cules at their natural abundance (1.11%) has been demonstrated ($\alpha \rightarrow 500$). However, similar selectivities have been observed in single-frequency irradiations (cf. ref 20). Which method offers the most efficient route to the separation of carbon isotopes awaits the quantitative determination of the photon absorption rates during the two irradiation pulses. Such measurements are under investigation.

Intensity and Pressure Effects in Infrared Multiphoton Dissociation. Photolysis of Hexafluoroacetone and Trifluoromethyl Bromide with 2-ns Laser Pulses

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We have carried out a study of the effect pulse length on the infrared multiphoton dissociation of hexafluoroacetone. A constant fluence of 1.8 J cm^{-2} was used, for both short-pulse (2-ns fwhm) and long-pulse (~120-ns fwhm, 5-μs tail, gain-switched, self-mode-locked TEA CO_2 laser) irradiations. The dissociation yields are *very significantly different* both in their magnitude and in their dependence on pressure of substrate or of added hexafluoroethane. At moderate pressures (>0.2 torr) *collisional effects dominate* the long-pulse irradiation. Possible explanations of these effects are discussed. A study of the isotopically selective dissociation of trifluoromethyl bromide revealed that, although the intensity is high, isotopic selectivity ($\alpha \approx 20$) is retained.

Introduction

In single-photon-induced photochemical studies one may conveniently separate the excited-state preparation process from its subsequent decay processes. In multiphoton-induced photochemistry this division is harder to make. This is particularly true for multiphoton-induced infrared photochemistry. For example, under certain experimental conditions (high pressure, low intensity) no chemical reactions occur, whereas under other conditions (molecular beam, high intensity) extremely endoergic reactions are driven; we cite a study of the multiphoton dissociation reaction $CH_2CHCN \rightarrow C_3N \rightarrow C_2$.[1] At intermediate conditions, one may favor bimolecular[2] or bulk thermal reactions of the vibrationally excited gas.[3] One may also design experiments in which up-pumping of molecules by the laser field competes with vibrational relaxation by unexcited molecules; this may lead to an increase in isotopic selectivity with pressure.[4] Clearly, one must take great care in defining the photolysis conditions (laser fluence, flux, and frequency and substrate pressure, temperature, and composition) before one may fully realize the potential of photolysis in the infrared to drive molecularly specific photochemically induced reactions, e.g., selective excitation of isotopically substituted molecules, isomers, or chemically different components of mixtures.

It has recently been demonstrated that photolysis with CO_2 laser pulses of moderate energy (2 J) and short pulse length (2 ns) leads to isotopically selective dissociation of trifluoromethane and that shortening the laser pulse length decreases the effect of "detrimental energy-removing collisions during the laser pulse".[5] In this paper we have studied the photolysis of hexafluoroacetone irradiated at a frequency close to the maximum of its ν_{15} dissociation spectrum as a function of substrate pressure and composition and of the length the laser pulse to ascertain whether other significant experimental advantages are conferred by photolysis with short-duration, high-intensity pulses. To conveniently assess the potential of short-pulse irradiation for inducing isotopically selective dissociaiton, we have also studied the selective dissociation of $^{13}CF_3Br$ at natural abundance, both in the presence and in the absence of inert gases.

Experimental Section

Short-pulse irradiations were performed with the output of a TEA CO_2 laser system designed to provide 2-ns pulses over a wide tuning range.[6] The system used a grating tuned injection mode-locked oscillator to produce a train of 4-ns pulses.[7,8] A single pulse was selected from the train by using (a) the characteristics of the module itself to obtain a large pulse-to-prepulse contrast ratio and (b) an air breakdown at a variable aperture to provide a high contrast ratio between the selected pulse and the post pulses. After amplification in the same gain module, a typical 2-ns (fwhm) pulse (Figure 1b,c) contained ~900 mJ and had a pulse-to-background energy contrast of ~ 50:1 when the laser was operated on the P(8) 10.6-μm transition.

