbing isotope, resulting in isotopic enrichment of the nonabsorbing isotopic species. Analogously, selective excitation of one isomer in a mixture of isomers can be used to effect conversion to products other than those obtained in a conventional thermal (or photochemical) reaction.

SELECTIVE ISOMERIZATION

A schematic energy level diagram for two component isomerization is shown in Fig. 1. Multiphoton excitation is generally described in terms of three energy regions which differ in state density. Starting at the lowest energy, these are (a) the region of discrete states, which converge due to anharmonicity, (b) the quasicontinuum, in which the density of states is sufficiently high to insure absorption of all incident irradiation, and (c) the continuum, which occurs above the dissociation threshold. The complex mech-

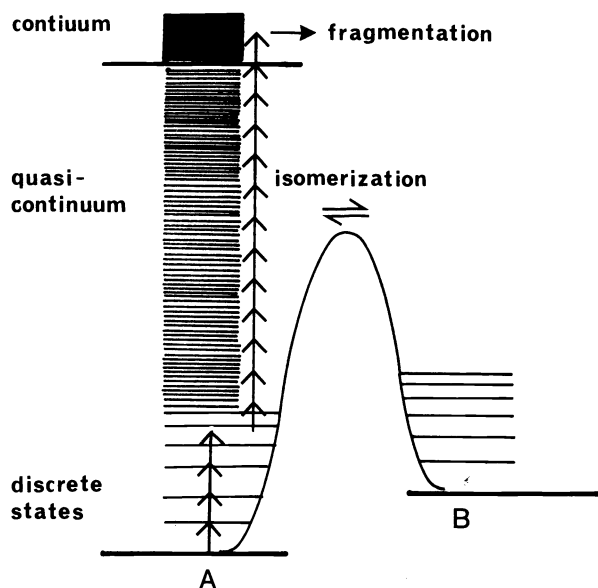


Fig. 1. Schematic energy level diagram for infrared excitation, isomerization, and fragmentation

anism of vibrational excitation and deexcitation is the subject of continuing experimental and theoretical investigation (3).

Reversible $A \rightleftharpoons B$ isomerization requires that A or B be excited into the quasicontinuum, above the isomerization threshold, but not above the dissociation threshold. This necessitates the use of a collimated laser beam of uniform and controlled intensity. Beam inhomogeneity or focusing results in "hot spots" or dielectric breakdown, which effect nonselective fragmentation. Selective contrathermodynamic $A \rightarrow B$ isomerization requires that A, but not B, be excited above the isomerization threshold. This requires that the infrared absorption cross section (σ) for A be greater than that for B and that the time between collisions of excited molecules with product molecules be longer than the laser pulse duration. For a laser pulse duration of 200 ns the pressure must be < 0.1 torr. The requirements of low pressure and laser beam homogeneity place severe restrictions on experimental design and the preparative yield of contrathermodynamic isomerization reactions.

Alkene cis-trans isomerization

Cis-trans isomerization is among the most extensively investigated of photochemical reactions (7). In the case of direct excitation, reversible isomerization ($A \rightleftharpoons B$) leads to a photostationary state governed by extinction coefficients and quantum yields (eq. 1). For isomers with similar electronic absorption spectra and quantum yields, such as cis and trans alkenes, photostationary states $[A]/[B] \sim 1$ are observed.

$$\frac{[A]}{[B]} = \frac{\epsilon_B}{\epsilon_A} \cdot \frac{\phi_{B \rightarrow A}}{\phi_{A \rightarrow B}} \quad (1)$$

Exothermic triplet energy transfer also results in photostationary states $[A]/[B] \sim 1$.

There have been numerous reported attempts to effect cis-trans isomerization using infrared multiphoton isomerization (8). Early efforts using focused lasers resulted in more fragmentation than isomerization. Using a defocused laser of controlled fluence, Steinfeld and co-workers (8) effected the trans \rightarrow cis isomerization of trans-dichloroethylene and trans-d₁-vinyl chloride. In neither case was a cis/trans ratio substantially larger than that expected for thermal equilibrium observed, possibly due to the occurrence of collisional energy transfer at the gas pressures used (ca 3 torr).

