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FREQUENCY-DEPENDENT BRANCHING RATIO IN THE INFRARED MULTIPHOTON PHOTOCHEMISTRY OF DIETHYL CARBONATES

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Unimolecular decomposition of 0·1 Torr of diethyl carbonate, diethyl-d_5 carbonate and diethyl-d_{10} carbonate induced by irradiation with a CO_2 TEA laser was investigated. In all cases only ethylene, ethanol and CO_2 were obtained. In the case of diethyl-d_5 carbonate, both ethylene-d_4 and ethylene-d_0 were observed together with the corresponding isotopic variants of ethanol. The chemical branching ratio was determined as a function of irradiation frequency and laser fluence by analysis of the ethylene-d_0/ethylene-d_4 ratio. RRKM theory applied to the branching ratio data requires very different average energies for two sets of fluence and frequency conditions that give identical total yields.

INTRODUCTION

Investigations of the infrared photochemistry of molecules that can decompose by more than one reaction pathway have proved to be especially useful in characterizing the multiphoton activation process.[1–10] Branching ratios from multichannel reactions are a sensitive function of the energy content of the reacting molecules. Comparison of the observed branching ratio with the predictions of statistical unimolecular rate theories allows the average energy of reacting molecules, $\langle E_r \rangle$, to be determined.[1,2] The change in branching ratio resulting from systematic variation in experimental parameters (e.g. laser fluence, laser intensity or bath gas pressure) constitutes perhaps the best available data on how sensitive $\langle E_r \rangle$ is to these parameters. This important information is useful for developing predictive versions of rate equation models of infrared multiphoton photochemistry,[11–13] and for designing infrared photochemistry experiments that yield one reaction pathway preferentially.[14]

One variable that has not been very thoroughly examined with respect to its effect on $\langle E_r \rangle$ is laser frequency. Theoretical models of multiphoton decomposition suggest that the average energy of reacting molecules should depend on the rates of absorption, chemical reaction and deactivation.[11] Laser frequency influences $\langle E_r \rangle$ through its effect on the rate of photon absorption. The rate of absorption from level i to level j is given by $R_{ij} = I\sigma_{ij}N_i$ where N_i is the population of molecules in the absorbing level, I is the laser intensity, and σ_{ij} is the absorption cross-section for the particular $j \leftarrow i$ transition. In the energy regime above the reaction threshold photons will continue to be absorbed until $R_{ij} \approx k(E_i)N_i$, the unimolecular reaction rate at energy E_i. When the branching ratio changes in response to changes in experimental parameters, information on how those parameters influence the up-pumping rates, R_{ij}, can be inferred.

In this paper we describe the infrared photochemistry of both diethyl-1,1,1,2,2-d_5 carbonate (DEC-d_5), a molecule with two unimolecular reaction channels that differ only by isotopic substitution, and the parent molecule DEC-d_0. The experiment is conceptually similar to work reported by other groups.[2,9,10] DEC-d_5 is an especially attractive molecule for this type of study for several reasons. (1) The two competitive reaction channels (k_H and k_D, Scheme 1) both yield stable, molecular products via mechanisms that are well established.[15]

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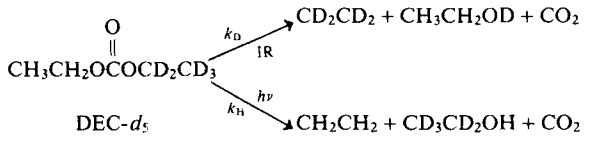

(2) The thermal chemistry of both DEC-d_0[16] and DEC-d_5 are well characterized and the Arrhenius parameters for both channels from DEC-d_5 have been determined.[17] This permits accurate RRKM calculations of the branching ratio as a function of internal energy to be performed. (3) DEC-d_5 possesses two distinct absorption bands in the region accessible with the CO_2 laser. (4) The molecule is closely related in structure to ethyl acetate, which is one of the most thoroughly investigated single-channel organic reactants in multiphoton photochemistry.[18,19] As a class, organic esters are important infrared photochemical reagents because of strong absorptions in the CO_2 laser region and useful unimolecular chemistry; pyrolysis of esters is a classical preparative method for olefins.[20]

