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Supplementary Material Available: The observed and calculated structure factors for **14** (7 pages). Ordering information is given on any current masthead page.

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Infrared Laser Induced Organic Reactions. 1. Irradiation of Ethyl Acetate with a Pulsed CO_2 Laser. Selective Inducement vs. Thermal Reaction[1]

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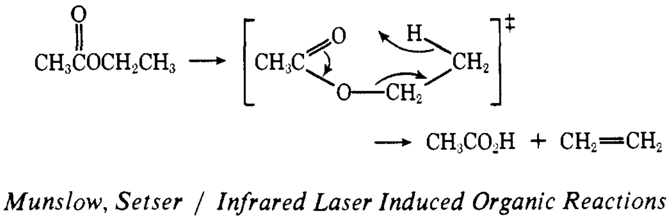
Abstract: Gas phase samples of ethyl acetate (**1**) were irradiated with a pulsed CO_2 laser to produce acetic acid and ethylene. The elimination of HBr from isopropyl bromide (**2**) was used as an internal standard to monitor thermal effects. Under nonfocused conditions (E_{irr} = 0.7–0.8 J/cm^2), ethylene was produced at 12–16% conversion per flash (CPF), nearly all of which was due to thermal processes. Under partially focused beam conditions (E_{irr} = 0.8–8.0 J/cm^2), it was possible to demonstrate laser-induced, nonequilibrium chemistry by showing that ethylene was produced in an amount that was greater than expected via the thermal route. These studies indicated that both low pressure and high energy of irradiations were necessary for the nonequilibrium pathway. Because of the similarities in Arrhenius parameters for the decomposition of **1** and **2,** it was possible to identify the amount of ethylene produced by both the thermal pathway and that produced via the nonequilibrium pathway.

Much interest has developed recently in the use of intense infrared radiation to augment chemical reactions. Considerable effort has been directed toward isotope separation[2] and understanding the multiple photon absorption process[3] using small molecules, while little has been done with relatively large organic molecules.[4] We wish to report the CO_2 laser augmented decomposition of ethyl acetate; a simple technique was employed by which the amount of laser-induced, nonequilibrium chemistry vs. simply heating was evaluated.[1]

The thermal decomposition of ethyl acetate proceeds through a cyclic transition state to yield ethylene and acetic acid with a rate constant of $k = 10^{12.59} \exp(-48\ 000/RT)$.[5a] This reaction can be induced with a pulsed CO_2 laser under both nonfocused and partially focused beam conditions; ethylene and acetic acid are the sole products as determined by gas chromatography and infrared spectroscopy of the reaction



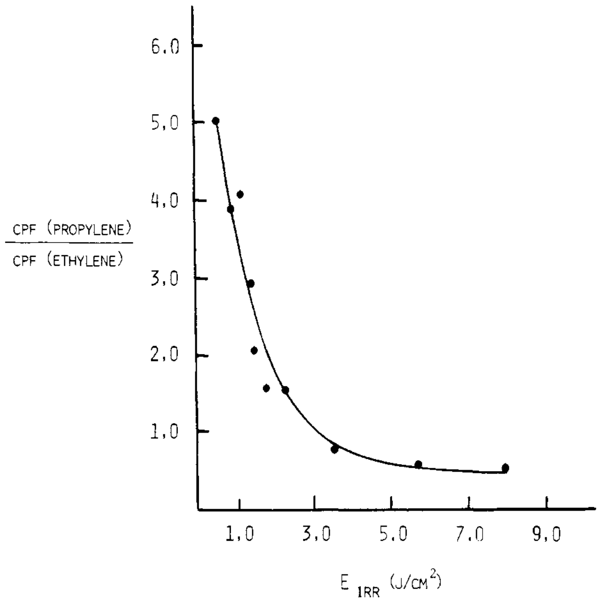


Figure 1. Plot of CPF(propylene)/CPF(ethylene) vs. laser intensity for 5 Torr of a 1:3 mixture of ethyl acetate and isopropyl bromide.

mixture. The irradiated absorption band centered at 1055 cm^{-1} is due mainly to the O-C_2H_5 stretching mode. Under nonfocused or weakly focused conditions at high (>20 Torr) pressure, ethyl acetate was shown to react in a thermal process in which all the molecules within the irradiated volume, regardless of whether they absorbed laser radiation, had become completely vibrationally equilibrated. Under more highly focused and lower pressure conditions, a nonequilibrium reaction occurred in the sense that only those molecules excited by the infrared radiation reacted and that *intermolecular V-V* and *V-T,R* transfer did not occur prior to reaction. The occurrence of this moderately complex rearrangement involving the rupture or formation of six bonds implies that at least a partial intramolecular redistribution of the deposited laser energy must occur even under focused conditions.[6-10]

