ferricyanide and H atoms. If (4′) is included, our value $k_4 = 6.5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ should be replaced by $k_4 + k_4' = 6.5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$.

Acknowledgment. We are indebted to Dr. M. S. Matheson for helpful discussions. We wish to thank Mr. U. Shainok of The Hebrew University for his help with the computer calculations. We wish also to thank the Linac group for their careful operation and Mr. S. Petrek of ANL for maintaining the electronic equipment.

The Photolysis of 1,3-Difluoro- and 1,1,3,3-Tetrafluoroacetone at Low Pressure[1]

by G. O. Pritchard and J. T. Bryant

Department of Chemistry, University of California, Santa Barbara, California 93106 *(Received October 17, 1967)*

1,3-Difluoroacetone and 1,1,3,3-tetrafluoroacetone, and their mixtures, were photolyzed at low pressures (about 0.1 torr). The disproportionation:combination ratio between two CF_2H radicals is redetermined to be 0.19–0.20, and that for $CFH_2 + CF_2H \rightarrow CFH_3 + CF_2$ is determined to be about 0.06; the alternative reaction to yield $CF_2H_2 + CFH$ does not occur, nor is there any disproportionation between two CFH_2 radicals. The elimination of HF from the vibrationally excited molecule $CF_2HCF_2H^*$ is discussed in terms of the RRK theory of unimolecular reactions, and an estimation of the activation energy of the process $C_2F_4H_2 \rightarrow C_2F_3H + HF$ of 56 kcal mol^{-1} is obtained. The elimination of HF from "hot" $CF_2HCFH_2^*$ leads to the formation of 1,1- and *cis*- and *trans*-difluoroethylenes. An effect of added nitrogen on the relative rates of formation of the three fluoroethylenes is observed, which is discussed in terms of the critical energies involved in the eliminations.

Introduction

In our previous investigation[2] of the photolysis of 1,1,3,3-tetrafluoroacetone (TFA), we observed the radical–radical interactions 1 and 2a but at the pressures used we were unable to observe the elimination of HF from the vibrationally excited molecule, reaction 2b. Part of this report constitutes an investigation under conditions of lower pressure, in order that reaction 2b may effectively compete with the collisional quenching process, 2a.

$$CF_2H + CF_2H \longrightarrow CF_2H_2 + CF_2 \tag{1}$$

$$CF_2H + CF_2H \xrightarrow{k_2} C_2F_4H_2^*\text{—}\left[\begin{array}{l} \xrightarrow[M]{k_{2a}} C_2F_4H_2 \\ \\ \xrightarrow{k_{2b}} C_2F_3H + HF \end{array}\right. \tag{2}$$

In a prior investigation[3] with 1,3-difluoroacetone (DFA) we observed the reaction sequences

$$CFH_2 + CFH_2 \xrightarrow{k_3} C_2F_2H_4^*\text{—}\left[\begin{array}{l} \xrightarrow[M]{k_{3a}} C_2F_2H_4 \\ \\ \xrightarrow{k_{3b}} C_2FH_3 + HF \end{array}\right. \tag{3}$$

but the importance of the disproportionation

$$CFH_2 + CFH_2 \longrightarrow CFH_3 + CFH \tag{4}$$

was not determined. The possible occurrence of this reaction is investigated.

In a preliminary communication[4] we have reported on the photolysis of mixtures of DFA and TFA at low pressures, where the reactions of interest are

$$CF_2H + CFH_2 \xrightarrow{k_5}$$

$$CF_2HCFH_2^*\text{—}\left[\begin{array}{l} \xrightarrow[M]{k_{5a}} CF_2HCFH_2 \\ \xrightarrow{k_{5b}} CF_2{=}CH_2 + HF \\ \xrightarrow{k_{5c}} cis\text{-}CFH{=}CFH + HF \\ \xrightarrow{k_{5d}} trans\text{-}CFH{=}CFH + HF \end{array}\right. \tag{5}$$

Herein we give more extensive data and describe the effect of added nitrogen on the various sequences de-

---

[1] This work was supported by a grant from the National Science Foundation, GP-4090.

[2] G. O. Pritchard and J. T. Bryant, *J. Phys. Chem.*, **70**, 1441 (1966).

[3] G. O. Pritchard, M. Venugopalan, and T. F. Graham, *ibid.*, **68**, 1786 (1964).

[4] J. T. Bryant, B. Kirtman, and G. O. Pritchard, *ibid.*, **71**, 1960 (1967).

picted in reaction 5. The possible disproportionation reactions and the cross-combination ratio between the two radicals are also discussed.

Experimental Section

The procedures have, in the main, been described elsewhere.[2,3,5] Chromatographically pure samples of DFA and TFA were used, and analysis was carried out by means of low-temperature fractionation and vpc. All compounds were identified by comparative retention times with known samples and by their mass spectra.[5] The *cis*- and *trans*-1,2-difluoroethylenes were distinguished by their infrared spectra.[6]

The low-pressure vacuum apparatus was mercury and grease free. Westef[7] Teflon stopcocks with Viton A O rings were used in place of conventional stopcocks. The cylindrical quartz reaction cell was 50 cm long by 5.8 cm in diameter, with a volume of 1321 cm^3, and it was fully illuminated by a collimated light beam in the 3130-Å region. Sufficient products for accurate analysis were thereby obtained at low total pressures and small percentage conversions. Reactant pressures were measured on a thermocouple gauge calibrated for TFA with a McLeod gauge in the range 0–0.36 torr. Higher pressures, and pressures of added N_2, were measured on a Wallace and Tiernan Bourdon-type gauge, which was calibrated in the range 0–110 torr. In the experiments with added N_2, the products were pumped into a large trap filled with glass beads at $-195°$. This prevented any loss of the 1,1-difluoroethylene, some of which was swept through an unpacked trap by the excess N_2.