EXPERIMENTAL

DEC-d_5 was prepared via the reaction of ethanol-d_6 (Stohler Isotope Chemicals, 99% D) with ethyl chloroformate (MCB Chemicals). Reaction was performed at 4–6 °C in methylene chloride solution containing pyridine (1 equiv.). The product was purified by preparative gas chromatography (GC). Mass spectral (MS) analysis (Finnegan 4000-EI) gave m/z = 96, 45, 93, 46, 50, 123, 124 in order of decreasing intensity. No peak is observed at m/z 118–122 (M^+ of DEC-d_0). IR (gas, Beckmann IR 4250): 2800–3050, 2100–2300, 1760, 1375, 1295, 1200, 1095, 1060, 1025, 990, 880 cm^{-1}.

DEC-d_{10} was prepared by refluxing 2·2 equiv. of ethanol-d_6 with carbonylimidazole (Aldrich) for 1 h followed by distillation).

Infrared photochemical experiments were performed on vapor-phase samples of the diethyl carbonates in a cylindrical Pyrex vessel (7·5 cm × 2·5 cm i.d.) fitted with KCl or NaCl windows. Sample pressures were measured with an MKS-Baratron 220 capacitance manometer. The samples were irradiated with a collimated beam from a Lumonics CO_2 TEA-101 laser, which was operated multimode. The beam emerging from the laser was reduced to 25 mm diameter with an iris and telescoped to 7 mm diameter with a combination of two ZnSe lenses. The beam was characterized using a Laser Precision KT-1510 pyroelectric detector, a Scientech (Model 38-0102) volume-absorbing calorimeter and an Optical Engineering 16A spectrum analyzer. At both experimental frequencies the pulse consisted of an initial *ca* 200-ns spike with a tail to *ca* 1·5 μs. The spatial characteristics of the beam were determined by two methods: (i) the beam was subdivided into quadrants, the fraction of laser energy in each quadrant being independent of frequency, and (ii) the intensity cross-section was obtained by moving a pinhole aperture across the horizontal and vertical axes of the beam. The profiles obtained by the latter method were roughly trapezoidal for both axes and identical within experimental error at the two experimental frequencies. When necessary, the laser beam was attenuated with a gas cell containing variable pressures of an absorbing material.

Reaction yields and product ratios were determined by GC [Varian 2400 equipped with an HP-3390A integrator, using 10% Carbowax 1540 on Chromosorb (60–80 mesh), 10 ft × 1/8 in i.d. column) GC–MS (Hitachi RMU-6MS) or GC–Fourier transform infrared spectroscopy (Digilabs FTS-10). The branching ratio was most conveniently determined from FTIR spectra of the photolysis mixture. Absorption intensities were determined at 950 and 722 cm^{-1}, the *Q*-branch maxima of the CH_2 and CD_2 out-of-plane deformation modes of ethylene-d_0 and ethylene-d_4, respectively. Spectral subtraction of DEC-d_5 and/or ethanol-d_0 or -d_6 did not change the absorbance ratios appreciably. The ratio of absorbances was converted to a concentration ratio using the Beer–Lambert Law. Absorptivities of C_2H_4 and C_2D_4 at these frequencies were obtained from C_2H_4–C_2D_4 mixtures at similar pressures and under analytical conditions identical with those used in photochemical product analyses. Comparable results for branching ratios could be obtained by analyzing ethanol-d_0 and -d_5 at specific frequencies between 3000–2900 and 2250–2100 cm^{-1} using GC–FTIR.

