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Infrared multiphoton induced isomerization of *cis*-3,4dichlorocyclobutene. I. Experimental results

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The yield and product distribution in the laser-induced isomerization of cis-3,4-dichlorocyclobutene (DCCB) have been measured as functions of laser fluence, DCCB pressure, and buffer gas pressure. Both Woodward-Hoffman allowed and "forbidden" isomers were observed. The fraction of "forbidden" products was found to increase linearly with fluence above a threshold of 3.5 J/cm^2 . At high fluence the yield increased quadratically with neat DCCB pressure. Both the yield and fraction of "forbidden" products declined monotonically with buffer gas pressure. These observations are explained in terms of a two-channel mechanism, in which the allowed isomer is formed in a concerted path and the forbidden isomers are produced from a diradical intermediate in a nonconcerted reaction.

I. INTRODUCTION

Infrared laser-initiated unimolecular reactions have been investigated intensively in recent years.^{1,2} In these reactions the parent molecule absorbs many photons in rapid succession, until the reaction rate becomes comparable to the optical pumping rate. In the case of unimolecular decomposition, since most of the absorbed energy is utilized in breaking one or more bonds, the resulting fragments usually contain only modest amounts of vibrational energy. In particular, if the threshold energy for reaction E_{th} and the reaction enthalpy ΔH are comparable in size, then the amount of energy available for partitioning between product translational and internal degrees of freedom will be fairly small. In contrast, for isomerization reactions ΔH may be positive or negative, while $|\Delta H|$ tends to be much smaller than $E_{\rm th}$. Consequently, the nascent products are born with a large amount of internal energy which can be removed only through radiation and collisions. Indeed, deactivation of the product species below the barrier for isomerization is required in order to define the isomeric state of the product. The essential role played by collisions even at low pressures distinguishes isomerization from other unimolecular processes.

A second interesting aspect of isomerization reactions is the possibility of obtaining stereospecific products. When more than one stereoisomer can be formed, it is possible to use the Woodward-Hoffmann rules³ to predict the outcome of the reaction. It has been conjectured, however, that these rules may be relaxed for molecules having very large amounts of vibrational energy.⁴ One might therefore expect to obtain symmetry-forbidden products by IR multiphoton excitation of the parent molecule.

To date there have been comparatively few detailed studies of IR multiphoton-induced isomerization reactions.⁵⁻²¹ Pioneering experiments in this area have been carried out by Yogev and co-workers.⁵⁻⁹ In their most recent work they investigated the CO_2 laser-induced ring-opening of perfluorocyclobutene.⁷⁻⁹ They observed a nonlinear dependence of the reaction yield on laser fluence. After many laser pulses they obtained up to 30% conversion of the neat gas and 100% conversion in a He bath. The isomerization was isotopically selective, with increased specificity in the presence of a buffer gas. These studies have motivated an information-theoretic treatment of multiphotoninduced isomerization reactions, formulated by Ben-Shaul and Haas.²²

The perfluoro compound studied by Yogev *et al.* is somewhat unique in that the ring-opening is endothermic. A study of the exothermic isomerization of 1-methyland 1, 2-dimethyl cyclobutene was carried out by Buechele *et al.*¹⁹ Although these reactions do not reveal any stereochemical information, the authors reported the very interesting finding that the reverse, endothermic ring closing of the butadienes can also be induced by laser excitation. Their work is a continuation of an earlier study of the CO_2 laser-initiated interconversion of the five hexadiene isomers.¹⁸

In order to test the stereospecificity of laser-initiated unimolecular reactions, Danen *et al.*²⁰ and Gordon and co-workers²¹ used a CO₂ laser to isomerize cis-3, 4-dichlorocyclobutene (DCCB). The principle objective of this study was to determine whether the Woodward-Hoffmann rules are satisfied by highly excited molecules. The thermally allowed reaction on the ground electronic surface produces only cis, trans-1, 4-dichloro-1, 3-butadiene (CT),



in a concerted, conrotatory mechanism. The thermally forbidden, photochemically allowed reaction yields the cis, cis (CC) and trans, trans (TT) isomers,

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in a disrotatory, concerted path.

