

Selective Isomerization of Alkenes, Dienes, and Trienes with Infrared Lasers

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Unimolecular isomerization reactions of unsaturated hydrocarbons have been a fertile research field for nearly a century.¹ In 1891² Skraup reported that cis-trans isomerization of maleic acid occurred upon heating, while the Claisen and Cope rearrangements date from 1912³ and 1939,⁴ respectively. Other now familiar electrocyclic and sigmatropic reactions provide the experimental foundation upon which the theory of pericyclic reactions of Woodward and Hoffman⁵ was based. This theory in turn kindled interest in both concerted and nonconcerted thermal isomerization reactions of hydrocarbons.

Kistiakowsky's⁶ series of papers on cis-trans isomerization reactions of alkenes provided initial evidence for the unimolecular nature of these reactions and the influence of molecular structure upon isomerization activation parameters. Early kinetic investigations of cis-trans isomerization with static reactors were frequently complicated by competing pyrolysis and by heterogeneous or free radical catalysis of the isomerization process.⁷ The development of flash vacuum pyrolysis⁸ and shock tubes⁹ has allowed the investigation of kinetics with minimal wall effects.⁹

Molecular gas lasers have become an important new tool for the investigation of thermal unimolecular reactions.¹⁰ The pulsed CO₂ laser is commonly used for infrared excitation. This laser has high power (ca. 10²⁰ photons/pulse or up to several gigawatts per centimeter squared in a focused beam), moderately short-pulse duration (<1 μs), and is tunable in the ranges 907-992 cm⁻¹ and from 1016 to 1092 cm⁻¹ (Figure 1), in which most organic molecules absorb.¹ High-power and short-pulse duration allow for the absorption of multiple photons from a single laser pulse, a phenomenon commonly referred to as infrared multiphoton (IRMP) excitation. Uniform heating of the irradiated volume (laser-powered pyrolysis) can be accomplished by direct absorption or by collisional energy transfer from a stable, strongly absorbing "sensitizer" molecule such as SiF₄ or SF₆. Although laser-powered pyrolysis differs from vacuum pyrolysis in that the reactor walls are not heated, the reaction products are normally the same.¹¹

Most of the initial chemical applications of infrared lasers have involved fragmentation reactions, especially those that result in isotopic enrichment of heavy isotopes.^{10,12} The tunability of the CO₂ laser and the finite vibrational frequency shifts observed for isotopic sub-

stitution allow selective IRMP excitation and fragmentation of a given isotope, resulting in enrichment of the nonabsorbing isotopic species.¹² The observation of selective fragmentation upon pulsed infrared laser excitation but not conventional thermolysis is indicative of fundamental differences in the activation process. In conventional thermal activation, be it with a Bunsen burner, tube furnace, or shock tube, energy is provided by collisions with other molecules and all molecules in a uniformly heated region are at the same average temperature. In pulsed infrared laser activation, energy is introduced into molecular vibrations and only those molecules which absorb at the laser frequency are initially excited. Collisions can degrade the vibrational energy into translational and rotational energy, producing a uniformly heated system. However, prior to collisional deactivation, the vibrational degrees of freedom are substantially "hotter" than the temperature after equilibration of the rotational, vibrational, and translational degrees of freedom. Thus if IRMP excitation and subsequent chemical reactions occur more rapidly than collisional energy transfer to nonabsorbing molecules, experimental conditions can be chosen so that only the absorbing molecules will be capable of undergoing chemical reactions.

Just as wavelength selective IRMP excitation allows selective excitation of one isotopic species in an isotopic mixture, it is possible to selectively excite one isomer in a mixture of isomers and thereby effect selective conversion to product mixtures different from those

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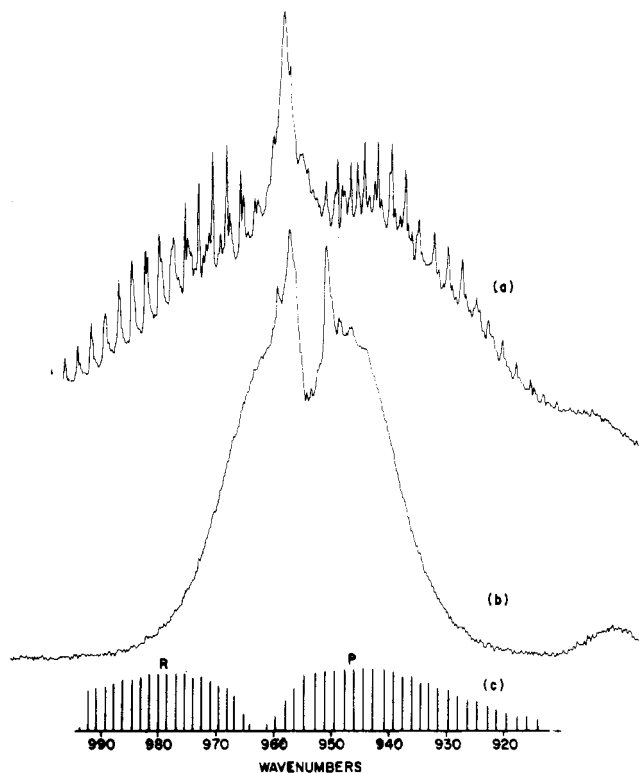
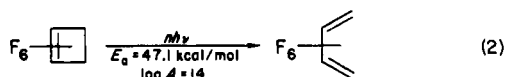
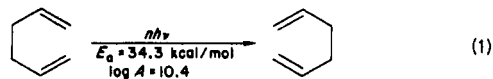


