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Photodecomposition of 1,2-difluoro-1,2-di-iodoethene: formation of 1,2-difluoroethyne

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Abstract

Photolysis of *trans*-1,2-difluoro-1,2-di-iodoethene with 248 nm radiation from an excimer laser yielded difluoroethyne, *cis*-1,2-difluoro-1,2-di-iodoethene and 1,2,3,4-tetrafluoro-3,4-di-iodocyclobutene. Potential pathways for these products are presented in terms of the energetics of the reaction, and the dependencies of product formation on pressure and extent of conversion are discussed.

Introduction

Difluoroethyne (DFE) has only recently been produced in sufficient quantities to obtain measurements of its physical properties. The products of the thermolysis of difluoromaleic anhydride were trapped in an Ar matrix, and an infrared absorption band at 1341 cm^{-1} was attributed to C_2F_2 [1]. A band at 1149 cm^{-1} had been attributed to DFE in earlier work [2], but this band was most likely due to trifluoromethane; HCF_3 has a band at 1152 cm^{-1} which is very much more intense than any other transition in that compound [3]. Thermolysis of perfluoro-1,2,3-triazine was used to produce DFE with higher yields, and infrared spectra of DFE in both the gas phase and in a matrix were obtained [4, 5]. High-resolution IR spectra of gas-phase DFE produced from the triazine [5, 6] and from difluoromaleic anhydride [7] have confirmed the assignment of a band at 1349 cm^{-1} as ν_3 of DFE.

In this work, we have produced DFE by photolysis of *trans*-1,2-difluoro-1,2-di-iodoethene (*t*-DFDIE) with 248 nm radiation produced by a KrF excimer laser. The products were DFE, *cis*-1,2-difluoro-1,2-di-iodoethene (*c*-DFDIE) and 1,2,3,4-tetrafluoro-3,4-di-iodocyclobutene (CYCB).

Results and discussion

Identification of photolysis products

Infrared spectra of gas-phase *t*-DFDIE and *c*-DFDIE are shown in Fig. 1 since they have not been reported previously. The two intense bands of the *trans* isomer are at 1182 and 685 cm^{-1} (1165 and 679 cm^{-1} in the liquid phase), and the four most intense bands of the *cis* isomer are at 1631, 1129, 1105 and 863 cm^{-1}. Note that each spectrum shows no detectable amounts of the other isomer. As expected, these spectra are very similar to those of the *cis* and *trans* isomers of $C_2Cl_2F_2$ [8]. The feature at 745 cm^{-1} and several other weaker bands are due to triethylsilylfluoride which was produced during the synthesis of both isomers.

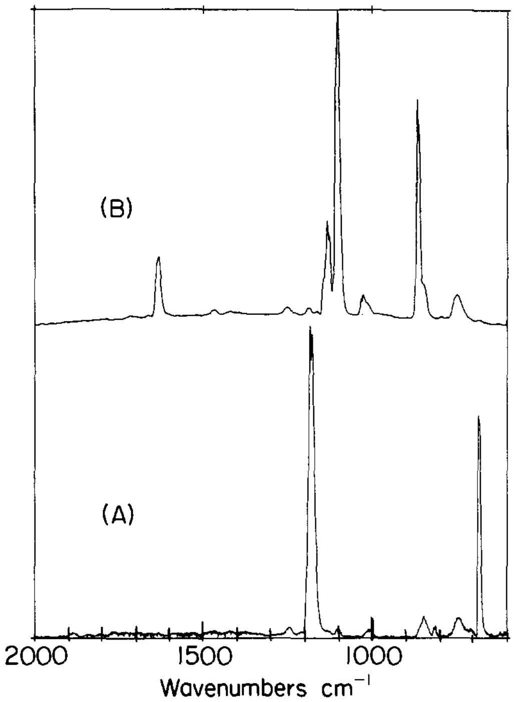

Fig. 1. Infrared absorbance spectra of (A) *trans*- and (B) *cis*-1,2-difluoro-1,2-di-iodoethene.

