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**KINETICS OF C<sub>2</sub>F<sub>4</sub> DISSOCIATION IN NITROGEN SHOCKS**

Prepared by

A. P. Modica and J. E. LaGraff

AVCO CORPORATION  
AVCO SPACE SYSTEMS DIVISION  
RESEARCH AND TECHNOLOGY LABORATORIES  
Wilmington, Massachusetts

for

AVCO EVERETT RESEARCH LABORATORY  
A DIVISION OF  
AVCO CORPORATION  
Everett, Massachusetts

AVSSD-0185-66-CR  
Contract DA-01-021-AMC-12005 (Z)

1 September 1966

Supported by

ADVANCED RESEARCH PROJECTS AGENCY  
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ARMY MISSILE COMMAND  
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This document consists of 21 pages,  
148 copies, Series A

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## FOREWORD

This report represents work performed by the Research and Technology Laboratories of the Avco Corporation Space Systems Division, 201 Lowell Street, Wilmington, Massachusetts, for the Avco Everett Research Laboratory, Everett, Massachusetts, supported by the Advanced Research Projects Agency monitored by the Army Missile Command, United States Army, Redstone Arsenal, Alabama, under Contract No. DA-01-021-AMC-12005 (Z) (part of Project DEFENDER).

### ABSTRACT

A kinetic study of the tetrafluoroethylene-difluorocarbene radical reaction was conducted in excess nitrogen behind incident shock waves over the temperature range from 1200 to 1600° K at total gas concentration around  $1.25 \times 10^{-5}$  mole/cc. The rate of formation of  $CF_2$  was observed spectrophotometrically and is reproduced by the rate law:

$$\frac{1/2 d [CF_2]}{dt} = k_f [N_2] [C_2F_4] - k_r [N_2] [CF_2] [CF_2]$$

with

$$k_f^{N_2} = (4.08 \pm 0.72) 10^{40} T^{-6.36 \pm 0.55} e^{\frac{-74900 \pm 3000}{RT}}$$

cc/mole-sec

and

$$k_r^{N_2} = (2.05 \pm 0.47) 10^{38} T^{-6.36 \pm 0.55} e^{\frac{-1840 \pm 263}{RT}}$$

cc<sup>2</sup>/mole<sup>2</sup> sec

Comparisons between the tetrafluoroethylene-difluorocarbene thermal equilibrium constants in  $N_2$  and Ar shocks indicate that  $N_2$  is vibrationally unrelaxed during chemical relaxation. The temperature determined from the chemical equilibrium constant and the time to reach 0.98 chemical equilibrium after shock compression are used to calculate the  $N_2$  relaxation time. The results show that  $N_2$  vibrational relaxation in the 1:00 tetrafluoroethylene-nitrogen mixture is about 10 to 50 times faster than in pure nitrogen.

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## I. INTRODUCTION

A shock tube kinetic study of the thermal dissociation of tetrafluorethylene in argon diluent was reported earlier.<sup>1</sup> Equilibrium and second-order rate constants for the reversible reaction



were determined by employing a spectrophotometric technique to monitor the production of  $\text{CF}_2$  radicals in absorption at 2536A. A similar kinetic investigation of the  $\text{C}_2\text{F}_4$  dissociation has been carried out in excess nitrogen in order to assess its collision efficiency as a second body. It was of interest also to note the effect of  $\text{C}_2\text{F}_4$  impurity on the vibrational relaxation of nitrogen molecules. Calculations had shown that over the temperature range of this study and near one atmosphere total pressure the  $\text{C}_2\text{F}_4$  chemical relaxation would be about 100 to 1000 times faster than vibrational relaxation of pure  $\text{N}_2$ . Hence, the measured  $\text{C}_2\text{F}_4$  equilibrium constant was used to obtain the temperature behind the shock wave, after a known time, to estimate the  $\text{N}_2$  vibrational relaxation time.

