Selective Trans to Cis Isomerization of Alkenes via Infrared Multiphoton Excitation

Peter P. Teng, Eric Weitz,[†] and Frederick D. Lewis*

Department of Chemistry, Northwestern University
Evanston, Illinois 60201

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It is now well established that infrared multiphoton excitation can effect the isomerization of thermodynamically more stable to less stable isomers in cases where the more stable isomer can be selectively excited.[1-3] Among the reported examples of such isomerization reactions are the conversions of hexafluorocyclobutene[1] to hexafluorobutadiene and methylbutadienes to methylcyclobutenes.[3] Infrared multiphoton excitation might be expected to result in more selective isomerization than ultraviolet single-photon excitation in cases where both isomers absorb at the excitation frequency. In the case of ultraviolet excitation, reversible isomerization ($A \rightleftharpoons B$) leads to a photostationary state governed by extinction coefficients and quantum yields (eq 1).

$$[A]/[B] = \epsilon_B/\epsilon_A(\phi_{B\to A}/\phi_{A\to B}) \qquad (1)$$

For isomers with similar electronic absorption spectra and quantum yields such as cis and trans alkenes, photostationary states near unity are observed.[4] In the case of multiphoton infrared excitation, reversible isomerization should yield a photostationary state governed by the absorption cross section (σ) for each step in the up-pumping process and cross sections for stimulated emission, collisional deactivation rate constants, and rates of isomerization.[3b] In cases where isomerization can be described by a master equation model, 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 $[A]/[B] \gg \sigma_B/\sigma_A$. We report here the preliminary results of our investigation of the multiphoton infrared isomerization of several unconjugated and conjugated alkenes.

Kinetic and thermodynamic parameters for cis → trans isomerization of 2-butene,[5] crotononitrile,[6] and 1,3-pentadiene[6b,7] are given in Table I. Under conditions of thermal equilibrium $[\text{cis}]/[\text{trans}] < 1$ for 2-butene and 1,3-pentadiene, whereas $[\text{cis}]/[\text{trans}] \sim 1.4 \pm 0.2$ for crotononitrile over the temperature range 300–560 °C. Direct and/or triplet-sensitized photoisomerization of all three alkenes results in photostationary states $[\text{cis}]/[\text{trans}] \lesssim 1$.[8-10] Infrared multiphoton reactions of *trans*-2-butene have been previously investigated by Yogev and Lowenstein-Benamair.[11] With a focused laser beam the yield of fragmentation was found to exceed that of trans → cis isomerization.

We have investigated the infrared multiphoton irradiation of several alkenes by employing a collimated laser beam under conditions previously found to effect the unimolecular isomerization reactions of hexadienes and butadienes without significant competing fragmentation.[2,3,12] Reported in Table II are laser excitation frequency and fluence, single-photon absorption cross sections, per pulse yields for trans → cis and cis → trans isomerization, and the percent cis isomer content of the steady state, obtained from the ratio of per pulse yields or by GC analysis following prolonged irradiation. Values obtained by these two methods are in good agreement. The same stationary state is obtained upon 931- or 953-cm^{-1} irradiation of either *trans*- or *cis*-1,3-pentadiene. Some fragmentation (ca. 20%) was observed for 2-butene but was not observed for the other alkenes under the conditions reported in Table II. Reported single-photon absorption cross sections, σ, for the butenes, pentenes, and pentadienes were obtained from gas-phase (5–20 torr) FTIR spectra. The spectra of *trans*- and *cis*-1,3-pentadiene are shown in Figure 1. In the case of crotononitrile, multiphoton absorption cross sections were determined both by calorimetric measurement of the attenuation of the laser beam intensity and by photoacoustic measurements. Values obtained by both methods are in reasonable agreement

Table I. Kinetic and Thermodynamic Parameters for Cis → Trans Isomerization

alkene	log A	E_a, kcal/mol	ΔH, kcal/mol	ΔS, cal/(mol K)
2-butene[a]	13.6	62	−0.75	−1.2
crotononitrile[b]	13.2	58	0.2	−0.4
1,3-pentadiene[c]	13.6	53	−0.5	

[a] Data from ref 5. [b] Data from ref 6. [c] Data from ref 7.