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The results of a typical experiments are shown in Fig. 2. In this example, the initial pressure of *t*-DFDIE was 0.7 Torr, and trace A in Fig. 2 is the infrared difference spectrum of the sample after exposure to 10 pulses (106 mJ pulse^{-1}) of the KrF laser, i.e. the spectrum after photolysis minus the spectrum before photolysis. The negative features at 1182 and 685 cm^{-1} correspond to a 0.1 Torr decrease of the *t*-DFDIE pressure, and the positive feature at 1345 cm^{-1} is due to DFE. Trace B in Fig. 2 shows a difference spectrum after exposure of the sample to 15 additional laser pulses; this is the spectrum after 15 additional pulses minus that obtained after the initial 10 pulses, so the difference spectrum shows the incremental changes in the spectrum rather than the total changes after 25 pulses. Traces C and D in Fig. 2 show similar difference spectra after 25 and 50 additional pulses, respectively. In each case, the gas cell was removed from the evacuated sample chamber of the IR instrument for photolysis, so the water vapor lines in the spectra are due to slight variations in the instrument background.

The wavenumbers of the band centers for all new features in the infrared spectrum are listed in Table 1 along with our assignments for the species responsible for each absorption. The band at 1345 cm^{-1} was also obtained at 0.03 cm^{-1} resolution as described below, and the rotational fine structure lines are the same as those obtained previously at higher resolution [5–7].

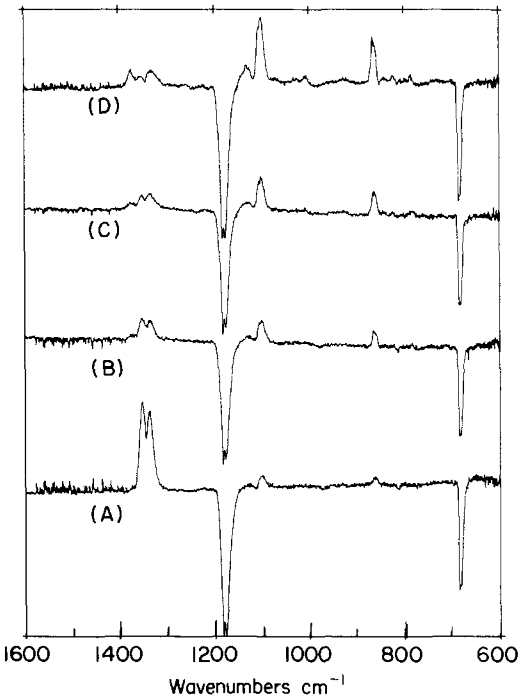

Fig. 2. IR difference absorbance spectra: (A) 10 pulses of the KrF laser at 106 mJ pulse^{-1}; (B) 15 additional pulses; (C) 25 additional pulses; and (D) 50 additional pulses.

TABLE 1. IR spectra of products of photolysis

Products[a]	TFA[b]	*c*-DFDIE	CYCB[c]
1779			1780
1631		1631	
1375			1365
1345	1349		
1323			
1129		1129	
1105		1105	
1070			1060
1029		1029	
1008			995
863		863	
842			845
822			820
785			785
705			700

[a] Band centers in cm^{-1} for gas-phase products at 1 cm^{-1} resolution.
[b] Band center for difluoroethyne determined by analysis of 0.004 cm^{-1} resolution spectra [5–7]; 1345 cm^{-1} is the location of the minimum between the P and R branch envelopes for a 1 cm^{-1} resolution spectrum.
[c] Spectrum of liquid 1,2,3,4-tetrafluoro-3,4-di-iodocyclobutene [9] with estimated uncertainties of ±0.05 μm, i.e. ±15 cm^{-1} at 1780 cm^{-1} and ±3 cm^{-1} at 700 cm^{-1}.