Figure 1. Partial FTIR spectra of (a) *trans*-crotononitrile (7 torr, $A_{958\text{cm}^{-1}} = 0.13$), (b) *cis*-crotononitrile (12 torr, $A_{958\text{cm}^{-1}} = 0.078$), and (c) the CO_2 10.6- μm laser gain.

obtained in conventional thermal reactions. Early reports of IRMP-induced reactions of unsaturated hydrocarbons were not encouraging in this respect. Excitation of *trans*-2-butene¹³ and *trans*-1,2-dichloroethylene¹⁴ resulted in low yields of the desired *cis* isomer along with substantial fragmentation: a result reminiscent of the difficulties encountered in early thermal studies using static reactors.

The initial examples of selective IRMP-induced isomerization reactions of unsaturated hydrocarbons were Glatt and Yogev's 1976 report of the quantitative Cope rearrangement of a deuterated 1,5-hexadiene (eq 1) and Yogev and Benmair's report of the quantitative ring opening of hexafluorocyclobutene (eq 2).^{15,16} In



both cases, the reactant but not the product strongly absorbs the incident radiation. Activation energies for both reactions are low, rendering competing fragmentation reactions less of a problem than in the case of alkene *cis*-*trans* isomerization. The remarkable aspect of these reactions is that under equilibrium conditions, the corresponding thermally initiated reactions produce similar amounts of reactant and product in eq 1 and predominantly the reactant in eq 2. Thus Yogev and co-workers successfully effected contrathermodynamic isomerization via IRMP excitation.

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During the last half-dozen years we have investigated several chemical applications of pulsed infrared laser excitation, including isomerization reactions of simple unsaturated hydrocarbons.^{17-24a} An objective was to determine the experimental and theoretical limitations of contrathermodynamic isomerizations in simple two-component systems. Investigation of multicomponent systems revealed that significantly different product ratios can be obtained from consecutive and competing reactions using IRMP vs. conventional thermal activation. Furthermore, the variation in product yields as a function of laser fluence and pressure can be used as a means of distinguishing between competing vs. consecutive reaction pathways. We have recently begun to investigate the effects of IRMP excitation of simple alkenes in the presence of catalytically active metal carbonyls and once again find results substantially different from those obtained upon conventional thermal activation.²³ The results of these investigations along with selected results from other workers in the infrared laser photochemical field provide the basis for this Account.

Contrathermodynamic Isomerization Reactions

We have investigated the IRMP-induced contrathermodynamic *trans*→*cis* isomerization reactions of several alkenes and dienes and the electrocyclic ring closure of several substituted butadienes. Activation and thermodynamic parameters for these systems are summarized in Table I and are reported for the reactions in the usual exothermic direction. Activation energies for the mildly endothermic *trans*→*cis* isomerization reactions range from 53 kcal/mol for 1,3-pentadiene to 66 kcal/mol for 2-butene.²⁵ Electrocyclic ring closure reactions of the substituted butadienes are endothermic by 9.6-11.4 kcal/mol, while activation energies are 45 ± 1 kcal/mol, substantially lower than the values for *trans*→*cis* isomerization.

In order for contrathermodynamic isomerization to occur, the following conditions must be fulfilled: (a) The more stable isomer must absorb infrared radiation more strongly than the less stable isomer at a CO_2 laser frequency. (b) The more stable isomer (but not the less stable isomer) must absorb sufficient infrared quanta within a single laser pulse to produce a finite population of molecules with sufficient energy to undergo reversible isomerization but not irreversible fragmentation. (c)

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Collisional deactivation of vibrationally excited reactant and product molecules must occur between laser pulses and provide a finite yield of product from each laser pulse.