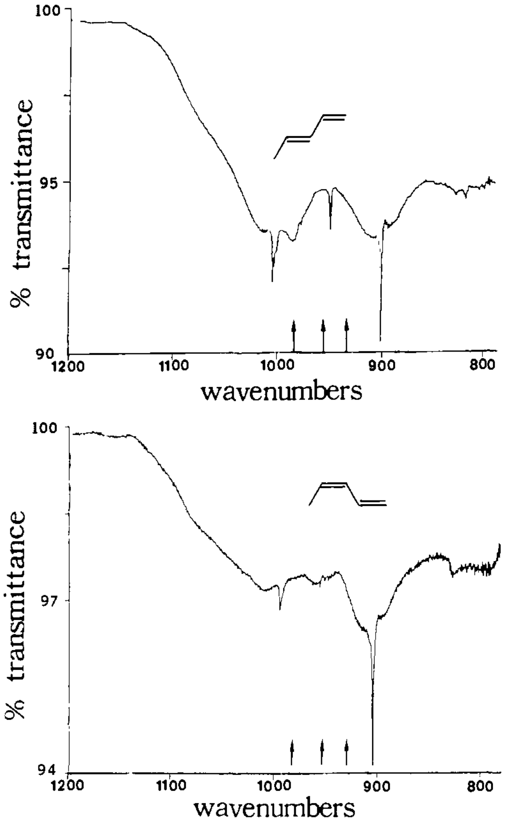

Figure 1. FTIR spectra of *trans*- and *cis*-1,3-pentadiene (5 torr). Arrows indicate laser excitation frequencies (Table II).

[†] Alfred P. Sloan fellow.

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(12) Samples (0.1 torr) contained in a 1-dm path length Pyrex cell with NaCl windows were irradiated with the collimated, unfocused output of a Lumonics K203-2 CO_2 TEA laser. Laser lines were determined with an Optical Engineering CO_2 laser spectrum analyzer and energies with a Scientech calorimeter. Irradiated samples were analyzed by FID GC. The mass balance for isomerization and/or fragmentation products was quantitative (±10%) as determined by GC analysis. When ethyl acetate was included as a transparent thermometer, it did not undergo fragmentation (E_a = 48 kcal/mol).

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Table II. Frequency and Fluence Dependence of per Pulse Yields and Stationary States

alkene	ν_{ex}, cm^{-1}	$10^{19}\sigma_t$, cm^2	$10^{19}\sigma_c$,[a] cm^2	fluence, J/cm^2	10^5(yield/pulse)[b] t → c	10^5(yield/pulse)[b] c → t	steady state,[c] % cis
2-butene	975	1.4	0.5	4.5	30	<0.1	(<95)
2-pentene	949	0.17	0.15	4.5	1.0	0.13	88
				6.0	7.0	0.69	91
crotononitrile	931	0.64	0.09	3.2	70	<0.1	99 (>95)
	951	1.0	0.41	5.5	90	1	98 (>95)
	978	0.45	0.04	3.4	80	<0.1	99 (>95)
1,3-pentadiene	931	2.7	2.4	2.7	310	210	60 (63)
	953	2.4	2.1	2.7	41	12	77 (80)
				2.9	145	44	77 (80)
				3.1	310	89	78 (80)
	982	3.2	2.1	2.7	300	<0.1	(<95)

[a] Single-photon absorption cross section obtained from infrared absorption spectrum (±10%). [b] Yield of molecules in irradiated volume converted per pulse at low conversions (<5%). [c] Values calculated from single-pulse yields or the observed stationary state (values in parentheses).

(±20%) with the single-photon absorption cross sections. Additionally, plots of the average number of photons absorbed per pulse vs. laser fluence are linear over the fluence range 1–3.5 J/cm^2. Such behavior is characteristic of large organic molecules for which excitation from the region of discrete states to the quasi-continuum occurs without the threshold behavior observed for small molecules.[2,3,13]

The most striking result of the present investigation is that essentially quantitative (>95%) contrathermodynamic conversion of trans to cis alkenes can be achieved in cases where the ratio of single-photon absorption cross section $\sigma_t/\sigma_c > 1.5$. Even in those cases where the difference in cross section is small ($\sigma_t/\sigma_c = 1.1 \pm 0.1$ for 2-pentene and for 1,3-pentadiene at 931 and 953 cm^{-1}), the percent cis isomer content of the stationary state is significantly higher than predicted from the ratio of cross sections. Thus substantial amplification of the difference in single-photon absorption cross section may occur in the multiphoton excitation process. The results for 1,3-pentadiene demonstrate that even with the limited selection of excitation frequency available with the CO$_2$ TEA laser, it is possible to control the isomer ratio by the choice of frequency.