RESULTS AND DISCUSSION

The infrared photochemistry of three isotopomers of DEC, DEC-d_0, DEC-d_5 and DEC-d_{10}, was examined. In DEC-d_5 one of the two ethyl groups is completely deuterated. In DEC-d_{10} all hydrogens are replaced by deuterium. The infrared spectra of DEC-d_0, DEC-d_5 and DEC-d_{10} are given in Figure 1. Significant differences are evident in these spectra in the region accessible with a CO_2 TEA laser (900–1100 cm^{-1}). The band centered at 1378 cm^{-1} (CH_3 deformation) in DEc-d_0 splits into two bands at 1377 and 1056 cm^{-1} in DEC-d_5 and disappears completely in favor of the lower frequency band in DEC-d_{10}. Bands appearing at 1056 ± 9 cm^{-1} for compounds structurally similar to DEC-d_5 have been assigned as CD_3 deformations.[21–23] Similarly, the band at 1031 cm^{-1} in DEC-d_0 appears to split into two bands at 1029 and 994 cm^{-1} in DEC-d_5. In DEC-d_{10} in a single band at 1016 cm^{-1} appears in this region. The 1031 cm^{-1} band in DEC-d_0 has been assigned as an O–C(H_2) stretch.[24] Changes observed in the DEC-d_5 spectrum appear to be consistent with this

assignment (reduced mass ratios indicate that an O–CH_2 stretch at 1031 cm^{-1} should shift to 996 cm^{-1} on deuterium substitution).

The infrared photodecomposition of the diethyl carbonates leads cleanly to the three products expected from pyrolysis studies, ethanol, ethylene and CO_2.[16] When DEC-d_5 is the reactant, branching occurs to yield both ethylene-d_0 and ethylene-d_4 together with the corresponding isotopic ethanols and CO_2 (Scheme 1). For each isotopomer and under all experimental conditions the ethanol-to-ethylene ratio was 1·02 ± 0·08. Irradiation of ethanol or ethanol-d_6 under identical photolysis conditions gave insignificant decomposition. Therefore, ethanol and ethylene are produced in equivalent amounts from DEC, and there is no significant secondary photochemistry. Scheme 1 adequately represents all routes to ethylene.

Photochemical reaction was investigated at two frequencies with each isotopomer: $P(14)$, 1052 cm^{-1}, and $P(38)$, 1029 cm^{-1}. Irradiation was generally done with