With regard to point a, we have observed that even modest differences in reactant and product single photon absorption cross sections are sufficient to allow selective reaction of the more strongly absorbing isomer.²¹ For example, excitation of *trans*-crotonitrile using the P(12) line of the 10.6- μm laser branch (951 cm^{-1}) and a laser fluence of 5.5 J/cm^2 results in >95% conversion to *cis*-crotonitrile even though the ratio of *trans/cis* single-photon absorption cross sections is only 2.4. The structured absorption of the *trans* isomer (Figure 1) is assigned to the out-of-plane deformation of vinyl hydrogen atoms. Even more pronounced differences in infrared spectra are observed for structural isomers such as 2-methyl-1,3-butadiene and 1-methylcyclobutene, permitting highly selective excitation of either isomer.¹⁹

With regard to point b, *trans*-2-butene must absorb at least 25 infrared photons (2.7 kcal/mol each) within a single laser pulse in order to overcome a barrier to isomerization of ca. 66 kcal/mol. This requires careful control of laser fluence and beam homogeneity. Too few photons fail to effect isomerization and too many lead to competing fragmentation.

While the theory of IRMP excitation is complex and is still being refined,²⁷ a brief discussion of selected aspects of the theory will suffice for the purposes of this article. A fundamental problem in IRMP excitation is that the vibrational energy level spacings for an anharmonic oscillator decrease with increasing energy, causing a photon which is resonant with the $0 \rightarrow 1$ transition to be of higher energy than the $1 \rightarrow 2$ transition. Several factors serve to mitigate the effect of anharmonicity and allow the absorption of subsequent photons. Among these are the fact that the P, Q, R branch structure of a vibrational level can compensate, at least in part, for the anharmonicity of a mode (rotational compensation), as well as other, more subtle effects such as the A. C. Stark effect and power broadening. However, the most significant factor is the increase in the number of vibrational states (density of states), and the mixing of these states, as the internal energy of a molecule increases. For large polyatomic molecules the density of states increases rapidly with internal energy. When the density of states approaches ca. 100 states/ cm^{-1} , there will typically be at least one state within the half-width of the laser line frequency. When this condition is met, the molecule is said to be in the quasi-continuum and absorption can occur at virtually any frequency.¹⁰

Due to their low density of internal energy levels, diatomic molecules have never been observed to undergo IRMP-induced reactions and reactions of triatomics have been observed only in very intense laser fields.²⁸ For small polyatomic molecules, the absorption of three or four quanta may be necessary for excitation from the region of discrete states into the

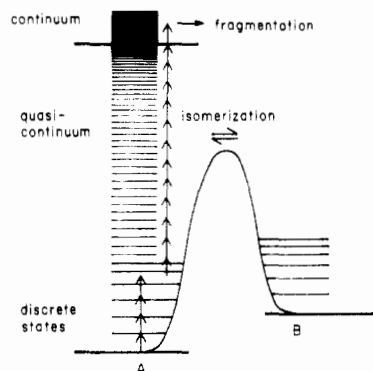


Figure 2. Schematic representation of the multiphoton excitation and isomerization process.

quasi-continuum. This results in a diminished cross section for absorption of quanta beyond the first until the quasi-continuum is reached, at which point cross sections typically increase. Thus, this region between the absorption of the first photon and the quasi-continuum can form a bottleneck in the IRMP absorption processes.²⁹

For large polyatomic molecules, state densities can increase so rapidly with increasing energy that it is possible to be effectively in the quasi-continuum upon absorption of a single photon.³⁰ For example, for molecules as small as 2,4-hexadiene the state density exceeds 100 cm^{-1} at a level of 2000 cm^{-1} .²⁰ Thus once a molecule is excited to $v = 1$, subsequent excitation will involve states in the quasi-continuum. Under these circumstances the number of photons absorbed should depend linearly on the fluence (energy/area). Interestingly, experimental results involving optoacoustic measurements of the average number of photons absorbed ($\langle n \rangle$) indicate that even for molecules where the quasi-continuum is entered at a level of $\sim 3000 \text{ cm}^{-1}$, the average number of absorbed photons is linear in the fluence.^{19,24} This result is compatible with, but does not necessarily require, an absorption coefficient that does not vary significantly with the level of excitation.^{10b} The very simple model discussed below, in which the absorption coefficient is invariant as a function of excitation level, does reproduce a variety of features of the IRMP systems we have dealt with.