The bands assigned to the *cis* isomer were identical to those of the pure *cis* sample shown in Fig. 1.

The bands assigned to CYCB were clearly associated with a single species because their relative intensities were the same in all experiments. The reference spectrum of CYCB* listed in Table 1 was for the neat liquid, and the agreement with our gas-phase spectrum is very good with the possible exception of the gas-phase bands at 1375 and 1323 cm^{-1}. The spectrum of the liquid had only one clearly resolved band in this region. The C=C stretch of perfluorocyclobutene in the gas phase is at 1799 cm^{-1} [9].

Product yields

Some examples of the relative yields of products after photolysis are shown in Table 2. An experimental value for the integrated intensity of the DFE band has not been determined, but theoretical calculations predict values ranging from 310 [10] to 380 [5] km mol^{-1} (a relative DFE intensity of 1.0 in Table 2 corresponds to about 0.1 Torr if the integrated intensity is 370 km mol^{-1}). Based on this value for the intensity of DFE, the yield of DFE ranged from 15 to 38% of the *t*-DFDIE consumed. Note that the production of DFE with the first few laser pulses was greater than that which occurred after some DFE was already present. The formation of *c*-DFDIE and CYCB increased after

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*We are indebted to Professor W.T. Miller for the IR spectrum of liquid 1,2,3,4-tetrafluoro-3,4-di-iodocyclobutene.

TABLE 2. Relative yields of photolysis products

No.	Relative pressures[c]					No. of pulses	mJ per pulse
	P_t[a]	ΔP_t[b]	DFE	*c*-DFDIE	CYCB		
1	0.5	−0.20	0.75	0.03	0.00	100	20
2	0.6	−0.26	1.13	0.26	0.21	200	20
3	0.5	−0.19	0.98	0.24	0.16	250	20
4	0.5	−0.26	1.40	0.31	0.18	100	130
5	1.0	−0.58	1.00	1.00	1.00	250	100
6	0.5	−0.41	1.04	0.60	1.27	1000	100
7	0.6	−0.19	1.43	0.22	0.06	50	100
8	0.8	−0.17	1.10	0.12	0.13	26	106
		−0.09	0.17	0.11	0.07	+24	
		−0.08	0.01	0.27	0.26	+60	
		−0.48	−0.07	0.17	0.27	+100	
9	0.7	−0.10	0.70	0.00	0.00	10	
		−0.07	0.14	0.10	0.06	+15	
		−0.08	0.14	0.09	0.13	+25	
		−0.36	0.07	0.17	0.14	+50	

[a] Initial pressure of *t*-DFDIE in Torr.

[b] Incremental change in *t*-DFDIE pressure after exposure to the number of pulses cited under No. of pulses. If a sample which had previously been photolyzed was exposed to an additional *N* pulses, the number of pulses is denoted as +*N*.

[c] The relative incremental changes in DFE, *c*-DFDIE and CYCB should be read vertically, not horizontally. Thus, the amount of each of these species present in example No. 5 was taken as the reference for that species, i.e. the actual pressures of the three species in No. 5 are not necessarily equal to each other.

some DFE had already been formed. The yield of DFE decreased while the yields of *c*-DFDIE and CYCB increased with an increase in initial pressure of *t*-DFDIE. These observations can be quantified by assuming that a quantity proportional to the normalized yield (the relative yield divided by the amount of *t*-DFDIE consumed) is a linear function of the *t*-DFDIE pressure and the irradiated energy (i.e. the number of pulses times the energy per pulse). For DFE, the normalized yield decreased by 3.3 per Torr *t*-DFDIE and 0.03 per mJ of photon energy, while *c*-DFDIE and CYCB showed increases of 1.0 and 1.3 per Torr *t*-DFDIE and 0.008 and 0.03 per mJ of photon energy. These results are complicated by the fact that DFE decays fairly rapidly in the dark as discussed below. In addition, it is possible that each of the iodine-containing products could be photolyzed by the 248 nm radiation, even though each of their concentrations increased so long as *t*-DFDIE was consumed by photolysis.

