High-Power Carbon Dioxide Laser-Induced Reactions of Cyclohexane, Methylcyclohexane, Hexane, and Benzene

M. Quinn, Z. Sabet, and N. Alyassini*

Quantum Electronic Group, Electronic Department, Kuwalt Institute of Scientific Research, Safat, Kuwalt (Received; July 13, 1981; In Final Form: March 2, 1982)

Static and dynamic experiments were conducted to study laser-induced reactions of cyclohexane, methylcyclohexane, *n*-hexane, and benzene using a focused high-energy pulsed carbon dioxide (CO_2) laser. The energy input and the sample vapor pressure were varied from 100 mJ to 1.5 J and from 5 to 50 torr, respectively. Two distinct regimes characterized by a faint and a bright luminescence were observed. Acetylene and ethylene were the major products in both reaction regimes. In the bright luminescence region where the maximum decomposition efficiency was obtained, results indicated that high concentrations of C₂ radicals and electronically excited hydrogen atoms were present. These latter results are consistent with a dielectric breakdown of the sample, under the high-power conditions utilized.

Introduction

During the past few years the possible applications of high-power pulsed CO₂ lasers to drive and control chemical reactions have been investigated by a number of researchers.¹⁻³ In the majority of the studies reported in the literature, the investigations have been primarily concerned with the following: (a) the bond-breaking selectivity⁴ and the chemical-reaction selectivity⁵ of the process; (b) the physical⁶ and chemical⁷ mechanisms through which the reactions occur; (c) the nature of the multiphoton absorption processes in collisionless^{8,9} regimes which cultimate in the molecular fragmentation of polyatomic organic molecules in the presence of intense infrared laser fields; (d) the nature of the fragments produced and their energy distribution immediately after their formation.¹⁰

Much of the work has been concerned with the collisionless regime. The greater emphasis on this line of study stems from the possible application of the technique to isotope separation and purification.^{11,12} Also mechanistic details are more easily studied and understood in this regime.¹³

There has also been some interest in chemical reactions driven by CO_2 lasers, using energy fluences well above the threshold required for multiphoton-induced molecular fragmentation.^{14,15} At such high energy fluences dielectric breakdown of the reactants can occur even at pressures

- (5) Fisk, G. A. Chem. Phys. Lett. 1978, 60, 11-5.
- (6) Bloembergen, N.; Yablonovitch, E. Phys. Today 1978, 31, 23-30.
 (7) Chekalin, N. V.; Letokhov, V. S.; Lokhman, V. N.; Shibanov, A. N.
- Chem. Phys. 1979, 36, 415-21.
 (8) Levy, M. R.; Reisler, H.; Mangir, M. s.; Wittig, C. Opt. Eng. 1980, (6) Levy, M. R., Reber, M. and E. Phys. Today 1980, 33, 43-50.
 (9) Zare, R. N.; Bernstein, R. B. Phys. Today 1980, 33, 43-50.
 (10) Reiser, C.; Steinfeld, J. I. Opt. Eng. 1980, 19, 2-9.
 (11) Letokov, V. S. Phys. Today 1980, 33, 34-41.
 (12) C. Delever, F. M. Lackev, V. A. Markin, F. P.

(13) Thiele, E.; Goodman, M. F. Stone, J. Opt. Eng. 1980, 19, 10-20.
(14) Ronn, A. M. Chem. Phys. Lett. 1976, 42, 202-4.
(15) Lin, S. T.; Ronn, A. M. Chem. Phys. Lett. 1978, 56, 414-8.

of the order of 1 torr.¹⁵ Evidence has been cited¹⁶ which suggests that reaction intermediates and products, formed in reactions induced by dielectric breakdown, may be similar to or identical with those produced in multiphoton-induced fragmentation reactions. To verify these conclusions, further experimental work will be required to characterize the nature of the products and intermediates formed in the dielectric breakdown regime.

To get an insight into the behavior of molecular systems in the higher energy fluence and pressure regimes, we investigated laser-induced reactions of cyclohexane, methylcyclohexane, *n*-hexane, and benzene. An investigation of the nature of the products, the efficiencies with which the products were obtained, and also the energy fluence dependence, the laser wavelength dependence, and the pressure dependence of these yields was undertaken. These investigations were conducted in two regimes, a static regime in which the reactant and resulting products were subjected to repetitive laser pulses and a dynamic regime in which the reactant was effectively subjected to a single laser shot.

The overall objective of these investigations was to evaluate the potential application of high-power pulsed CO_2 lasers to drive the gas-phase chemical reactions in a pressure regime very much higher than that required for excitation-specific reactions. Reaction processes of this nature may find useful applications in the petrochemical industry.

