Vibrational Excitation of the Reaction between Vinyl Bromide and Fluorine in Solid Argon

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A number of unsuccessful attempts to induce bimolecular addition reactions with selective vibrational excitation in cryogenic solids are reported here: 1,3-butadiene with Cl_2 , ClF, Br_2 , I_2 , and XeF_2 ; vinyl chloride with F_2 . One system, vinyl bromide with fluorine in solid argon, did respond by showing reaction product growth upon laser excitation at 3116, 3098, 1849, 1808, and 1605 cm⁻¹. Identification of reaction products suggests F_2 addition across the double bond followed significantly by HF elimination but apparently without HBr elimination. Relative quantum yields display a monotonic dependence upon photon energy that is even more dramatic than that found earlier for the ethylene–fluorine reaction. Thus excitation of the C–H stretching modes either at 3116 or 3098 cm⁻¹ is 10^2 times more effective than excitation at 1849 or 1848 cm⁻¹ and 10^3 times more effective than at 1605 cm⁻¹.

Introduction

Infrared-induced bimolecular reactions in cryogenic matrices present some intriguing possibilities but, to date, there have been only a few clear-cut successful examples. Frei et al.¹ summarize earlier work (hereafter, ref 1 will be called I) and they describe studies of five additional systems, only two of which display infrared-induced reaction. Continued investigation of the C_2H_4/F_2 system² has revealed mode specificity, which enhances interest in extending this type of study to other systems (hereafter, ref 2 will be called II). Consequently, we have examined several additional reactions suggested by the C_2H_4/F_2 example. We present these studies here, with special emphasis on $F_2 + C_2H_3Br$, the most responsive reactants of the group.

Experimental Section

The experimental apparatus and techniques have been described in I. Dual-jet depositions were used to minimize gas-phase prereaction; the CsI substrate was held at 12 K during deposition, irradiation, and spectroscopic study. Reactants were premixed with argon at mole ratios in the range 400:1 to 5:1 and 1-2 mmol of sample was deposited at a rate of 1-2 mmol/h.

The closed-cycle refrigerator, CO and CO_2 lasers, and Nicolet 7199 FT IR apparatus were used exactly as in I. In addition, an F center continuously tunable laser (Burleigh, Model FCl 10) was used for excitation in the spectral range 3000–3200 cm⁻¹, exactly as in II.

Mixtures were prepared in a glass vacuum line except for F_2/Ar and ClF/Ar which were mixed and deposited by using a previously passivated stainless steel vacuum line equipped with a 2.4-L stainless steel reservoir, 30-in. Ashcroft pressure gauge, and Whitey stainless steel valves.³ These last two mixtures passed through a stainless steel coil immersed in liquid N₂ just before deposition. Iodine was sublimed before use. All other chemicals were used without purification: 1,3-butadiene (Matheson 99.86%), vinyl chloride (Matheson, 99.5%), vinyl bromide (Matheson, 99.5%), F₂ (Matheson, 98%), ClF³, Cl₂ (Matheson, 99.9%), Br₂ (Mallinckrodt, A.R.), 1,1-, *cis*-1,2-, and *trans*-1,2-difluoroethylenes, and Ar (Matheson, 99.998%).

Results

1,3-Butadiene Experiments. 1,3-Butadiene mixed with argon (Ar:C₄H₆ = 50) was codeposited with an Ar:F₂ = 50

TABLE I:	Attempts to Induce Halogenation of	
1,3-Butadie	he in Argon at 12 K (C_4H_6 :R:Ar = 1:5:100))

excita- tion freq, cm ⁻¹	power (mW/cm²), time (min)	R	excitation freq, cm ⁻¹	power (mW/ cm ²), time (min)	R
globar	50, 180-960	all	1827.2 1825.6	587, 60	XeF ₂ XeF ₂
3113	7.5, 30	Cl,	1823.5	1133, 90	XeF,
3111	7.5, 20	Cl_2	1819.7	422 190	ClF
3109	7.5, 20	Cl_2	1817.6	435, 160	ClF
3107 3105.3	7.5, 40 7.5, 30	Cl_2 Cl_3	1815.9	1067, 60	Cl_2, ClF
3101	7.5, 60	Cl,	1633.5	287, 120	Ι,
3099	7.5, 60	Cl_2	1591.4	393, 90	
3097.1	7.5, 60	Cl_2	1587.9	313, 150	$\operatorname{Br}_2, \operatorname{I}_2$
1834	800, 70	I ₂	1091.0	310, 15	XeF ₂

mixture in equimolar amounts at 12 K. Immediately after deposition and without irradiation (except for 10 min by the globar source during spectral study), the spectrum included many absorptions not present in the spectrum of butadiene. We believe that these absorptions signal prereaction during deposition but cannot rule out positively the unlikely possibility that only 10 min of globar exposure is sufficient to deplete all reactive pairs.

Similar 1,3-butadiene experiments were carried out with $Ar:C_4H_6 = 50$ mixtures codeposited with equimolar amounts of Ar:R = 5 mixtures with $R = Cl_2$, CIF, Br_2 , I_2 , and XeF_2 . Under none of the irradiation conditions described in Table I were any new features detected. Each reactant matrix was exposed to the globar irradiation for at least 10 min during spectroscopy and, as well, to sustained laser irradiation at one or more butadiene absorption frequencies, as shown in Table I. In none of these experiments was there detectable product growth.