Multiphoton infrared excitation should yield a photostationary state governed by the absorption cross section (σ) for each step in the up-pumping process, cross sections for stimulated emission, collisional deactivation rate constants, and rates of isomerization. In cases where isomerization can be described by a master equation model (3), small differences in single photon absorption cross sections may be amplified in the absorption process. Thus modest differences in σ may lead to photostationary states with $[A]/[B] \gg \sigma(B)/\sigma(A)$. Such is apparently the case for the isomeric 2-butenes.

The infrared absorption spectra of trans- and cis-2-butene in the region accessible with the CO₂ laser are shown in Fig. 2. Alkene absorption in the region 1000-800 cm⁻¹ is attributed to the out-of-plane deformation of vinyl hydrogen atoms (9). Irradiation of trans-2-butene at 975 cm⁻¹ with 3,000 pulses of fluence = 4.5 J/cm² results in 98% conversion to cis-2-butene (80%) and fragments (18%). The threshold fluence below which the isomerization yield per laser pulse is too low to be accurately measured is ca 3.5 J/cm². Irradiation of cis-2-butene under identical conditions (4.5 J/cm²) results in inefficient isomerization (< 1%) and fragmentation (3%). The lower single photon absorption cross section for the cis (4.8 \cdot 10⁻²⁰cm²) vs. trans (1.4 x 10⁻¹⁹cm²) isomer apparently results in a higher threshold fluence than can be obtained without focusing of our laser.

Irradiation of trans- or cis-crotonitrile at 931 cm⁻¹ and a fluence of 2.0 J/cm² results in the formation of a stationary state cis/trans isomer ratio of 1.0 (Fig. 3). The lower threshold fluence for isomerization and the absence of fragmentation probably are due to the lower activation energy for isomerization of crotonitrile (51 kcal/mole) vs. 2-butene (63 kcal/mole) (10). The single photon absorption cross sections for trans- (6.4 x 10⁻²⁰cm²) and cis-crotonitrile (8.9 x 10⁻²¹cm²) are smaller than the values for trans-2-butene. Based on the observed cross sections a stationary state cis/trans ratio > 7 might be expected. As seen in Table I, the observed values and the values calculated from the ratio of single pulse yields increase with increasing fluence reaching a value of 5.7 for J = 3.6. The observation of a lower cis/trans product ratio than absorption cross section ratio was unexpected. It is possible that the up-pumping process is less efficient for the trans vs. cis isomer. Plots of the average number of photons absorbed per pulse $\langle n \rangle$ vs. fluence show little deviation from linearity over the fluence range investigated (Fig. 4). Such behavior is characteristic of large organic molecules for which excitation from the region of discrete states to the quasicontinuum occurs without the threshold behavior observed for small molecules (11). Photoacoustic measurements of σ provide results similar to those obtained calorimetrically (Fig. 4). It is important to note that these measurements probe the energy content of the average molecule, while isomerization occurs from the small population of molecules with energies above the reaction threshold ($\langle n \rangle > 19$).

We find that multiphoton infrared excitation of 2-butene and crotonitrile results in substantially higher cis/trans product ratios than previously obtained for thermal or triplet sensitized irradiation (12). Attempts to effect the trans \rightarrow cis isomerization of α,β -unsaturated esters met with less

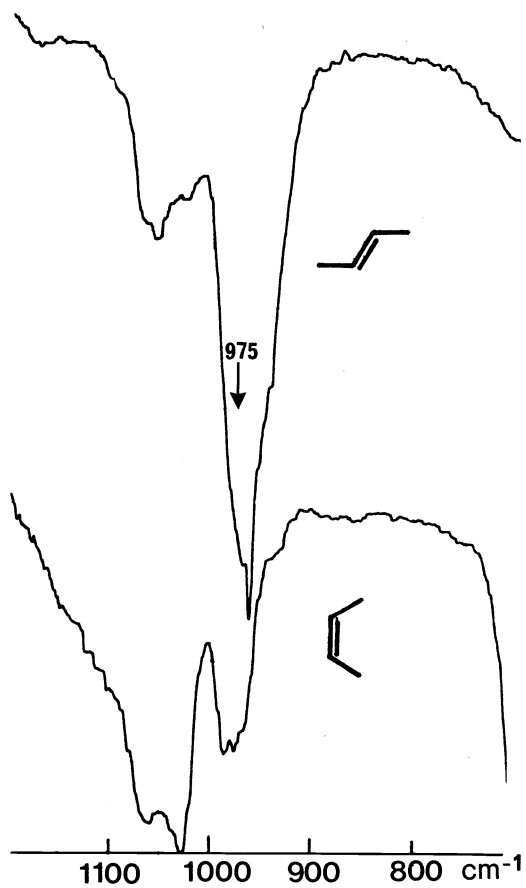


Fig. 2. Infrared spectra of *trans*- and *cis*-butenes (20 torr).