Experimental Section

All experiments were conducted in a reaction vessel which consisted of a cylindrical Pyrex tube of 1-cm path length and 3-cm diameter fitted with NaCl windows and a vacuum stopcock. Irradiation was accomplished with a Lumonics TEA 103 pulsed CO_2 laser. The laser beam was directed through an iris of 1-in. diameter to remove the outer fringes of nonuniform energy density. The energy of the nonfocused beam was determined to be 0.7–0.8 J/cm^2 with a Lumonics Model 20D pyroelectric detector; <15% of the energy was absorbed per pulse. The pulse duration was measured with a Rofin Model 7415 photon drag detector and full width at half maximum found to be ~150 ns.

All quantitative analyses were by gas phase chromatography.

Results and Discussion

Pulsing 20 Torr of ethyl acetate three–five times under nonfocused conditions produced acetic acid and ethylene at 14 ± 2% conversion per flash (CPF) where CPF = (ethylene)/((ethylene) + (EtOAc)). The CPF was, within experimental error, independent of the CO_2 rotational line used within the frequency range 1050.5–1035.5 cm^{-1} provided that the energies of irradiation were comparable.

The following experiments were performed to check for thermal effects. With 20 Torr of ethyl acetate and varying amounts (10–80 Torr) of CF_4 the CPF was reduced to ~2% at high pressures of added bath gas. This result is consistent with either a temperature drop of the system due to the increased heat capacity or collisional deactivation of the vibrationally excited ethyl acetate.

To evaluate thermal effects further, the HBr elimination from isopropyl bromide ($k = 10^{13.6}\exp(-47\,800/RT)$)[5b] was used as an internal standard. Since the activation energies for the acetate and bromide reaction are very similar, the ratio of the thermal rate constants is essentially temperature independent. For a 1:3 mixture of isopropyl bromide and ethyl acetate the expected product ratio is ~4 for a thermal process; experimentally we found a ratio of 4 ± 1 from a mixture of 5 Torr of isopropyl bromide and 15 Torr of ethyl acetate irradiated at 1049.6 cm^{-1} under nonfocused conditions. In the absence of ethyl acetate, isopropyl bromide did not undergo any reaction under either focused or nonfocused conditions when irradiated at this wavelength.

As a check on the thermal ratio obtained from the Arrhenius equation, a mixture of 10 Torr of SF_6 and 10 Torr of 1:3 mixture of isopropyl bromide and ethyl acetate was irradiated at 945.0 cm^{-1}. Neither ethyl acetate nor isopropyl bromide reacted at this wavelength when irradiated in the absence of SF_6. The SF_6 absorbed the radiation but did not itself undergo reaction at these laser intensities; hence, it served only as a thermal sensitizer. An average of three experiments yielded a value of 5.5 ± 1 for the ratio of CPF(propylene)/CPF(ethylene). These experiments showed that the majority of the ethylene produced from irradiation of ethyl acetate alone under nonfocused conditions arose from thermal processes rather than from any selective, nonequilibrium laser initiation.

In order to demonstrate unambiguously laser-induced chemistry prior to collisional redistribution of energy, it was necessary to focus the laser beam,[9] thereby increasing the energy density of the pulse. The effect produced is displayed by Figure 1. As expected, at low energies of irradiation the CPF(propylene)/CPF(ethylene) ratio was near the thermally calculated value of ~4, but the ratio dropped dramatically as the intensity of radiation was increased. At 8 J/cm^2, the ratio was only 0.6. Higher irradiation intensities were precluded by cracking of the NaCl windows under the more highly focused conditions. These experiments demonstrated that, as the energy density of incident infrared radiation was increased, the nonequilibrium laser-induced pathway became increasingly important.

The CPF(propylene)/CPF(ethylene) ratio was also monitored as a function of reactant pressure at a constant laser intensity of 2.1 J/cm^2. The ratio decreased linearly from a value of 1.6 at 60 Torr to 0.8 at 5 Torr. This result demonstrated that as the number of collisions/second was reduced, the rate at which thermal equilibrium is reached was decreased, again allowing the nonequilibrium laser-induced pathway to become increasingly important.