Vinyl Chloride-Fluorine Experiments. In a dual-jet deposition experiment with final concentration ratio $C_2H_3Cl:F_2:Ar = 1:2:150$, irradiation was conducted for 60 min with each of the two CO laser lines 1808.5 and 1812.4 cm⁻¹ (respectively, with power 1200 and 1000 mW/cm²). These lines coincide with vinyl chloride absorption due to binary combinations. Definitive growth of product bands could not be confirmed.

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⁽²⁾ H. Frei and G. C. Pimentel, J. Chem. Phys., in press.

⁽³⁾ We thank Dr. G. Richmond for preparing the ClF sample.

TABLE II: Absorptions of Vinyl Bromide in Argon at 12 K ($C_2H_3Br:Ar = 1:100$ or $C_2H_3Br:F_2:Ar = 1:20:140$)

	freq, ci					
C.H.Br	(C.H.Br).	$(C_2H_3Br(F_2)_n^a)$				
(isolated)	(dimer, polymer)	before $h\nu$	by difference	assignment		
 585.5 ms	583.4 sh	585.0 ms				
		588.6 sh	589.2	CH ₂ twist, a''		
605.9 s	607.9 ms	605.9 s	605.5	CBr stretch, a'		
898.7 s	899.0 sh	900.3 s	903.5	CH, wag, a''		
948.0 s	939,9 sh	940.3 sh	942.6 sh	2 0,		
		945.9s	948.1	CH, wag, a''		
1003.6		1003.1	1003.8	CH, rock, a''		
1259.2 s	1256.7 sh	1250.1 s		2 ,		
		1254.3 sh	1258.0	CH, rock, a'		
1370.0 s		1370.2 s	1370.9	CH, deformation, a'		
1483.7 m		1484.4 m		twist + wag, a'		
1599.5 vs		1598.8 vs	1597.8	CC stretch, a'		
1602.5 s		1602.3 s	1607.8 sh	,		
1799.4 ms	1801.7					
1800.6 sh						
			1833.6			
1838.6 sh		1843.1 sh		twist + CH, rock, a'		
1843.6		1844.2		wag + wag, a'		
			1861.6	5 57		
1888.2 vw		1883.3 vw		2 imes a'' wag, a'		
1896.7 vw				C /		
			1938.5			
			1979.1			
2007.7 vw		2006.9 vvw		$2 \times CH_2$ rock, a'		
2518.5 vvw		2517.0 vw		$2 \times CH$ rock, a'		
2593.6 vvw		2592.7 vvw		CH, rock + CC stretch, a'		
2626.1 vvw		2626.5 vvw		CH rock + CH_{2} deformation, a'		
2732.7 vvw		2739.4 vvw		$2 \times CH_{2}$ deformation, a		
2952.3 vvw		2952.3 vvw		CH, deformation + CC stretch, a'		
3023.0 w	3085.0	3023.6 w		CH stretch, a'		
3102.0 w		3100.5		CH stretch, a'		
3119.7 w		3118.7		CH stretch, a'		
3711.1				CBr + CH stretch, a'		
3725.2				CBr + CH stretch, a'		
				,		

^a In a $C_2H_3Br:F_2:Ar = 1:20:140$ mixture, if a C_2H_3Br has 12 nearest neighbors, a random distribution would give $C_2H_3Br:(F_2)_n$ complexes with probabilities: isolated, $n = 0, 0.19; n = 1, 0.32; n = 2, 0.25; n \ge 3, 0.24$.

Vinyl Bromide-Fluorine Experiments. Vinyl bromide was suspended in argon at two matrix ratios, $C_2H_3Br:Ar$ = 1:50 and 1:250. These spectra permitted the identification of absorption frequencies of isolated C_2H_3Br and, for a few bands, C_2H_3Br in dimeric or higher aggregates, as listed in the first two columns of Table II. Probable assignments are listed in the last column.

A series of experiments with varying amounts of fluorine gave some information about where C_2H_3Br absorbs in the presence of one or more F_2 neighbors. The concentrations studied were $C_2H_3Br:F_2:Ar = 1:1.5:60, 1:6:90$, and 1:20:140. Only in the case of the third, most concentrated sample were new features detected that could be attributed to C_2H_3Br with F_2 nearest neighbors (one or more). These features are listed in the third column of Table II.

There was, however, information about the absorptions of reactive sites provided in the difference spectra in those laser experiments in which reaction products were observed. These are frequencies at which the difference spectra show loss of absorbance which can be attributed to consumption of reactive pairs. They were all obtained with $C_2H_3Br:F_2:Ar = 1:20:140$ and are listed in the fourth column of Table II. This technique enables the detection of quite weak features, some too weak to be identified with confidence except in the expanded scale, difference spectra (e.g., 1833.6, 1861.6, 1938.5, and 1979.1 cm⁻¹). At this high fluorine concentration, less than one-fifth of the C_2H_3Br molecules will be isolated (assuming 12 randomly selected nearest neighbors). About one-third will have a single F_2 neighbor, a quarter will have two F2 neighbors, and the remaining one-fifth will have three or more.

