

IR MULTIPHOTON-INDUCED RETRO DIELS-ALDER DISSOCIATION OF DECAFLUOROCYCLOHEXENE BY A PULSED CO₂ LASER

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Summary

The retro Diels-Alder dissociation of decafluorocyclohexene into tetrafluoroethylene and hexafluorobutadiene was experimentally investigated. The nascent hexafluorobutadiene formed after dissociation isomerizes to thermodynamically stable hexafluorocyclobutene. The wavelength-dependent and energy-dependent dissociations were studied. Experiments over a range of pressure showed that collisions have a detrimental effect on the rate of dissociation. Under collisionless conditions, the threshold fluence for the decomposition of decafluorocyclohexene at the R(20) line of the 10.6 μm CO₂ laser line was found to be 0.92 J cm⁻².

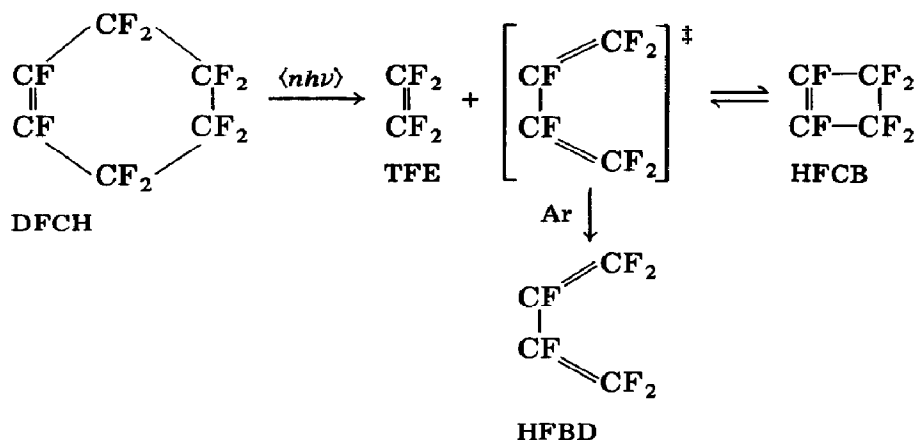
1. Introduction

A retro Diels-Alder (RDA) reaction is a typical example of the generalized pericyclic reaction of Woodward and Hoffmann [1], which passes through a minimum activation energy barrier when it proceeds in a concerted fashion in the ground electronic state. The activation energy required for the unimolecular decomposition may be supplied exclusively as vibrational excitation by means of IR laser irradiation and thereby the role of vibrational activation in RDA reactions may be assessed. Garcia and Keehn [2] have recently reported the IR laser-induced RDA decomposition of a few organic molecules including cyclohexene. In this paper, we report a novel RDA decomposition of decafluorocyclohexene (DFCH).

Thermal decomposition of DFCH, investigated in the temperature range 480 - 550 °C by Dvornikova *et al.* [3], gave among other products perfluorinated 1-methylcyclopentene, 1,2-dimethylcyclopentene and mesitylene, whereas photodecomposition at 1849 Å, studied by Camaggi and Gozzo [4], led to the formation of perfluorinated 1-methylcyclopentene, methylene cyclopentane and other perfluorinated liquids.

In contrast, however, we report a new channel in the IR laser-induced photodecomposition of DFCH into tetrafluoroethylene (TFE) and hexafluorobutadiene (HFBD). This decomposition is followed by isomerization

of the vibrationally energized HFBD to the thermodynamically more stable hexafluorocyclobutene (HFCB). Addition of argon as a buffer gas arrested the isomerization reaction and facilitated the identification of the initial RDA product HFBD. The observed reactions are as follows:



2. Experimental details

A grating-tuned multimode Lumonics 103 transversely excited atmospheric pressure CO_2 laser was used, a typical pulse consisting of a 100 ns spike followed by a 2 μs tail. About two-thirds of the pulse energy was contained in the spike, as measured by a photon drag detector (Rofin model 7415). A spectrum analyser supplied by Optical Engineering Company was used for identifying the tuned laser frequency. A factory-calibrated Lumonics 20 D pyroelectric detector was used for energy measurements. The energy of the incident beam was attenuated by introducing polyethylene films of various thicknesses.