Before illuminating the sample the beam passed through a NaCl beam splitter where a portion of the laser output was used to monitor pulse duration and pulse-to-background contrast on a photon drag detector. The beam was then compressed with an R = 18-m concave radius of curvature mirror before entering the cell with a cross

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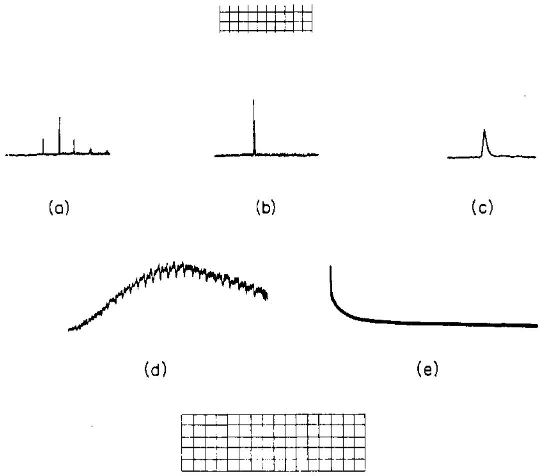

Figure 1. Pulse shapes of laser pulses used in this study. The upper graticule applies to traces a–c, and the lower to traces d and e. (a) Output of regenerative amplifier operated without air breakdown; horizontal scale, 100 ns/division. (b) As in trace a but with air breakdown. (c) As in trace b; horizontal scale, 2 ns/division. (d) Output of gain-switched TEA laser; horizontal scale, 20 ns/division. (e) As in trace d; horizontal scale, 5 μs/division; vertical scale expanded by 2.

section of 0.6 cm^2. The cross section was determined by examining the burn pattern of a suitably attenuated beam. The long radius of curvature mirror ensured that the beam cross section was constant through the 18-cm long cell (cell diameter was 2.5 cm). Finally the beam was reexpanded and was incident upon a pyroelectric detector for routine monitoring of pulse energy. Two irradiation frequencies were used: the P(8) line of the 10.6-μm band at 954.6 cm^{-1} was used to irradiate hexafluoroacetone, and the P(20) line of the 9.4-μm band at 1046.9 cm^{-1} was used to irradiate trifluoromethyl bromide.

Long-pulse irradiations were performed with the conventional TEA CO_2 laser described before.[9] Parallel beams of moderate fluence were obtained by compressing the beam with a 2-m focal length germanium lens. The temporal profile of the laser pulse varied from shot to shot but consisted of the typical gain-switched, self-mode-locked spike (fwhm 80 ns), followed by 5-ms tail. Typical profiles are shown in Figure 1d,e.

Reactions in hexafluoroacetone were followed by measuring the increase in pressure per pulse and the pressure of noncondensable carbon monoxide produced per pulse. Reaction yields are reported as the probability of dissociation per pulse for all irradiated molecules, calculated as in earlier work.[9] When experiments were performed by using the 2-ns laser, reaction yields were measured after each single shot as the energy variation from pulse to pulse was quite large (±15%). The output energy of the long-pulse laser was extremely stable (±0.5%), and hence multiple-pulse irradiation could be used as the pressure decreased. These considerations allowed dissociation probabilities to be measured to much lower hexafluoroacetone pressures in the case of long-pulse irradiation even though the magnitude of the yield was an order of magnitude less than for short-pulse irradiation. In the case of trifluoromethyl bromide, only product isotopic enrichments (α) are reported. The isotopic composition of the product hexafluoroethane was assessed by exposing the total contents of the cell after irradiation to a Leybold Heraeus Inficon IQ200 quadrupole mass spectrometer. Peaks at m/e 119, 120, and 121 were measured; corrections were made for small contributions from the substrate at these mass peaks. α values were calculated as previously reported.[10]

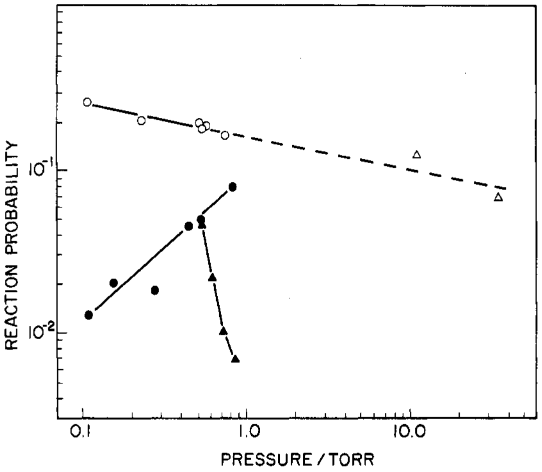

Figure 2. Reaction probability as a function of pressure. Open symbols refer to single 2-ns irradiation; filled symbols refer to long-pulse (see text) irradiation. Circles are data for neat hexafluoroacetone; triangles are data for 0.5 torr of hexafluoroacetone + hexafluoroethane. Incident fluence, 1.8 J cm^{-2}; frequency, 954.6 cm^{-1}; temperature, 22 °C.