Initial irradiation experiments were conducted with the spectrometer globar for exposure times exceeding 1 h. When $C_2H_3Br:F_2:Ar = 1:1.5:140$ and 1:6:140, no reaction could be discerned whereas at 1:20:140, weak product absorptions were observed in the region 1000–1200 and 1620–1650 cm⁻¹. Hence all of the subsequent irradiation experiments were conducted with the 1:20:140 mixture.

Table III displays the laser irradiation experiments that were performed.

For all excitation frequencies except 942.4 cm⁻¹, distinct product absorbances appeared. Reaction may have been excited by 942.4 cm⁻¹ also, but not in sufficient amount to measure in the presence of the growth during spectroscopy. Figure 1 shows six spectra in the frequency range 500-1700 cm⁻¹. The bottom spectrum (f), was recorded immediately after deposition and before laser irradiation. Spectra a-e are difference spectra showing the absorbance after laser irradiation minus the absorbance before irradiation. Upward excursions reveal product growth and downward excursions show loss of reactive pair absorption due to reaction. Irradiation times are given in the caption. The irradiation frequencies for (a), (b), (c), (d), and (e) were, respectively, 3116, 3097.8, 1849.0, 1808.2/1809.2, and 1605 cm⁻¹. Table IV lists, in the first column and footnote b, all of the product absorptions detected.

The highly expanded optical density scales in Figure 1 show that only a small fraction (perhaps 1 or 2%) of the vinyl bromide molecules react, even though statistical distribution would guarantee that over 80% of the CH₂-CHBr molecules have at least one F_2 nearest neighbor. This is in contrast to the results in II, in which perhaps

TABLE III: Laser Irradiation Experiments Conducted ($C_2H_3Br:F_2:Ar = 1:20:140, T = 12$ K)

ν , cr	1			Dower		
laser	C_2H_3Br in 1:20:140 mixture	irradn time, h	power, mW	absorbed, mW	quanta absorbed/ (s cm²)	
942.4	945.87	1	410	107	3.9×10^{18}	
1605.2	1597.79/1607.77	1	450	138	$3.07 imes10^{18}$	
1808.2/1809.2	1801.71	1	1600	20	$0.40 imes10^{18}$	
1849.0	1844.21	1	1060	14	$0.27 imes10^{18}$	
3097.8	3100.45	0.5	1	0.044	$2.5 imes10^{15}$	
3110, 3112, 3116, 3117.04,	3118 3118.67	0.3 each	2 each	0.044	$2.5 imes10^{15}$	

10% of the ethene molecules react and almost all of those with an F_2 nearest neighbor react. Because of the relatively high F_2 concentration in the present work (~50% of the CH₂CHBr molecules have two or more F_2 neighbors) we do not attribute this small yield to a small reservoir of reactive pairs (for example, those with a particular cage orientation). More likely this small yield reflects quite low absolute quantum yields, so our experiments do not come close to exhausting the reservoir.

These spectra become meaningful when expressed in terms of quantum yields. Absolute quantum yields were not measured, but the experiments conducted provide some information about relative quantum yields. The product absorbance growth ΔA divided by the time of irradiation approximates the slope of the growth curve. If this time is converted to moles of laser photons absorbed, $N^{\rm L}$, the quotient $\Delta A/N^{\rm L}$ is determined by (but is not equal to) the quantum yield, $\phi^{\rm L}$. If two such quantities are compared for the same product frequency, $\nu_{\rm p}$, but for a different laser excitation frequency $\nu_{\rm L'}$, the ratio $\phi_{\nu_{\rm L'}}^{\nu_{\rm L}}$ ($\nu_{\rm p}$) will approximate the ratio of the quantum yields:

$$\phi_{\nu_{\mathrm{L}}}^{\nu_{\mathrm{L}}}(\nu_{\mathrm{p}}) = \frac{\Delta A^{\mathrm{L}}(\nu_{\mathrm{p}})/N^{\mathrm{L}}}{\Delta A^{\mathrm{L}'}(\nu_{\mathrm{p}})/N^{\mathrm{L}'}} \approx \frac{\phi^{\mathrm{L}}(\nu_{\mathrm{p}})}{\phi^{\mathrm{L}'}(\nu_{\mathrm{p}})}$$

The quantity $\phi_{r_L'}^{\nu}(\nu_p)$ will closely approximate the quantum yield ratio if the two laser irradiation periods are comparable in duration and if the calculation of photons absorbed accurately corresponds for both ν_L and $\nu_{L'}$ to absorption by reactive pairs (not, for example, by isolated parent molecules). Uncertainty in the latter quantity (photons absorbed by reactive pairs) limits the quantitative significance of our relative quantum yields. Nevertheless, we feel confident that the data so interpreted have at least qualitative meaning and that they reveal interesting behavior. Table IV shows the experimental results, all based on peak absorbance measurements and calculated relative to $\nu_{L'} = 3116 \text{ cm}^{-1}$. Notice that, except for the first three columns, the entries have been multiplied by 10^3 .