We are now in a position to formulate a mathematical model of the IRMP absorption and isomerization process. The model, a schematic of which is shown in Figure 2, considers a manifold of vibrationally excited reactant states separated by the energy of a CO_2 laser photon, 1000 cm^{-1} . The degeneracy of each state is determined by a sum over all states within $\pm 500 \text{ cm}^{-1}$. A molecule in state i can be excited to state $i + 1$ by absorption of a photon and can be deactivated to state $i - 1$ by stimulated emission or collisional relaxation. Once above the isomerization threshold the reactant molecules can form isoenergetic product at a rate, k_i , and be reformed from isoenergetic product at a rate, k_j . Since reaction rates near the isomerization threshold

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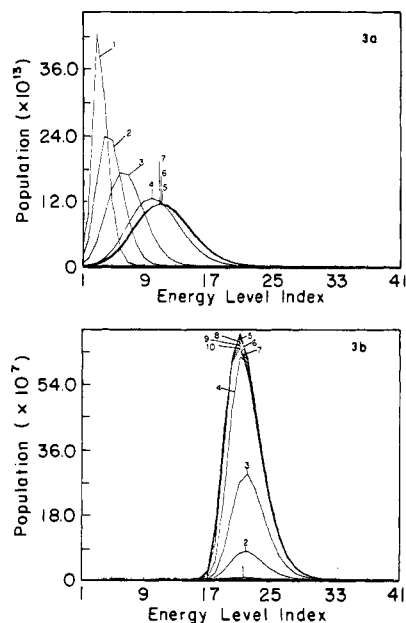


Figure 3. Time evolution of vibrational level populations. For isoprene (**3a**) the times (ns) are (1) 30, (2) 60, (3) 90, (4) 150, (5) 240, (6) 470, and (7) 970. For 1-methylcyclobutene (**3b**) the times (ns) are (1) 120, (2) 160, (3) 180, (4) 240, (5) 470, (6) 570, (7) 670, (8) 770, (9) 870, and (10) 970. The calculations assume a collision rate of 10^6 s^{-1} . Excitation of isoprene is with the $P(42)$, $10.6\text{-}\mu\text{m}$ laser line at 3 J/cm^2 .

are often slower than the rate of photon absorption, it is possible to excite a molecule to energies far above the isomerization threshold. Spontaneous emission and collisional activation are small cross section processes and are neglected. Reactant (N_i) and product (N_j) state populations can be described by a set of coupled differential equations (eq 3 and 4), where σ_i^a and σ_i^e are

$$dN_i/dt = -[I(\sigma_i^a + \sigma_i^e) + \alpha k_z + k_i]N_i + \alpha k_z N_{i+1} + I\sigma_{i+1}^e N_{i+1} + I\sigma_{i-1}^a N_{i-1} + k_j N_j \quad (3)$$

$$dN_j/dt = -[\alpha k_z + k_j]N_j + \alpha k_z N_{j+1} + k_i N_i \quad (4)$$

absorption and emission cross sections for optical transitions originating in level i . These are related to one another by eq 5, where g_i is the degeneracy of state

$$\sigma_{i+1}^e = (g_i/g_{i+1})\sigma_i^a \quad (5)$$

i . The gas kinetic collision rate k_z is weighted with an efficiency factor α , and k_i and k_j are the RRKM rate constants for states i and j , respectively.

Equations 3 and 4 can be numerically integrated with a suitable choice of parameters to obtain a time-resolved picture of the evolution of an IRMP isomerization reaction.¹⁹ Despite the simplicity of this model, calculated yields agree quite well with experiment for large molecules. The results of such a calculation for the excitation of 2-methyl-1,3-butadiene with a simulated 100-ns fwhm 3 J/cm^2 laser pulse are shown in Figure 3, where the energy level index corresponds to the number of infrared photons absorbed by the reactant. Figure 3 illustrates a number of features which are pertinent to IRMP isomerization reactions in general. The reactant energy distribution is seen to evolve with time to a maximum value of $\langle n \rangle = 12$ (32.4 kcal/mol). Only those reactant molecules with energies above the isomerization threshold (46 kcal/mol ≈ 17 quanta) yield product; however, the average product energy level is

21 quanta (57 kcal/mol), well above the isomerization threshold. The isomerization yield from each reactant energy level is limited by the steady-state relation $N_i k_i = N_j k_j$. Since reactant state i will have a higher density of states than the isoenergetic product state j in a contrathermodynamic reaction, the equilibrium will favor the reactant, particularly for states near the isomerization threshold. Increasing the laser fluence increases the population of reactant states far above the reaction threshold, for which the balance between reactant and product is less biased toward the reactants. However, a good thing can be pushed too far; reactant molecules excited into the continuum (Figure 2) can undergo irreversible fragmentation in competition with reversible isomerization, thus reducing the relative yield of the isomerization product.