In our preliminary study of DCCB isomerization we found that with fluences greater than 3.5 J/cm^2 , at a wavelength of 10.812 μ m, substantial amounts of symmetry-forbidden products were formed. The fraction of forbidden isomers increased linearly with fluence above the threshold, reaching a value of 18% at 8.2 J/cm^2 . Danen *et al.*²⁰ failed to observe the forbidden products; however, their highest fluence corresponds to our reported threshold. In the present paper we explore in more detail the laser-induced isomerization of DCCB. We have investigated systematically the effects of fluence, reactant pressure, and buffer gas pressure on the reaction yield and the product branching ratios. A quantitative explanation of these results, using a thermal RRKM model, will be presented in a forthcoming publication.²³

II. EXPERIMENTAL METHODS

The experiments were carried out using a pulsed CO_2 laser to irradiate samples of DCCB contained in Pyrex cells. The composition of the irradiated samples was determined by gas chromatography, while the total yield was measured by UV spectroscopy.

The TEA CO₂ laser used in this study (Lumonics 103K) was grating tuned to the P(40), 10.812 μ m line. This wavelength, which lies on the shoulder of the ν_{18} fundamental of DCCB, ²⁴ was selected as a compromise between the increase in absorptivity and the decrease in laser fluence with increasing wavelength. The laser was pulsed at a rate < 0.2 Hz, with a typical fluence of 1.0 J/cm^2 . Higher fluences were usually obtained by focusing the 3.8×1.6 cm² rectangular beam with an AR coated, 5.1 cm diam, 77 cm focal length, Ge lens. The fluence entering the cell was adjusted by varying the distance between the lens and cell. The volume irradiated by the laser was determined by measuring burn patterns on heat sensitive paper placed at the position of the center of the cell. The actual fluence delivered to the cell was determined by measuring the average energy reaching a calibrated disk calorimeter (Scientech 362) through a 0.457 cm diam aperture placed at various points along the optical path. Based on these measurements we determined that the fluence along the length of a 2.5 cm long cell varied by no more than $\pm 5\%$ of the fluence at the center of the cell.

The irradiation cells were constructed from 2.54 cm

o.d. Pyrex tubes cut to 2.04 cm lengths and connected to ballast bulbs having volumes ranging from 0.1 to 2.4 1. NaCl windows were attached to the tubes with soft (Techkits E-7) epoxy. The ballast volume was needed to keep the total conversion of DCCB below 5% after multiple laser pulses. To promote efficient mixing of the gas in the irradiation and ballast volumes, the connecting Pyrex channels were kept as short (< 0.6 cm) and as wide (1.7 cm i.d.) as feasible. For gc measurements at low DCCB pressures, the ballast volume was at least 1.5 l, and in addition a condensation side arm was attached to the ballast bulb in order to increase the amount of injected material. For the UV absorption measurements, a 10 cm Pyrex tube fitted with S-1 quartz windows was attached to the ballast bulb.

The chemical composition of the gas after irradiation was determined with a Varian 2700 gas chromatograph equipped with a flame ionization detector. The reactant and product isomers were separated on a 3 m long, 0.22 cm i.d. stainless steel column filled with 5% $\beta\beta'$ oxyproprionitrile on firebrick. The gas flow rates were 317, 10, and 17.1 cm³ min⁻¹ for N_2 , air, and H₂, respectively. For most of the measurements the column temperature was maintained at 70 °C. In some cases, however, 50 °C was used to reduce the background noise and to increase the separation between the CT and TT peaks. Peak assignments on the chromatogram were established by running pure samples of each compound separately. These samples were themselves identified by NMR, IR, and (in the case of DCCB) FTIR spectroscopy.

The total reaction yield was determined by measuring the absorption at 232.5 nm using a Cary 14 spectrophotometer. A calibration run showed that CT has an absorption peak at this wavelength, with an extinction coefficient of $2.8 \times 10^4 1 \text{ mol}^{-1} \text{ cm}^{-1}$, in good agreement with the literature value.^{25,26}

The reaction vessels were routinely evacuated to pressures below 10⁻³ Torr, using a 2 in. oil diffusion pump. Prior to each run the vessel was filled with the reactant gas, evacuated, and then refilled. Gas pressures were measured with either a 10 Torr Datametrics capacitance manometer or a 760 Torr Wallace and Tiernan mechanical pressure gauge.

