

The choice of supporting electrolyte for the electrochemical preparation of **1** was critical. Tetraethyl- and tetrabutylammonium salts produced substantial amounts of tertiary amine and olefin, presumably from a Hofmann reaction of the intermediate carbanion.¹³ These products were difficult to separate from **1**. A reaction using platinum cathode with tetraalkylammonium salts followed a different course and gave little or no olefin.

Studies on the mechanism of formation of **1** and its chemical behavior are in progress.

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- (6) Normally the catholyte volume is 25 mL, anolyte 15 mL.
- (7) The use of this supporting electrolyte was suggested Professor S. Mazur, and its preparation will be described elsewhere.
- (8) The counterelectrode was a 1-cm² platinum foil, and the mercury surface area was 11.3 cm².
- (9) CCl₃ appeared to react with **1** and induce polymerization. Similar behavior has been observed for other strained bridgehead olefins (Professor D. Aue, private communication).
- (10) Using C₆D₅CD₃ the peaks appeared at 163.3 and 44.1 ppm relative to Me₄Si. The low field peak was small compared with the ¹³CH₂ resonance, possibly owing to a long spin-lattice relaxation time.
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Enthalpy Limit in The Laser-Induced Reaction of CH₃CF₂Cl

Sir:

Recently, Tardieu de Maleissye et al.¹ reported on the pyrolysis of ethylene induced by a CO₂ laser. At a continuous laser intensity of 660 W/cm² and ethylene pressure above 200 Torr, the number of absorbed photons per decomposed molecule reached a limiting value of 16.7, corresponding in total absorbed energy per mole to the thermal activation energy measured by standard pyrolytic techniques. Similar results were claimed for ethane,² with added SF₆ as the laser absorber. The thermodynamic limit is set, however, not by the activation energy E_A , but by the enthalpy difference, ΔH . In the experiments just described, there is energy per mole $E_A - \Delta H$ being lost or unused. We wish to report that in similar experiments on the compound CH₃CF₂Cl the number of photons absorbed per molecule dissociated is considerably less than the activation energy equivalent and approaches ΔH for the reaction.

The pyrolytic elimination of HCl from CH₃CF₂Cl to yield

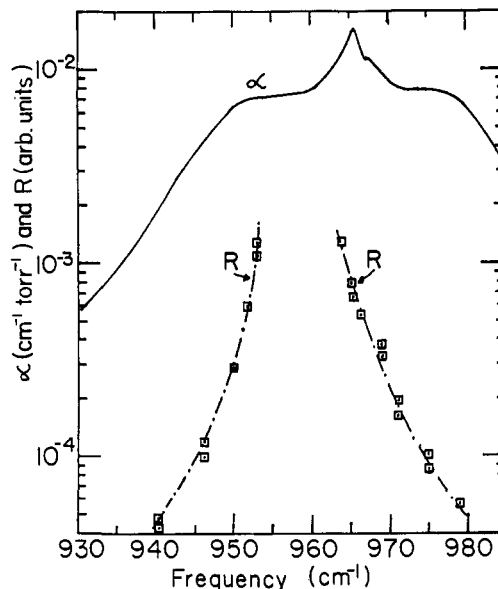


Figure 1. Optical absorption coefficient α and laser-induced reaction rate R for various frequencies over the 966-cm⁻¹ band of CH₃CF₂Cl. The gap in R is due to lack of laser output at those frequencies.

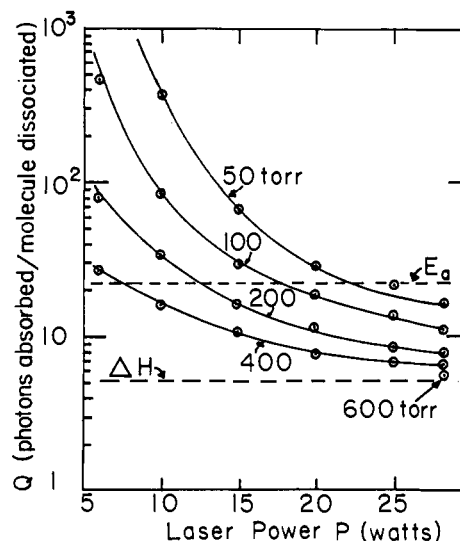


Figure 2. Quantum requirement Q as a function of laser beam power P for several gas pressures. The horizontal dotted lines indicate the activation energy and enthalpy in units of photons/molecule. The laser frequency is 953 cm⁻¹.

CH₂CF₂ occurs with an enthalpy change³ and activation energy⁴ of 59.4 and 252 kJ/mol, respectively. There is a competing reaction, namely HF elimination, which can amount to 30% of the total in reactors with quartz or inconel walls, but only to 2 or 3% of the total for some seasoned Ni-Cr alloy walls.⁴ In our experiments, the beam interaction region is far from the Pyrex cell walls, and we observe only HCl elimination with no evidence of the competing HF elimination reaction.