With regard to point c, vibrationally excited reactant and products are deactivated by collisions, which occur slowly on the time scale of Figure 3, but rapidly relative to the time between pulses. The collision rate can be increased by increasing the pressure of the reactant or an inert buffer gas, thus decreasing the time required for collisional deactivation between laser pulses. However, an increase in the collision rate (pressure) also results in deactivation of the reactant during the excitation process, thereby decreasing the yield of vibrationally excited product. Further increases in the collision rate can lead to very rapid vibrational relaxation and rapid heating of the gas in the irradiated region similar to that observed in shock tubes. This type of process generally leads to thermodynamic control of the reaction.

All of the alkenes, dienes, and trienes listed in Table I meet the first condition for contrathermodynamic isomerization; viz., a frequency accessible with a CO_2 laser can be chosen at which the more stable isomer absorbs infrared radiation more strongly than the less stable isomer. A practical limitation on the yield of infrared laser-induced contrathermodynamic isomerization reactions is the unfavorable steady-state equality between excited reactant and product. As the isomerization reaction becomes increasingly endothermic, the steady-state population of excited product should become increasingly smaller. This effect is responsible for the low yields per laser pulse observed for butadiene \rightarrow cyclobutene isomerization.^{18,20}

A second practical limitation on the yield of laser-induced contrathermodynamic isomerization reactions is that, in real systems, fragmentation often occurs at average beam energies well below the expected threshold for isomerization due to laser beam inhomogeneities which cause local hot spots. Improved beam homogeneity is doubtless responsible for the observation of higher isomerization/fragmentation product ratios in more recent investigations of alkene isomerization.^{21,31} Preexponential factors for unimolecular fragmentation reactions of the molecules in Table I are likely to be substantially larger than those for isomerization. Thus low activation energy, low preexponential isomerization reactions are normally favored at low reactant energies, whereas high activation energy, high preexponential

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Table I.
Kinetic and Thermodynamic Parameters for Unimolecular Isomerization Reactions

reaction	log A	E_a , kcal/mol	ref	ΔH , kcal/mol	ΔS , cal/(mol K)	ref
<i>cis</i> -2-butene \rightarrow <i>trans</i> -2-butene	14.6	66.2	<i>a</i>	-1.04	-1.22	<i>b</i>
<i>cis</i> -2-pentene \rightarrow <i>trans</i> -2-pentene	13.6	58	<i>c</i>	-1.17	-0.85	<i>b</i>
<i>cis</i> -2-hexene \rightarrow <i>trans</i> -2-hexene	14.6	66.2	<i>a</i>			
<i>cis</i> -crotonitrile \rightarrow <i>trans</i> -crotonitrile	13.2	58	<i>c</i>	+0.17	-0.39	<i>d</i>
<i>cis</i> -methyl crotonate \rightarrow <i>trans</i> -methyl crotonate	13.2	58	<i>e</i>	-0.2	2.7	<i>e</i>
<i>cis</i> -1,3-pentadiene \rightarrow <i>trans</i> -1,3-pentadiene	13.6	53	<i>b</i>	-1.04	-0.14	<i>f</i>
cyclobutene \rightarrow 1,3-butadiene	13.3	32.7	<i>g</i>	-11.4	+3.6	<i>h</i>
1-methylcyclobutene \rightarrow 2-methyl-1,3-butadiene	13.8	35.1	<i>g</i>	-10.6	+3.9	<i>h</i>
1,2-dimethylcyclobutene \rightarrow 2,3-dimethylbutadiene	13.8	36.0	<i>g</i>	-9.6	+3.6	<i>h</i>
<i>trans,trans</i> - \rightarrow <i>cis,trans</i> -2,4-hexadiene	13.0	53.2	<i>i</i>	+1.10	+1.56	<i>i</i>
<i>cis,cis</i> - \rightarrow <i>cis,trans</i> -2,4-hexadiene	13.9	49.6	<i>i</i>	-0.84	-1.33	<i>i</i>
<i>cis</i> -1,3- \rightarrow <i>cis,trans</i> -2,4-hexadiene	10.8	32.5	<i>i</i>	-3.48	+1.48	<i>i</i>
<i>trans</i> - \rightarrow <i>cis</i> -1,3,5-hexatriene	12.7	43.3	<i>j</i>	1.0	<i>k</i>	
<i>cis</i> -1,3,5-hexatriene \rightarrow 1,3-cyclohexadiene	11.8	29.9	<i>j</i>	-9.7	<i>k</i>	