Results and Discussion

TFA and DFA at Low Pressures. i. Disproportionation. The results of a number of runs with TFA are given in Table I. The disproportionation:combination ratio for CF_2H radicals, k_1/k_2, at pressures where reaction 2b is negligible (note that $k_{-2} \ll k_{2b}$[8]) is well established at about 0.19.[2,9,10] The data in Table I, where k_1/k_2 is now $R_{CF_2H_2}/(R_{C_2F_3H} + R_{C_2F_4H_2})$ and R is rate of formation, gives an average value of 0.20 for the 20 experiments between 303 and 516°K. From this and the variation in TFA pressure, *e.g.*, tenfold at ~515°K, it is evident that reaction 6, abstraction

$$CF_2H + TFA \longrightarrow CF_2H_2 + CF_2COCF_2H \quad (6)$$

from the ketone, is unimportant, under the experimental conditions. The activation energy for this reaction is also considerably higher[10] than we have given previously.[2] At 551°K and above the ratio is >0.2, which may indicate the onset of reaction 6. Alternatively, the consumption of C_2F_3H by CF_2H radicals may occur[11] ($CF_2H + C_2F_3H + CF_2H$) and this will become of increasing importance at elevated temperature. This is borne out somewhat by the decrease in the mass-balance ratios with temperature, shown in Table I, since the ratio would not be affected if the acetonyl radical produced in reaction 6 combined with a CF_2H radical. Radicals will also be consumed by the CF_2 species produced in reaction 1; however, no temperature dependence would be assumed in this case.[12] An attempt was made to identify any C_3 and C_4 fluorohydrocarbon products in the reaction mixture at 306°, but it was inconclusive. Products may also be formed and radicals lost by addition to the >C=O in the ketone.

Table I: Data on CF_2HCOCF_2H Photolysis

Temp, °K	Pressure, torr	Time, sec	Products, 10^6 mol C_2F_3H	CF_2H_2	$C_2F_4H_2$	CO	Mb[a]
303	0.273	20	0.642	0.940	4.078		
362	0.273	20	1.164	0.842	3.868		
399	0.360	10	0.993	0.750	3.417		
401	0.051	20	0.452	0.156	0.337		
402	0.098	20	0.941	0.341	0.974		
402	0.178	20	1.032	0.448	1.540		
402	0.273	20	1.416	0.814	3.272		
441	0.247	20	1.484	0.730	1.960		
482	0.260	20	1.685	0.860	2.236		
513	0.221	20	1.407	0.572	1.232		
513	0.273	20	1.837	0.724	1.965		
514	0.034	20	0.542	0.120	0.110		
514	0.070	20	0.865	0.244	0.335		
514	0.095	20	0.958	0.360	0.498		
514	0.140	20	0.812	0.290	0.454		
515	0.302	20	1.826	0.948	2.471		
516	0.181	20	1.772	0.586	1.265		
516	0.347	20	2.050	1.180	3.264		
551	0.273	20	1.539	0.772	1.368		
590	0.277	20	1.443	0.896	1.221		
478	0.143	20	0.790	0.280	0.616		
477	0.153	20	1.390	0.470	1.111	3.31	0.90
573	0.169	20	1.172	0.424	0.724	3.46	0.67
579	0.160	20	1.070	0.450	0.674	3.51	0.62
577	0.150	20	0.951	0.425	0.505	2.88	0.65

[a] Mass balance = $(R_{CF_2H_2} + R_{C_2F_3H} + R_{C_2F_4H_2})/R_{CO}$.

Benson[13] has effectively summarized the evidence against the "common transition state" assumption for disproportionation and recombination reactions of

---

[5] J. T. Bryant, Ph.D. Thesis, University of California, Santa Barbara, Calif., 1967.

[6] H. G. Viehe, *Chem. Ber.*, **93**, 1697 (1960).

[7] West-glass Corp., South El Monte, Calif.

[8] S. W. Benson and G. Haugen, *J. Phys. Chem.*, **69**, 3898 (1965).

[9] M. G. Bellas, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.*, **43**, 1022 (1965).

[10] M. J. Perona, J. T. Bryant, and G. O. Pritchard, unpublished data.

[11] See R. D. Giles and E. Whittle, *Trans. Faraday Soc.*, **61**, 1425 (1965), for a discussion of the possible loss of $CF_2{=}CH_2$ in the $CF_3 + CH_3$ system.

[12] $C_3F_6H_2$ has been identified in the Hg-sensitized decomposition of CF_2HCl formed by $CF_2H + CF_2 + CF_2H$,[9] and C_3F_8 and C_3F_7H formed *via* $CF_3 + CF_2 + CF_3$ and $CF_3 + CF_2 + CF_2H$, respectively, in the photolysis of pentafluoroacetone: J. B. Hynes, R. C. Price, W. S. Brey, Jr., M. J. Perona, and G. O. Pritchard, *Can. J. Chem.*, **45**, 2278 (1967).

[13] S. W. Benson, *Advan. Photochem.*, **2**, 1 (1964).

alkyl radicals. It is evident from the present work that the reaction channel that leads to disproportionation is an alternative one to that which leads to the "hot" ethane intermediate.

Data on DFA are presented in Table II. The only observed products were CO and vinyl fluoride. The complete absence of CFH_3 rules out the occurrence of reaction 4 and abstraction from the ketone, under the reaction conditions. The absence of $C_2F_2H_4$ indicates that $k_{3b} \gg k_{3a}[M]$; at higher ketone concentrations, *i.e.*, at higher [M], it is readily observable.[3] The decreasing mass-balance ratios with temperature may be attributed to the addition of CFH_2 radicals to C_2FH_3. A search for the fluorobutane was again inconclusive.