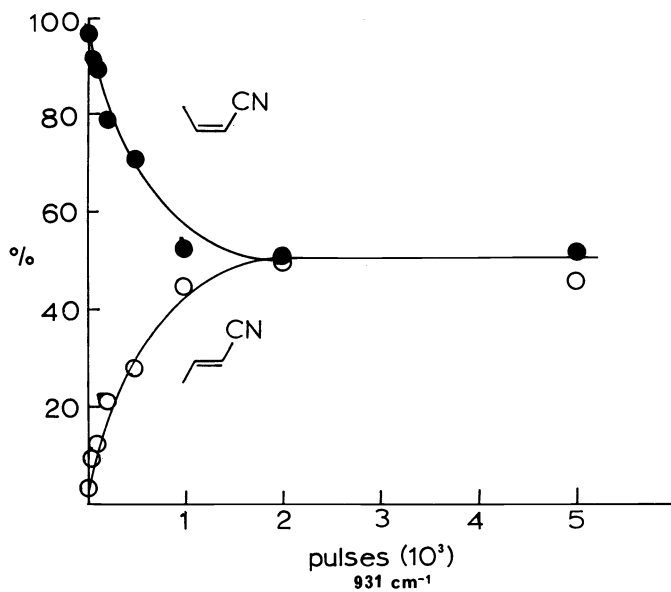


Fig. 3. Conversion of *cis*-crotonitrile to the photostationary state.

TABLE I. Fluence dependence of yields and stationary states for crotononitrile

Fluence, ^a J/cm ²	Yield ^b trans+cis	Yield ^b cis+trans	cis/trans	
			calcd. ^c	obs. ^d
2.0	1.1	0.95	1.2	1.0
2.5				1.0
3.0	4.0	2.7	1.5	1.9
3.2	7.0	3.0	2.3	
3.6				5.7

a P(34) (931 cm⁻¹) irradiation.

b Average of first 300 pulses. Values invariant from 200-800 pulses. 10⁴ x yield/pulse-cm².

c Stationary states calculated from ratio of per-pulse yields.

d Stationary states obtained with both cis and trans parents ($\pm 10\%$).

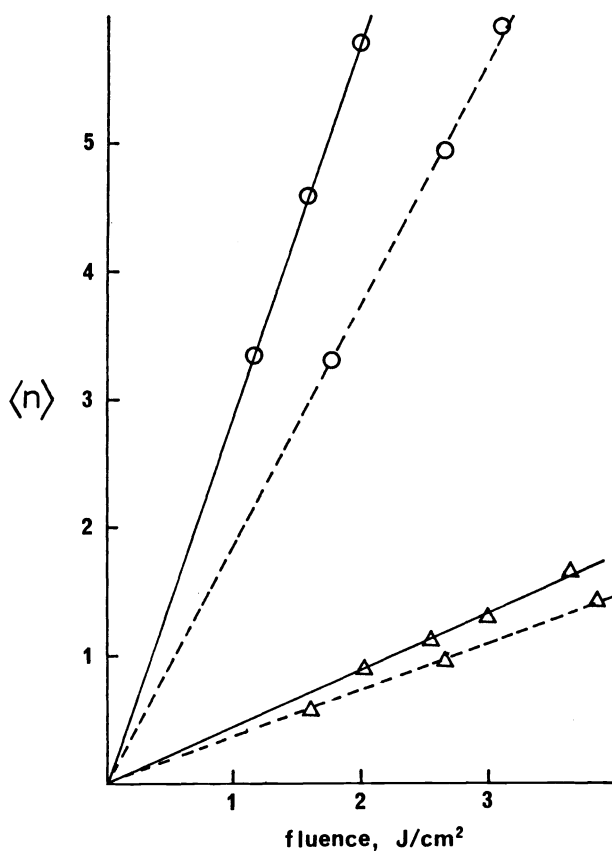
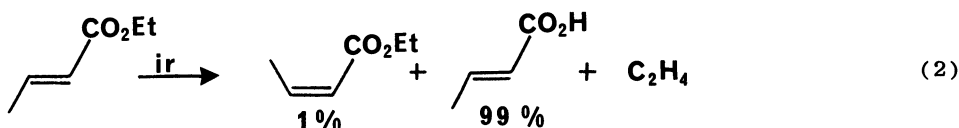