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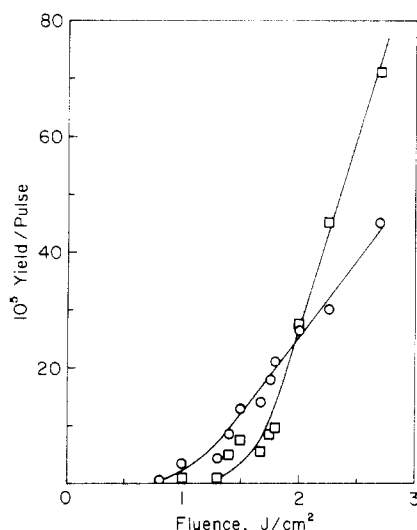


Figure 4. Fluence dependence of the yields per pulse of isomerization (O) and fragmentation (□) products from *trans*-methyl crotonate.

fragmentation reactions are favored by high reactant energies.³¹ This is clearly demonstrated by the fluence dependence of the isomerization and fragmentation yields for *trans*-methyl crotonate shown in Figure 4.³² Similar results have been obtained for the fluence dependence of the isomerization and fragmentation yields from *trans*-2-pentene.^{21b}

Rate constants for the isomerization and fragmentation reactions can be calculated by using the classical RRK model (eq 6), where s is typically taken to be half

$$k_j = A \left(\frac{E_j^* - E_a}{E_j^*} \right)^{s-1} \quad (6)$$

the total number of vibrational modes. The rates of *trans*-2-pentene isomerization and fragmentation³³ are calculated to be equal when $E_j^* = 102$ kcal/mol, far

(32) Fragmentation is reported to compete with isomerization at all temperatures for which *cis*-*trans* isomerization occurs at measurable rate in a static reactor (>350 °C); however, activation parameters for fragmentation are not reported; Butler, J. N.; Small, G. J. *Can. J. Chem.* **1963**, *41*, 2492-2499.

(33) Activation parameters for loss of $\cdot\text{CH}_3$ are assumed to be the same as for 1-butene pyrolysis (log $A = 16.3$, $E_a = 71.5$ kcal/mol); Trenwith, A. B. *Trans. Faraday Soc.* **1970**, *66*, 2805-2811.

above the threshold for either reaction. The series of *trans*-alkenes 2-butene, 2-pentene, and 2-hexene has similar single photon absorption cross sections and isomerization activation parameters (Table I); however, the activation energies of fragmentation decrease with increasing molecular weight.³⁴ As expected on the basis of classical RRK model calculations for the isomerization vs. fragmentation process, the experimental isomerization/fragmentation ratio decreases in the same order.

A particularly interesting case of competing isomerization and fragmentation reactions is that of the isomeric 1,3-pentadienes. Clean and quantitative fragmentation to cyclopentadiene and H_2 occurs at fluences (>3 J/cm²) only modestly higher than the *trans*-*cis* isomerization threshold (1.5 J/cm²). Non-selective fragmentation is observed at substantially higher fluence (>5 J/cm²). This behavior is compatible with the kinetic parameters for dehydrogenation. Loss of H_2 from *cis*-1,3-pentadiene is reported to proceed with activation parameters log $A = 13.0$ and $E_a = 65$ kcal/mol, estimated from low-pressure pyrolysis data.³⁵ The loss of H_2 may occur in a stepwise or concerted fashion via a cyclic transition state similar to that for the degenerate 1,5 hydrogen shift (log $A = 11$, $E_a = 35$ kcal/mol).³⁶

Consecutive and Competing Isomerization Reactions

In the preceding section we have seen how the yields of IRMP-induced contrathermodynamic unimolecular isomerization reactions are limited by the unfavorable equilibrium between vibrationally excited reactant and product and by competing fragmentation reactions. Pulsed laser excitation has also proven to be a powerful technique for the investigation of competing and consecutive unimolecular isomerization reactions. As in the case of competing isomerization and fragmentation reactions, increasing laser fluence can allow the observation of high activation energy isomerization pathways which are not normally observed with conventional

(34) Activation parameters for loss of $\cdot\text{CH}_3$ from *cis*-2-butene are log $A = 16$, $E_a = 80$ kcal/mol; Jeffers, P.; Bauer, S. H. *Int. J. Chem. Kinet.* **1974**, *63*, 763-771.

(35) Nguyen, T. T.; King, K. D. *Int. J. Chem. Kinet.* **1982**, *14*, 623-629.

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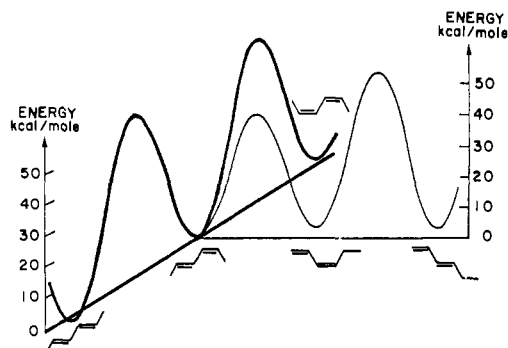


Figure 5. Schematic of proposed isomerization pathways in the conjugated hexadiene isomer system. Also depicted are the barriers to isomerization and the relative thermodynamic stabilities of the species.