The per pulse yields for trans → cis isomerization (Table II) are dependent upon alkene structure, absorption cross section, and laser fluence. Both *trans*-2-butene and *trans*-2-pentene display a threshold fluence of ca. 4 J/cm^2, below which the per pulse yield is too small to permit accurate measurement ($<10^{-6}$). Threshold fluences for *trans*-crotononitrile and *trans*- or *cis*-1,3-pentadiene are 1.5 J/cm^2. Above these threshold values, yields increase with increasing laser fluence, as shown in Table II for 953-cm^{-1} irradiation of 1,3-pentadiene and 1049-cm^{-1} irradiation of 2-pentene. Irradiation of *trans*-2-butene with fluence >6 J/cm^2 induces more fragmentation than isomerization, while irradiation of *cis*- or *trans*-1,3-pentadiene at 982 cm^{-1} and at fluences >3 J/cm^2 results in loss of H$_2$ to quantitatively and irreversibly yield cyclopentadiene.[14] This in itself is an interesting result. It is another example[2b] where merely changing laser parameters can drastically alter the course of a reaction. Comparison of the results for *trans*-2-butene and *trans*-2-pentene demonstrates that the yield increases with increasing absorption cross section for molecules with similar activation barriers irradiated with the same laser fluence. While differences in cross section and fluence preclude quantitative comparison of results for the different alkenes, it is clear that the per pulse yield also increases with decreasing thermal activation energy (Table I). These observations are consistent with a simple rate equations model for reversible multiphoton isomerization in which the yield is determined by the convolution of state populations (determined by absorption cross section and laser fluence) and isomerization rate constants.[3b]

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Registry No. *cis*-2-Butene, 590-18-1; *cis*-crotononitrile, 1190-76-7; *cis*-1,3-pentadiene, 1574-41-0; *trans*-2-butene, 624-64-6; *trans*-crotononitrile, 627-26-9; *trans*-1,3-pentadiene, 2004-70-8; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8.

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[14] (a) Loss of H$_2$ in the low-pressure pyrolysis of 1,3-pentadiene is reported to yield 1,2,4-pentatriene on the basis of a *m/e* 66 peak in the mass spectrum.[14b] We found that the IR spectrum, mass spectral fragmentation, and GC retention time of the *m/e* 66 product were identical with those of cyclopentadiene. (b) Nguyen, T. T.; King, K. D. *Int. J. Chem. Kinet.* **1982**, *14*, 623–629.

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^{252}Cf Fission Fragment Ionization Mass Spectrometry of Chlorophyll *a*

B. T. Chait* and F. H. Field

Rockefeller University, New York, New York 10021

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In a recent communication, Hunt et al.[1] report on the fission fragment induced ionization mass spectra of chlorophyll *a* (Chl *a*). They conclude that the fragmentation reactions observed must have occurred on an extremely short time scale (10^{-12}–10^{-14} s). We have made an independent investigation of Chl *a* by fission fragment ionization mass spectrometry. We obtain new results, and our conclusions differ substantially from those of the aforementioned authors.[1]

The mass spectra were obtained with the spectrometer described previously,[2] modified[3] by the addition of retarding grids to allow the measurement of reactions and rates of decompositions occurring during flight. A flux of 3000 fission fragments s^{-1} was used. Samples with a thickness of ~15 μg/cm^2 were prepared by evaporation of Chl *a*[4] from benzene and CCl$_4$ solutions on 1 μm thick Ni and 2 μm thick aluminized polyester, respectively.

Our unretarded spectra of Chl *a* correspond closely to those given in ref 1. The molecular ion regions of the sharpened spectra obtained with retarding potential are shown in Figure 1, top (positive), and Figure 1, bottom (negative). The Chl *a* sample contained a small amount of pheophytin *a* (Pheo *a*), which serves a useful comparative function.

The following observations were made:

(1) Only 1.3% of the positive and 4.7% of the negative Chl *a* molecular ions survive intact the 67-μs flight to the ion detector.

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[4] Samples of Chl *a* were obtained from the Laboratory of D. C. Mauzerall at The Rockefeller University, The Sigma Chemical Co., St. Louis, MO, and United States Biochemical Corp., Cleveland, OH.

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