The laser frequencies used were primarily those in near resonance with the 966-cm⁻¹ absorption band of CH₃CF₂Cl, which has been characterized as a CH₃ rocking mode.⁵ The laser beam diameter was 1 mm, while the reaction cell had an inner diameter of 22 mm and a total volume of 50 cm³. Reaction rates were obtained by observing the growth of the 1731-cm⁻¹ absorption band of the product CH₂CF₂, and only initial rates were recorded, corresponding to small product concentrations. Above 10 W of laser power, rates were too rapid to measure in the pure continuous mode, and pulses of ~10⁻¹-s duration were used. This duration exceeds even the

thermal relaxation time of the gas; so the operational mode can be treated as continuous. As a check, we verified that the amount of product produced was proportional to pulse duration, and, that at intermediate power levels, pulsed and CW operation gave consistent results.

Measurements were made first to determine the laser frequency giving the most efficient reaction. Figure 1 shows the optical absorption coefficient over the 966-cm⁻¹ band (obtained from spectrophotometer measurements) and the reaction rate *R* for various laser frequencies (at fixed input power of 4.5 W into the cell with 200-Torr initial gas pressure). There is a gap in the *R* data because the CO₂ laser has no output in the 956–963-cm⁻¹ range. We note that the reaction rate maximizes at a frequency ~7 cm⁻¹ below the 966-cm⁻¹ absorption band peak. This effect, termed "red shift", is observed in other compounds⁶⁻⁹ and has been ascribed to vibrational anharmonicity and "hot-band" absorption.

On the basis of the rate data the laser frequency 953 cm⁻¹ was used for measurements of the quantum requirement *Q*, defined as the number of photons absorbed per product molecule produced. This is identical with the ratio of the photon absorption rate to the reaction rate (in units of product molecules per second). Both of these quantities, it should be noted, are directly and easily measurable. The photon absorption rate comes simply from a measurement of the total power absorbed in the cell (corrected for window losses), while the rate of product molecule production is derived from the rate data using only the cell volume and the optical absorption coefficient of the CH₂CF₂ product at 1731 cm⁻¹.

Figure 2 shows the dependence of *Q* on laser power and initial CH₃CF₂Cl pressure. At 28 W and 600 Torr, *Q* reaches the value 5.6 photons per molecule dissociated, which is very close to the ΔH equivalent³ of 5.2 photons per molecule (at 953 cm⁻¹) and which is nearly four times smaller than the activation energy equivalent⁴ of 22 photons per molecule. In the high power, high pressure limit it appears that virtually all the energy $E_A - \Delta H$ released per reacting molecule is utilized by unreacted molecules in the beam, with negligible rate of energy loss due to thermal diffusion and convection or fluorescence.

Whereas the minimum *Q* value is set by ΔH in endothermic reactions, *Q* could approach 0 in exothermic reactions. The results of Basov et al.¹⁰ support this conclusion. In studies of eight reactions, it was found that irradiation by a single 10⁻²-s pulse at intensities above a threshold level produced nearly 100% conversion in the exothermic reactions, while for endothermic reactions the product yield was proportional to the number of pulses.

The reason why the "enthalpy limit" was not reached in the reported reactions of ethylene¹ and ethane² is not yet clear. The ethylene reaction mechanism is complicated, with numerous products, and appropriate values of E_A and ΔH are not clearly defined, while close inspection of the ethane data² indicates a limiting value of *Q* that is less than the claimed E_A equivalent. Perhaps the determining factor lies in having an efficient mechanism for feeding the released energy $E_A - \Delta H$ back to unreacted molecules. In the present case for example, most of $E_A - \Delta H$ may reside in vibrational excitation of the HCl product which is quickly transferred in collisions with CH₃CF₂Cl molecules.

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Product Control by Light Intensity. The Photoaddition of Aldehydes to α -Diketones

Sir:

The product(s) formed in a photochemical reaction can depend markedly on experimental variables such as wavelength of exciting light, concentration(s) of reactant(s), temperature, and solvent. Except for cases involving intense irradiation, variation in light intensity may affect quantum yield but is generally¹ not considered to be an important factor in determining products of reaction. We wish to report an example of a reaction in which product composition can be affected considerably by variation of light intensity over a moderate range readily accessible with conventional light sources.

Irradiation of benzene solutions of bicyclo[2.2.2]octane-2,3-dione (BOD) and aldehydes produces²⁻⁵ mixtures of keto ester **1** and hydroxy diketone **2**. As part of an investigation of mechanism, the reaction with *p*-chlorobenzaldehyde was studied in detail. Both quantum yield and product ratio (**1**:**2**) were shown to vary with intensity of absorbed light for identical conversions (20%) of BOD. As shown in Table I, at the lowest light intensity used **1** constituted 94% of the reaction product, while at the highest intensity **2** was 71% of the total. This dramatic effect can be preparatively useful and is clearly of