Stainless steel cells of volume about 45.5 ml provided with KCl windows at each end were used to contain the material during irradiation. The laser beam was focused inside the cell by a KCl lens with a focal length of 13 cm. In some experiments a BaF_2 lens with a focal length of 50 cm was used where a nearly uniform fluence was maintained within the 5 cm path length of the cell.

The DFCH, supplied by PCR Research Chemicals Inc. (Gainesville, FL), was used after outgassing using four freeze-pump-thaw cycles. The progress of the dissociation was monitored after the laser irradiation, with a Perkin-Elmer model 577 IR grating spectrophotometer, by recording the decrease in the 1006 cm^{-1} absorption peak ($\epsilon = 3.578 \times 10^{-2} \text{ cm}^{-1} \text{ Torr}^{-1}$) of DFCH.

A home-made gas chromatograph equipped with a flame ionization detector and with a 10% dodecylphthalate column 5.5 ft long coupled in series to a 20% diethyl glycol succinate column 5.5 ft long was used for the

product analysis. Nitrogen was used as the carrier gas. Comparisons and identifications of the products were made with standard samples and with reported data [5].

3. Results

3.1. Neat decafluorocyclohexene

The decomposition of DFCH was studied at various laser frequencies which lie within the range of the absorption spectrum of the compound shown in Fig. 1, curve a. The laser beam was focused inside the stainless steel cell containing DFCH at a pressure of about 1 - 2 Torr and the sample was repetitively irradiated. The decrease in the optical absorption of DFCH was monitored periodically after every 100 laser pulses. Perfluorinated ethylene and cyclobutene were found as products, as determined by gas chromatographic analysis of the contents of the cell after irradiation. The same products were obtained irrespective of the laser line used for irradiation. Nearly complete conversion of the DFCH into TFE and HFCB was observed after about 1200 laser pulses, using the R(20) line (976 cm^{-1}) which is red shifted by 2 cm^{-1} from the absorption maximum of DFCH at 978 cm^{-1} . The energy per pulse was maintained at 100 mJ.

The IR absorption spectrum of the irradiated sample, in the range $800 - 1050\text{ cm}^{-1}$, is shown in Fig. 1, curve b. The absorption peaks at 980 and 985 cm^{-1} together with the peak at 1418 cm^{-1} (not shown in the figure) identify the HFCB product. The TFE absorption peaks at 1186 , 1332 and 1342 cm^{-1} were also detected after irradiation but are not shown in Fig. 1, curve b. Perfluorobutadiene has IR absorption peaks at 972 , 1330 and 1766 cm^{-1} . The irradiated samples show very little absorption at 1766 cm^{-1} , indicating that less than 5% butadiene was present in the products. However, when the irradiation was carried out in the presence of added argon, all the absorption peaks typical of butadiene grow at the expense of those typical of cyclobutene.

An exponential decrease in the optical density D of DFCH was observed as a function of the number n of laser pulses given to the sample, *i.e.*

$$D = D_0 \exp(-\alpha n) \quad (1)$$

where D_0 and D are the initial and the final optical densities of DFCH after n pulses. The exponent α denotes the fraction of the molecules decomposed per pulse. Such an exponential decay of the irradiated reactant, shown in the present case in Fig. 2, is commonly observed in the IR laser-induced decomposition of polyatomic molecules in cases where the fraction α decomposed per pulse is small and the fraction remaining undecomposed, *i.e.* $1 - \alpha$, can be approximated as $\exp(-\alpha)$ [6].