TABLE I: Reaction Probabilities for Low-Pressure CF_3COCF_3

press., torr	reaction probability
0.041	0.022[a]
0.042	0.029[a]
0.066	0.021[a]
0.110	0.013[a]
0.103	0.260[b]

[a] 20 °C; 1.8 J cm^{-2}; P(8), 954.6 cm^{-1}; conventional gain-switched TEA CO_2 laser, ~80-ns fwhm, 5-μs tail. [b] 20 °C; 1.8 J cm^{-2}; P(8), 954.6 cm^{-1}; injection-locked TEA CO_2 laser, ~2-ns fwhm, no tail.

TABLE II: Effect of Fluence on Dissociation Probability for 2-ns Irradiation[a]

fluence, J cm^{-2}	reaction probability[b]
1.61-1.80	0.18
1.81-2.00	0.19
2.01-2.20	0.20
2.21-2.40	0.22

[a] 0.50 torr of hexafluoroacetone; 20 °C; 1.8 J cm^{-2}; P(8), 954.6 cm^{-1}; 2-ns fwhm. [b] Results averaged over six pulses.

Results and Discussion

Hexafluoroacetone. The most significant results are shown in Figure 2. The most dramatic feature of these results is that at constant fluence (1.8 J cm^{-2}) increasing substrate pressure decreases the dissociation probability for short-pulse irradiation (2 ns), while for long-pulse irradiation the dissociation increases in the range 0.1–1.0 torr and is constant below 0.1 torr (Table I). For long-pulse irradiation the dissociation probability is dramatically reduced by addition of small amounts of hexafluoroethane (half-quenching pressure ≈ 0.12 torr), whereas for short-pulse irradiation the dissociation probability is far less sensitive to hexafluoroethane, or to hexafluoroacetone pressure, and both gases appear to have equal effect (half-quenching pressure ≈ 1.2 torr). Not shown in Figure 1 is the fluence dependence, which for long-pulse irradi-

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ation was typically of high order, whereas the data in Table II show only a mild fluence dependence when short pulses are used.

The results may all be explained by postulating the preparation of two different distributions of excited molecules. For short-pulse irradiation we postulate that the laser field drives all molecules accessible to the field to levels of internal vibrational excitation which are above the dissociation limit. Dissociation may then occur at a rate characterized by the RRKM expression in competition with deactivation by unexcited hexafluoroacetone molecules or by added inert hexafluoroethane. The observed quenching efficiencies would suggest RRKM lifetimes of $\sim$200 ns for a reasonable quenching rate constant of 1×10^{11} L/ms (40-Å^2 cross section) although molecules with a range of dissociation lifetimes are probably formed. The fraction of molecules accessible to the laser field is controlled by the laser intensity ($\sim$1 GW cm^{-2}; Rabi Frequency, 2 cm^{-1}) and the ambient pressure and temperature which determine the rate at which nonresonant states are converted to resonant states through the rotational relaxation cross section. A typical value for this cross section for large molecules is the value 170 Å determined recently by Jensen et al.[11] for SF_6–SF_6 collisions in three-level infrared double resonance (IRDR) experiments. However, these workers carried out a high-resolution time-resolved IRDR experiment and found no effect of rotational relaxation for 0.08 torr of SF during the first 500-ns period. It therefore would appear reasonable that rotational relaxation can be neglected for all of the 2-ns irradiation experiments at substrate pressures up to 32 torr reported here.

The fraction of molecules accessible to the infrared field is then simply controlled by the power-broadened line width, which can be approximated by

$$\delta\nu_{1/2} \simeq \mu\epsilon_0/\hbar \qquad (1)$$

where $\delta\nu_{1/2}$ is the line width at half-height of the field-broadened transition, μ is the transition dipole moment, and ϵ_0 is the electric-field strength associated with the laser field. The transition dipole moment is not known for the ν_{15} band of hexafluoroacetone; we use a reasonable estimate of 0.2×10^{-18} esu cm obtained by comparing the integrated absorption coefficient for the ν_{15} band with that of the ν_3 band of SF_6 (μ = 0.388 D) with proper allowance for symmetry and calculate $\delta\nu_{1/2} \approx 2$ cm^{-1} applicable to the 2-ns experiments. The ν_{15} band of hexafluoroacetone at 972 cm^{-1} appears as a smooth rotational contour with defined P, Q, and R structure with a full width at half-maximum of 15 cm^{-1} and a width at its base of 30 cm^{-1}. The excitation frequency underlies the P branch of the transition. It is not unreasonable that at 1 GW cm^{-2} 20% of the molecules are accessible to the field; furthermore, this fraction is expected to increase only as (fluence)$^{1/2}$, in agreement with the small increases reported in Table II (reaction probability/(fluence)$^{1/2}$ = 0.142 ± 0.003 cm J$^{-1/2}$) although we accept that the variation in fluence (1.5) is too small to provide a significant test.