The various compounds used in this study were synthesized by standard methods. DCCB was prepared by the method of Pettit and Henery²⁷ and purified by preparative gc. The CT isomer was prepared by heating DCCB in a sealed tube at 175 °C for 4 h. The CC and TT isomers were prepared by heating a sample of CT to 100 °C in the presence of a trace of I_2 , according to the method of Bartlett and Wallbillich.²⁸ The three isomers were then separated chromatographically.

III. RESULTS

The principal result of this study is that under suitable experimental conditions a substantial fraction of "forbidden" isomers can be formed by infrared multiphoton excitation. Except at very low and very high pressures



FIG. 1. Branching ratios Γ (open circles) and r (filled circles) as functions of the number of laser pulses. Data are for 0.25 Torr of neat DCCB irradiated with 8.2 J/cm² at 10.812 μ m.

of neat DCCB (P_{DCCB}) , the only products observed chromatographically were the three isomers (CC, TT, and CT) of dichlorobutadiene. Conventional IR spectroscopy did not reveal any HCl product. An upper limit for HCl elimination is 2% of the total products formed at $P_{\text{DCCB}} = 0.25$ Torr and a laser fluence ϕ of 8.2 J/cm². When P_{DCCB} was low enough that the mean free path in the gas was comparable to the cell radius, some low molecular weight products were also formed. Thus at $P_{\text{DCCB}} = 0.020$ Torr and $\phi = 8.2$ J/cm², approximately 1% of the products were dissociation fragments. When a Teflon insert (0.95 cm i.d.) was placed in the cell, this fraction increased to 8%, while the relative amounts of CC, TT, and CT isomers were unchanged. Fragmentation was also observed at high DCCB pressures. For example, at $P_{\text{DCCB}} = 0.60$ Torr and $\phi = 8.2$ J/cm², the fraction of decomposition products was 12.5%.

Before measuring systematically the product isomer distribution, a number of experiments were carried out to test for possible artifacts. In particular, two tests were performed to determine the extent of heterogeneous effects which have been observed in other studies.^{29,30} First, we found that reducing the Pyrex cell diameter from 2.5 to 1.25 cm had no effect on the product yield or composition. Second, changing the laser wavelength to 10.285 μ m, where DCCB does not absorb, completely suppressed the reaction. These tests, performed with $P_{DCCB} = 0.25$ Torr and $\phi = 8.2$ J/cm², demonstrate that wall and window reactions were negligible.

Another possibility we examined is that the forbidden isomers are the products of secondary reaction of cold CT produced by earlier laser pulses. To test this hypothesis, we measured the branching ratios,³¹

$$\Gamma = \{ [CC] + [TT] \} / \{ [CC] + [TT] + [CT] \}, \qquad (1)$$

and

$$r = [CC]/[TT]$$
,

as functions of the number of laser pulses N. As shown

in Fig. 1, both quantities increase monotonically with N. The positive intercepts confirm that CC and TT are indeed primary products. There is, however, a gradual conversion of CT to CC and TT. In a separate experiment we found that irradiation of pure CT at the same wavelength and fluence resulted in slow conversion to CC. In practice N was kept small enough to minimize the extent of secondary isomerization. The yields and branching ratios reported in this paper were always extrapolated back to N=1.

Following these preliminary studies we measured the dependence of the fractional yield Y, and the branching ratios Γ , and r, on ϕ , P_{DCCB} , and buffer gas pressure P_{M} . Throughout this paper Y is defined as the fractional conversion of DCCB per laser pulse within the irradiated volume of gas.

The fluence dependence of Y at $P_{\text{DCCB}} = 0.25$ Torr of neat gas is shown in Fig. 2. There is an apparent threshold for ring opening at $\phi = 3.0 \text{ J/cm}^2$, although very small concentrations of products were observed at fluences as low as 1.0 J/cm^2 (see Figs. 5 and 6). The fluence dependence of Γ is shown in Fig. 3. No forbidden products were seen for $\phi < 3.5 \text{ J/cm}^2$, while at higher fluences Γ increased linearly with ϕ . The open circle in Fig. 3 is the highest fluence measurement of Danen *et al.*²⁰ The fluence dependence of r is shown in Fig. 4. The rapid falloff of r at low ϕ indicates a threshold for TT formation at approximately 4 J/cm².