Table II: Data on CFH_2COCFH_2 Photolysis[a]

Temp, °K	Pressure, torr	Products, 10^6mol CO	Products, 10^6mol C_2FH_3	Mb[b]
395	0.169	1.210	1.098	0.91
396	0.130	1.015	0.850	0.84
476	0.157	1.152	0.976	0.85
572	0.160	1.182	0.830	0.70
576	0.164	1.733	1.200	0.69

[a] Time of all runs was 20 min. [b] Mass balance = $R_{C_2FH_3}/R_{CO}$.

ii. HF Elimination. From reaction scheme 2 we may write

$$\frac{R_{C_2F_4H_2}}{R_{C_2F_3H}}\frac{1}{[M]} = \frac{k_{2a}}{k_{2b}}\ \text{mm}^{-1} \tag{7}$$

where [M] is the pressure of ketone, P_{TFA}, in mm. A plot of the data at two temperatures is given in Figure 1, in accord with eq 7,[14] and a plot of k_{2a}/k_{2b} *vs.* temperature is given in Figure 2. The temperature dependence for k_{stab}/k_{elim} has been treated by the simple-collision theory and the Rice-Ramsperger-Kassel theory of unimolecular decompositions for the "hot" molecules $CFH_2CFH_2^*$,[8] $C_2FH_5^*$,[15] and $CF_2HCH_3^*$,[16] and we may treat $CF_2HCF_2H^*$ in a similar manner. Details of the method and definition of the parameters can be found elsewhere.[8,15,16] The upward curvature seen at low temperatures in Figure 2 was not observed in the previous systems[8,15,16] over the same temperature range, but would presumably occur if experiments could be extended to lower temperatures. The region in which curvature occurs will be determined by the characteristics of the "hot" molecule and the nature of the moderating environment, as given by the theoretical equation[8,15,16]

$$\frac{k_{2a}}{k_{2b}} = \frac{QZ}{A}\left(\frac{E}{E - E^*}\right)^{n-1} \tag{8}$$

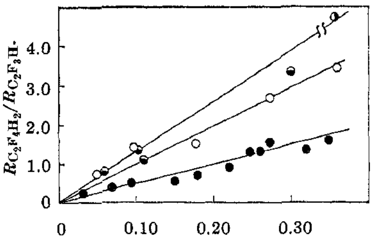

Figure 1. $R_{C_2F_4H_2}/R_{C_2F_3H}$ *vs.* ketone pressure, in mm: ○, TFA (399–402°K); ●, TFA (513–516°K); ◒, approximately 1:1 mixture of TFA + DFA (370–372°K); ◐, same conditions but ratio is 9.56 at a total ketone pressure of 0.72 mm.

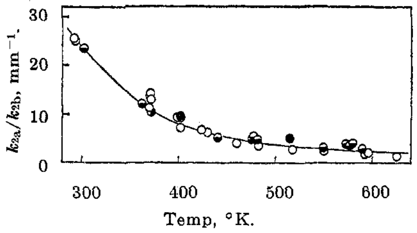

Figure 2. k_{2a}/k_{2b}, in mm^{-1}, *vs.* absolute temperature: ◒, TFA; ●, derived from slopes in Figure 1; ○, approximately 1:1 mixture of TFA + DFA; ◑, derived from slope in Figure 1.

For $CF_2HCF_2H^*$ we take E (internal energy) to vary between 85.4 kcal mol^{-1} at 298°K and 93.9 kcal mol^{-1} at 560°K.[5] Taking n (number of effective oscillators) = 15,[8] the theoretical and experimental curves are fitted in Figure 3.[17] Some representative curves for values of the critical energy, E^*, of 50, 56, and 62 kcal mol^{-1} are given. The best over-all fit appears to be with $E^* \cong 56$ kcal mol^{-1}. A similar result is obtained by taking a value of $n = 14$, and from a consideration of the number of effective (lower frequency) C–F oscillators in $CF_2HCF_2H^*$, a value of $n = 14$–15 is certainly very reasonable.[8,15,16] Assuming $n = 15$ and $E^* = 56$ kcal mol^{-1}, and taking the preexponential factor for the unimolecular decomposition, A, as $10^{13.5}$ sec^{-1}, and the collision frequency, Z, as 1.35×10^7 collisions mm^{-1} sec^{-1}, we may calculate a collisional quenching efficiency factor, Q, of 18, which is meaningless. (Previously,[8,15,16] values of Q in the range 0.1–1 were obtained, based on similar assumptions.) Smaller values of Q may be obtained[8] by either raising E^* or n. If $n = 15$ is retained and $E^* = 62$ kcal mol^{-1} is adopted, $Q \cong 1.0$, but from Figure 3 it is seen that these parameters do not give a good fit. If $E^* = 56$ kcal mol^{-1} is retained, n must be raised to 18 before Q decreases below unity. If the low-temperature points in Figure

---

[14] At pressures below 0.10 torr, where mean free paths approach 1 mm, some wall stabilization may occur.

[15] G. O. Pritchard and R. L. Thommarson, *J. Phys. Chem.*, **71**, 1674 (1967).

[16] J. T. Bryant and G. O. Pritchard, *ibid.*, **71**, 3439 (1967).

[17] The quantity $^1/_2(1 - \text{Mb})R_{CO}$ has been added to $R_{C_2F_3H}$ to allow for the loss of C_2F_3H by radical addition. Mb at each temperature was estimated from the data in Table I, and it was assumed to be unity at 298°K.

Table III: Data on CF_2HCOCF_2H and CFH_2COCFH_2 Photolysis

Temp, °K	Reactant pressure, torr		Products, 10^8mol								
	TFA	DFA	CF_2CH_2	$CFHCH_2$[a]	CF_2CFH	*trans*-CFHCFH	CF_2H_2	*cis*-CFHCFH	$C_2F_4H_2$	CO	Mb[b]
395	0.155	0.159	12.04	28.89	43.21	43.15	27.30	67.71	93.84	405.6	0.78
475	0.150	0.160	14.79	43.70	55.42	46.22	26.80	72.64	63.81	421.8	0.77
574	0.151	0.160	19.63	54.00	72.77	41.61	47.00	65.69	62.75	467.6	0.78
573	0.150	0.153	15.84	33.67	79.19	36.76	42.60	54.78	67.56	437.1	0.76
471	0.160	0.150	8.48	9.38	88.05	27.07	42.60	40.16	124.3	423.3	0.80
371	0.146	0.164	13.17	24.66	41.76	44.28	33.30	68.76	152.2	433.4	0.87

[a] The vinyl fluoride also contains small amounts of CFH_3. In the mass-balance calculation, they are assumed to have equal sensitivities on the vpc. [b] Mass balance = $(\Sigma R_{C_2F_2H_2} + R_{CFH_3} + R_{C_2FH_3} + R_{C_2F_3H} + R_{CF_2H_2} + R_{C_2F_4H_2})/R_{CO}$.