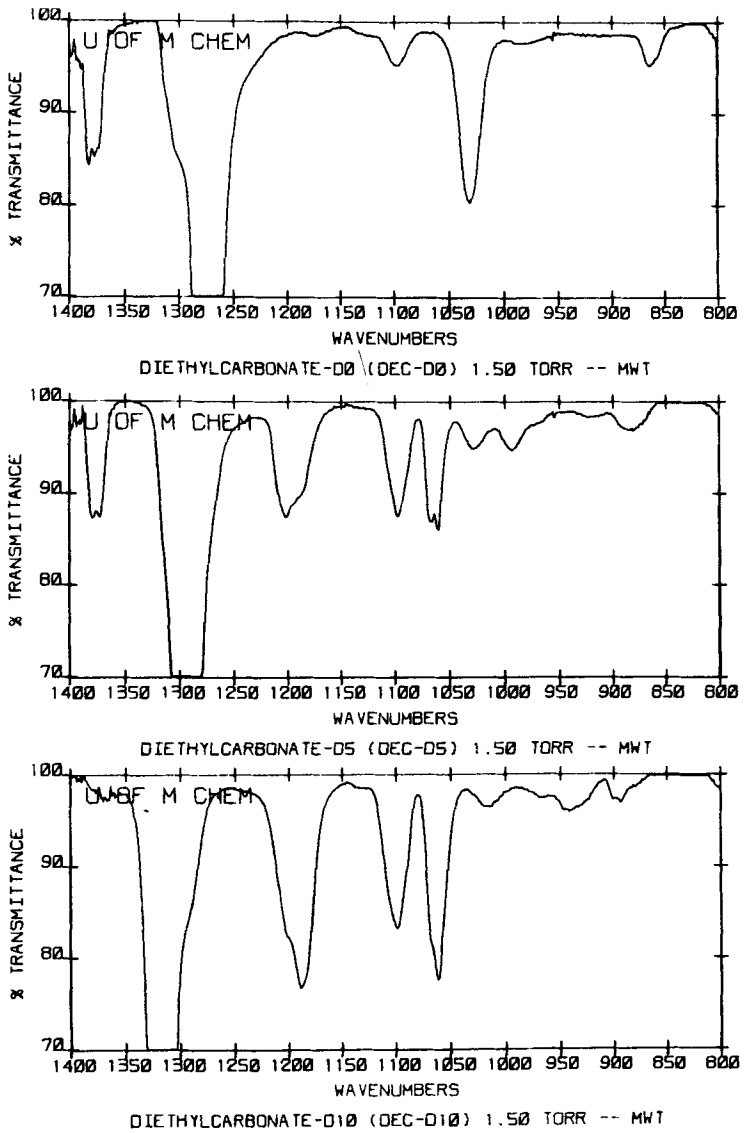

Figure 1. Vapor-phase infrared spectra of DEC-d_0, DEC-d_5 and DEC-d_{10}. The irradiation frequencies, $P(38)$, 1052 cm^{-1}, and $P(14)$, 1029 cm^{-1}, are indicated on each spectrum

0·100 ± 0·004 Torr of reactant using the telescoped beam of a CO_2 TEA laser at the photolysis source. At both frequencies and with each isotopomer, the extent of reaction up to at least 25% conversion was well described by an equation analogous to a first-order decay, $[DEC]_n/[DEC]_0 = \exp(-kn)$, where n is the number of pulses and k is the fraction of DEC decomposed per pulse within the irradiated volume. The irradiated volume was estimated from cell dimensions and the laser beam diameter observed on thermal paper placed at the entrance window. Values of k are given in Table 1. At 0·400 Torr of reactant some deviations from this apparent first-order behavior were observed. Since reaction produces three molecules of product per decomposed reactant, significant pressure changes occur over the course of the reaction. As products are formed the ambient pressure increases and reaction occurs less efficiently, and this effect becomes significant at lower conversions when the initial pressure is increased.

For the same frequency and at identical fluences, the decomposition rate constants for DEC-d_0, DEC-d_5 and DEC-d_{10} are very different. These differences are in accord with expectations based on the single photon absorption spectra (see above). Thus, at 1029 cm^{-1} the strongest absorber, DEC-d_0, reacts faster than either DEC-d_5 or DEC-d_{10}. Similarly, at 1052 cm^{-1}, where DEC-d_{10} is the strongest absorber, it is the most reactive. At both frequencies, the reactivities of DEC-d_5 is intermediate between those of DEC-d_{10} and DEC-d_0.

The dependence of reaction yields on fluence is also unexceptional. Figure 2 shows yield vs fluence behavior for DEC-d_0 at $P(38)$, 1029 cm^{-1}, and DEC-d_5 at both $P(38)$, 1029 cm^{-1}, and $P(14)$, 1052 cm^{-1}. The slopes of these plots are DEC-d_0 $P(38) = 5·3$, DEC-d_5 $P(14) = 4·4$ and DEC-d_5 $P(38) = 5·4$. These values are

Table 1. Percentage conversion of DEC-d_n in laser beam per pulse

Laser frequency	DEC-d_0	DEC-d_5	DEC-d_{10}
$P(14)$[a]	≪ 0·10	4·29 ± 0·12	6·51 ± 0·95
$P(38)$[b]	6·12 ± 1·05	1·14 ± 0·10	1·08 ± 0·06

[a] 0·100 ± 0·004 Torr DEC-d_n, 1·29 ± 0·02 J cm^{-2}.
[b] 0·100 ± 0·004 Torr DEC-d_n, 1·49 ± 0·02 J cm^{-2}.