The neat pressure dependence of Y at fluences of 1.0, 1.7, and 8.2 J/cm² is shown in Figs. 5-7. At 1.0 and 8.2 J/cm², Y varied as P_{DCCB}^2 , while at $\phi = 1.7$ J/cm² Y varied approximately as $P_{DCCB}^{3.3}$. At $\phi = 8.2$ J/cm² and $P_{DCCB} > 0.4$ Torr, yields greater than unity were observed, indicating that molecules outside of the irradiated volume were also isomerized. Indeed, at P_{DCCB} = 1.5 Torr and $\phi = 8.2$ J/cm² (not shown in the figure), 75% of the molecules in the entire cell were isomerized by a single laser pulse.

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(2)



FIG. 2. Total product yield per laser pulse as a function of laser fluence. Data are for 0.25 Torr of neat DCCB. The filled circles indicate yields $\ll 1\%$.



FIG. 3. Branching ratio (fraction of forbidden products) as a function of laser fluence. Data are for 0.25 Torr of neat DCCB. The open point is the highest fluence measurement of Danen *et al.* (Ref. 20).



FIG. 4. Ratio of *cis*, *cis* to *trans*, *trans* isomers as a function of laser fluence. Data are for 0.25 Torr of neat DCCB.



FIG. 5. Total product yield vs neat DCCB pressure for a fluence of 1.0 J/cm^2 . Open and filled symbols were measured with a different DCCB sample. The line indicates a quadratic pressure dependence.

The neat pressure dependence of Γ at 8.2 J/cm² is shown in Fig. 8. Γ was found to decline from a value of 28% at 0.020 Torr to a minimum value of 18%, and then gradually to increase at higher pressures. The very weak dependence of Γ on P_{DCCB} is remarkable, considering that the total number of molecules converted per pulse varied by five orders of magnitude. Over this pressure range r was constant, within ex-



FIG. 6. Total product yield vs neat DCCB pressure for a fluence of 1.7 J/cm^2 .

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FIG. 7. Total product yield vs DCCB pressure for a fluence of 8.2 J/cm^2 . The line indicates a quadratic pressure dependence.

perimental error.

In another series of experiments the effects of different buffer gases on the yield and branching ratios were studied. In these measurements P_{DCCB} was fixed at 0.25 Torr and ϕ was set at 8.2 J/cm². The variation of Y with P_{M} is shown in Fig. 9 for M = He, Ar, N₂, and O_2 . In each case Y decreased monotonically with P_{yy} with the relative "quenching" efficiencies in the order $He < Ar < N_2 < O_2$. The branching ratios were not measurably affected by He for pressures up to 25 Torr. The effects of Ar, N₂, and O₂ on Γ and r are shown in Fig. 10. In each case Γ decreased and r increased monotonically with P_{M} . The large effect of O_2 on r suggests that in this case chemical as well as physical quenching may be important. We note that the overall effect of increasing P_{M} is qualitatively similar to that of decreasing ϕ .



FIG. 8. Branching ratio (fraction of forbidden products) vs neat DCCB pressure at a fluence of 8.2 J/cm^2 . Open circles indicate a product yield greater than unity.



FIG. 9. Total reaction yield vs pressure of buffer gas for 0.25 Torr of DCCB and a fluence of 8.2 J/cm^2 .



FIG. 10 Branching ratios Γ (open circles, ordinate on left) and r (solid circles, ordinate on right) vs buffer gas pressure for a DCCB pressure of 0.25 Torr and a fluence of 8.2 J/cm².

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In addition to the experiments reported here, two further studies relevant to DCCB isomerization have been carried out and will be published separately. In the first study³² the average number of photons \overline{n} absorbed by DCCB was measured using optical absorption and optoacoustic techniques. The main findings of this study are that \bar{n} is independent of $P_{\rm DCCB}$ for the pressures used in the present study, and that \overline{n} increases approximately linearly with ϕ , reaching a value of 27 ± 4 at 8.2 J/cm.² In the second study, ³³ the thermal rate constant for the isomerization of DCCB was measured over the temperature range 400-475 K. The high pressure rate constant was found to be $k_{\infty} = 1.1 \times 10^{14}$ exp(-36.0/RT). In addition, a measurement of the equilibrium distributions of isomers at 298 K revealed that CC is more stable than CT by 0.9 kcal/mol, while CT is more stable than TT by 0.7 kcal/mol.