Decay of DFE

The decay of DFE with time was monitored by periodically recording infrared spectra with the cell in the instrument. No new strong bands appeared in the IR spectrum as DFE decayed, and the intensity of all bands decreased with time as illustrated in Fig. 3. The decay of DFE did not follow first-order kinetics; second-order plots gave better fits, but the slopes showed considerable variation. With an initial pressure of about 0.1 Torr, typical half-lives were about 30 min when the sample was in a glass cell and about 10 min in an aluminum cell. For example, in entry No. 9 in Table 2, 85 min after the last photolysis the pressure of *t*-DFDIE, *c*-DFDIE, CYCB and DFE had decreased by 17%, 30%, 27% and 78%, respectively.

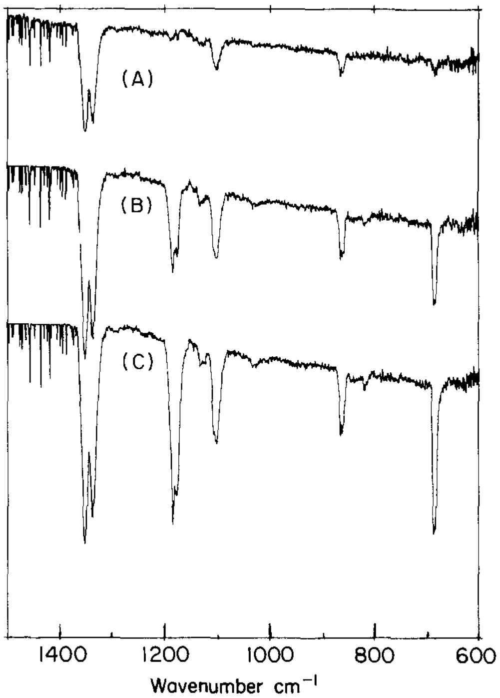

Fig. 3. Change of IR spectrum with time following the last entry for No. 9 in Table 2. (A) 18 min, (B) 52 min and (C) 87 min. Absorbance scale for each plot is −0.025 to +0.005 absorbance units.

The decomposition of DFE at higher pressures than those used in our work was found to lead to the formation of C_3F_4 isomers [4], and CF_2 was found to be present in a matrix-isolated sample of DFE [5]. If CF_2 were produced in a primary step, then its addition to DFE would yield 1,2,3,3-tetrafluorocyclopropene (TFC), and the latter would be formed with sufficient energy to isomerize to tetrafluoroallene and tetrafluoropropyne, as observed for the multiple photon excitation of TFC [11]. However, at lower pressures of DFE, McNaughton and Elmes [7] found no evidence for the formation of C_3F_4 isomers in the decomposition of DFE. We obtained infrared spectra of C_3F_4 isomers and of C_2F_4 at known pressures in previous work [11, 12], so the pressures of these species could be determined by spectral subtractions. In most cases, the C_3F_4 isomers were not detectable, but for a case in which over 80% of the initial *t*-DFDIE had been consumed (No. 6 in Table 2), trace amounts (<0.02 Torr) of

TFC and C_2F_4 were found. Because the species present at the highest pressure in most of our experiments was *t*-DFDIE, we would have expected a cyclopropane, $C_3F_4I_2$, to form in the presence of CF_2; however, we found no evidence for its presence in any of our spectra. A unimolecular fluorine migration to form difluorovinylidene is predicted to be endothermic by about 25 kcal mol^{-1} [10] with an activation energy of about 60 kcal mol^{-1} [13, 14]. Presumably, the unimolecular formation of CF_2+C would be even less favorable.