Experimental System

The experimental procedure is described briefly below. Static samples at known pressures (1-54 torr) and flowing samples at $\simeq 20$ torr (dynamic experiments) were irradiated in a stainless-steel cell by a grating tuned CO₂ TEA laser (Lumonics 103). The cell had a cylindrical geometry with a length of 16 cm, a diameter of 4 cm, and a total volume of $\simeq 0.2$ L. A 13-cm focal length lens (ZnSe) was used to focus the laser pulse into the reaction cell via a ZnSe window tilted at the Brewster angle. An adjustable aperture placed ahead of the lens was used to control the energy input to the reaction cell (100 mJ-1.5 J). The calculated energy fluence was 50 J cm⁻² per 100 mJ of laser excitation energy, assuming a uniform distribution of energy across the focused laser spot. A focal spot size of

⁽¹⁾ Gauthier, M.; Hackett, P. A.; Willis, C. J. Chem. Phys. 1980, 45, 39-46.

⁽²⁾ Danen, W. C.; Munslow, W. D.; Setser, D. W. J. Am. Chem. Soc. 1977, 99, 6961-3.

⁽³⁾ Lesiecki, M. L.; Guillory, W. A. J. Chem. Phys. 1977, 66, 4317-23.
(4) Avouris, P. H.; Chan, I. Y.; Loy, M. M. J. Photochem. 1980, 13, 13 - 9

 ⁽¹²⁾ Basov, N. G.; Belenov, E. M.; Isakov, V. A.; Markin, E. P.; Ora-evskii, A. N.; Ramanenko, V. I. Sov. Phys. - Usp. (Engl. Transl.) 1977, 20, 209-25.

⁽¹⁶⁾ Ronn, A. M. U.S. Patent 4 230 546, Oct 28, 1980.



Figure 1. Plot of relative energy transmitted through a 100- μ m pinhole scanned in 200- μ m steps across the CO₂ laser wave front. The laser was tuned to 9.714 μ m and the total energy in the beam was 1.5 J.

0.5-mm diameter (close to theoretical for a Gaussian beam) was also assumed for the average aperture diameter of 5.5 mm.

The temporal behavior of the laser pulse was monitored with a photon drag detector Rofin Model 7455), the energy with a pyroelectric detector (Lumonics Model 20D 111), and the laser wavelength with a CO_2 spectrum analyzer (Optical Engineering Inc.). The laser was operated in the multimode regime and a 100- μ m diameter pinhole scan across the laser beam showed no "hot" spots (Figure 1). The pulse consisted of an initial fast-rising spike with a duration of 80-ns fwhm. The spike was followed by a longer-duration component which contained about 15% of the total laser energy and which decayed to zero after 1.5 μ s. The measured temporal profiles of the laser pulses did not change appreciably with laser wavelength and were found to be reproducible to at least 10%. The laser pulse energy was found to be reproducible to better than 5%. The spatial properties of the laser pulses were also reproducible for any particular wavelength but showed wide variation from one wavelength to another. In static experiments the reaction cell was filled to the desired reactant pressure by first evacuating to 10⁻³ torr and then allowing the reactant vapor pressure to drive vapor into the cell until the desired pressure was reached.

In dynamic experiments, the required sample flow rate and pressure were achieved by controlling both the evaporation rate of reactant into the cell and the condensation rate of products in two series coupled cold traps operating at -70 and -177 °C, respectively. Unreacted starting material and relatively high boiling point products (i.e., bp > 40 °C at 1 atm) were primarily collected in the first in-line cold trap (-70 °C).

Reaction products were identified qualitatively by online infrared spectrophotometry (Perkin-Elmer Model 577) and gas chromatography (Hewlett Packard Model HP5710A) analysis.

A 3-m stainless-steel column packed with phenylisocyanate on Porasil C (mesh size 80/100) was utilized in the GC system. Quantitative analysis was achieved by calibration of the gas-chromatography system using pure standard samples of the known products. Important reaction transients or intermediates were also identified from luminescence studies. Sample luminescence produced during laser irradiation was collected from the reaction cell via side-mounted quartz windows and led to a spectrally resolved analyzer for integrated spectral measurements (Princeton Applied Research, OMA2) and a photomultiplier/monochromator system for temporal measurements. The photomultiplier system (Hammamatsu 955) had a rise



INITIAL PRESSURE OF CYCLOHEXANE.TORR

Figure 2. Plot of threshold energy fluence required for transition from a faint to bright luminescence, as a function of reactant pressure. The results relate to CO₂ laser-irradiated cyclohexane. The threshold energy fluence shows approximately a p^{-2} dependence at lower pressures and a $p^{-1/3}$ dependence at higher pressures (i.e., >10 torr). The laser was tuned to 9.714 μ m.

time of $\simeq 1$ ns when operated as a five-stage multiplier. Where higher gain was required, nine stages were used with a system rise time of < 20 ns.