The problem is much more complex for long-pulse excitation. To begin with, the pulse profile is far less well-defined. If we assume that the N_2 tail contains 30% of the energy and accept the 80-ns fwhm for the initial spike, then we may estimate that the peak intensity is reduced by a factor of 90 from the 2-ns irradiations; accordingly, we expect that the power-broadened line width will be reduced by a factor of $\sim$10. This may be reflected in the low-pressure dissociation probabilities reported in Table I, which are in reasonable agreement with this expectation. However, the most interesting feature in the comparison between the short- and long-pulse irradiations if the effect of increasing hexafluoroacetone pressure. There are at least two explanations for this behavior. The first involves competition between rotational relaxation and vibrational relaxation. We may test this postulate by calculating the number of collisions during the 1-μs pulse (arbitrary), using the rotational relaxation cross section referred to earlier. We find 20 μs^{-1} torr^{-1}. Hence, it is not unreasonable that rotational relaxation increases the number of accessible states with concomitant increase in dissociation probability in the pressure range (0–1.0 torr) for long-pulse irradiation. We then have to explain the effect of hexafluoroethane. It is reasonable that hexafluoroacetone/hexafluoroacetone rotational relaxation cross sections will be much larger than those for hexafluoroacetone/hexafluoroethane, a consequence of long-range dipole–dipole forces compared to dipole-induced dipole forces for nonpolar collision partner. However, one is then drawn to the conclusion that vibrational quenching is the explanation for the decrease in reaction probability with hexafluoroethane pressure. There is no reason to suppose that the vibrational quenching rate constant for the partners hexafluoroacetone/hexafluoroacetone will be less than that for hexafluoroacetone/hexafluoroethane. Indeed we have seen, vide supra, that these rates are equivalent. Therefore, to explain the observed differences in pressure effect, one has to assume a small rotational relaxation rate for hexafluoroacetone/hexafluoroethane collisions (<40-Å cross section). This is unreasonable in light of the large cross section observed in SF_6–SF_6 collisions.[11]

These problems are avoided by a second plausible explanation, one we have previously invoked to explain entirely analogous effects observed in long-pulse photolysis of hexafluoroacetone at its ν_{15} band center (970.56 cm^{-1} at 2 J cm^{-2}).[2] Here, it was observed that the average degree of excitation was high (19 000 cm^{-1} molecule) while the dissociation probability was still low ($\sim$0.08). The explanation which we advanced then, and one that we expand upon now, is that excitation with lower-intensity pulses creates a different distribution of excited molecules. Collisional effects during the irradiation pulse assume a greater significance, both in terms of increasing the number of accessible molecules (rotational relaxation) and in terms of transfer of energy from resonant molecules to nonresonant molecules (vibrational relaxation). The net result is that after the termination of the pulse much energy is deposited in vibrational levels of molecules with insufficient total internal energy to undergo unimolecular decomposition. The only routes for relaxation of this energy are by diffusion to unirradiated regions or by thermal decomposition (collision-induced decomposition). This situation explains qualitatively both the increase in yield with hexafluoroacetone pressure (increase in diffusional time constant) and the decrease in yield with added hexafluoroethane (decrease in effective vibrational temperature).

As a final comment on the significance of the observed pressure dependence, we note that the two explanations become kinetically similar if we postulate that the rotational relaxation process referred to in the former explanation requires the interaction of two *vibrationally* excited molecules. This interaction would involve a pooling of energy so that one of the pair has sufficient internal energy that rapid pumping by the radiation field is ensured. The two explanations then only differ in the time scale of the