Table IV: Data on CF_2HCOCF_2H and CFH_2COCFH_2 Photolysis

Temp, °K	Reactant pressure, torr		Products, 10^8mol					
	TFA	DFA	CF_2CH_2	CF_2CFH	*trans*-CFHCFH	CF_2H_2	*cis*-CFHCFH	CF_2HCF_2H
399	0.178	0.169	20.28	64.00	64.96	47.00	103.8	202.0
401	0.160	0.160	19.07	60.75	63.27	41.80	96.80	179.5
402	0.155	0.157	18.83	49.54	56.32	35.00	93.16	130.9
424	0.160	0.143	18.58	78.65	57.37	42.80	89.04	166.5
431	0.160	0.160	21.65	71.69	63.91	38.00	111.8	139.3
461	0.273	0.287	30.06	99.44	85.65	65.80	137.8	222.3
518	0.160	0.160	18.75	78.11	45.25	37.40	71.59	72.13
593	0.049	0.051	4.484	26.22	10.87	12.75	16.40	4.774
595	0.273	0.287	25.21	88.41	48.32	88.40	76.60	89.51
594	0.160	0.178	21.01		42.66		64.64	
595	0.094	0.103	14.46		27.31		42.99	
591	0.052	0.051	5.818		12.40		18.46	
371	0.360	0.360	17.78	30.01	57.37	52.80	86.94	286.8
372	0.051	0.052	7.151	25.67	18.26	11.75	28.08	33.17
370	0.150	0.150	13.57	37.97	43.47	31.60	70.54	127.1
371	0.030	0.033	3.434	15.23	11.57	6.15	15.82	13.63
371	0.053	0.057	4.646	20.34	16.64	9.85	23.67	22.44
482	0.151	0.188	15.03	60.57	42.82	32.50	66.34	73.11
550	0.143	0.169	14.54	54.69	35.15	37.60	54.22	43.98
625	0.198	0.198	16.32	55.60	30.78	54.10	48.16	29.87
295	0.198	0.198	8.807	22.42	32.89	45.20	51.71	220.9
294	0.159	0.157	7.110	22.37	27.35	39.00	43.35	181.3

Table V: Data on CF_2HCOCF_2H and CFH_2COCFH_2 Photolysis

Temp, °K	Reactant pressure, torr		Products, 10^8mol				$CFH_3/\Sigma C_2F_2H_2$[a]
	TFA	DFA	CF_2CH_2	CFH_3	*trans*-CFHCFH	*cis*-CFHCFH	
393	0.160	0.152	14.87	8.29	45.65	68.44	0.064
389	0.054	0.053	4.85	2.31	16.67	19.90	0.056
387	0.302	0.302	19.98	9.83	66.90	110.8	0.050
402	0.155	0.157	18.83	11.89[b]	56.32	93.15	0.071

[a] No $C_2F_3H_3$ was observed until the pressure was increased to 0.72 torr. [b] In this experiment CFH_3 and C_2FH_3 were collected together and analyzed mass spectrometrically.

3 are omitted, a very good fit is obtained with $E^* = 50$ kcal mol^{-1} and $n = 15$; however, Q is in excess of 150.

Recently we have pointed out[4] the possibility of an alternative reaction path that leads to HF elimination. The simultaneous occurrence of both reactions would render the RRK equation used here invalid, as the two eliminations would have different A factors and critical energies. The measured Arrhenius parameters would then represent some weighted average values. This

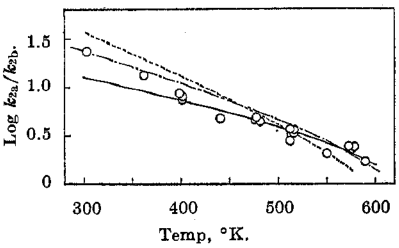

Figure 3. Comparison of the theoretical and observed temperature dependence of k_{2a}/k_{2b} for $n = 15$: ○, experimental points (corrected, see ref 17); ———, $E^* = 50$ kcal mole^{-1} (log $(QZ/A) = -4.15$); — · —, $E^* = 56$ kcal mol^{-1} (log $(QZ/A) = -5.12$); - - - -, $E^* = 62$ kcal mol^{-1} (log $(QZ/A) = -6.29$).

may well be the case with $CF_2HCF_2H^*$; note that if $A = 10^{12}$ sec^{-1} is adopted, $Q = 0.56$ for $E^* = 56$ kcal mol^{-1} and $n = 15$.

DFA and TFA Mixtures at Low Pressures. i. Disproportionation. Data on the DFA and TFA mixtures are collected in Tables III–V. No CF_2HCFH_2 or CFH_2CFH_2 was observed in the systems below a total pressure of 0.7 torr, indicating the unimportance of collisional quenching in reaction sequences 3 and 5 at these pressures. CO was measured in a number of experiments and the mass-balance ratios are given in Table III. The constancy of these with temperature indicates that radicals are being lost in the system by a predominantly temperature-independent reaction, presumably involving the CF_2 species.[12] Some further data are given in Table IV. The value of the disproportionation:combination ratio for CF_2H radicals, $R_{CF_2H_2}/(R_{C_2F_4H_2} + R_{C_2F_3H})$, calculated for 13 experiments between 294 and 461°K is 0.19 ± 0.02, indicating no extraneous source of CF_2H_2. (At higher temperatures, the ratio is >0.2, for reasons already discussed.) This rules out the possible disproportionation

$$CF_2H + CFH_2 \longrightarrow CF_2H_2 + CFH \qquad (9)$$

and also abstraction by CF_2H from DFA under the reaction conditions. The further disproportionation

$$CFH_2 + CF_2H \longrightarrow CFH_3 + CF_2 \qquad (10)$$

must also be considered. By adjusting the chromatographic conditions,[5] it was possible to resolve the CFH_3 and C_2FH_3 peaks, and the data are given in Table V. The ratio $R_{CFH_3}/\Sigma R_{C_2F_2H_2} = 0.06 \pm 0.01$ independent of pressure (attack by CFH_2 on TFA would not, in any case, be expected, considering the previous results) which may be taken as k_{10}/k_5. It is seen that only the disproportionation reactions 1 and 10, in which CF_2 is produced, occur, while those which lead to the formation of CFH do not occur. These observations may be correlated with the considerable stabilization of CF_2 which has been noted.[18] We[10] have also observed the reaction