IV. DISCUSSION

A. Thermochemical considerations

A number of reaction mechanisms could contribute to the multiphoton isomerization of DCCB. These include (i) conrotatory reaction on the ground (singlet) electronic surface; (ii) disrotatory reaction on the first electronically excited (triplet) surface; (iii) nonconcerted rupturing of the 1, 2 carbon-carbon single bond; and (iv) a serial mechanism in which concerted ringopening is followed by rotation about a vibrationally hot double bond. In order to evaluate these mechanisms it is necessary to estimate the energetics associated with each of them. In doing so we will use the isomerization of cyclobutene (CB) as a reference reaction from which related quantities in the DCCB system may be estimated. In the discussion which follows the reader will find it helpful to refer to Fig. 11, in which the energetics of the CB and DCCB reactions are plotted schematically.

Consider first the enthalpy of isomerization. For CB, ΔH° was found calorimetrically to be -11.5 kcal/mol.³⁴ ΔH° should be more negative for DCCB because the Cl atoms stabilize butadiene relative to cyclobutene. Benson's bond additivity rules³⁵ predict that ΔH° for DCCB is reduced by 9 kcal/mol. A simple comparison of ΔH_f for C₂H₆, C₂H₅Cl, C₂H₄, and C₂H₃Cl, however, predicts a net stabilization of only 2 kcal/mol for each Cl atom.³⁶ In our analysis we assumed that ΔH° for DCCB is reduced by a total of 4 kcal/mol, resulting in $\Delta H^{\circ} = -15.5$ kcal/mol.

Next, consider the activation energy E_a along each of the proposed reaction paths. (i) For the concerted reaction on the ground electronic surface $E_a = 32.9$ kcal/mol for CB, ³⁷ while for DCCB $E_a = 36$ kcal/mol.³³ The larger activation energy for DCCB may be attributed to steric hindrance in the concerted rotation of Cl and H atoms into the molecular plane, which offsets the stabilizing effect which the Cl atoms may have on the transition state. (ii) The activation energy for the photochemically allowed disrotatory reaction is at least as large as the separation between the ground state and the first electronically excited state. For CB this separation is 85 kcal/mol, ³⁸ and for DCCB it should be



FIG. 11. Thermochemical estimate of the energetics of various possible reaction mechanisms. Solid curves are for the isomerization of unsubstituted cyclobutene (CB), while the dashed segments refer to DCCB. Zero energy corresponds to *cis,trans* butadiene and *cis,trans* dichlorobutadiene. Barrier (a) is for the concerted, conrotatory ring opening [mechanism (i)]; barrier (b) is for a nonconcerted formation of a diradial intermediate [mechanism (iii)]; barrier (c) is for rotation about a hot double in the CT isomer [mechanism (iv)]. Note that for the unhalogenated molecules TT is more stable than CC, while for the chlorinated species the reverse is true. This is indicated to the right of barrier (c), but is omitted for clarity on the left side of the figure. Also, for clarity, the potential wells corresponding to the diradical intermediates are not shown.

comparable.

(iii) The third reaction path involves nonconcerted rupturing of the carbon-carbon single bond to produce a diradical intermediate. Working backwards from butadiene we find that E_a is the sum of three terms: the energy for rupturing and rotating about the double bond, the allylic stabilization energy of the intermediate, and the repulsion energy for ring-closure.³⁹ For butadiene these three quantities are 65.0, ⁴⁰ - 10.2 to - 12.6, ⁴¹ and ~5, ³⁵ kcal/mol, respectively. Assuming - 10 kcal/mol for allylic stabilization, we obtain $E_a = 60$ kcal/mol for ring closing and 48.5 kcal/mol for ring opening of CB. The difference, ΔE_a , between the diradical and concerted activation energies for the ring opening of CB is therefore 16 kcal/mol.⁴²