High-resolution spectra

Spectra of samples containing DFE at about 0.1 Torr were also obtained at 0.03 cm^{-1} resolution. The spectrum of ν_3 exhibits the 3:1 intensity variations expected for a molecule which obeys Fermi–Dirac statistics, but is complicated by overlapping hot bands; about 50% of the molecules are in excited vibrational states at room temperature. An initial fit to the spectrum for the ν_3 fundamental was obtained using a quartic equation [15] in m using the parameters reported by Burger *et al.* [5]; here $m=-J$ for $\Delta J=-1$ and $m=J+1$ for $\Delta J=+1$. The calculated values agree with the observed values in the range of $m=-40$ to $m=40$, but the R branch lines show a large divergence above $m=40$. Using the method of combinations and differences [15], the values for the rotational parameters shown in Table 3 were obtained. The ground state parameters were obtained using 30 PR pairs and the excited state parameters using 32 pairs of lines, all with $|m|<40$; the uncertainties were estimated using 500 random selections of the PR pairs. Although our values are not as accurate as those obtained previously at higher resolution [5–7], they do provide confirmation of the assignment of the band at 1345 cm^{-1} (band center at 1349.5 cm^{-1}) as due to DFE.

Mechanism of photolysis

The dependence of the yields of DFE, *c*-DFDIE and CYCB on the pressure of *t*-DFDIE and the extent of reaction (i.e. No. of photons used for the irradiation) indicate that DFE is a primary product while both *c*-DFDIE and CYCB result from secondary reactions. Although the photochemistry of *t*-DFDIE has not been reported, Lee and coworkers [16] have studied the dynamics for the photodissociation of C_2F_5I (PFIE) at 248 nm. Analogous to the PFIE system, the absorbed photon provides 115 kcal mol^{-1} to *t*-DFDIE via an n–σ^* transition; the UV absorption curves for DFDIE and PFIE are similar above 200 nm. The C–I bond dissociation energy is estimated to be on the order of 53 kcal mol^{-1}, so that the excess energy (approximately 62 kcal mol$^{)1}$) after dissociation is distributed between the internal modes of the *t*-C_2F_2I radical, electronic excitation of I atoms (21.7 kcal mol^{-1}) and relative translation. Lee *et al.* [16] observed that I* is the predominant channel and approximately 21 kcal mol^{-1} is partitioned into relative translational energy; this leaves approximately 20 kcal mol^{-1} of internal energy in the C_2F_5 radical. Analogously, the *t*-C_2F_2I radical would have approximately 20 kcal mol^{-1}; this energy should be sufficient to break the C—I bond (the formation of the δ bond decreases this bond energy to approximately 15 kcal mol^{-1}). This second unimolecular decomposition would not have sufficient energy to form I* at 248 nm. Collision of the vibrationally excited *t*-C_2F_2I radical formed in the initial decomposition with other molecules would reduce its energy so that reaction forming DFE would be diminished; this accounts for the observed decrease of the DFE yield with increasing pressure. The energetics also dictate that DFE would be vibrationally cold, so that it would not have the 60 kcal mol^{-1} necessary to isomerize to difluorovinylidene.

TABLE 3. Effective rotational parameters (cm^{-1})^a

State	B	$D\times10^8$	Ref.
(00000)	0.11856857(11)	1.1504(7)	5
	0.11856970(59)	1.1908(115)	7
	0.11865(6)	3.4(2.4)	this work
(00100)	0.1182284(8)	−3.64(5)	5
	0.11829(5)	−3.6(2.3)	this work

^{a}Effective band center taken to be at 1349.524 cm^{-1}.