$$CF_3 + CF_2H \longrightarrow CF_3H + CF_2 \qquad (11)$$

but data on

$$CH_3 + CF_2H \longrightarrow CH_4 + CF_2 \qquad (12)$$

were inconclusive.[16] The series of reactions 1, 10, 11, and 12 will be discussed more fully.[10]

ii. Cross Combination. In the absence of H-atom abstraction from the ketones and the collisional stabilization of $C_2F_2H_4^*$ and $C_2F_3H_3^*$ the cross-combination ratio, Ψ, for the two radicals is given by

$$\Psi = \frac{\Sigma R_{C_2F_2H_2} + R_{CFH_3}}{R_{C_2FH_3}^{1/2}(R_{CF_2H_2} + R_{C_2F_3H} + R_{C_2F_4H_2})^{1/2}} \qquad (13)$$

Since $k_{10}/k_5 = 0.06$, we may use the data in Table III to redefine Ψ in eq 14

$$\Psi = \frac{1.06\Sigma R_{C_2F_2H_2}}{(R_{C_2FH_3} - 0.06\Sigma R_{C_2F_2H_2})^{1/2}(R_{CF_2H_2} + R_{C_2F_3H} + R_{C_2F_4H_2})^{1/2}} \qquad (14)$$

Again considering only the experiments below 500°K, eq 14 leads to a value of $\Psi = 2.15 \pm 0.16$, which is the collision-theory prediction.[19]

iii. HF Elimination. The "hot" molecules of interest are $C_2F_4H_2^*$ and $C_2F_3H_3^*$. Data taken from Table IV on $R_{C_2F_4H_2}/R_{C_2F_3H}$ at 371°K are plotted in Figure 1 as a function of total pressure in the system $P_{DFA} + P_{TFA}$. The temperature variation of the function given in eq 7 is shown in Figure 2, where $[M] = P_{TFA} + P_{DFA}$, in mm. It is evident that the quenching efficiencies of the two ketones with respect to $C_2F_4H_2^*$ must be very similar. This is further shown for $C_2F_3H_3^*$ by the data presented in Table VI and Figure 4, where for the "hot" molecule in reaction sequence 5, we have

$$\frac{R_{C_2F_3H_3}}{\Sigma R_{C_2F_2H_2}} = \frac{k_{5a}[M]}{k_{5b} + k_{5c} + k_{5d}} \qquad (15)$$

and $[M]$ is $P_{TFA} + P_{DFA}$. The data are well described by eq 15, even though there are large variations in the relative ketone pressures, indicating that the deactivating efficiencies are not very different.[16]

Data on the predicted[8] and experimental k_{stab}/k_{elim} for the vibrationally excited fluoroethanes at 298°K together with the critical energies obtained by the RRK method are given in Table VII. The agreement is satisfactory, except for $CF_2HCF_2H^*$, where the predicted ratio is not approached until a temperature of 600°K; see Figure 2. However, as we have already noted, the frequency factor for this particular elimination could be a factor of 30 less than that assumed by Benson and Haugen.[8]

---

(18) I. P. Fisher, J. B. Homer, and F. P. Lossing, *J. Amer. Chem. Soc.*, **87**, 957 (1965); J. P. Simons, *Nature*, **205**, 1308 (1965).

(19) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 105 (1961).

Table VI: Data on CF_2HCOCF_2H and CFH_2COCFH_2 Photolysis

Temp, °K	Ketone pressure, torr		Products, 10^8mol			
	TFA	DFA	CF_2CH_2	*trans*-CFHCFH	*cis*-CFHCFH	CF_2HCFH_2
391	0.9	1.2	79.51	215.3	384.0	490.6
390	2.3	2.7	59.47	136.1	258.6	698.7
391	3.7	1.2	33.13	73.69	131.9	338.0
391	0.2	4.8	34.34	75.95	120.7	383.0
391	0.2	2.4	32.24	91.14	148.6	209.8

Table VII: Comparison of Predicted and Experimental $k_{\text{stab}}/k_{\text{elim}}$ Ratios[a]

"Hot" molecule	$k_{\text{stab}}/k_{\text{elim}}$ (298°K), mm^{-1}		Quencher [M]	E^*, kcal mol^{-1}	Ref
	Predicted[b]	Exptl			
CFH_2CH_3	5.9×10^{-3}	5×10^{-3}	CFH_2COCH_3	59	15
		10^{-2}	?	51	*c*
CFH_2CFH_2	4.1×10^{-2}	2×10^{-2}	CFH_2COCH_3	59	15
		4.1×10^{-2}	DFA	62	3, 8
CF_2HCH_3	4.1×10^{-2}	1.4×10^{-2}	TFA + CH_3COCH_3	53	16
		$\sim 10^{-2}$	$CH_2CO + CF_2H_2$	...	*d*
CF_3CH_3	2.9×10^{-1}	3.4×10^{-2} (423°K)	CF_3COCF_3	...	
		1.5×10^{-2} (423°K)	CH_3COCH_3	...	
CF_2HCFH_2	2.9×10^{-1}	3.1×10^{-1} (390°K)	DFA + TFA	...	This work
CF_2HCF_2H	1.8	24.2	TFA	56 (?)	This work

[a] Since the completion of the manuscript, a further report has been given on the kinetics of decomposition of "hot" alkyl fluorides by the authors in ref *b* at the Faraday Society Meeting, Toronto, Sept 1967. We shall reserve further comment until the results are made generally available. [b] Reference 8. [c] J. A. Kerr, A. W. Kirk, B. V. O'Grady, and A. F. Trotman-Dickenson, *Chem. Commun.*, 365 (1967). [d] G. O. Pritchard, J. T. Bryant, and R. L. Thommarson, *J. Phys. Chem.*, **69**, 2804 (1965).