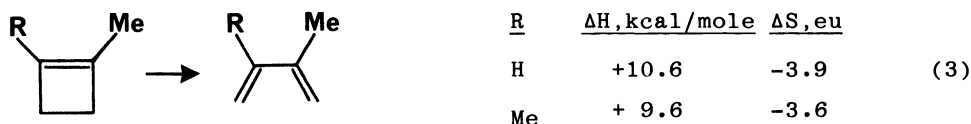
Fig. 4. Fluence dependence of the average number of photons absorbed per molecule, $\langle n \rangle$ by 0.1 torr trans-crotononitrile (O) and cis-crotononitrile (Δ) using 931 cm⁻¹ (—) and 978 cm⁻¹ (----) irradiation.

success even though its thermal isomerization activation energy (58 kcal/mole) is lower than that for 2-butene (10). Trans-ethyl crotonate yields ca. 99% crotonic acid and 1% cis-ethyl crotonate over the fluence range 0.9-3.0 J/cm² (eq. 2). This result is in accord with the lower activation energy for ester pyrolysis (48 kcal/mole) and the similar preexponentials for the fragmentation and isomerization processes.



Butadiene-cyclobutene electrocyclic isomerizations

The use of multiphoton infrared excitation to effect the ring opening isomerization of hexafluorocyclobutene to hexafluorobutadiene was reported by Yogev and Benmair in 1977 (13). This reaction is endoenthalpic but exoentropic. A more demanding test of laser-induced contrathermodynamic isomerization is the ring closure of butadiene to cyclobutene, a process which is both endoentropic and endoenthalpic (eq 3). We (14) have in fact been able to effect the electrocyclic reaction of 2-methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene to 2-methylcyclobutene and 1,2-dimethylcyclobutene by selective multiphoton infrared excitation (see Note a). The IR spectra



shown in Fig. 5 illustrate that highly selective excitation of 2-methyl-1,3-pentadiene can be achieved using 923 cm^{-1} ($P(42)$) laser excitation, while clean ring opening can be effected using 944 cm^{-1} ($P(20)$) irradiation.

Representative data for the ring closure reaction yield (molecules per pulse per cm^2 of irradiated area) as a function of laser fluence and buffer gas pressure are reported in Table 2. Per pulse yields increase with increasing

Table 2. 2-Methyl-1,3-butadiene isomerization yields^a

fluence, J/cm^2	helium pressure, torr	$10^6 \times \text{yield/pulse cm}^{-2}$
1.0	0	1.0
2.0	0	2.9
3.0	0	19.0
4.0	0	35.0
4.0	5	21.4
4.0	10	17.8

^a 944 cm^{-1} irradiation, 0.1 torr diene.

fluence and decrease with increasing helium pressure. The low reaction threshold (ca 1 J/cm^2) is in accord with the low activation energy for isomerization (46 kcal/mole) and the moderate single photon absorption cross section ($6.2 \times 10^{-20} \text{ cm}^2$). The salient experimental parameters for this system can be reproduced using a simple rate equation model (16). Several interesting features of the multiphoton infrared isomerization process emerge from these calculations. At low pressure (0.1 torr) and a fluence of 3 J/cm^2 , up-pumping leads to an average vibrational energy content of 11 quanta/molecule. Isomerization only occurs from the small fraction of excited molecules with energies above the reaction barrier (46 kcal/mole ~ 17 quanta/molecule). The peak in the relatively narrow product vibrational energy distribution occurs at 21 quanta/molecule, 4 quanta above the reaction barrier. Most of the product is formed during or shortly after the laser pulse, establishing a steady state between excited reactant and product. Increasing the fluence to 6 J/cm^2 increases the average energy content of the reactant to 16 quanta/molecule and the product to 23 quanta/molecule

Note a. Electronic excitation remains the method of choice for effecting this isomerization on a preparative scale (15).