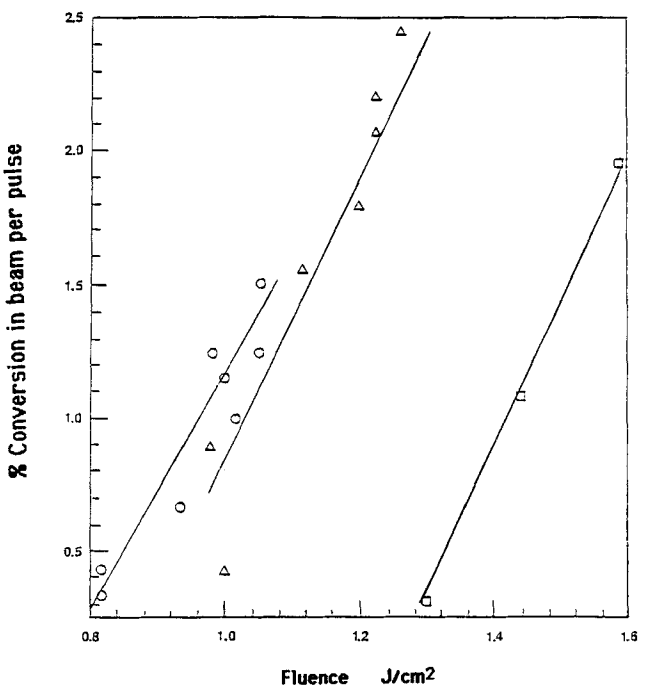

Figure 2. Yield vs fluence for (△) DEC-d_0 $P(38)$, (□) DEC-d_5 $P(38)$ and (○) DEC-d_5 $P(14)$

in good agreement with work on ethyl acetate under similar conditions. Danen and Jang[13] reported a slope of *ca* 4·2 in the intermediate fluence range (*ca* 1 J cm^{-2}) when the reaction probability is of the order of 10^{-2} as it is here. Higher fluences are required at *P*(38) than at *P*(14) to achieve comparable conversion of DEC-d_5. Nevertheless, the slope of the fluence vs percentage conversion plot is not significantly different within experimental error at these two frequencies.

Both total yields and branching ratios (k_H/k_D, Scheme 1) for the photodecomposition of DEC-d_5 were determined. A comparison of branching ratios at the two experimental frequencies reveals interesting differences. Data are given in Table 2. When the total yields are identical (entry 2 vs entry 5), the branching ratio is considerably smaller for reaction at *P*(14) ($\beta = 1{\cdot}26 \pm 0{\cdot}17$) than for reaction at *P*(38) ($\beta = 1{\cdot}63 \pm 0{\cdot}15$). In spite of scatter in the data, these two values are significantly different in the 99·9% confidence level by a standard *t*-test [the total number of degrees of freedom was 19; 8 runs at *P*(38), 13 runs at *P*(14)]. When the two frequencies are compared at the same fluence (entry 4 vs entry 5), the differences are even greater. Clearly, the average reacting molecule absorbs more photons during irradiation at *P*(14) than at *P*(38) under otherwise identical conditions.

RRKM theory has been used to calculate the branching ratio from DEC-d_5 as a function of internal energy. The general formulation for using RRKM theory to calculate a branching ratio, β, in this way is given by

$$\beta = \frac{[C_2H_4]}{[C_2D_4]} = \frac{k_H}{k_D} = \sum_{E}^{\infty} = E_0^{N(E)k_H(E)/k_D(E)}$$

where $N(E)$ is the number of reactant molecules that decompose at energy E, $k_H(E)$ and $k_D(E)$ are RRKM-calculated unimolecular rate constants for a reactant activated to internal energy E and E_0 is the threshold for reaction. Assuming a delta distribution among reacting molecules, $\beta = k_H(E)/k_D(E)$.