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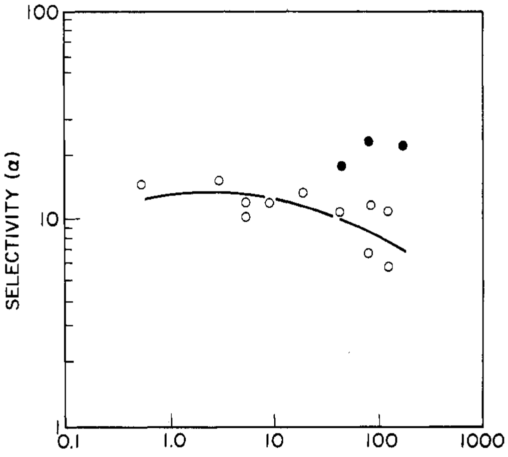

Figure 3. Isotopic selectivities from 2-ns-pulse photolysis of trifluoromethyl bromide. Open circles are for neat trifluoromethylbromide; filled circles are for 5.0 torr of trifluoromethyl bromide + argon. Incident fluence, 2 J cm^{-2}; frequency, 1047 cm^{-1}; temperature, 22 °C.

yield enhancement. In the former the yield must be enhanced during the pulse; in the latter the yield may increase after the pulse. Both explanations are supported by the observation that, when the excitation frequency is removed from the central frequency of the dissociation spectrum, an increase in hexafluoroacetone pressure decreases the observed yield.[9]

Although a precise kinetic explanation for the results presented above may be a matter for some debate, the demonstration that changing the laser pulse length at constant fluence leads to entirely different kinetic dependence is unequivocal. Thus, we have demonstrated significant flux effects of a kind not usually discussed. The low-pressure data ($\leq$0.11 torr) of Table I may be used to demonstrate the importance of intensity effects of a more conventional nature;[12] at constant fluence (1.8 J cm^{-2}) we observed that the dissociation probability for 2-ns pulses is over an order of magnitude greater than that for long-pulse irradiation. This observation could only be amplified or treated in a more quantitative fashion if the temporal profile of the "long" pulse were better defined. Experiments designed to quantify this effect are being considered. We note that two other groups have reported evidence for intensity effects in infrared multiphoton dissociation.[13,14]

Trifluoromethyl Bromide. The experiments reported above have indicated that irradiation by short-pulse CO_2 laser pulses at moderate fluences, at pressures where collisions may be neglected during the irradiaiton time, leads to a kinetically simple situation in which dissociation probabilities are determined solely by power broadening and collisional quenching of molecules above the dissociation threshold. Isotopically selective dissociation has been inferred for 2-ns irradiation of CF_3H/CF_3D mixtures where the isotope shift is large ($\Delta\nu_5$ = 182 cm^{-1}).[5] However, no direct measurements of isotopic selectivity have been made in a situation where the isotope shift is comparable to the power broadening. Such measurements were not possible with the present system for hexafluoroacetone, so trifluoromethyl bromide was used as a test molecule. The ν_1 absorption band of $^{12}CF_3Br$ lies at 1084 cm^{-1}; that for $^{13}CF_3Br$ lies at 1058 cm^{-1}. Figure 3 shows α values observed when CF_3Br at natural abundance is irradiated with 2-ns pulses at 1047 cm^{-1} at 2 J cm^{-2}. Isotopically selective dissociation of ^{13}C-bearing molecules is demonstrated. We note that recently workers in other laboratories have found similar results.[15] In agreement with the discussion presented above, there is little effect of pressure on the isotopic selectivity.

Acknowledgment. We thank J. B. Marling for providing us with a preprint of a paper on trifluoromethane photolysis and for communicating results on trifluoromethyl bromide photolysis.

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Electrogenerated Chemiluminescence. 38. Emission Intensity–Time Transients in the Tris(2,2′-bipyridine)ruthenium(II) System

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Ecl transients for potential step experiments on the $Bu(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) system in acetonitrile solutions conform well to the behavior predicted for the case in which the emitting species is produced in the electron-transfer step (i.e., an "energy-sufficient" or "S-route" system). Possible explanations for the deviation of the slope/intercept ratio of the linear ecl intensity vs. $(t_r/t_f)^{-1/2}$ plot (t_f = forward pulse duration, t_r = time during reverse pulse) found for longer pulse lengths and at higher temperatures are examined.

Although transient techniques and the detailed analysis of current–time curves have been very important in the elucidation of reaction mechanisms in electrochemical investigations, the analogous intensity–time (I–t) transients observed in studies in electrogenerated chemiluminescence (ecl) have been less informative. The usual potential step experiment involves a step for a duration t_f, to a potential where one of the reactants, e.g., the reduced form $A^{-}\cdot$, is produced at a rate controlled by its diffusion to the electrode. The potential is then stepped to a value where the

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