There are several potential pathways that could account for the production of *c*-DFDIE and CYCB. The addition of the C_2F_2I radical to *t*-DFDIE to form the $C_4F_4I_3$ radical, which could react unimolecularly to form *c*-DFDIE or CYCB, is unlikely since the quantities of the latter products are negligible during the initial decomposition. This result also indicates that most of the C_2F_2I radicals decompose to form DFE, i.e. that its lifetime is less than 100 μs. Another possible route to CYCB would be the dimerization of DFE to form perfluorocyclobutadiene, followed by the homogeneous or heterogeneous (on the walls of the reactor) addition of I_2. In a similar manner, the formation of *c*-DFDIE could occur via the homogeneous or heterogeneous addition of I_2 to DFE. Finally, cyclobutene formation as a result of both thermal and photolytic cycloaddition of alkenes to alkynes has long been known [17]. If the reaction between *t*-DFDIE and DFE proceeds stepwise through a diradical, it could decompose to form *c*-DFDIE or cyclize to form CYCB; at high pressure this radical would be stabilized and produce CYCB.

Experimental

c- and *t*-DFDIE were prepared by the cleavage of *c*- and *t*-IFC=CFSiEt$_3$ with KF and I_2 in DMSO. Details of these preparations will be reported elsewhere.

The output of a Tachisto 400 XR excimer laser operating at 1 Hz was directed onto the gas cells described below. To maintain laser output energy the gas mixture (krypton, fluorine and helium) was circulated through an Applied Photonics cryogenic purifier. The pulse energy was measured with a Gentec joulemeter (ED-500).

Infrared spectra were obtained with a Bruker 113V FT-IR instrument with a Ge/KBr beamsplitter and a liquid-nitrogen-cooled MCT detector. All gas cells had NaCl or KCl windows; Al-body cells with 2.5- and 5.1-cm path lengths, a glass cell with a 15-cm path length and a 11.8-cm path length tee with CaF_2 windows were used. Initial sample pressures were measured by means of an MKS Baratron 10-Torr capacitance manometer. Subsequent relative pressures were determined by classical least-squares, principle component regression, or by the instrument interactive graphics routines.

Acknowledgements

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References

1 J.C. Brahms and W.P. Dailey, *J. Am. Chem. Soc., 111* (1989) 8940.
2 J. Heicklen and V. Knight, *J. Phys. Chem., 69* (1965) 2484.
3 A. Ruoff, H. Burger and S. Biedermann, *Spectrochim. Acta, 27A* (1971) 1359.
4 H. Burger and S. Sommer, *J. Chem. Soc., Chem. Commun.,* (1991) 456.
5 H. Burger, W. Schneider, S. Sommer, W. Thiel and H. Willner, *J. Chem. Phys., 95* (1991) 5660.
6 H. Burger and S. Sommer, *J. Mol. Spectrosc., 151* (1992) 148.
7 D. McNaughton and P. Elmes, *Spectrochim. Acta, 48A* (1992) 605.
8 N.C. Craig and D.A. Evans, *J. Am. Chem. Soc., 87* (1965) 4223.
9 J.R. Nielsen, M.Z. El-Sabban and M. Alpert, *J. Chem. Phys., 23* (1955) 324.
10 M.M. Gallo and H.F. Schaefer III, *J. Chem. Phys., 93* (1990) 865.
11 H.B. Friedrich, D.J. Burton and D.C. Tardy, *J. Phys. Chem., 91* (1987) 6334.
12 H.B. Friedrich, D.J. Burton and P.A. Schemmer, *Spectrochim. Acta, 45A* (1989) 181.
13 M.J. Frisch, R. Krishnan, J.A. Pople and P.R. Schleyer, *Chem. Phys. Lett., 81* (1981) 421.
14 J.D. Goddard, *Chem. Phys. Lett., 83* (1981) 312.
15 H.C. Allen, Jr. and P.C. Cross, *Molecular Vib-Rotors,* John Wiley, New York, 1963.
16 D. Krajnovich, L.J. Butler and Y.-T. Lee, *J. Chem. Phys., 81* (1984) 3031.
17 R. Fuks and H.G. Viehe, in H.G. Viehe (ed.), *Chemistry of Acetylenes*, Marcel Dekker, New York, 1969.