Results and Discussions

Laser-induced reactions in cyclohexane, methylcyclohexane, hexane, and benzene were found to show similar general characteristic features. Two distinct reaction regimes were always observed over the energy fluence $(50-750 \text{ J cm}^{-2})$, pressure (5-50 torr), and exposure ranges (1-3500 pulses) investigated: a low decomposition yield region characterized by a faint luminescence and a high decomposition yield region characterized by a bright luminescence (typically 6 orders of magnitude brighter than the faint luminescence). The faint luminescence was only observed at laser wavelengths overlapping the infrared absorption region of the reactant. The bright luminescence could be achieved over the entire tuning range of the CO_2 laser (9.2–11.0 μ m). These distinct regions were separated by a well-defined laser energy/power threshold. The threshold energy required to reach the bright luminescence regime was found to show the characteristic pressure dependence depicted in Figure 2. The curve in Figure 2 shows approximately a p^{-2} dependence at lower pressure (<10 torr) which gradually develops into a $p^{-1/3}$ dependence at higher pressures (>10 torr).

In carrying out threshold energy measurements, it was found necessary to ensure that the reaction cell and cell windows were thoroughly clean and free of carbon and other dust particulates. For all reactants investigated under these conditions, the threshold energy showed a weak laser wavelength dependence over the entire tuning range of the CO_2 laser (9.2–11 μ m). There appeared to be no detectable direct correlation of threshold energy with the structured infrared absorption bands of any of the reactants. However, throughout the wavelength region 9.3–9.9 μ m, where infrared absorption is relatively strong

TABLE I. Threshold Energies (mJ) for Transition from a Faint Luminescence to Bright Luminescence, Observed at Four Different CO_2 Excitation Wavelengths in CO_2 Laser-Irradiated Cyclohexane, Methylcyclohexane, Benzene, and Hexane at the Initial Pressure of 15 torr

CO₂ laser wavelength, µm	threshold energy in				
	cyclohexane	methylcyclo- hexane	benzene	hexane	
10.591	780	780	1050		
10.365	712	740	990		
9.714	420	465	495	370	
9.552	590	550	620		

in these materials,¹⁷ lower threshold energies were always observed. In fact, the measured threshold energies were found to be lowest at wavelengths which overlapped the peak in the infrared absorption spectrum of the reactant, red shifted by about 25 cm^{-1} (ref 18), (i.e., close to 9.716 μm in all reactants). The threshold energies observed in the reactants at 15 torr, measured by using four different CO_2 laser wavelengths, are shown in Table I. Since the laser was operated in a multimode condition, the spatial distribution of energy fluence across the wave front did vary with laser wavelength tuning. This variation may have been partially responsible for the observed threshold energy dependence on excitation wavelength. The breakdown volume always occurred in the focal plane of the lens when the laser excitation wavelength overlapped the red-shifted ($\simeq 25 \text{ cm}^{-1}$) infrared absorption bands of the reactants.¹⁸ This was not generally the case when the laser was tuned to wavelengths outside these absorption bands. Optical breakdown under these latter conditions may therefore have been influenced by impurities in the cell or residual carbon particulates which were difficult to eliminate entirely from the system.

Nature of Intermediates

Typical time-integrated spectra of the bright and faint luminescence emissions are shown in Figure 3. The bright luminescence emission was found to be at least 6 orders of magnitude brighter than the faint luminescence.

An analysis of the luminescence from each regime indicated that C_2 and CH radicals were responsible. The C_2 radicals were easily identified from their well-known Swan bands $(a^3\Pi_u \leftarrow d^3\Pi_g)$ involving the electronic-vibrational transition sequences at 438, 470, 516, and 568 nm, corresponding respectively to $\Delta V = +2, +1, 0, -1$. The CH radicals were identified from their characteristic spectral transition peaks near 389 nm ($X^2\Pi_r \leftarrow B^2\Sigma$) and 428 nm $(X^2\Pi_r \leftarrow A^2\Delta)$. The spectral features of C_2 and CH species were identified in both luminescence regimes. Luminescence emission from electronically excited hydrogen atoms (Balmer series) was only present in the high-yield, bright luminescence regime. One important feature of the luminescence emission in the faint luminescence regime concerned its intensity dependence on the laser excitation wavelength. When the luminescence intensity in the wavelength band 430-475 nm (due to C_2 radicals) was measured as a function of CO₂ laser wavelength, during laser-induced decomposition of each hydrocarbon at 10torr pressure, an action spectrum was always observed which resembled the normal infrared absorption spectrum of the reactant.¹⁸ The energy fluence was maintained at a constant value of 75% of the faint luminescence to bright luminescence threshold level, throughout these latter



Figure 3. Time-integrated spectra of the bright luminescence (solid curve) and faint luminescence observed in cyclohexane at 10 torr. The CO₂ laser input energies were 500 and 320 mJ per pulse, respectively. The laser was tuned to 9.714 μ m. The bright luminescence intensity was at least 6 orders of magnitude more intense than the faint luminescence observed below the optical breakdown threshold. The possible assignments of the emission lines and bands are appropriately shown. Ordinate: (left) relative luminescence intensity, arbitrary units; (right) relative luminescence intensity, arbitrary units; wavelength, nanometers.

measurements. In all molecules studied, the observed action spectra were red shifted by about 25 cm^{-1} from the corresponding infrared spectra. To illustrate this effect, the action spectrum observed in benzene vapor at 10-torr pressure is presented with the normal infrared absorption spectrum in Figure 4.