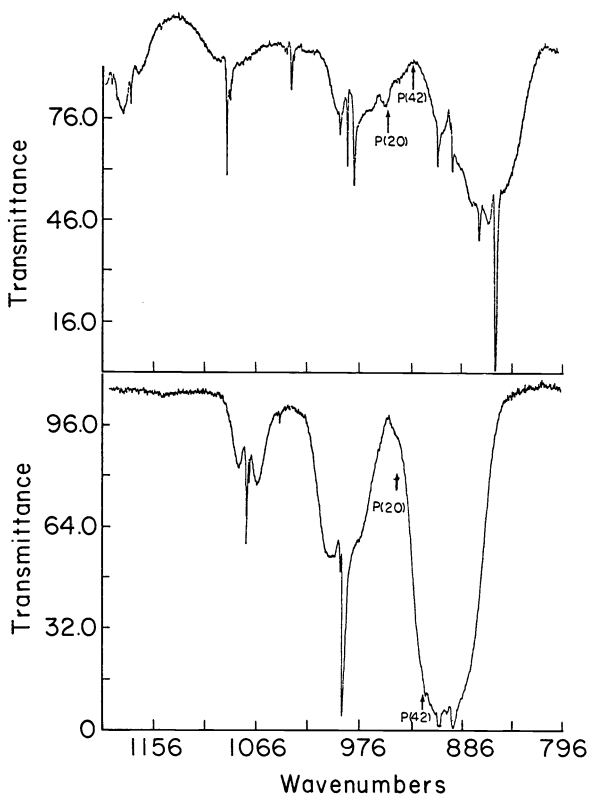


Fig. 5. Infrared spectra of 1-methylcyclobutene (upper) and 2-methyl-1,3-butadiene (lower) vapor (50 torr). Arrows indicate laser lines employed.

and thus substantially increases the equilibrium concentration of the product. Added helium buffer gas serves to collisionally deactivate vibrationally excited reactant and product and also diminishes the rate of reactant up-pumping below the reaction barrier. Thus the yield of product is reduced by added buffer gas. Detailed results of kinetic modeling will be published elsewhere.

Isomerization of conjugated hexadienes

The five isomeric conjugated hexadienes can be interconverted by *cis* \leftrightarrow *trans* isomerization and [1,5] sigmatropic rearrangement as shown in Chart 1. The

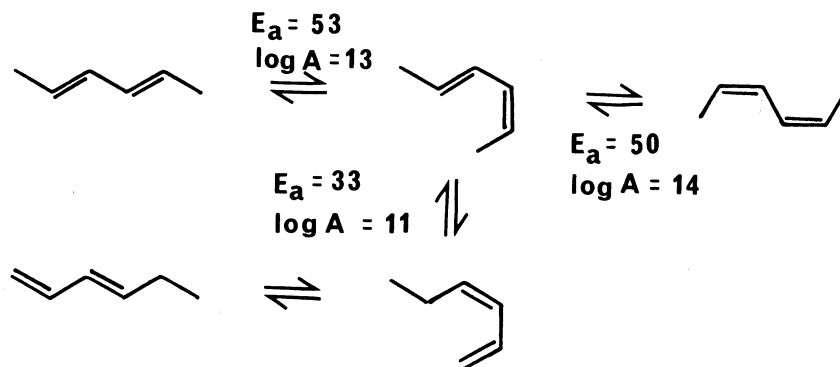
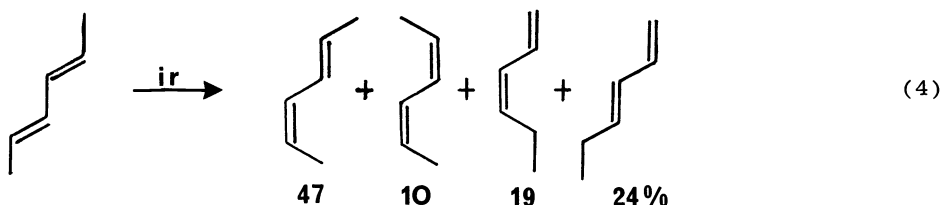


Chart 1.