At the bottom of Table IV, the average values of $\bar{\phi}_{3116}^{*}$ are given together with the standard deviation for each set of nine entries. The standard deviations indicate variability of about 25%. Each parenthetic entry indicates by how many standard deviations its value of ϕ_{3116}^{*} differs from the average $\bar{\phi}_{3116}^{*}$.

Discussion

1,3-Butadiene Experiments. Table I shows that the C_4H_6/Cl_2 system was the most thoroughly explored. Even at photon energies of 3100 cm⁻¹ (8.6 kcal/mol), no reaction could be initiated in an argon matrix. The highest photon energy attempted for three of the other reactants (I_2 , XeF₂, and ClF) was 1825 cm⁻¹ (5.2 kcal/mol) and, for Br₂, 1590 cm⁻¹ (4.5 kcal/mol). Among the possible explanations for this lack of success are rapid relaxation, high activation energy, or unfavorable reaction geometry in the matrix cage. In considering the first of these, our experience with the ethylene/fluorine system is helpful. In II, sizeable



Figure 1. CH_2 ==-CHBr:F₂:Ar ~ 1:20:140, 12 K: growth of product absorptions in the spectral range 1700–500 cm⁻¹ after laser irradiation at (a) 3116 cm⁻¹, 1.5 h, 0.044 mW absorbed; (b) 3097.8 cm⁻¹, 0.5 h, 0.044 mW absorbed; (c) 1849.0 cm⁻¹, 1 h, 14 mW absorbed; (d) 1809.2/1808.2 cm⁻¹, 1 h, 20 mW absorbed; (e) 1605.2 cm⁻¹, 1 h, 138 mW absorbed. Spectrum f was taken after deposition, and before laser irradiation. X: atmospheric CO₂ absorption.

reductions in quantum yield were found going from C_2H_4 to trans-1,2- $C_2H_2D_2$ and then again to cis-1,2- $C_2H_2D_2$. These order of magnitude effects were rationalized in II on the basis of more rapid relaxation caused by increased level density. Plainly, butadiene has an energy level density much higher than that of ethylene since it has 24 vibrational degrees (instead of 12) and a less rigid skeleton. Nevertheless, it seems likely that the activation energies play a role as well. Compare, for example, the C_4H_6/F_2 system, which prereacts during deposition, with the

TABLE IV: Relative Quantum Yields $\phi_{3116}^{\nu_{\rm L}}(\nu_{\rm P})$ and Deviation from the Average

						_
$\nu_{\rm P}^{b,c}$ (identity)	$\phi^{3116}_{3116}a$	φ ³⁰⁹⁸ 3116	φ ¹⁸⁴⁹ 3116	$10^{3}\phi_{3116}^{1808}$	$10^{3}\phi_{3116}^{1605}$	
738 (cis-CHFCHBr)	$(1.00) (+0.3\sigma)^d$	$1.41(-0.4\sigma)$	$6.9(-0.2\sigma)$	$6.1(-0.3\sigma)$	$0.50(-0.5\sigma)$	
1073	$(1.00)(+0.6\sigma)$	$1.29(-0.7\sigma)$	$6.3(-0.5\sigma)$	$6.0(-0.4\sigma)$	$0.49(-0.6\sigma)$	
1116 (trans-CHFCHBr)	$(1.00)(+0.4\sigma)$ $(1.00)(-1.9\sigma)$	$1.43(-0.3\sigma)$ 1.66(+0.3\sigma)	$9.2(-1.1\sigma)$ 9.6(+1.2 σ)	$6.6(+0.2\sigma)$ 81(+1.8 σ)	$0.52(-0.2\sigma)$ 0.63(+1.4 σ)	
1032 (<i>cis</i> CHFCHBr) 1090	(1.00)(-1.20) $(1.00)(-0.3\sigma)$	$1.92 (+0.9\sigma)$	$7.8(+0.3\sigma)$	$6.8(+0.4\sigma)$	$0.49(-0.6\sigma)$	
1649 (cis, trans-CHFCHBr)	$(1.00)(-0.9\sigma)$	$2.04(+1.2\sigma)$	$8.2(+0.5\sigma)$	$7.2(+0.8\sigma)$	$0.61(+1.1\sigma)$	
1202 (cis-CHFCHBr)	(1.00) (~0.9 0)	$2.08(+1.3\sigma)$	$10.7 (+1.7\sigma)$	$6.5(+0.1\sigma)$	$0.57 (+0.5\sigma)$	
1023 (CH ₂ FCHFBr)	$(1.00)(+0.7\sigma)$	$1.06(-1.3\sigma)$	$5.3(-1.0\sigma)$	$5.5(-0.9\sigma)$	$0.57 (+0.5\sigma)$	
$1122 (CH_2 CFBr)$	$(1.00)(+1.3\sigma)$	$1.11(-1.1\sigma)$	5.6 (-0.9o)	4.8 (-1.7σ)	$0.42(-1.7\sigma)$	
$\operatorname{av} \overline{\phi}^{\nu}_{3116}, \sigma$	(1.00)	1.56, 0.39	$7.29 imes10^{-3},\ 1.95 imes10^{-3}$	$\begin{array}{c} 6.40 imes 10^{-3}, \\ 0.96 imes 10^{-3} \end{array}$	$0.533 imes 10^{-3}, \ 0.067 imes 10^{-3}$	