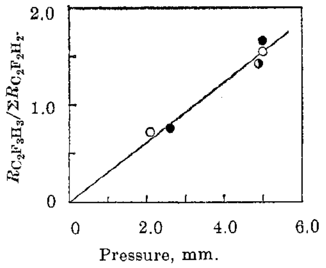

Figure 4. $R_{C_2F_3H_3}/\Sigma R_{C_2F_2H_2}$ *vs.* ketone (DFA + TFA) pressure, in mm, at 390–391°K: ○, 1:1 mixture; ●, 0.2 mm of TFA + DFA (see Table VI); ◑, 3.7 mm of TFA + 1.2 mm of DFA.

Discussion of runs, based on the data in Table IV, on the molecule $CF_2HCFH_2^*$ has already been presented by us.[4] Although these dehydrohalogenations are generally accepted as proceeding *via* a four-center transition state,[20] α,β elimination, from our observation[4,10] of the formation of d_3- as well as d_2-vinyl fluoride in the interaction of CF_2H with CD_3 radicals, we have suggested that the "hot" molecule $CF_2HCD_3^*$ may decompose by elimination of HF from the same carbon atom in a three-center process, α,α elimination. No evidence has previously been presented for an α,α process in the dehydrohalogenation of haloethanes in either thermal or chemical activation systems,[21] and it should be noted that in chemical activation systems involving $CHCl_2$ with CH_3 or CH_2Cl radicals[22] chloroethylenes can be formed by pathways not involving "hot" chloroethane intermediates. If the α,α elimination is established, detailed quantitative conclusions will depend upon an analysis of the isotope effects. These experiments are currently being undertaken by us.[10] An α,α elimination does occur[23] in the photolysis of CH_3CD_3 at 1470 Å where

$$CH_3CD_3^* \longrightarrow CHD{=}CD_2 + H_2 \qquad (16)$$

is the major molecular hydrogen elimination process.

iv. Experiments with Added N_2. Data on runs conducted in the presence of varying pressures of N_2 are given in Table VIII. The total pressure of ketones is such that no collisional stabilization of $C_2F_3H_3^*$ occurs in the absence of added N_2, so that we may apply eq 15 to the data, where [M] is now P_{N_2}. This is shown in Figure 5. The slope of the line at 391°K is 0.074 mm^{-1}, which may be compared to the slope of the line in Figure 4 which is 0.31 mm^{-1}. Assuming an average molecular weight and collision diameters of 6.0 Å for the ketones,

---

(20) S. W. Benson and A. N. Bose, *J. Chem. Phys.*, **39**, 3463 (1963); S. W. Benson and G. R. Haugen, *J. Amer. Chem. Soc.*, **87**, 4036 (1965); J. C. Hassler and D. W. Setser, *J. Chem. Phys.*, **45**, 3246 (1966).

(21) D. W. Setser, private communication, 1967.

(22) J. C. Hassler and D. W. Setser, *J. Chem. Phys.*, **45**, 3237 (1966).

(23) H. Okabe and J. R. McNesby, *ibid.*, **34**, 668 (1961).

Table VIII: Data on CF_2HCOCF_2H and CFH_2COCFH_2 Photolysis with Added N_2

Temp, °K	Reactant pressure, torr TFA	DFA	N_2	Products, 10^8mol CF_2CH_2	*trans*-CFHCFH	*cis*-CFHCFH	CF_2HCFH_2
390	0.148	0.198	46.0	4.20	6.87	14.58	87.07
392	0.155	0.198	61.4	3.27	4.04	8.08	62.74
392	0.156	0.198	11.5	9.70	22.62	42.90	80.24
391	0.117	0.198	20.8	6.59	13.21	25.65	68.17
391	0.136	0.198	32.1	5.01	8.57	17.13	76.13
392	0.169	0.210	4.9	13.90	39.59	69.73	57.04
579	0.146	0.210	69.7	3.68	5.45	10.26	37.25
577	0.160	0.198	29.9	7.51	15.84	27.63	42.52
577	0.160	0.274	16.1	12.48	25.73	48.28	33.72
576	0.155	0.198	4.9	13.74	32.52	56.03	8.73
575	0.150	0.198	2.5	13.94	32.40	52.76	6.60
622	0.136	0.210	5.0	14.50	30.22	47.95	
620	0.130	0.210	10.4	11.11	24.32	41.53	
619	0.143	0.210	15.05	9.70	20.32	35.19	19.75
621	0.140	0.198	20.0	7.47	14.02	22.14	18.74
620	0.151	0.198	30.9	9.41	15.11	26.91	33.45
621	0.143	0.210	50.5	5.13	9.25	16.73	33.87
622	0.143	0.210	2.4	16.93	35.31	57.49	
621	0.136	0.198	7.8	12.44	22.87	39.59	

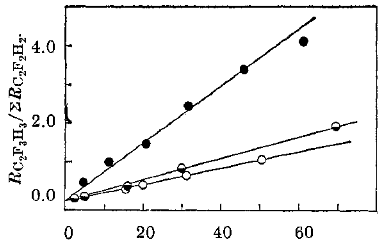

Figure 5. $R_{C_2F_3H_3}/\Sigma R_{C_2F_2H_2}$ *vs.* N_2 pressure, in mm: ●, 390–392°K; ◒, 575–579°K; ○, 619–621°K.

3.7 Å for N_2, and 5.5 Å for $CF_2HCFH_2^*$, we obtain a relative quenching efficiency of N_2 to ketone of 0.36 on a collision-for-collision basis. Similarly Giles and Whittle[11] find relative efficiencies of N_2 with CH_3COCH_3 and CF_3COCF_3 of 0.19 and 0.10, respectively, for the quenching of $CF_3CH_3^*$. These results demonstrate the "stronger" collision assumption for polyatomic and the "weaker" collision assumption for atoms and diatomic molecules.[24] Although the two fluoroethanes are formed with roughly the same energy of excitation, the two systems are not directly comparable. It should be noted that there will be a lower critical energy for HF elimination from the $CF_3CH_3^*$, as opposed to the $CF_2HCFH_2^*$ "hot" molecule.[25] Setser and Hassler[26] have also suggested that the relative N_2 quenching efficiency given by Giles and Whittle[11] is too low. In collisional quenching experiments on chemically activated $CH_2ClCH_2Cl^*$ with added N_2, they find that about 6 kcal mol^{-1} of energy is transferred per collision, whereas about 2.5 kcal mol^{-1} would more normally be expected.[24] Our data in Figure 5 support "stronger" deactivating collisions, since some curvature would be expected[15] in the plots at low pressures if "weaker" collisions were taking place.