For all reactants investigated, the luminescence, due to C₂ radicals and electronically excited hydrogen atoms, was extremely intense in the bright luminescence region. For example, C₂ radical luminescence in cyclohexane was measured from a known solid angle ($\simeq 10^{-2}$ sr), using a vacuum photodiode (Instrument Technology Model HSD 50). The luminescence showed the following behavior. It started about 30 ns after the onset of the laser pulse, reached a peak in about 20 ns, and decayed gradually in approximately 300 ns. Before it reached zero, a second component was observed, reaching an equally intense peak 600 ns after the onset of the laser pulse and gradually decaying to zero in approximately 2 μ s. The measured optical peak power output for each component, in the solid angle subtended by the photodiode (i.e., 10^{-2} sr), was >60 mW. These values indicate a relatively high concentration of emitting species. Since the reaction-zone volume was estimated to be <0.1 cm³ (based on visual observations of the plasma) and the reactant concentration 6×10^{-7} mol cm⁻³ (at 10-torr pressure), a sizable fraction of this reactant was probably decomposed to C2 radicals, thus accounting for the observed luminescence behavior. The occurrence of high concentrations of electronically excited hydrogen atoms also indicated that high-energy fragments (i.e., >12 eV) were produced in the bright luminescence regime.

In these experiments, the calculated ranges of power densities required to produce the bright luminescence were $10^{13}-5 \times 10^{13}$ W m⁻² over the pressure range of 5-50 torr. These latter results are probably consistent with a dielectric breakdown of the organic material.¹⁶ Ronn¹⁶ reported CO₂ laser-induced dielectric breakdown in benzene vapor at 25-torr pressure. In his work the laser was tuned to 10.6 μ m, was operated in a multimode condition, had an energy per pulse of 2 J, and was focused into the sample by using a 13-cm focal length lens.

Nature of Products

In laser-induced decomposition of cyclohexane, methylcyclohexane, and hexane, the major products observed in the faint and bright luminescence reaction regimes were

⁽¹⁷⁾ Pouchert, Charles J. "Aldrich Laboratory of Infrared Spectra";
Aldrich Chemical Co.: Milwaukee, WI, 1970. Pierson, Raymond H.;
Fletcher, Aaron N.; Gantz, E. St. Clair, Anal. Chem. 1956, 28, 1218.
(18) Quinn, M. F.; Alyassini, N., to be submitted for publication.



WAVELENGTH, MICROMETRES

Figure 4. Plot for benzene (10 torr), showing relative emission intensities from C2 radicals in the faint luminescence regime (•) and the normal infrared absorption spectrum of benzene vapor at 10 torr (O). The emission intensities of the C2 radicals, measured in the wavelength band 430-470 nm, are shown as a function of CO2 laser wavelength. The laser input energy was maintained consant at 300 mJ for each laser wavelength in the range investigated, i.e., 9.422-9.773 µm. The observed emission intensities for laser excitation wavelengths <9.676 μ m (P34) were magnified by 10 for easier interpretation and are plotted as the broken curve. The infrared absorption spectrum of benzene was measured in a 55-cm path length cell using a low-power (1-W) tunable CW CO, laser. The relative positions of the CO, laser lines corresponding to benzene infrared absorption peaks and C2 radical emission peaks are presented. Ordinate: (left) relative luminescence intensity, arbitary units; (right) normal infrared absorbance. Abscissa: wavelength, micrometers.

acetylene, ethylene, and hydrogen. However, in the faint luminescence regime only trace amounts of these products were detected after irradiation with 10^3-10^4 laser pulses. These observations were made in all pressure ranges investigated, irrespective of excitation wavelength.

Above the energy fluence threshold, where a bright luminescence occurred, high yields of products were observed. In addition to acetylene and ethylene, butadiene was present as a major product in laser-irradiated samples of hexane, cyclohexane, and methylcyclohexane. Methane was also detected, as a minor product, in laser-irradiated methylcyclohexane. Acetylene, hydrogen, and carbon particulates were the only major components observed in laser-irradiated benzene. These results are consistent with those of Ronn¹⁶ although he did not report the detection of H₂. Small carbon deposits were also observed in the cyclohexane and methylcyclohexane systems.