^a 3116 cm⁻¹ is the central value of ν_L ; radiation was conducted for equal times, 18 min, at laser frequencies 3110, 3112, 3116, 3117, and 3118 cm⁻¹. ^b Probable product absorptions too weak to permit quantum yield measurements were also observed at 572, 715, 1052, 1267, 1320, 3834, and 3911 cm⁻¹. ^c The product frequencies are listed in order of decreasing absorbance. ^d For 3116 cm⁻¹, the entry given is the negative of the average standard deviation associated with the other four irradiation features.

 C_4H_6/Cl_2 system, which shows no reaction even with excitation at 3100 cm⁻¹. This absence of both prereaction and reaction under excitation could indicate a raised activation energy associated with the relatively high Cl₂ bond energy (57 kcal/mol compared to 36 for F_2) and the lowered exothermicity (\sim -41 kcal/mol compared to \sim -113 for F_2 addition). This same argument would extend, though lessened, to ClF and Br_2 (with bond energies, respectively, of 61 and 46 kcal/mol). However, it should not be influential for I_2 or XeF_2 for which the bond energies and exothermicities are quite close to those of F_2 . In these instances, it is possible that reaction geometry plays an inhibiting role. It is conceivable that the matrix cage restricts the $FXeF \cdot C_4H_6$ pairs to molecular orientations unsuited to a concerted fluorination reaction.

Vinyl Chloride-Fluorine. None of the above three explanations seems to rationalize the absence of reactivity of C_2H_3Cl with F_2 since C_2H_3Br does react. While this contrasting behavior surely piques interest in this system, it must be noted that only two laser excitation frequencies were attempted. Conceivably the CO laser frequencies available are not propitious relative to the absorption frequency of the reactive pair. More study is needed before detailed interpretation is warranted.

Vinyl Bromide-Fluorine. Possible Reactions. In analogy to the results in I and II, reactions can be expected to begin with concerted addition of F_2 across the double bond followed by stabilization or elimination of one or more diatomic molecules. The reactions to be considered, all of those energetically possible within this scheme, are given in Scheme I. Notice that elimination products obtainable through $\alpha \alpha$ -elimination are identical with those listed if it is assumed that only H atom migration is possible.

Identification of Products. The most easily identifiable products would be HF and HBr, each through its characteristic absorption perturbed by its olefinic or acetylenic cage partner. In I, HF with C_2H_3F nearest neighbor in N_2 was found to absorb at 3795.5 cm⁻¹, 84.0 cm⁻¹ below the isolated HF absorption. With both C_2H_3F and C_2H_4 neighbors, HF absorbs at 3682.0 cm⁻¹, a shift of 197.5 cm⁻¹. This much larger shift suggests that HF hydrogen bonds preferentially to C_2H_4 and with a much stronger interaction than for C_2H_3F ·HF. This deduction is supported by the study of Andrews et al.⁶ who find that C₂H₄·HF complexes

Scheme I

		∆H°,⁵	
		kcal/mol	
$CH_{2}CHBr + F_{2}$	\rightarrow CH, FCHFBr	-132	(1)
CH,FCHFBr [‡]	\rightarrow HF + <i>cis</i> -CHFCHBr	17	(2a)
•	\rightarrow HF + trans-CHFCHBr	17	(2b)
	\rightarrow HF + CH ₂ CFBr	17	(2c)
	\rightarrow HBr + <i>cis</i> -CHFCHF	17	(3a)
	\rightarrow HBr + trans-CHFCHF	17	(3b)
	\rightarrow H ₂ + cis-CHFCFBr	30	(4a)
	\rightarrow H ₂ + trans-CHFCFBr	30	(4b)
	→ FBr + CH ₂ CHF	64	(5)
	$\rightarrow 2\text{HF} + \text{HCCBr}$	43	(6)
	\rightarrow HF + H ₂ + FCCBr	57	(7)
	\rightarrow HBr + $\dot{H_2}$ + FCCF	57	(8)
	\rightarrow HF + HBr + HCCF	74	(9)
	\rightarrow HF + FBr + HCCH	90	(10)
	\rightarrow H, + FBr + HCCF	103	(11)

in N_2 absorb at 3664.3 cm⁻¹, shifted 216.3 cm⁻¹ from isolated HF. We conclude that vinyl fluoride is a much weaker electron donor than is ethylene.

It is reasonable to expect, then, that the dihaloolefinic products from reactions 2a-c will be more like vinyl fluoride than like ethylene. Andrews et al.⁶ have also measured HF stretching frequencies in argon: HF isolated, 3953.8 cm⁻¹ and C₂H₄·HF, 3730.7 cm⁻¹ (shift, 223.1 cm⁻¹). Thus our two product frequencies at 3838.4 and 3910.6 cm⁻¹ are shifted from the monomer position by 115.4 and 43.2 cm^{-1} . These are plausible shifts for HF in the same cage with one or another of the C_2H_2FBr isomers.