The best fit of calculated to observed values of β gives $\langle E_r \rangle$, the mean internal energy of reacting molecules. Parameters for the calculation of individual RRKM rate constants, $k_{H(D)}(E)$, are given in the Appendix. The calculations use Arrhenius parameters for the two channels that we determined in an independent series of pyrolysis experiments.[17] The RRKM calculations using the parameters described in the Appendix reproduce the temperature dependence of both the high-pressure rate constant for DEC-d_5 disappearance and the branching ratio in the thermal experiments to within the experimental accuracy.

The results of the RRKM calculations are shown in Figure 3. The solid line shows branching ratios (β) calculated using threshold energies for the two channels, E_{0H}, E_{0D}, determined from thermal activation energies. The broken lines represent values of β for E_{0H} and $E_{0D} + \sigma$ and E_{0H}, $E_{0D} - \sigma$, where σ is the standard deviation of the difference in activation energies from the thermal experiments. Clearly, the calculated branching ratio is sensitive to small changes in the threshold energy difference. The calculation is much less sensitive to other parameters. The best fit of the observed to cal-

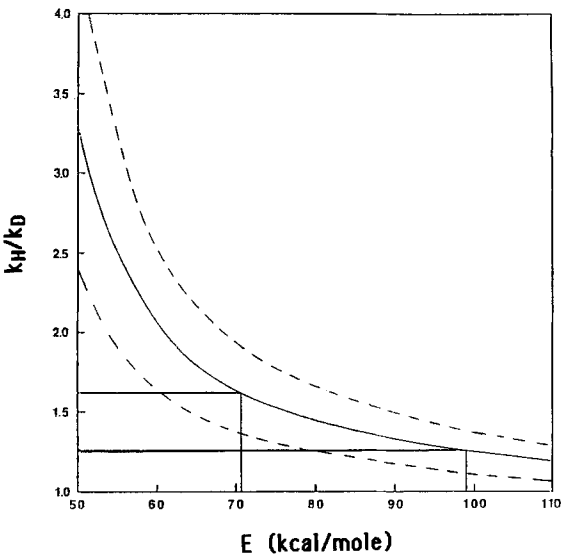

Figure 3. Branching ratio (k_H/k_D) vs internal energy for DEC-d_5. Best fits to *P*(14) and *P*(38) data are shown. Broken curves represent upper and lower limits for calculated branching ratio based on error limits of E_D (see text)

Table 2. Yields and branching ratios in DEC-d_5 IR photochemistry

Frequency (cm^{-1})	Fluence (J cm^{-2})	Yield per pulse (%)	Branching ratio, C_2H_4/C_2D_4
1052 *P*(14)	0·86 ± 0·02	0·5 ± 0·2	1·51 ± 0·15
1052 *P*(14)	1·00 ± 0·02	1·0 ± 0·3	1·26 ± 0·17
1052 *P*(14)	1·32 ± 0·02	2·5 ± 0·3	1·12 ± 0·10
1052 *P*(14)	1·40 ± 0·02	2·9 ± 0·2	1·09 ± 0·10
1052 *P*(38)	1·44 ± 0·04	1·0 ± 0·3	1·63 ± 0·15

culated branching ratio gives $\langle E_r \rangle = 99$ kcal mol^{-1} at $P(14)$ and $\langle E_r \rangle = 71$ kcal mol^{-1} at $P(38)$. The absolute magnitudes of these energies have fairly large uncertainty owing to the uncertainty in the Arrhenius parameters. However, their differences, $\langle E_r \rangle_{P(14)} - \langle E_r \rangle_{P(38)}$, is at least 20 kcal mol^{-1}.