As a result of the similarities of Arrhenius parameters, the amount of ethylene produced via the laser-induced reaction and that produced via the thermal reaction may be calculated as follows for low percentage CPF. Assuming the CPF(ethylene)/CPF(propylene) ratio can be partitioned as follows

$$\frac{\mathrm{CPF(ethylene)}}{\mathrm{CPF(propylene)}} = \frac{(\mathrm{CPF(ethylene)})_{\mathrm{thermal}} + (\mathrm{CPF(ethylene)})_{\mathrm{laser}}}{\mathrm{CPF(propylene)}}$$
$$= \frac{(\mathrm{EtOAc})(3.89 \times 10^{12}\exp(-48\,000/RT))}{(\text{isopropyl bromide})(3.98 \times 10^{13}\exp(-47\,800/RT))} + \frac{(\mathrm{CPF(ethylene)})_{\mathrm{laser}}}{\mathrm{CPF(propylene)}}$$

all values of the equation may be measured experimentally except the $\mathrm{CPF(ethylene)}_{\mathrm{laser}}$. For a typical experiment with a laser intensity of 2.1 J/cm^2 and 5-Torr total pressure, the observed CPF(ethylene)$_{\text{total}}$ = 19% and CPF(propylene) = 28%. For a thermal rate constant ratio of 0.08, this yields a CPF(ethylene)$_{\text{laser}}$ of 12%, indicating 64% of the ethylene produced was via the nonthermal, laser-augmented pathway under these conditions.

Summary

Our results demonstrate that under appropriate conditions a moderate-sized organic molecule can be induced to undergo a nonequilibrium reaction by multiple photon absorption from a high energy infrared laser pulse. The need to conduct such experiments at lower pressure and rather high laser intensities to minimize V–V and V–T,R intermolecular relaxation may be a general requirement particularly for large polyatomic molecules for which V–V relaxation rates are ≥ 0.1 of the gas kinetic collision frequency. Since the nonequilibrium laser-induced reaction pathway follows the unimolecular pathway of lowest energy and since the laser pathway is competitive with collisional relaxation in the 1-Torr range, *intramolecular* relaxation of the absorbed laser energy is implied.[6,10]

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References and Notes

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Ester Aminolysis. Structure–Reactivity Relationships and the Rate-Determining Step in the Aminolysis of Substituted Diphenyl Carbonates[1]

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Abstract. The rates of reaction of quinuclidines with substituted diphenyl carbonates in aqueous solution increase sharply with increasing amine basicity ($\beta_{\text{nuc}} = 1.0$) until the amine is 3–5 units more basic than the leaving aryl oxide ion and then break to a small dependence on amine basicity ($\beta_{\text{nuc}} = 0.3$); corresponding breaks, with $\beta_{\text{lg}} = -1.3$ and -0.2, are found with changing pK of the leaving group. This behavior is interpreted in terms of a change in rate-determining step from breakdown to formation of the addition intermediate, as in the similar reactions of substituted phenyl acetates. The structure–reactivity data are described in terms of "effective charges" on the reacting groups and it is shown that the pK difference at which the change in rate-determining step occurs is a function of the absolute basicity of the attacking and leaving groups. In the reactions of phenyl acetates the kinetic partitioning of the intermediate through the transition states for expulsion of amine and aryl oxide reflects the thermodynamic partitioning of the reaction products at equilibrium.

Structure–reactivity relationships in acyl transfer reactions are of interest in themselves and for the light they shed on the mechanism of the reactions. Structure–reactivity correlations for the reactions of primary, secondary, and tertiary amines with substituted phenyl acetates show a break from a large ($\beta_{\text{nuc}} = 0.9 \pm 0.1$) to a small ($\beta_{\text{nuc}} = 0.2 \pm 0.2$) dependence of the rate on the basicity of the attacking amine when the amine becomes some 4–5 pK units more basic than the leaving aryl oxide ion.[2] This break has been interpreted as a consequence of a change in rate-determining step, from rate-determining amine attack with the most basic amines ($\beta_{\text{nuc}} \sim 0.2$) to rate-determining aryl oxide expulsion from an addition intermediate, T$^{\pm}$, with less basic amines ($\beta_{\text{nuc}} \sim 0.9$) (eq 1).[3,4]

The experiments reported in this and the subsequent paper were directed toward the goal of testing this interpretation directly in the closely related reactions of substituted diphenyl carbonates by generating the tetrahedral intermediate T$^{\pm}$ from