From such exponential plots, α has been evaluated and plotted in Fig. 1, curve c, as a function of the laser frequency used for irradiation in

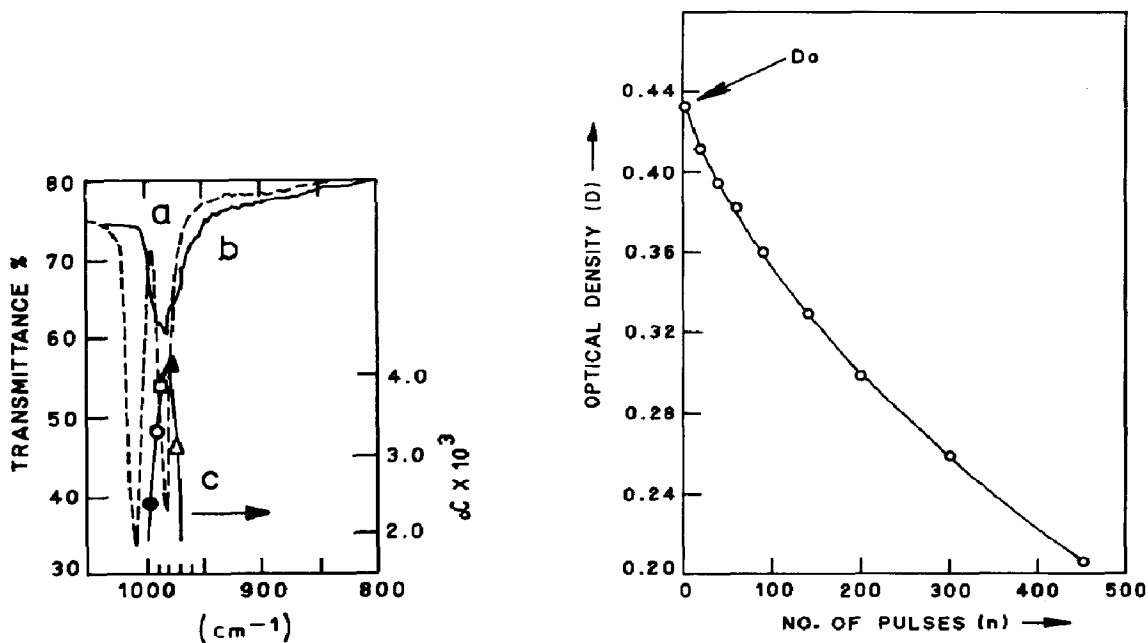


Fig. 1. Plots of transmittance of DFCH vs. wavenumber in the range 900 - 1050 cm^{-1} (curve a, ---) and after dissociation of DFCH (curve b, —) and the values of α at various CO_2 laser lines used for irradiation (curve c) (energy per pulse, 86.5 mJ): \bullet , R(38); \circ , R(32); \square , R(26); \blacktriangle , R(20); \triangle , R(10).

Fig. 2. A typical plot of optical density D vs. number n of pulses monitored at an IR absorption peak at 1006 cm^{-1} (energy per pulse, 86.5 mJ at the R(20) line of the $10.6 \mu\text{m}$ CO_2 laser).

which the energy per pulse was attenuated to the same value of 86.5 mJ by introducing polyethylene films of a suitable thickness before the entrance window of the sample cell. The maximum α and hence the maximum decomposition per pulse were found to occur at 976 cm^{-1} .

After Keefer and Allen [6] the threshold fluence for DFCH decomposition was obtained from the equation

$$\phi_{\text{th}} = \left(\frac{8}{9} \pi^{-1/2} \right)^{2/3} E \left(\frac{f}{\alpha V} \right)^{2/3} \quad (2)$$

where V is the irradiation cell volume, f is the f number of the lens, α is the fraction decomposed per pulse and E is the energy of the laser pulse. The threshold fluence and intensity were found to be 0.92 J cm^{-2} and 4.6 MW cm^{-2} respectively for the R(20) line (*i.e.* 976 cm^{-1}).

The dependence of α on the DFCH pressure was evaluated and the results shown in Fig. 3 indicate that α decreases as the DFCH pressure is increased. Figure 4 shows the dependence of α on the laser pulse energy E . For the focused geometry used in our experiments, α was found to be proportional to $E^{3/2}$ in agreement with eqn. (2).