A large number of experiments were carried out in which the effect of laser energy, laser wavelength, sample pressure, and exposure period were investigated in detail with respect to product yields. Results pertinent to irradiated TABLE II:Product Yields, as a Function of ExposurePeriod and Laser Energy, Observed in High-Power CO2Laser-Irradiated Samples of Cyclohexane Vapor at anInitial Pressure of 34 torr^a

		reactant and product partial press., torr	
		500-mJ	750-mJ
0		laser	laser
no of		pulse	pulse
pulses	products and reactant	energy	energy
50	cyclohexane decomposed	1.43	2.08
	acetylene	1.73	2.86
	ethylene	0.32	0.86
	butadiene	$\simeq 0.2^{b}$	
75	cyclohexane decomposed		3.15
	acetylene		4.15
	ethylene		1.3
	butadiene		
100	cyclohexane decomposed	2.72	
	acetylene	2.39	
	ethylene	0.47	
	butadiene	≃0.3 ^b	
150	cyclohexane decomposed	4.45	6.6
	acetylene	3.88	9.5
	ethylene	0.85	2.3
	butadiene	0.48	0.75
300	cyclohexane decomposed	9.15	13.4
	acetylene	6.9	16,3
	ethylene	1.55	4.0
	butadiene	0.63	1.15
500	cyclohexane decomposed	15.0	22.4
	acetylene	13.0	22.2
	ethylene	3.72	4.4
	butadiene	1.03	1.04

^a The laser was tuned to 9.714 μ m (P38). The reaction cell volume was 0.2 L. The partial pressures of hydrogen were not accurately measured and are therefore not included in the table. ^b Not accurately measurable. The instrument detection limit for butadiene and cyclohexane was approximately 100 mtorr, and for ethylene and acetylene approximately 50 mtorr.

cyclohexane are discussed below. Results from laser-irradiated methylcyclohexane and hexane were found to be similar.

Effect of Laser Energy and Exposure Period. In Table II product yields are listed as a function of exposure period (number of laser pulses) for irradiated samples of cyclohexane at an initial pressure of 34 torr (static experiments). The results relate to two energies, i.e., 500 mJ per pulse and 750 mJ per pulse, incident on the reaction cell entrance window. An important feature of the results in Table II is that the partial pressure of cyclohexane decomposed in an exposure cycle is directly proportional to the total laser radiation adsorbed by the sample. In contrast, the reaction products, particularly ethylene and butadiene, show a rapid departure from linearity with respect to adsorbed laser energy, probably indicating their decomposition during exposure. The data for acetylene indicates a departure from linearity only when the total energy input to the reaction exceeds approximately 250 J, i.e., after 500 pulses with pulse energy of 500 mJ or 330 pulses with pulse energy of 750 mJ.

In the dynamic experiments, where flowing samples at a pressure of approximately 20 torr were subjected to laser pulses of similar energies, yields of ethylene and butadiene relative to acetylene (shown in Table III) were higher than those observed in static experiments. In these latter experiments the flow rate was adjusted such that the reactant in the reaction zone was changed between consecutive laser pulses. The results of these dynamic experiments support the conclusion that ethylene and butadiene undergo de-

TABLE III: Relative Yields for Products Collected in a Liquid-Nitrogen Cold Trap, at the Termination of Typical Dynamic Experiments in Which Cyclohexane Was Subjected to High-Power CO_2 Laser Pulses^a

exposure conditions	products collected	relative ratios of products
1500 pulses of 750-mJ energy	acetylene ethylene butadiene	1.0 0.33 0.11
600 pulses of 500-mJ energy	acetylene ethylene butadiene	1.0 0.39

 a The reactant pressure was approximately 20 torr. The laser was tuned to 9.714 $\mu m.$



INITIAL PARTIAL PRESSURE OF CYCLOHEXANE REACTANT, TORR

Figure 5. Plot showing the partial pressures of laser-induced reaction products, as a function of initial pressure of reactant. The results relate to laser-induced reactions of static samples of cyclohexane. A similar set of results were observed in laser-irradiated methylcyclohexane and hexane. These product yields were achieved by exposing the reactant to 100 laser pulses (750 mJ per pulse). The laser was tuned to 9.714 μ m.

composition during exposure to repetitive laser pulses, probably to acetylene.