To calculate the corresponding energies for DCCB isomerization it is necessary to take into account both stabilizing and destabilizing effects that the Cl atoms have on the diradical intermediate. A comparison of E_a for the isomerization of trans-1, 2-dideuteroethylene and trans-1, 2-dichloroethylene shows that the two Cl atoms stabilize the transition state by a total of 10.7 kcal/mol.⁴¹ If the Cl atom and the allylic effects are additive, the diradical would be extensively stabilized by resonance delocalization of the unpaired electrons, with the two free spins tending to reside on the terminal Cl atoms. However, in the transition state leading to the diradical intermediate, the planar array of atoms

required for this extensive delocalization is not yet achieved. Hence the total stabilization is likely to be less than 21 kcal/mol, though it should be greater than the 10 kcal/mol contributed by the allylic stabilization alone. In addition to these stabilizing effects, for a nonplanar transition state there is the added effect of Cl-Cl steric repulsion. From the torsional barriers of chlorinated ethanes we estimate this destabilization energy to be ~5 kcal/mol.⁴³ Taking all these contributions into account, we estimate that $E_e = 54$ to 65 kcal/ mol for ring-closure, 38.5 to 49.5 kcal/mol for ring opening, and $\Delta E_e = 2.5$ to 13.5 kcal/mol.

(iv) The fourth proposed mechanism is a concerted ring opening to form CT, followed by rotation about a vibrationally hot double bond to produce the other isomers. The barrier for this process is the same as in mechanism (iii), except that the 5 kcal/mol repulsion energy for ring-closure is absent. Since experimentally we observe only the concerted product at low fluence, it is unlikely that $\Delta E_a < 0$, indicating that the stabilization of the intermediate is considerably less than the upper value of 21 kcal/mol. In Fig. 11 we arbitrarily assumed a diradical stabilization energy of 15 kcal/mol, yielding $\Delta E_a = 8.5$ kcal/mol for mechanism (iii) and 3.5 kcal/mol for mechanism (iv).

B. Reaction mechanism

We consider next which of the proposed mechanisms are consisted with our observations. The concerted production of CC and TT on the ground electronic surface [mechanism (i) is forbidden by the Woodward-Hoffman rules. Ross and co-workers⁴ pointed out, however, that strong vibrational motion introduces into the Hamiltonian non-Born-Oppenheimer terms which could relax the symmetry requirements. Although it is difficult to estimate the contribution of this mechanism, our observation that [CC] > [TT] (r > 1 in Figs. 4 and 10) suggests that the reaction is largely nonconcerted. Of the three product isomers, CC is thermodynamically the most stable because rotation about the carbon-carbon single bond allows two hydrogen bonding interactions.²⁸ Since in a nonconcerted reaction steric effects should not be a dominant factor, we would expect the product distribution to approach thermodynamic equilibrium, thus favoring CC. In a concerted mechanism, however, production of the TT isomer is kinetically favored because initial formation of the cisoid conformer necessary for producing CC is sterically hindered.

Mechanism (ii) requires absorption of 40 to 50 photons on the ground electronic surface, followed by inverse electronic relaxation to the first electronically excited state of DCCB. Although it is possible that a sufficiently large population of the irradiated molecules do absorb this number of photons, such highly excited molecules would have enough energy, while still in the ground electronic state, to undergo fragmentation and elimination reactions at all DCCB pressures. This was not observed experimentally.

The remaining pathways involve a diradical intermediate. Mechanism (iii) is a "parallel" process,



in which the allowed and forbidden products are formed independently. The alternative [pathway (iv)] is a "serial" process

$$DCCB \xrightarrow{c} CT^{\dagger} \xrightarrow{d'} CC, TT$$

in which CT[†] is formed vibrationally hot and goes on (perhaps by absorbing additional photons) to produce CC and TT. Such a mechanism has been shown to occur in the laser-induced isomerization of the hexadiene isomers.¹⁸ It might also be important in the laser-induced isomerization of DCCB because the activation energy for reaction d' is ~5 kcal/mol lower than for step d. However, there are a number of indications that under our experimental conditions the parallel mechanism dominates. In the serial mechanism, vibrational relaxation should compete very effectively with secondary reaction (step d') since only a few collisions would be needed to deactivate CT below the barrier for rotation about the double bond. Thus one would expect for this mechanism that Γ^{-1} would increase linearly with pressure. In fact we observed that Γ is insensitive to P_{DCCB} (see Fig. 8) and P_{He} . The branching ratio does decline with the addition of other buffer gases (Fig. 10); however, Stern-Volmer plots display marked curvature in Γ^{-1} vs P_M . In addition, experiments with more conventional excitation sources indicate that the parallel mechanism dominates. In the photochemically induced isomerization of 1, 3-cis-dimethylcyclobutene, Srinivasan³⁹ demonstrated that TT is guenched before secondary isomerization can occur. A similar effect in the thermally induced isomerization of this molecule was implied by Brauman and Archie.⁴³