There is also the possibility that one or both of these absorptions might be attributable to HF with an acetylenic nearest neighbor. Andrews et al.⁶ again help us by reporting that in Ar the C_2H_2 ·HF complex absorbs at 3746 cm⁻¹. This shift, 207.8 cm⁻¹, is close to that of C_2H_4 ·HF. Hence we can conclude that we have not observed HF bonded to C_2H_2 , as would result from reaction 10. However, without reference spectra we cannot rule out the possibility that our product features at 3838.4 and 3910.6 cm⁻¹ might be due to HF in the same cage with HCCBr, FCCBr, or HCCF, as would be produced by reactions 6, 7. and 9.

No corresponding absorption of HBr is detected. In argon, isolated HBr absorbs at 2559 cm⁻¹ while the complexes C_2H_4 ·HBr and C_2H_2 ·HBr absorb,⁷ respectively, at 2453 and 2467 cm⁻¹. We find no product features in this

⁽⁴⁾ We thank Mr. Ben Gordon for conducting these gas chromatographic analyses.

⁽⁵⁾ Calculated by assuming bond energy additivities with bond ener-gies (kcal/mol) as follows: C—C, 83; C—C, 146; C—C, 200; C—H, 99; C—F, 116; C—Br, 68; H₂, 104; H—Br, 87; H—F, 135; Br—F, 57; F₂, 37.

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spectral region. While this absence of HBr absorption speaks against reactions 3, 8, and 9, its significance is lessened by the relatively low extinction coefficient of HBr, approximately one-seventh that of HF.⁸ That difference, probably accentuated by a reduced enhancement due to hydrogen bonding to its cage partner, implies a lowered sensitivity by about a factor of ten. Fortunately, other products of reactions 3, 8, and 9 provide more sensitive evidence about the occurrence of these reactions.

Three potential products were available to provide matrix reference spectra, cis- and trans-1,2-difluoroethylene and 1,1-difluoroethylene. Though the gas-phase spectra have been reported,^{9,10} we suspended each of these substances in solid argon for reference use. The most intense features of cis-1,2-CHFCHF in Ar (1:180) are at 1714, 1128, 1009, 985, and 766 cm⁻¹. There is no product absorption near 1714 cm⁻¹ and the product band closest to 766 cm⁻¹ is at 738 cm⁻¹. Their absence indicates cis-1,2-CHFCHF is not a significant product (reaction 3a).

In a similar way, trans-1,2-difluoroethylene would be indicated by its strongest absorption in Ar (1:215) at 1153 cm^{-1} , strong absorptions at 1275, 1140, and 877 cm^{-1} , and its medium strong absorption at 3118 cm⁻¹. There is weak product absorption at 1267 cm⁻¹ but the absence of product bands at any of the other characteristic frequencies and, in particular, at 1153 cm⁻¹ indicates that trans-1,2-CHFCHF is also not a detectable product (reaction 3b).

Though none of the reactions 1-11 produce 1,1-difluoroethylene, it is worthy of mention that its known spectrum (CF_2CH_2 :Ar = 1:180) indicates that it, too, is not an observed product (the most decisive missing absorptions are its two most intense features at 1734 and 1721 cm⁻¹).

The difluoroethylenes have quite significant extinction coefficients. Hence, the absence of their product absorptions adds strength to the conclusions, suggested by the absence of HBr product, that elimination of a single HBr molecule in either reaction 3a or 3b is disfavored.

The observation of HF product absorption focusses attention on reactions 2, 6, 7, 9, and 10. The spectra of the cis- and trans-CHFCHBr products of reactions 2a and 2b are reported,¹¹ so identification was based upon the gas-phase frequencies. The five most intense absorptions of the cis isomer are found at 1672, 1219, 1055, 1035, and 733 cm^{-1} . There are product absorptions at frequencies reasonably close to all of these: 1649, 1201, 1052, 1032, and 738 cm⁻¹. The trans isomer has its three most intense absorptions at 1655, 1117, and 800 cm⁻¹. These can be compared to product features at 1649 and 1116 cm⁻¹. From these coincidences we conclude that probably both cis- and trans-CHF=CHBr are formed in reactions 2a and 2b.

Reaction 5 would produce vinyl fluoride, whose spectrum in solid N_2 is shown in I. The most intense product band intensities in that earlier study are, in order of decreasing intensity, 1649, 1119, 906, 878, and 928 cm⁻¹. In the present work, two absorptions correspond well, at 1649 and 1116 cm⁻¹. However, both of these can be equally well assigned to trans-CHFCHBr. More important, there are no distinct product bands between 1023 and 738 cm⁻¹, so the two prominent vinyl fluoride features 906 and 928 cm⁻¹ are not represented in the spectrum. These absences seem to eliminate vinyl fluoride as a product, and we conclude reaction 5 is not an important reaction.