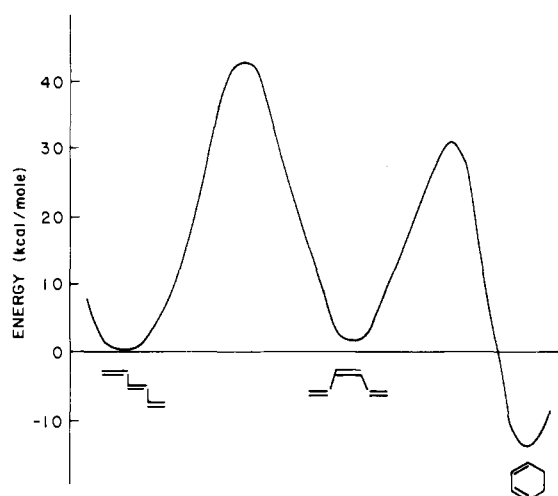


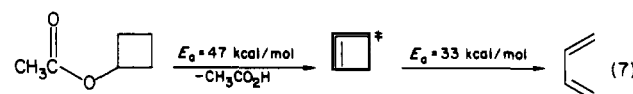
Figure 6. Schematic of isomerization pathways in the 1,3,5-hexatriene-1,3-cyclohexadiene system.

heating. A noteworthy example is the report of the symmetry-forbidden (disrotatory) electrocyclic ring opening of *cis*-3,4-dichlorocyclobutene upon IRMP excitation at high fluence.^{37a} The threshold fluence for the forbidden products is presumably substantially higher than that for the allowed (conrotatory) product, thus explaining the previously reported failures to observe disrotatory IRMP-induced ring opening of cyclobutenes.^{37b}

We have investigated the effects of laser fluence upon the branching ratios for the competitive *cis*-*trans* vs. 1,5-sigmatropic isomerization reactions of *cis,trans*-2,4-hexadiene (Figure 5)²⁰ and *cis*-*trans* vs. electrocyclic isomerization of *cis*-1,3,5-hexatriene (Figure 6).²² In both cases the lower activation energy process proceeds via a cyclic transition state and has a lower preexponential factor than the competing *cis*-*trans* isomerization process. As a consequence, the rate of the higher activation energy process may exceed that of the lower activation energy process at sufficiently high reactant energies. The results of RRK calculations indicate equal rates for the competitive reactions within the *cis,trans*-2,4-hexadiene system²⁰ and the *cis*-1,3,5-hexatriene system²² at reactant energies of ca. 85 and 140 kcal/mol, respectively. Experimental results for these systems provide ratios of high activation energy to low

activation energy products under optimized conditions of fluence and pressure of 1.0 for *cis,trans*-2,4-hexadiene at 6.5 J/cm² and 0.1 for *cis*-1,3,5-hexatriene at 2.5 J/cm². While the latter ratio may not seem impressive, it should be borne in mind that conventional heating of *cis*-1,3,5-hexatriene yields *only* cyclohexadiene.

A particularly exciting application of IRMP methods to the investigation of consecutive unimolecular reactions is based upon the ability to collisionally deactivate intermediate products which are kinetically labile under normal excitation conditions. The initial report of the IRMP-induced production of a labile product was provided by Nguyen and Danen,³⁸ who observed that upon elimination of acetic acid from cyclobutyl acetate the ratio of primary cyclobutene product to secondary butadiene product (eq 7) increased with decreasing laser



fluence and increasing CF₄ buffer gas pressure. Under normal gas-phase thermal activation conditions, butadiene is the exclusive reaction product due to the substantially lower activation energy for the secondary reaction.

We have observed the formation of thermally labile products upon IRMP-induced isomerization of both *trans*-1,3-hexadiene²⁰ and *trans*-1,3,5-hexatriene.²² Conventional heating of *trans*-1,3-hexadiene yields predominantly *cis,trans*-2,4-hexadiene, presumably via sequential *trans*-*cis* isomerization and 1,5-sigmatropic reactions. Pulsed laser excitation of *trans*-1,3-hexadiene at high fluence and low pressure yields all four isomeric hexadienes (Figure 5); however, *cis*-1,3-hexadiene becomes the major product at moderate fluence (3.5 J/cm²) and Ar buffer gas pressure (5 torr). Similarly, conventional heating of *trans*-1,3,5-hexatriene yields only cyclohexadiene (Figure 6), whereas *cis*-1,3,5-hexatriene is the major product of the IRMP-induced reaction at moderate fluence (≤ 3.5 J/cm²) and Ar buffer gas pressure (1 torr). The basic principle of stabilization of thermally labile products in an $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ reaction scheme is straightforward. When the rate of collisional deactivation of excited B becomes comparable to k_2 , B will accumulate even if k_2 exceeds k_1 . Further stabilization occurs as the collisional deactivation rate is increased; however, the yield of both B and C decreases due to the concomitant deactivation of A.