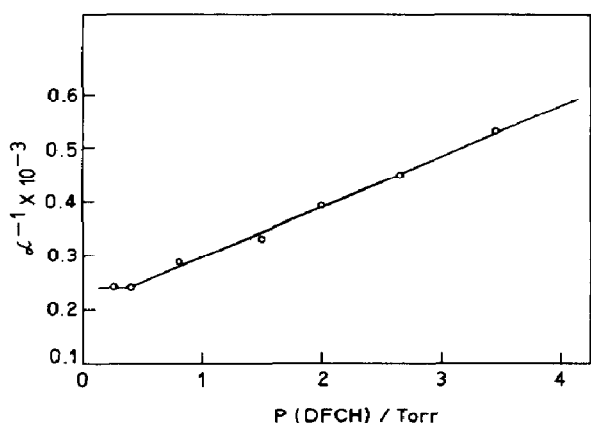


Fig. 3. Plot of α^{-1} vs. pressure of DFCH using the R(20) laser line for irradiation (energy per pulse, 86.5 mJ).

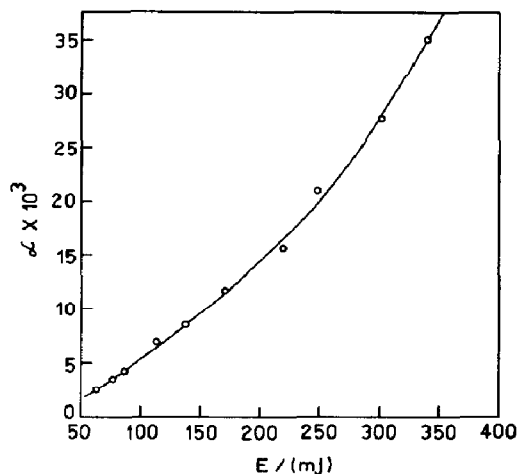


Fig. 4. Plot of α vs. incident laser R(20) energy (irradiation using DFCH at 0.4 Torr).

3.2. Decafluorocyclohexene-argon mixtures

A significant change in the reaction was observed when DFCH at a pressure of 1 - 2 Torr was diluted with argon and irradiated. In addition to TFE, HFBD was obtained and no HFCB could be observed. The fraction α dissociated per pulse decreased as shown in Fig. 5.

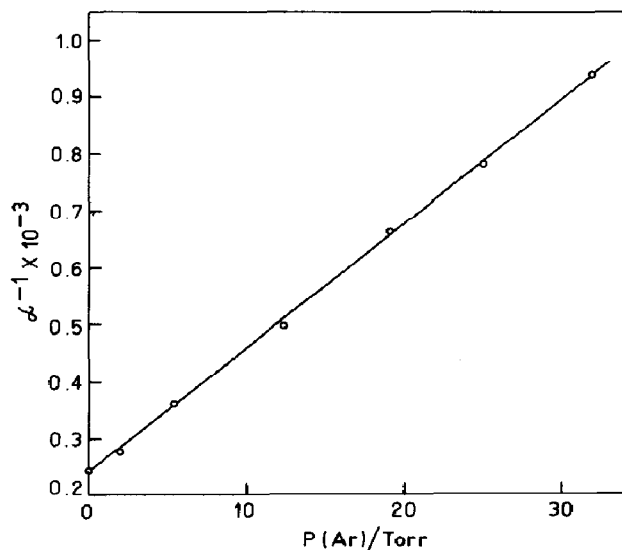
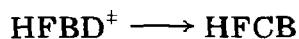


Fig. 5. Plot of α^{-1} vs. pressure of argon added with DFCH at 0.4 Torr (irradiation using R(20) laser line containing an energy per pulse of 86.5 mJ).

4. Discussion

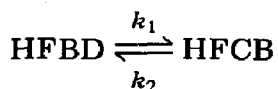
TFE and HFBD are expected as products in the RDA reaction of DFCH. However, in our experiments in which decomposition of DFCH is induced by IR laser light, the isomeric HFCB was obtained instead of HFBD. The initial RDA products could be obtained only in the presence of an appreciable pressure of an added buffer gas (argon). Apparently the product HFBD has sufficient internal energy, at the time of its formation, to undergo isomerization to HFCB, unless it is deactivated by collisions with a buffer gas. In this sense, two consecutive Woodward–Hoffmann-type pericyclic reactions occur on pulsed laser irradiation of DFCH:



The isomerization reaction takes place after the laser-induced primary reaction.