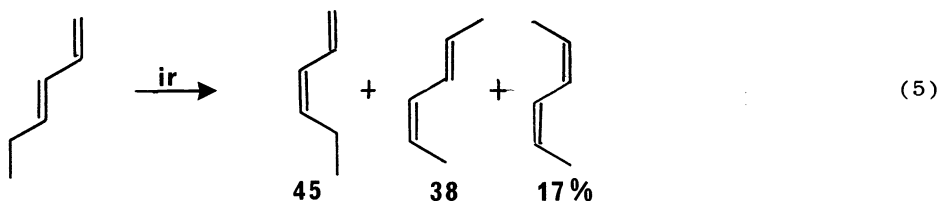
activation energies for these processes are substantially lower than for bond homolysis, allowing infrared multiphoton isomerization to occur without extensive fragmentation (17). The infrared spectra of the five isomers are suf-

ficiently different to allow at least partially selective isomerization. For example, irradiation of the thermodynamically most stable isomer, trans,trans-2,4-hexadiene, at 956 cm^{-1} with 3,000 pulses of 1.6 J/cm^2 fluence resulted in $> 98\%$ conversion to a mixture of the less stable but less strongly absorbing isomers (cis,cis-2,4-hexadiene and cis- and trans-1,3-hexadiene) with 89% mass balance.

While the hexadiene system is too complex to allow highly selective isomerization, it is well suited for the investigation of consecutive and competing reactions. For example, irradiation of trans,trans-2,4-hexadiene with a single laser pulse (946 cm^{-1} , 3.5 J/cm^2) produces all four isomers (eq 4). Decreasing the laser fluence or adding neon buffer gas reduces the yield of all products but increases the selectivity for formation of cis,trans-2,4-hexadiene. The available evidence indicates that the other products are formed sequentially via vibrationally excited cis,trans-2,4-hexadiene (Chart 1) in a vibrationally adiabatic process. There is no evidence for the occurrence of electrocyclic ring closure and reopening (eq 3).



An interesting example of the use of infrared multiphoton isomerization to control the products of consecutive reactions is provided by the irradiation of trans-1,3-hexadiene. The single pulse yields (0.1 torr, 946 cm^{-1} , 3.5 J/cm^2) given in eq 5 show comparable yields of the initial product,



cis-1,3-hexadiene, and secondary product, cis,trans-2,4-hexadiene. Since the activation energy for the secondary reaction (sigmatropic rearrangement) is substantially lower than for the primary reaction (trans + cis isomerization), the primary product would never be observed in a conventional thermal reaction. Control of laser fluence and buffer gas pressure allows optimization of the yield of thermally labile primary products (11, 18).

Irradiation of cis,trans-2,4-hexadiene (0.1 torr, 946 cm^{-1} , 2.0 J/cm^2) yields cis-1,3-hexadiene as the sole product. With increasing fluence, cis,cis- and trans,trans-2,4-hexadiene comprise an increasing fraction of the product isomer mixture. At a fluence of 7 J/cm^2 the yield of these products, which are formed via high activation energy and high preexponential cis-trans isomerization, exceeds the yield of cis-1,3-hexadiene, which is formed via a low activation energy and low preexponential sigmatropic rearrangement (Chart 1). This result can be predicted from the dependence of the calculated RRKM rate constants upon the average energy deposited in the reactant molecule by a single laser pulse. Thus it is possible to control the branching ratios for competing reactions by varying the laser fluence and buffer gas pressure (18, 19).

FRAGMENTATION REACTIONS

While most of our investigations of multiphoton infrared chemistry have focused on isomerization reactions, the bulk of the literature in this field is devoted to dissociation reactions. Infrared laser-induced dissociation is known to yield vibrationally excited (20) and in a few cases electronically

excited (21) fragments. The use of a pulsed CO₂ laser permits the observation of time resolved emission from the excited fragments.

We have investigated the vibrational energy content of CO₂ produced in the laser-induced fragmentation of several carboxylic acids. The experimental apparatus (Fig. 6) permits detection of infrared emission through a KBr win-