Effects of Initial Sample Pressure and Laser Wavelength. The trends outlined above were observed at all other sample pressures investigated. The partial pressures of acetylene, ethylene, and butadiene, measured in cyclohexane samples irradiated with 100 laser pulses (energy per pulse, 750 mJ), are shown in Figure 5. The initial pressure of cyclohexane was varied from 19 to 54 torr. The corresponding partial pressures of cyclohexane decomposed in these experiments are given in Figure 6. The results in Figure 6 indicate the following. As the initial partial pressure of reactant is increased, the percentage of decomposed reactant converted to acetylene, ethylene, and butadiene appears to decrease. This decrease is much more rapid above \simeq 40-torr reactant pressure. This latter trend may partially be due to errors in our analysis of decomposed reactant, brough about by reactant conden-



Figure 6. Plot of the partial pressures of cyclohexane consumed during laser irradiation of static samples, as a function of initial pressure of cyclohexane. For each initial cyclohexane pressure, the reactant was subjected to 100 laser pulses (750 mJ per pulse). The laser was tuned to 9.714 μ m. The solid curve indicates the measured parameters. Since some condensation of cyclohexane occurred on the walls of the reaction cell and in the analysis system, at the relatively higher pressures (i.e., >40 torr), the measured partial pressures of cyclohexane consumed in the reactions are too large. The extrapolated broken curve would probably be more realistic in the absence of condensation.

sation on the walls of our reaction cell and sampling systems.

Results outlined above were found to be approximately independent of the laser wavelength, over the tunability range of the CO₂ laser (9.2–11.0 μ m).

The product yields from the laser-irradiated n-hexane were found to follow trends similar to those observed in cyclohexane. Similar determinations were not attempted with methylcyclohexane because of its relatively low vapor pressure at laboratory temperature and with benzene because the chromatography column would not allow separation.

Decomposition Efficiencies. An approximate estimate of the maximum reaction efficiency was carried out as follows for the faint luminescence region observed in CO₂ laser-irradiated cyclohexane at 20-torr pressure. For a total input to the sample of 3.5 kJ (10000 pulses) at 9.714 μ m and with energy fluences up to about 50% of that required for threshold (see Figure 2), there was no detectable faint luminescence. In addition there was no detectable decomposition of the reactant and no detectable products. As the energy fluence was increased to the threshold point, the faint luminescence gradually increased in intensity. At an energy fluence of 75% of the threshold value, reactant decomposition was just about detectable and traces of acetylene and ethylene (the only products observed) appeared with cyclohexane or methylcyclohexane as reactant. From GC analysis sensitivity considerations and using the 3.5-kJ total energy input to the reaction cell, we calculated the energy required to decompose the reactants to be >5 \times 10⁴ kcal mol⁻¹ for an energy fluence equivalent to 75%

of the breakdown level at 9.714 μ m. The enthalpy for the reaction which gave the observed products in approximately the correct ratios was calculated to be 150 kcal mol⁻¹. The maximum achievable efficiency for the process was therefore <0.3%. The low efficiency may have been primarily due to the fact that <1% of the incident laser energy was adsorbed. By utilizing an optical system to couple laser energy into the reaction more efficiently, while simultaneously maintaining a constant energy fluence, one might achieve higher reaction efficiencies.

In the bright luminescence regime (i.e., above the optical breakdown threshold), the product yields were considerably higher. Assuming the observed products to be produced in the following sequence of fragmentation processes¹⁹

the percentage of decomposed cyclohexane converted to the products acetylene, ethylene, and butadiene was calculated as follows. For short exposure periods, when less carbon is being produced, such as 50 pulses of energy with 500 mJ per pulse (Table II), the 1.73 torr of C_2H_2 would account for 0.58 torr of decomposed C_6H_{12} , according to the proposed equations. Similiarly, if it is assumed that C_2H_4 is produced according to the first step in the reaction sequence above, the 0.32 torr of C_2H_4 would account for 0.32 torr of decomposed cyclohexane. On this basis, the products ethylene and acetylene account for 62% of the decomposed cyclohexane. However, according to Table II, the butadiene concentration always appears to be smaller than the ethylene concentration, and this should be included in the calculation. If this procedure is adopted and the smaller butadiene concentration is considered, the calculated efficiency will be >50%.

For each laser shot, at 9.714 μ m, 15% of the laser pulse energy was reflected off the cell's entrance window, 30% was transmitted through the exit window, and approximately 15% was adsorbed by the sample outside the 0.1cm³ reaction volume. The 15% adsorbed energy in the sample was determined by measuring the transmission through the sample of a low-power (1-W), CW CO₂ laser at 9.714 µm.

Thus, the estimated laser energy absorbed in the decomposition of cyclohexane given in Table II was calculated to be typically 180 kcal mol⁻¹. From the trend outlined in the text, it would appear that, in a dynamic system, reaction yield efficiencies of >50% (for acetylene, ethylene, and butadiene) can be achieved for a reaction enthalpy of 180 kcal mol⁻¹ of reactant decomposed (cyclohexane, methylcyclohexane, and hexane). This corresponds to about 70 CO_2 laser photons per molecule of cyclohexane decomposed.