Another unique feature of IRMP excitation is illustrated by the hexadiene isomer system shown in Figure 5. In our initial investigation of IRMP-induced isomerization reactions we observed that excitation of any one of the five isomeric 2,4- or 1,3-hexadienes resulted in the formation of all four isomeric products after only a single excitation pulse.¹⁷ Inspection of the schematic energy surface shown in Figure 5 indicates why this is the case: activation parameters for all of the *cis*-*trans* isomerization processes are similar (Table I) while the 1,5-sigmatropic hydrogen shift that interconverts *cis,trans*-2,4-hexadiene and *cis*-1,3-hexadiene has a smaller preexponential and activation energy. Thus a molecule excited several quanta above the barrier for one isomerization reaction is also expected to be above the

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barrier for competing isomerization reactions and may yield vibrationally excited products with sufficient energy to undergo a second isomerization reaction. Clearly, the product distributions obtained in such a reaction will depend upon the reactant energy distribution, which is fluence and pressure dependent, and the rate of collisional deactivation of the product(s), which is pressure dependent. This has been shown to be the case in our subsequent detailed investigations of the hexadiene system²⁰ and in Farneth's³⁹ investigations of the IRMP-induced reactions of vinylcyclopropane.

Concluding Remarks

The examples that we have presented, while limited to unimolecular isomerization and fragmentation reactions of unsaturated hydrocarbons, serve to illustrate some of the unique characteristics of IRMP excitation. The finite infrared frequency shifts or intensity differences between isomeric molecules make it possible to selectively excite one molecule in an isomeric mixture and thus generate distinctly nonthermal product distributions in competing and consecutive reactions. Application of IRMP excitation to the synthesis of kinetically labile intermediates has been amply demonstrated. This latter capability can be employed to help distinguish between competing and consecutive reaction pathways. We have also utilized IRMP excitation to study the competition between low-energy isomerization vs. high-energy isomerization and fragmentation pathways, which are not observed under normal steady-state thermolysis conditions.

In addition to the applications we have discussed, IRMP excitation continues to be extensively utilized for separation of isotopes via selective fragmentation.^{10,12} It is also widely used to generate transient species, particularly those of interest in catalytic and combustion processes, by photolysis of appropriate precursors.⁴⁰ This has allowed the spectroscopic characterization of these species and the measurement of their reaction kinetics. Despite this multiplicity of uses it is also clear that the scope of the technique still has not been exhausted. Along these lines we now conclude with the description of a new, potentially very exciting, application of IRMP excitation which is in its early stages

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of development and understanding.

While a remarkable degree of product selectivity has been observed in some of the reactions described in this Account, the low-energy unimolecular isomerization pathways available to an IRMP-excited molecule are limited to those available upon continuous heating. The scope of thermal hydrocarbon isomerization has been greatly expanded by the use of transition-metal catalysts.⁴¹ For example, 1,3-sigmatropic hydrogen shifts are rarely observed for acyclic alkenes upon thermal activation; however, coordinatively unsaturated metal carbonyl catalysts are able to effect the positional isomerization of alkenes as well as their hydrogenation and hydrosilation.⁴²

We have recently initiated an investigation of the IRMP-induced homogeneous vapor-phase reactions of some simple alkenes in the presence of $\text{Fe}(\text{CO})_5$.²³ Whereas steady-state thermolysis of such reaction mixtures results in decomposition of $\text{Fe}(\text{CO})_5$ without alkene isomerization, we observe both alkene cis-trans and positional isomerization upon pulsed laser excitation. Moreover, the isomer ratios obtained appear to be kinetically controlled and differ significantly from the thermodynamically controlled isomer ratios observed upon ultraviolet irradiation in the solution phase.⁴² The initial attempt to combine IRMP methods with heterogeneous catalysis was recently reported by Farneth and co-workers.⁴³ They observe that laser excitation of 2-propanol vapor in the presence of solid cupric oxide results in the formation of both the unimolecular (propene and water) and catalyzed (acetone and hydrogen) reaction products. While attempts to combine IRMP methods with homogeneous and heterogeneous catalysis are still at a preliminary stage, the promise of such combined technology has clearly been established. We anticipate the development of numerous additional applications of IRMP methods.

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