The activation energy for the first reaction, *i.e.* the RDA decomposition of DFCH, is not known. The hydrogen analogue, C_6H_{10} , has an overall activation energy of about 66 kcal mol^{-1} . In view of the fact that C–C bonds are only involved in the RDA reaction, the activation energy for DFCH decomposition is expected to be close to that for cyclohexene. Further, the multiphoton excitation of the molecule by the IR laser must impart an appreciably larger amount of energy to the molecule than is required to traverse the energy barrier for dissociation to induce rapid unimolecular decomposition before vibrational–translational and/or rotational relaxation occurs. At a DFCH pressure of 1 Torr a meaningful collisionless decomposition rate constant k would be about 10^8 s^{-1} . As can be seen from Fig. 3, the fraction α decomposed per pulse decreased to about one-half when the DFCH pressure increases from 0.5 to 4 Torr.

The excess multiphoton excitation energy, over and above that required for the decomposition of DFCH, will be available as internal energy of the product molecules, *i.e.* TFE and HFBD, and can be utilized for driving the isomerization reaction



From the thermal work of Schlag and Peatman [7], the rate constants k_1 and k_2 for the forward and reverse reactions are known to be $10^{12.03} \exp(-35\,380/RT) \text{ s}^{-1}$ and $10^{14} \exp(-47\,080/RT) \text{ s}^{-1}$ respectively.

An insight into the internal energy associated with the HFBD product, in the present work, can be obtained from the following considerations. The criteria which determine such a decomposition level are on the one hand the up-pumping rate of excitation and on the other hand the internal energy-dependent rate of decomposition. At any particular laser intensity, the optical excitation rate constant decreases, as higher excitation levels are reached, because of a decrease in the absorption cross section, while the

unimolecular decomposition rate constant rapidly increases with increases in the internal energy of the molecules. The probability of further multiphoton excitation beyond a certain excitation level decreases sharply since the lifetime of the molecule with respect to decomposition would be too short. In other words a limiting multiphoton excitation level (or narrowly spaced levels) would be reached where the molecule decomposes before it can absorb the next laser photon [8]. The addition of inert gas limits the number of molecules reaching such an excitation level during the laser pulse and consequently decreases the net decomposition per pulse.

Nevertheless, the primary product energy distribution remains unaffected, at the time of formation, by the presence or absence of an inert gas. This occurs because the reactant molecule which decomposes is energized to the same multiphoton excitation level. In view of this we consider that the initial internal energy available with the primary products TFE and HFBD is independent of inert gas addition. Subsequent collisions of HFBD with argon would de-energize the HFBD molecule and prevent its isomerization to HFBC, however. An estimate of the initial energy content of HFBD can be obtained by assuming that the isomerization and the collisional deactivation are competitive processes. The experimental observation that HFBD is completely trapped at a pressure of argon of 100 Torr suggests that the ratio $k_i/100k_q$ of rate constants for isomerization and quenching is very much less than unity. At an argon pressure of 1 Torr, about 10^7 collisions s^{-1} would occur for every molecule of HFBD. Although vibrational-translational and/or rotational relaxation, by collisions with the monatomic inert gas, may require 100 - 1000 collisions, the vibrational energy of the HFBD molecule may be decreased below its threshold energy for isomerization with fewer collisions only.

From the above consideration and the experimental result that the cyclic isomers account for less than 5% of the product (in the presence of argon at 100 Torr) it appears that $k_i \approx 5 \times 10^6 s^{-1}$, if ten collisions are required for deactivation.