Conclusions

The most interesting aspects of the results presented above relate to the higher input energy fluence regime. where bright luminescence was observed. The characteristic features of the bright luminescence suggest that a dielectric breakdown was probably responsible.¹⁶ The interesting feature of this behavior was the low power levels at which a dielectric breakdown was achieved, i.e., $10^{9}-5$ $\times 10^9$ W cm⁻². To produce a dielectric breakdown in

methane over the same pressure range, power levels at least 1 order of magnitude higher were required. Furthermore, at power levels greater that 10¹⁰ W cm⁻², dielectric breakdown in pure argon gas could only be achieved at pressures of >80 torr. When argon was doped with one of the hydrocarbons investigated above (>5%), dielectric breakdown was observed in argon at pressures down to 15 torr, using power levels of approximately 5×10^9 W cm⁻². These results are consistent with results reported by Deutsch²⁰ and Crim and Kwei.²¹ Deutsch²⁰ reported a visible luminesxcence from CO₂ laser-irradiated samples of silane at pressures in the range 2-20 torr. Characteristic Balmer series spectral lines of atomic hydrogen were detected in the luminescence. When an electrode system was incorporated into the reaction cell, ions were also detected. Estimated energy fluences and power densities used in this work were 14–150 J cm⁻² and 3.5×10^{8} – 3.75×10^{9} W cm⁻², respectively. In these studies, dielectric breakdown in argon gas was achieved at a power density of 6×10^9 W cm^{-2} when the gas pressure was >66 torr. Furthermore, the threshold for the observed luminescence was found to be approximately 6 times larger when the CO₂ laser was tuned to wavelengths outside the absorption bands of the reactant. The author concluded from these latter observations that the production of the luminescence did involve resonant laser-induced dielectric breakdown.

Crim and Kwei²¹ reported CO₂ laser-induced ionization in flowing mixtures of SF_6 (1-torr pressure) containing 1% hydrocarbon. The hydrocarbons used in this work $(CH_4,$ C_2H_6 , and C_3H_8) did not directly absorb CO_2 laser radiation but were found to be necessary for the ionization process to occur. Considerably higher efficiencies for ion production were observed when the laser was tuned to the absorption bands of SF_6 . The production of F atoms by multiple-photon fragmentation was found to be essential to the ionization, and a likely mechanism was thought to involve F atom reactions with the hydrocarbon to produce energetic C_2 and CH radicals which undergo subsequent chemiionization. The presence of electronically excited C₂ and CH radicals in SF₆-hydrocarbon mixtures was verified by Orr and Keentok.²² Energy fluences in the range 16-3500 J cm⁻² were used in this work.

A possible explanation for the breakdown behavior observed in our work may be the involvement of multiphoton absorption processes which are expected to be prominent in the high-power laser irradiation of the cyclohexane, hexane, and benzene vapors. These molecules have relatively intense infrared absorption bands throughout the 9–11- μ m wavelength range whereas methane does not.¹⁷

Multiphoton absorption processes are known to lead to the formation of C₂ and CH radicals,⁸ and these were observed in the faint and bright luminescence regimes investigated in this work. Experimental evidence¹⁹⁻²¹ suggests that these radicals, in electronically excited states, may induce chemiionization in collisions between themselves and with neutral molecules.²¹ Once a critical concentration of electrons is formed, classical collision heating of electrons (via the inverse Bremsstrahlung mechanism) is capable of propagating a breakdown process. A mechanism of this nature could explain the transition from the faint luminescence region to the bright luminescence region.

Finally, since the start of this breakdown was always observed <50 ns after the initiation of the laser pulse, the involvement of laser thermal heating in the production of

⁽¹⁹⁾ Gillespie, H. M.; Gowenlock, B. G.; Johnson, C. A. F. J. Chem. Soc. Perkin Trans. 2 1979, 317-24.

⁽²⁰⁾ Deutsch, T. F. J. Chem. Phys. 1979, 70, 1187-92.

⁽²¹⁾ Crim, F. F.; Kwei, G. H. Chem. Phys. Lett. 1977, 49, 526-9. (22) Orr, B. J.; Keentok, M. V. Chem. Phys. Lett. 1976, 41, 68-72.

electronically excited radicals or collisional ionization was probably unimportant. In the faint luminescence regime, just below breakdown, the temperature of the reactant was <4000 K as calculated from specific heat data, the minimum excitation zone volume $(0.5\pi \times 10^{-2} \text{ cm}^3)$, the maximum adsorbed laser energy ($<10^{-3}$ cal), and the reactant pressure. From this calculation and from collision frequency and vibrational to translational energy transfer considerations, it is unlikely that thermalization times for cyclohexanes at 10-torr pressure would be <100 ns.

Acknowledgment. We acknowledge the financial support of the Kuwait Institute for Scientific Research for this project. We also thank Dr. Firas Rasoul for his contributions during the early phases of this work, Dr. Jamal Manassa and Dr. Samir Ahmed for their interesting discussions pertinent to the project, and Mr. Joseph D'Souza for his technical assistance.