From the data in Table VIII it can be shown that the *cis*:*trans* 1,2-difluoroethylene ratio rises gradually from the average value of 1.55 (obtained from Table IV, quoted in ref 4) with increasing N_2 pressure. The data above 50 torr are not very accurate, owing to the small amount of elimination products formed, but the experiments at 575–579°K and 619–622°K generally tend toward a *cis*:*trans* ratio of about 1.8 with increasing pressure. The effect is greater at lower temperatures and the data are presented in Figure 6, together with additional data from Table IX, for a temperature of about 391°K. It is seen that values in excess of 2.0 are obtained for the *cis*:*trans* ratio with increasing pressure.[27] With increasing ketone pressure, Table VI, the ratio also increases, the five runs giving an average value of 1.74 ± 0.15.

Our previous report on the low-pressure data (given in Table IV) showed the *cis*:*trans* ratio to be 1.55 ± 0.1 independent of temperature, indicating that $E^*_{cis} = E^*_{trans}$. (The experimental scatter could conceal a difference in the activation energies[4] of about 1 kcal mol^{-1}.) A possible explanation of the variation of the *cis*:*trans* ratio with added N_2 may be due to the fact that

---

(24) F. J. Fletcher, B. S. Rabinovitch, K. W. Watkins, and D. J. Locker, *J. Phys. Chem*, **70**, 2823 (1966).

(25) α- and β-halogenation effects have been fully discussed by A. Maccoll, *Advan. Phys. Org. Chem.*, **3**, 91 (1965); "Studies on Chemical Structure and Reactivity," Methuen, London, 1966, pp 53–72. Note also the experimental values of k_{stab}/k_{elim} for the two molecules in Table VII.

(26) D. W. Setser and J. C. Hassler, *J. Phys. Chem.*, **71**, 1364 (1967).

(27) If $E^*_{cis} = E^*_{trans}$, the *cis*:*trans* ratio would not be expected to be a function of pressure.

Table IX: Data on CF_2HCOCF_2H and CFH_2COCFH_2 Photolysis with Added N_2

Temp, °K	Reactant pressure, torr			Products, 10^7mol		
	TFA	DFA	N_2	$CF_2{=}CH_2$	*trans*-CFH=CFH	*cis*-CFH=CFH
572	0.160	0.188	11.2	1.05	2.36	3.66
570	0.160	0.199	4.9	1.34	2.74	4.91
571	0.199	0.199	20.8	1.07	1.75	3.07
571	0.199	0.199	30.8	0.88	1.26	2.59
576	0.178	0.199	50.6	0.48	0.66	1.11
393	0.178	0.199	15.8	0.99	1.69	3.07
391	0.199	0.199	4.9	1.45	3.56	5.89
392	0.199	0.199	32.3	0.53	0.70	1.61
391	0.199	0.199	44.1	0.57	0.58	1.45

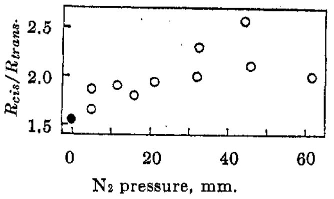

Figure 6. R_{cis}/R_{trans} for 1,2-difluoroethylenes *vs.* N_2 pressure, in mm: ○, 390–393°K: ●, average value from ref 4 (Table IV) with no N_2.

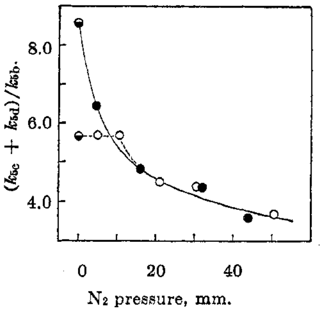

Figure 7. $(R_{cis} + R_{trans})/R_{1,1}$-for difluoroethylenes, $(k_{5c} + k_{5d})/k_{5b}$, *vs.* N_2 pressure, in mm: ●, 391–393°K; ○, 570–576°K; ◒, from published data (ref 4) with no N_2.

the initially formed 1,2-difluoroethylene is sufficiently energized that it undergoes isomerization. This process is quenched more rapidly by the addition of excess N_2, so that the *cis*:*trans* ratio approaches that value which may be expected from reaction path degeneracy considerations.[28] Alternatively, Rabinovitch and his coworkers[29] have studied the effect of pressure on the competitive unimolecular decomposition of vibrationally excited 3-hexyl radicals into 1-pentene and 1-butene. Application of these considerations[27] to the *cis*:*trans* ratios does not seem warranted until we can establish the possible extent of any *cis* ⇄ *trans* isomerization in this complex nonequilibrium system.

The ratio (*cis* + *trans*):1,1- for the difluoroethylenes, $(k_{5c} + k_{5d})/k_{5b}$, is shown as a function of N_2 pressure at two temperatures in Figure 7. The data are obtained from Table IX. The data in Table VIII show a similar

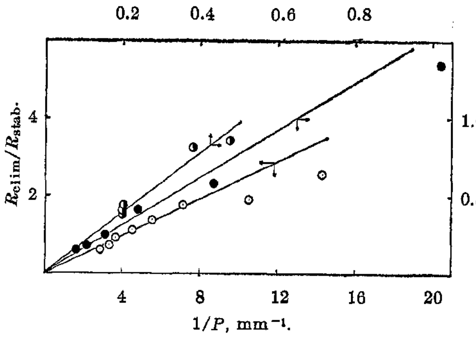

Figure 8. R_{elim}/R_{stab} *vs.* reciprocal pressure, mm^{-1}: ◑, $\Sigma R_{C_2F_2H_2}/R_{C_2F_3H_3}$ *vs.* $1/(P_{TFA} + P_{DFA})$ (390–391°K); ●, $\Sigma R_{C_2F_2H_2}/R_{C_2F_3H_3}$ *vs.* $10^2/P_{N_2}$ (390–392°K); ○, $R_{C_2F_3H}/R_{C_2F_4H_2}$ *vs.* $1/P_{TFA}$ (513–516°K).

dependence, but are scattered due to the loss of small amounts of $CF_2{=}CH_2$ in some of the experiments, see the Experimental Section. The ratio behaves similarly with increasing total ketone pressure, Table VI. Under conditions of no collisional stabilization the function $(k_{5c} + k_{5d})/k_{5b}$ shows a strong temperature dependence (shown as Figure 1 in ref 4), indicating a higher critical energy for $E^*_{1,1}$- than for E^*_{cis} and E^*_{trans}.