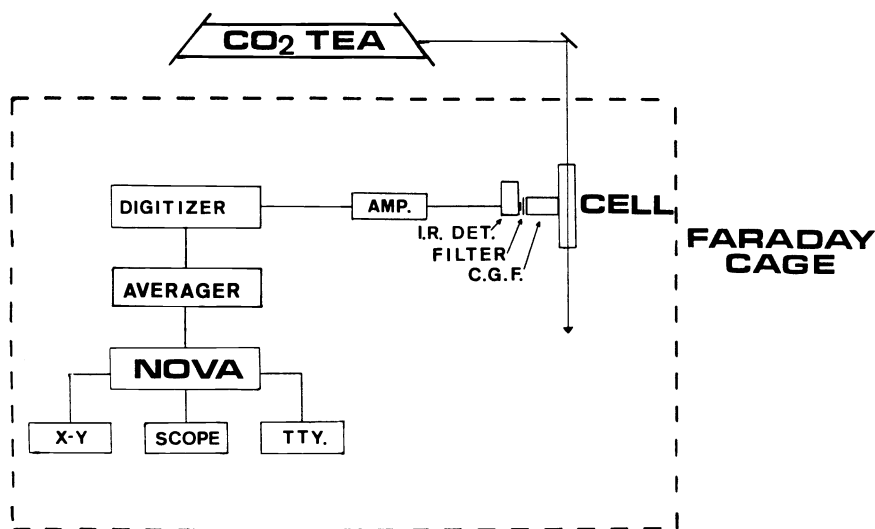
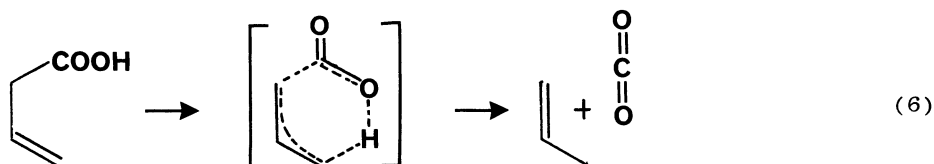


Fig. 6. Schematic diagram of the experimental apparatus.

dow perpendicular to the laser beam path using infrared detectors, narrow bandpass filters, and a cold gas filter (C.G.F.). Pyrolysis of 3-butenic acid is known to proceed via a concerted mechanism to yield propylene and CO₂ (eq 6) (22). Upon pulsed irradiation of 3-butenic acid strong



emission rising with the laser pulse is observed in the bending mode region of CO₂ (650 cm⁻¹) whereas weak emission with a slow rise time is observed in the asymmetric stretch region (2340 cm⁻¹) (Fig. 7). Investigation of the extent of self-trapping of the infrared emission with a cold gas filter confirms that the extruded CO₂ initially possesses a "hot" bending mode (>> 1 quanta/molecule) and a cold asymmetric stretching mode (< 1 quanta/molecule).

Such data provides valuable information about energy transfer and disposition in the fragments and may supply information about the transition state for decarboxylation (eq 6). According to a recent calculation by Dewar (23), the transition state possesses an O-C-O bond angle of 140° and nearly identical C-O bond lengths. It is attractive to speculate that the transition state geometry determines the vibrational energy distribution in the fragments.

In contrast to the results obtained for 3-butenic acid, laser induced fragmentation of pyruvic acid yields CO₂ with significant amounts of vibrational excitation in both the asymmetric stretching and bending modes. While the mechanism of thermal decomposition of pyruvic acid in the low pressure gas phase is unknown, we suspect on the basis of our observations that it differs substantially from that for 3-butenic acid.

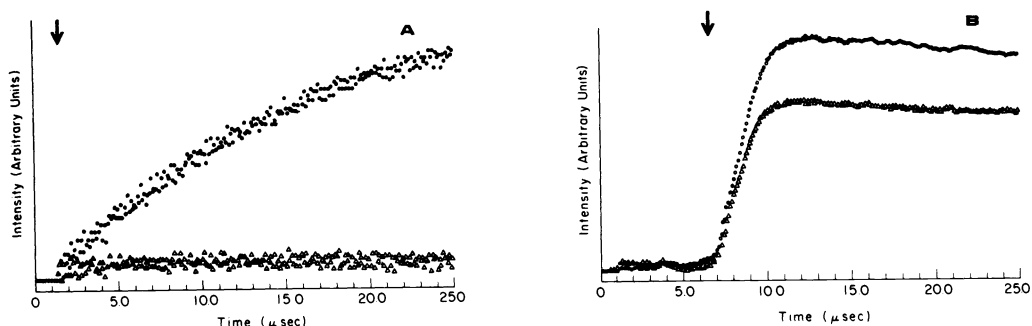


Fig. 7. Time resolved emission in the asymmetric stretching (a) and bending mode (b) regions of CO_2

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