Nonuniform Transfer of Electron Spin Polarization in Reaction Centers of the Photosynthetic Bacterium Rhodopseudomonas sphaeroldes

Peter Gast,* Richard A. Mushlin, and Arnoid J. Hoff*

Department of Biophysics, Huygens Laboratory of the State University, 2300 RA Leiden, The Netherlands (Received: August 5, 1981; In Final Form: March 18, 1982)

The light-induced emissively polarized electron spin resonance signal at g = 2 in reaction centers of photosynthetic bacteria is further characterized, by employing conventional electron spin and electron spin echo resonance techniques. These new data confirm our model that describes the polarized signal as originating from transfer by exchange interaction of the net polarization of the spin-polarized intermediary electron acceptor I (a bacteriopheophytin) to the prereduced primary acceptor, U⁻ (a ubisemiquinone). The modulated echo decay envelope of the dark signal of U- and that of the light-induced polarized signal are identical, establishing the latter signal as a polarized form of U. The spin-spin and spin-lattice relaxation times of the dark and polarized signals of U⁻ are found to be identical and uniform over the lines i.e., $(T_1)_{dark} = (T_1)_{pol}, (T_2)_{dark} = (T_2)_{pol}$. A small difference in the line shape of the two signals appears to be caused by nonuniform transfer of polarization; this effect is responsible for the previously reported difference in g value of the dark and polarized ESR spectra of U⁻.

Introduction

The primary act of bacterial photosynthesis is that of initial charge separation:

$$P I \xrightarrow{h_{\nu}} P^*I \xrightarrow{< s \ ps} P^+I^-$$
(1)

in which P is a bacteriochlorophyll dimer, and I, the intermediary acceptor, is a bacteriopheophytin molecule. Both P and I are embedded in a protein forming the socalled reaction center. The state P⁺I⁻ is a radical-pair (RP) state: the individual members can develope cage electron spin polarization as described by CIDEP theory.¹⁻⁵ For a simple model in which the exchange interaction giving rise to the energy splitting between the singlet and the triplet RP states, $J(P^+I^-)$, is independent of time, the polarization is given by^5

$$\mathcal{P}_{\rm pi}({\rm P}^+) = -\mathcal{P}_{\rm pi}({\rm I}^-) = \frac{-4QJ({\rm P}^+{\rm I}^-)\tau^2}{1+4\omega^2\tau^2}$$
(2)

with

$$2Q = (g_{P^+} - g_{I^-})\beta\hbar^{-1}H + \sum_{j}^{P^+}A_jM_j - \sum_{k}^{I^-}A_kM_k \qquad (3)$$

Equation 2 gives the polarization of radical P⁺ in nuclear spin configuration $p(A_i, M_i)$ with hyperfine coupling constants A_i and nuclear quantum numbers M_i when the intermediary acceptor I^- is in the nuclear spin configuration $i(A_k, M_k)$ and the initial RP state is a pure singlet state; Q is half the difference in ESR resonance frequency between the two radicals at fixed magnetic field H; τ is the lifetime of the RP and $\omega^2 = Q^2 + J^2(P^+I^-)$. It can be seen from eq 2 and 3 that the net polarization of either radical, i.e., the contribution to the polarization that is independent of hyperfine fields (first term on the right-hand side of eq. 3), can be nonzero (it is of equal amplitude and of opposite sign for the counterradical) and that this polarization will be distributed among the hyperfine (hf) components of that radical in an asymmetric pattern which depends on the overlap of the two radical spectra. This type of polarization that develops within the geminate radicals has been called static.6

The next step in the primary photosynthetic reaction is a further stabilization of the separated charges

$$I^-U \xrightarrow{200 \text{ ps}} I U^-$$
 (4)

in which U is a guinone molecule.⁷ Pedersen⁶ has pointed out that, since eq 4 is an actual electron transfer, the net polarization of I⁻ should be transferred to U and distributed among the hf components of U⁻ in a pattern determined only by the line shape of unpolarized U^- . The hf

⁽¹⁾ F. J. Adrian in "Chemically Induced Magnetic Polarization", L. T.

⁽¹⁾ P. J. Millard M. Onemically induced magnetic round in p. 1. 1.
Muus et al., Eds., D. Reidel, Dordrecht, 1977, pp 77-105.
(2) R. E. Blankenship, T. J. Schaafsma, and W. W. Parson, Biochim. Biophys. Acta, 461, 297 (1977).
(3) A. J. Hoff, H. Rademaker, R. van Grondelle, and L. N. M. Duysens, Biochim Einspine Acta, 460, 547 (1077).

⁽⁴⁾ A. J. Hoff, P. Gast, and J. C. Romijn, FEBS Lett., 73, 185 (1977).
(5) J. B. Pedersen, "Theories of Chemical Induced Magnetic Polarization", Odense University Press, Odense, 1979.

⁽⁶⁾ J. B. Pedersen, FEBS Lett., 97, 305 (1979).

⁽⁷⁾ Note: in some species of photosynthetic bacteria U is a menaquinone; these species are not considered in this work.