Equations 7 and 15 are tested in the form of R_{stab}/R_{elim} *vs.* pressure in Figures 1, 4, and 5 which demonstrates that R_{stab} approaches zero with decreasing pressure, in accord with reaction sequences 2 and 5. However a plot of R_{elim}/R_{stab} *vs.* reciprocal pressure is required[22] to demonstrate that R_{elim} approaches zero at infinite pressure, as predicted by our mechanism. Some of the data presented in Figures 1, 4, and 5 are shown in this manner in Figure 8, and the lines are arbitrarily drawn to intersect at zero. The test of reaction 2 for $C_2F_4H_2^*$ is good[30] and to within the

---

(28) The small temperature effect, if real, may reflect a temperature dependence of the deactivation efficiency of the added N_2.

(29) D. C. Tardy, B. S. Rabinovitch, and C. W. Larson, *J. Chem. Phys.*, **45**, 1163 (1966).

(30) The scatter at high $1/P$ may be due to the relatively small values of $R_{C_2F_4H_2}$ obtained at low pressures.

experimental scatter it would also appear that the test for reaction 5 for $C_2F_3H_3^*$ is valid.[31] A more critical test would be to examine $R_{1,1\text{-}}/R_{C_2F_3H_3}$ and $(R_{cis} + R_{trans})/R_{C_2F_3H_3}$ as functions of $1/P$, but such plots of our data (corresponding to those given in Figure 8 and Table VIII at 575–579°K and 619–621°K) lead to intercepts which are very close to zero in all cases.[32] It is, therefore, evident that the data depicted in Figure 7 cannot be rationalized on the basis that any appreciable amount of $CF_2{=}CH_2$ is formed in a process which does not involve elimination from a "hot" intermediate, and the "hot" molecule mechanism for the formation of all three isomers is satisfactorily established.

Our data on the total 1,2 elimination *vs.* 1,1 elimination are satisfactorily explained in terms of Rabinovitch's treatment,[29] since $E^*_{1,1\text{-}} > E^*_{1,2\text{-}}$ and the average energy of the *reacting* species increases with increasing pressure.[33]

An additional complicating consideration is provided by the fact that our data[10] on the dehydrohalogenation of the "hot" molecule $CD_3CF_2H^*$ in the presence of added quenchers indicate that the d_3-vinyl fluoride arises *only via* a "hot" molecule mechanism. The possibility, therefore, of the formation of any, or all, of the difluoroethylene isomers *via* a competing α,α elimination process from $CF_2HCFH_2^*$ cannot be ruled out at this juncture.

Acknowledgments. We thank Dr. Bernard Kirtman, Dr. R. M. Martin, and M. J. Perona for several helpful discussions.

---

(31) The data on $\Sigma R_{C_2F_2H_2}/R_{C_2F_3H_3}$ with added N_2 at 391°K may well be better represented by a small positive intercept at ~0.05, but it is apparent that a large number of runs would have to be performed (see for instance ref 22) to permit a clear-cut determination as to the existence of an intercept, or not.

(32) Similarly, so did plots of $R_{cis}/R_{C_2F_3H_3}$ and $R_{trans}/R_{C_2F_3H_3}$, although any difference in behavior of these two functions would certainly not be anticipated.

(33) The data in Figure 7 only show the ratio of the products, but the absolute amount of elimination products is, of course, reduced with increasing pressure.

Dissociation Energy of PN and Other Thermodynamic Properties for the Vaporization of P_3N_5[1a,b]

by O. Manuel Uy, Fred J. Kohl,[1c] and K. Douglas Carlson

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106 *(Received October 18, 1967)*

The chemistry of the phosphorus–nitrogen system has been the subject of a number of studies in past years. Nevertheless, some of the published data on this system are contradictory or questionable. In particular the dissociation energy of the PN molecule is uncertain and the available thermodynamic properties of the solid phases are very questionable. This article describes a mass spectrometric study of the solid–vapor equilibria in the vaporization of solid P_3N_5 to clarify some of these questions. The equilibrium vapor of P_3N_5 was found to consist of PN and N_2 with relatively minor concentrations of P_2. The $D_0°$ of PN was determined to be 7.57 ± 0.03 eV, and the heat of formation of solid P_3N_5 was found to be −230 ± 20 kcal mole^{-1}.

Introduction

Elements of the group Va nitrogen family combine among themselves to form a number of condensed phases and a wide variety of gaseous polyatomic molecules.[2,3] As a class of chemically related substances, however, these have been studied incompletely. The P–N system has been the most extensively studied of the mixed pnictides,[4–7] but the data are questionable and incomplete. This article describes a study of the solid–vapor equilibria in this system by molecular beam sampling of the vapor above solid P_3N_5 to establish a reliable value for the dissociation energy of the PN molecule and to clarify certain questionable thermodynamic data for the solid phase.

The known molecules of nitrogen and phosphorus are

---

(1) (a) Research sponsored by the U. S. Army Research Office (Durham), Department of the Army, Contract No. DA-31-124-ARO-D-304. (b) Based in part on the Ph.D. Thesis submitted by O. M. Uy to Case Institute of Technology, Cleveland, Ohio, 1967. (c) National Aeronautics and Space Administration Predoctoral Fellow.

(2) K. D. Carlson, F. J. Kohl, and O. M. Uy in "Applications of Mass Spectrometry in Inorganic Chemistry," Advances in Chemistry Series, American Chemical Society, Washington, D. C., in press.