There are two important implications of these data. First, yield vs fluence plots for DEC-d_0 or DEC-d_5 at either frequency are very similar to yield/fluence data for a variety of other 'large' molecules.[13,25,26] These data could surely be successfully fitted by an approximate rate equation model of the type that has been used to rationalize very similar yield data in a number of single-channel multiphoton decomposition experiments.[12c,13,26] Basically these models describe how the energy distribution function of the absorbing population evolves with time. Because the complete rate equation matrix is difficult to solve, models are usually applied to the data in some approximate form. Since the basic elements of the theoretical model are well established, the most important remaining questions concern what approximations can be made that retain the chemically significant effects. For example, an approximate model, which is very appealing in its simplicity, has been suggested by Danen and Jang.[13] This model has been used to rationalize simultaneously bulk absorption and yield/fluence data for several organic esters.[13,27] Multiphoton activation is presumed to produce a Boltzman distribution of internal energies among reactant molecules within the irradiated volume. All reaction occurs after the pulse from the high-energy tail of this distribution. Molecules with sufficient energy such that unimolecular reaction rates (RRKM) are greater than the collisional deactivation rates are assumed to react. Increased fluence raises the average energy of the Boltzman distribution, which increases the population in the tail and thereby the yield.

This model yields the clear prediction that changes in yield which result from variations in laser parameters (fluence, intensity, frequency) must always be accompanied by changes in branching ratio and vice versa. This result is required because the only parameter remaining in the model that is sensitive to irradiation conditions is the average energy of the entire ensemble $\langle E \rangle$. Any set of frequency–fluence conditions that produces a given yield must also, according to this one-parameter model, produce a unique branching ratio. In fact, the same conclusion applies to any approximate master equation treatment that assumes a homogeneous ensemble of absorbers, a statistical theory for reaction rate constants and a simple functional form such as $R_{ij} = I\sigma_0 \exp(-\gamma E_i)$ for the absorption rates, where γ is independent of frequency. To fit the DEC-d_5 data, a model must be able to change simultaneously both the average energy and the shape of the ensemble distribution function when frequency and fluence are changed.

Two *ad hoc* ways to build the required flexibility into the model would be first to postulate an inhomogeneous sample incorporating subsets of absorbing ('hot') molecules and non-absorbing ('cold') molecules,[28,29] and allow the relative populations of the subsets to change with frequency . In the case of DEC-d_5, a larger fraction of the sample would be required in the absorbing (hot) population at $P(38)$ but, because of the smaller value of $I\sigma_0$, the average energy of the absorbing population lags behind that for $P(14)$. Secondly, permit γ to be frequency dependent.[25] At $P(14)$, γ may be negative and R_{ij} therefore an increasing function of energy. At $P(38)$, γ could be positive and R_{ij} therefore a decreasing function of energy. These differences will tend to produce a broader, higher energy distribution for molecules that react at $P(14)$ and one that is bunched at lower energies for $P(38)$. There may be some physical justification for a difference of this type in the energy dependence of the $P(14)$ and $P(38)$ absorption cross-sections. Rossi *et al.*[25] showed that for C_3F_7I the absorption spectrum at high energies has the same features as the small signal absorption spectrum but is red-shifted by *ca* 20 cm^{-1}. A progressive red shift in the DEC-d_5 spectrum would lead to continuously decreasing cross-sections at $P(38)$ but sharply increasing cross-sections at $P(14)$ over 20 cm^{-1} of red shift. Independent of the details required to fit the DEC-d_5 data successfully with an approximate model, the first implication is that the simplest approximations that have been usefully applied to single-channel reactants are probably not adequate for branching systems, at least over a range of reaction conditions. More remains to be learned about up-pumping rates, R_{ij}, and the characteristics of the ensemble energy distribution before models can be considered to be predictive, especially for chemically interesting cases involving multiple reactant channels.