The initial internal energy E associated with the excited HFBD can be evaluated using Kassel's expression [9] for the energy-dependent unimolecular rate constant, *i.e.*

$$k(E) = A \left(\frac{E - E_0}{E} \right)^{s-1} \\ = 5 \times 10^6 s^{-1} \quad (3)$$

where $E_0 = 35\,800 \text{ cal mol}^{-1}$ is the activation energy for the isomerization to the cyclic form. Assuming that all the 24 vibrational modes of HFBD contribute equally to the randomization of the internal energy, the number s of oscillators is taken as 24 and E is calculated to be $85.5 \text{ kcal mol}^{-1}$. This would be the upper limit for the vibrational energy associated with the HFBD product from the RDA decomposition of multiphoton-excited DFCH. It is generally observed that all the vibrational modes are not equally

TABLE 1

Results of unfocused IR laser photolysis of decafluorocyclohexene

Experiment	Sample	Laser line used (10.6 μm)	Energy per pulse (J)	Number of pulses	Conversion (%)	Products
1	DFCH at 1.08 Torr	R(20)	1.45	230	99	TFE and HFCB
2	Products of experiment 1 and Ar at 26 Torr	P(6)	0.95	600	99 ^a	TFE and HFBD
3	DFCH at 1.38 Torr and Ar at 100 Torr	R(20)	1.45	400	65	TFE and HFBD

^aWith respect to HFCB.

coupled. If the effective number of oscillators is about half of the total number of oscillators, *i.e.* the effective number of oscillators is 12, the energy associated with HFBD would be 52.6 kcal mol⁻¹ which may be considered as the lower limit.

To test whether HFCB could be reisolomerized to HFBD, an experiment was carried out in which neat DFCH was decomposed and after complete conversion argon at a pressure of 26 Torr was added to the irradiated sample and irradiation was continued. Table 1 shows the observed results. It is seen that argon addition drives the HFCB \rightarrow HFBD reaction to near completion, confirming the results from other laboratories [10].

No enhancement in the DFCH decomposition rate was observed as a result of an increase in the DFCH or argon pressure in the pressure range studied. This rules out vibrational energy pooling and rotational hole filling as bottle-necks for laser-induced decomposition.

5. Conclusions

In summary, we have carried out a sequential cycloreversion and electrocyclization reaction induced by multiphoton absorption of IR laser radiation by DFCH. The threshold fluence for the decomposition was found to be 0.92 J cm⁻². We have studied the dependence of the rate of dissociation on the energy flux and on the DFCH and argon pressures. An increase in the pressure of either DFCH or argon quenches the reaction. Under focused conditions, the dissociation rate was found to be proportional to $E^{3/2}$. The rate of dissociation was found to have a maximum at the R(20) laser line of the 10.6 μm CO₂ laser which is red shifted by 2 cm⁻¹ from the absorption peak of DFCH.

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References

- 1 R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, 1970.
- 2 D. Garcia and P. M. Keehn, *J. Am. Chem. Soc.*, **100** (1978) 6111.
- 3 K. V. Dvornikova, V. E. Platonov, V. P. Urasimova and G. G. Yakobson, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, **10** (1971) 2361.
- 4 G. Camaggi and F. Gozzo, *J. Chem. Soc., Chem. Commun.*, (5) (1967) 236.
- 5 J. H. Simons, *Fluorine Chemistry*, Vol. II, Academic Press, New York, 1954.
J. R. Nielsen, H. H. Classen and D. C. Smith, *J. Chem. Phys.*, **18** (1950) 812.
J. R. Nielsen, M. J. El-Sabban and M. Albert, *J. Chem. Phys.*, **23** (1955) 324.
J. C. Albright and J. R. Nielsen, *J. Chem. Phys.*, **26** (1957) 370.
- 6 D. R. Keefer and J. E. Allen, Jr., *Chem. Phys. Lett.*, **43** (1976) 394.
- 7 E. W. Schlag and W. B. Peatman, *J. Am. Chem. Soc.*, **86** (1964) 1676.
- 8 E. R. Grant, M. J. Coggiola, Y. T. Lee, P. A. Schulz, A. S. Sudbo and Y. R. Shen, *Chem. Phys. Lett.*, **52** (1977) 595.
- 9 L. S. Kassel, *J. Phys. Chem.*, **32** (1928) 225.
- 10 A. Yogev and R. M. J. Benmair, *Chem. Phys. Lett.*, **46** (1977) 290.
A. Ben-Shaul and Y. Haas, *J. Chem. Phys.*, **73** (1980) 5107.