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Having found no evidence of double elimination in I or II, we feel that reactions 6-11 seem unlikely. Nevertheless, they must be considered, since reaction 1 may be more exothermic than the corresponding reaction in I. The spectrum of acetylene in Ar is, of course, known¹² and it is dominated by the intense feature at 729 cm⁻¹ followed by the weaker, but highly characteristic C-H stretching mode at 3287 cm⁻¹. There is a product band at 738 cm⁻¹ and possibly another weak feature at 715 cm⁻¹, either of which could be acetylene shifted by the cage partners reaction 10 would provide. The absence of absorption at 3287 cm⁻¹ cannot be taken as definitive since all C-H stretching modes are weak. Thus it is possible that acetylene is a product.

Fluoroacetylene has intense absorptions^{13,14} at 3355. 2255, and 1055 cm⁻¹ as well as less intense absorptions at 1156 and 578 cm⁻¹. Although there is weak absorption at 1052 cm⁻¹, the absence of product absorptions near 2255 cm^{-1} speaks against reaction 9. Similarly, reaction 6 can be ruled out because of the absence of product absorptions near any of the three most intense absorptions of $HC \equiv$ CBr, 2085, 618, and 3325 cm^{-1.14}

Difluoroacetylene¹⁵ has its most intense band at 1149 cm⁻¹ and its next most intense at 1370 cm⁻¹, the latter coincident with a strong parent absorption. The closest product absorption is at 1122 cm⁻¹, rather far from coincidence to be comfortably assigned to C_2F_2 . We conclude that reaction 7 is probably not important.

Thus, the only evidence for double elimination is the near correspondence of the 738- and 715-cm⁻¹ product absorptions to the 729-cm⁻¹ absorption of acetylene. However, it does not seem likely that reaction 10 would take place but none of the other double elimination reactions 6–9 and 11. More plausibly, 738 cm^{-1} is due to cis-CHFCHBr and 715 cm⁻¹ to some other, unidentified product.

There remain reactions 1, 2c, 4a, and 4b to discuss. For none of these reactions is the product molecule infrared spectrum reported. The situation is complicated for reaction 1 by the fact that 1-bromo-1,2-difluoroethane has three rotational conformers, each of which will have its own spectrum. Thus the only information available about the remaining possible products is provided by the characteristic spectral regions in which prototype molecules absorb.

For example, olefinic C-F stretching modes tend to absorb strongly in the spectral region¹⁶ 1100-1150 cm⁻¹. In contrast, alkyl C-F stretching modes tend to be lower in frequency,¹⁷ in the region $1010-1040 \text{ cm}^{-1}$. It is, then, plausible to attribute the product features at 1052 and 1023 cm⁻¹ to C-F stretching modes of two of the rotameric isomers of CH₂FCHFBr produced in reaction 1. In a similar way, alkyl C-Br stretching modes²⁰ tend to fall in the region 570-645 cm⁻¹, so the product feature at 575 cm⁻¹

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(20) Prototype alkyl C-Br stretching frequencies (cm⁻¹): CH₃CH₂Br, 605.8; CH₂BrCH₂F,¹⁹ 588; and CH₂BrCH₂Cl,²¹ 571 (gauche), 630 (trans).

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(16) Prototype olefinic C—F stretching frequencies (cm⁻¹): CH₂CHF,¹
1145; cis-CHFCHF, 1125; trans-CHFCHF,⁹ 1153; trans-CHFCHBr,¹¹
1117; and cis-CHFCHBr,¹¹ 1219, 1055.
(17) Prototype alkyl C—F stretching frequencies (cm⁻¹): CH₃CH₂F,¹⁸
1048; CH₂ClCH₂F,¹⁹ 1026; CH₂BrCH₂F,¹⁹ 1026; and CH₂ICH₂F,¹⁹ 1018.
(18) D. C. Smith, R. A. Saunders, J. R. Nielson, E. E. Ferguson, J. Cham. Phys. 20, 8472 (1952).

Chem. Phys., 20, 847 (1952).

⁽¹⁹⁾ M. F. El Bermani and N. Jonathan, J. Chem. Phys., 49, 340 (1968)

could also be assigned to $CH_2FCHFBr$. These features offer the most significant evidence that reaction 1 takes place and that not all of the excited ethane so produced is lost through subsequent elimination reactions.

The presence of CH₂CFBr as a product of reaction 2c might be signalled by absorption near 850–900 cm⁻¹, a usual region for the out-of-plane wagging motion of olefins with a single CH₂ group,²² and/or absorption in the range 1100–1150 cm⁻¹, the before mentioned olefinic C-F stretching region. Thus the latter provides a plausible assignment of the product feature at 1122 cm⁻¹ to CH₂-CFBr, suggesting that reaction 2c is taking place.

If we take at face value the assignments given in Table IV, there remain a number of product absorptions still unassigned: 1320.0, 1267.1, 1090, 1073.1, and 715 cm⁻¹. Some of these are undoubtedly associated with products already identified by comparison to prototype molecules but whose spectra in this so-called "fingerprint region" are not known. In the same way, these bands may also indicate products of reactions 4a and 4b, whose spectra are also not reported.

Summarizing, product identification shows that HF eliminations (reactions 2a, 2b, and, probably, 2c) do take place but probably not double eliminations (reactions 6-11). There is ample evidence to indicate that the product of reaction 1 is stabilized and retained to some extent. The evidence seems to indicate that HBr elimination does not occur. No product bands provide convincing evidence about whether reactions 4a and 4b take place.