The second implication of the branching ratio data is that $\langle E_r \rangle$ at these two freuqencies is very different even when the total yields are the same. The best fitting branching ratios in Figure 3 correspond to the absorption of *ca* 24 and *ca* 34 photons at $P(14)$ and $P(38)$, respectively. The total unimolecular rate constants $(k_H + k_D)$ at these energies differ by about two orders of magnitude: $k\langle E_r \rangle_{P(14)} = 9{\cdot}0 \times 10^4$ s^{-1} and $k\langle E_r \rangle_{P(38)} \approx 1{\cdot}1 \times 10^7$ s^{-1}. It is becoming increasingly apparent that very large differences in the mean unimolecular reaction rate constant can be achieved with fairly modest alterations to the reaction conditions in multiphoton excitation experiments. In addition to these data, recent work on other branching systems has shown differences of over three orders of magnitude in $k\langle E_r \rangle$ in response to bath gas pressure changes for CH_2DCH_2Cl[2] and approximately two orders of magnitude in response to laser intensity with ethyl vinyl ether.[10] These observations foster the hope that once the details of pressure, intensity and frequency effects in

infrared multiphoton excitation are known, it can become a flexible method for activating chemical reactions capable of delivering known and variable amounts of energy to specific components of reacting mixtures.

APPENDIX

RRKM rate constants for each reaction channel from DEC-d_5 were calculated from the equation[30]

$$k_a(E^*) = L^* \frac{Q_1^+}{Q_1} \frac{\sum_{E^+=0}^{E^+} P(E_{VR}^+)}{N^* E^*}$$

where

L^* = reaction path degeneracy = 3;

Q_1^+/Q_1 = ratio of adiabatic partition functions = 1;

$\sum_{E^+=0}^{E^*} P(E_{VR}^+)$ = sum of vibrational states of the activated complex from the threshold energy E_0 to E^*;

$N^*(E^*)$ = density of vibrational states of the reactant at internal energy E^*.

State sums and densities were calculated using the algorithm described by Stein and Rabinovitch.[31] All internal degrees of freedom were assumed to be harmonic oscillators. Frequencies for DEC-d_5 were chosen based on normal mode assignments for dimethyl carbonate[32] and characteristic frequencies for carbonate skeletons.[33] Harmonic oscillator approximations to torsional frequencies were calculated from

$$\nu = \frac{n}{2\pi} \left(\frac{V_0}{I_r}\right)^{1/2}$$

using estimates for V_0 and I_r. These frequencies give a value for $\Delta S^\circ_{(600)}$ in good agreement with group additivity calculations.[34] Frequencies for the activated complexes were obtained by dropping a C–C–O bending mode as the reaction coordinate and adjusting the torsional frequencies to fit the experimental values of $\Delta S^{\ddagger}$. Frequencies are listed in Table 3.

Arrhenius parameters were determined from pyrolysis experiments:[17] $\log k_H = 12{\cdot}6 - 43\,300/\phi$; $\log k_D = 12{\cdot}7 - 44\,400/\phi$ ($\phi = RT$). Values of the critical energies, E_0, were calculated from the Arrhenius activation energies. RRKM calculations were carried out over a range of critical energy differences, $\Delta E_{0(D-H)}$, that reflected the error in the thermal data[17]. High-pressure thermal rate constants and branching ratios calculated with RRKM theory using these parameters are in excellent agreement with the pyrolysis data.

Table 3. Frequencies and degeneracies for RRKM calculations

DEC-d_5 (cm^{-1})	k_H (transition state)	k_D (transition state)
3000 (5)	3000 (5)	3000 (5)
2150 (5)	2150 (5)	2150 (5)
1760	1760	1760
1430 (2)	1430 (2)	1430 (2)
1295	1295	1295
1150 (3)	1150 (3)	1150 (3)
1060 (3)	1060 (3)	1060 (3)
1030 (2)	1030 (2)	1030 (2)
1025	1025	1025
1000 (2)	1000 (2)	1000 (2)
990	990	990
950 (3)	950 (3)	950 (3)
857	857	857
801	801	801
634	634	634
579	579	579
518	518	518
400 (2)	400	400
222	320	222
190	190	260
90	140	90 (2)
70	70	60 (2)
60	75	
50	50	

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