The pressure dependence of the total yield is a direct indication of the importance of collisions in the reaction mechanism. But unlike the behavior observed for dissociative reactions, ⁴⁵⁻⁵⁴ the pressure effect reported here persists down to very low values of P_{DCCB} . Two possible effects of collisions, both of which could increase the yield by increasing the amount of energy absorbed, are pressure broadening of the absorption line and rotational hole filling.^{2,48} The optoacoustic measurements, however, revealed that \overline{n} is independent of P_{DCCB} and P_{M} . Also, Fig. 9 shows that Y decreases monotonically with P_M , whereas these collisional processes should cause Y initially to increase with P_{μ} . Another possible collisional effect is energy pooling of two partially activated molecules. 53-55 Such a mechanism could explain the threshold behavior at low fluence (Figs. 5 and 6). At higher fluences, however, where \overline{n} exceeds the activation energy for concerted reaction (36 kcal/mol, or 14 $h\nu$), a substantial fraction of the molecules should react without the need for energy pooling. Moreover, if pooling were significant, fragmentation would be expected to occur to a much greater extent than actually observed.

In the mechanism which we propose, collisions are important only after termination of the laser pulse,

which serves primarily to initiate the reaction. A fraction of the DCCB molecules absorb 14 or more infrared photons in the ground electronic state. Molecules formed with energy above the barrier for diradical formation are free to shuttle back and forth above the different wells. These excited species must be collisionally deactivated before they can drop down into one of the isomeric states. As pointed out in the Introduction, the requirement of collisions to stabilize the newly formed molecules is a unique feature of isomerization reactions.²² If the collision partner itself is activated, it may acquire sufficient energy to isomerize. Thus an energy chain will result, which can be terminated either by diffusion out of the irradiation zone, or by collision with cold buffer gas molecules. Indeed, at high P_{DCCB} most of the reaction will occur after the end of the laser pulse. Moreover, if the isomerization reaction is exothermic and the substrate pressure is high enough, the energy chain will be thermally unstable and an explosion may result.^{14,56-58} This phenomenon could explain the very large yields and the fragmentation products observed at high pressures of DCCB.

The quadratic pressure dependence of the yield at high fluence could be explained by a kinetic model in which most of the reaction occurs during the thermal pulse initiated by the laser. One factor of P_{DCCB} is due to the pressure dependence of the unimolecular rate constant in the falloff region, while the second factor comes from the linear pressure dependence of the time constant for thermal relaxation of the laser-heated gas. In this model, the effect of the buffer gas is to increase the heat capacity, and hence decrease the temperature of the reacting gas. It is difficult to explain, however, the very low yields at low DCCB pressure. One would expect Y to level off at low P_{DCCB} to some constant value characteristic of the "active" DCCB population excited by the laser. Work on this problem is continuing in this laboratory.

C. Concluding remarks

We have found experimentally that both Woodward-Hoffmann allowed and forbidden products can be formed by homogeneous, gas phase irradiation of DCCB with a pulsed infrared laser. It is argued that the symmetry allowed product is formed in a concerted conrotatory ring-opening on the ground electronic surface, while the forbidden isomers are produced by rupture of a carbon-carbon single bond to form a diradical intermediate. The final identity of the product is determined only after deactivating collisions quench the vibrationally excited nascent molecule.

To explain our results we have proposed a kinetic model in which it is assumed that the reaction occurs thermally after termination of the laser pulse. This model can be used to explain a number of our observations, including the threshold for forbidden product formation, the magnitude of the branching ratio, and the effects of DCCB pressure and buffer gas pressure on the reaction yield and branching ratio. A quantitative application of this model will be presented in a forthcoming paper.²³

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