Relative Quantum Yields. Just as reported in I, the difference spectra show that hole burning does not occur. Instead the absorbance-loss spectrum has a typical band width of a few wave numbers. Since there is ample reason to expect that this width is due to inhomogeneous broadening, we attribute the absence of hole burning to energy transfer in the matrix. Experiments relevant to this transfer have been performed for the ethylene-fluorine system and will be discussed in a forthcoming paper.²³ This energy transfer does not prevent measurement of relative quantum yields, as reported here.

The average values of ϕ_{3116}^{ν} and their associated standard deviations (see Table IV) indicate that, within about $\pm 25\%$, the relative quantum yields are independent of the product band studied. Comparing the magnitude of the averages, we find a large and monotonic dependence of ϕ on photon energy, just as discovered in II. In fact ϕ changes by more than three orders of magnitude going from excitation at 1605 cm⁻¹ to excitation at 3116 cm⁻¹. This is even more dramatic than the two orders of magnitude change shown by the ethylene-fluorine reaction over the same excitation range.

A search for mode specificity is limited by the uncertainties provided by photometric accuracy and by the extent to which absorbed photons can be connected with CH₂CHBr·F₂ reactive pairs rather than CH₂CHBr isolated molecules. If we make the assumption that the fraction of absorbed photons that reach reactive pairs is the same for each excitation frequency, then the changes in ϕ might reveal mode specificity. Thus we find a 12-fold change in $\overline{\phi}$ going from 1605 to 1808 cm⁻¹ but only in 14% change from 1808 to 1849 cm⁻¹. This would suggest a specially low contribution to the quantum yield by 1849 cm⁻¹ compared to that added through excitation at 1808 cm⁻¹. While this suggests mode selectivity, the uncertainties mentioned above do not permit a conclusive interpretation. Even less can be drawn from the relative quantum yields at 3098 and 3116 cm⁻¹. Since these frequencies are quite close together, only a small change in quantum yield is expected under any circumstance, so the large uncertainty limits would mask any mode-selective effects.

We can also search for excitation-specific changes in branching ratios within the uncertainty limits of the data. Statistically about one-third of the entries can be expected to differ by more than one σ from the average and, indeed, 12 out of the 36 values in Table IV so differ. Also noteworthy is the fact that the differences are smallest for the first five product bands, the entries associated with the features which can be most accurately measured because they are the most intense. Thus, the data suggest that, within about $\pm 25\%$, the product distribution is independent of excitation frequency. The only spectral anomaly that seems to be surely outside the photometric uncertainty is the change in the relative intensities of the features at 1023, 1032, and 1073 cm⁻¹ when the excitation frequency is changed from 3116 to 1808 cm⁻¹. The differences are consistent with an interpretation that 1808 cm⁻¹ favors the product absorbing at 1032 cm⁻¹ over that absorbing at 1023 cm⁻¹ (or, conceivably, 1808-cm⁻¹ excitation converts the 1023-cm⁻¹ product into 1032 cm⁻¹).

Conclusions

The vinyl bromide/ F_2 reaction reiterates the finding in I and II that the quantum yield shows a general and large increase as photon energy increases. In fact, this effect is larger than is found for ethylene since the quantum yields for the 3- μ m excitations (3116 and 3098 cm⁻¹) are more than 10² larger than found for excitation at 1849 and 1808 cm⁻¹ and about 10³ larger than at 1605 cm⁻¹. Within our experimental uncertainty, no reaction is observed with excitation at 942 cm⁻¹, indicating at least another factor of 10 lower quantum yields. It is conceivable that this larger contrast in quantum yields indicates that the activation energy barrier for reaction is close to 1605 cm⁻¹ so that the lower frequency excitations have only a little excess energy.

Because of the low product growth rate, the signal-tonoise limitation is really too severe to provide a favorable opportunity to search for excitation mode-specific behavior. While there may be some manifestation of such in the quantum yields seen with excitation at 1605, 1808, and 1849 cm⁻¹, it is not conclusive. Further, there is only one clear-cut indication of a mode-sensitive product distribution. Nevertheless, the vinyl bromide-fluorine system is of significant interest because of the relatively small number of cases for which single-photon vibrational excitation of bimolecular reactions of polyatomic molecules has been demonstrated under any experimental conditions.

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 (22) Prototype olefinic out-of-plane CH₂ frequencies (cm⁻¹): CH₂CF₂,¹⁰
 803; CH₂CHF,¹ 868; and CH₂CHBr, 900.

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Registry No. C₄H₆, 106-99-0; Cl₂, 7782-50-5; ClF, 7790-89-8; Br₂, 7726-95-6; I₂, 7553-56-2; XeF₂, 13709-36-9; F₂, 7782-41-4; Ar, 7440-37-1; C₂H₃Cl, 75-01-4; C₂H₃Br, 593-60-2; *cis*-CHFCHBr, 2366-31-6; *trans*-CHFCHBr, 2366-32-7; CH₂FCHFBr, 1800-81-3; CH₂CFBr, 420-25-7.