## II. EXPERIMENTAL

The shock-tube and optical absorption-spectroscopy apparatus used in these experiments was identical to the setup described in Reference 1. The concentration of  $\text{CF}_2$  radicals generated behind the shock wave was determined from Beer's law according to the expression

$$\begin{aligned} I/I_0 &= \exp(-\epsilon L [\text{CF}_2]) \\ &= \exp(-2\epsilon L a \rho_{21} [\text{C}_2\text{F}_4]_1) \end{aligned} \quad (1)$$

where  $I_0$  and  $I$  are the incident and transmitted light intensity;  $\epsilon$  is the molar extinction coefficient in cubic centimeter per mole-centimeter;  $L = 3.91$  centimeters, the path length of light through the shock tube;  $a$  is the degree of  $\text{C}_2\text{F}_4$  dissociation;  $\rho_{21}$  is the density ratio across the shock; and  $[\text{C}_2\text{F}_4]_1$  is the concentration ahead of the shock front. Measurements of the  $\text{CF}_2$  radical UV absorption were made at 2536A where  $\epsilon$  was taken to be  $(1.25 \pm 0.10)10^6$  cc/mole-cm over the temperature interval 1200° to 1600°K.<sup>2</sup> A general profile of the  $\text{CF}_2$  absorption behind a nitrogen shock wave is indicated by the oscillogram record in Figure 1. It is observed that after chemical relaxation, the  $\text{CF}_2$  equilibrium absorption appears to overshoot slightly at first, and then to decay gradually later on. The effect here is attributed to the  $\text{C}_2\text{F}_4$  equilibrium following the decrease in temperature behind the shock wave as the  $\text{N}_2$  molecules vibrationally relax. This behavior was not observed behind similar shocks in argon.

The shock conditions of temperature and density ratio were calculated from the Rankine-Hugoniot equations with the incident shock velocity and the state of the gas ahead of the shock, and as a function of the degree of  $\text{C}_2\text{F}_4$  dissociation behind the shock wave.<sup>3</sup> The dissociation energy of  $\text{C}_2\text{F}_4$  was taken to be 74.9 kcal/mole (Reference 1) so that the temperature drop behind the shock wave due to complete dissociation was 100°K for the 1:100 (mole ratio)  $\text{C}_2\text{F}_4$ - $\text{N}_2$  mixtures used. For the same degree of dissociation, the difference in temperature between vibrationally unrelaxed and relaxed  $\text{N}_2$  shocks was about 70°K. Attenuation of shock velocity under conditions of interest amounted to a decrease of  $0.22 \pm 0.08$  percent per 20 cm length of tube, which introduced at most a 5°K uncertainty in the analyzed data.

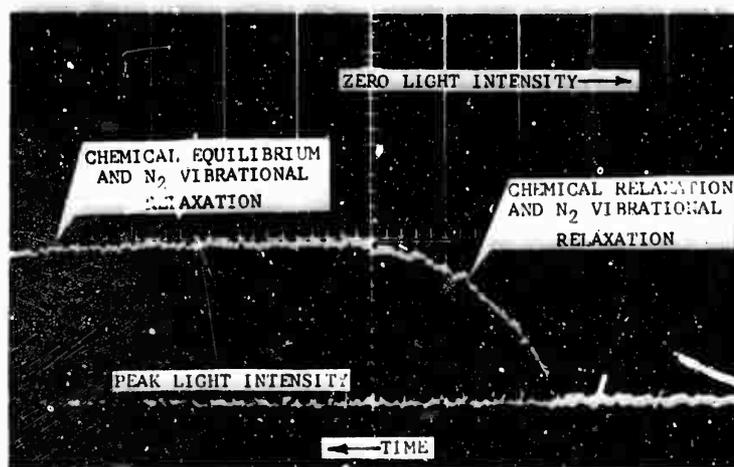


Figure 1 UV ABSORPTION PROFILE OF  $CF_2$  RADICAL BEHIND INCIDENT SHOCK WAVE INTO 1:100  $C_2F_4-N_2$  GAS MIXTURE.  $P_1 = 5.0$  CM HG.  $U_s = 1.472$  mm/ $\mu$ SEC.  $T_2$  (UNRELAXED  $N_2$ ) = 1290°K. WRITING SPEED = 20  $\mu$ SEC/CM

### III. N<sub>2</sub> VIBRATIONAL RELAXATION

Vibrational relaxation of molecules in gas mixtures involves energy to be exchanged between translational-vibrational and vibrational-vibrational degrees of freedom. Most polyatomic molecules with many vibrational modes usually exhibit short relaxation times of less than one microsecond at pressures around one atmosphere.<sup>4</sup> This behavior is attributed to the efficient transfer of translational energy to the low-frequency vibrational states followed by rapid internal distribution to the other modes of the molecule. For binary gas mixtures where near-resonant and resonant vibrational-vibrational exchange occurs, it is found that the faster relaxing molecule goes first to some fraction of its final equilibrium energy and then proceeds to equilibrium at the same relaxation time with the slower relaxing molecule.<sup>5, 6</sup>

In reference to the vibrational relaxation of a dissociated C<sub>2</sub>F<sub>4</sub>-N<sub>2</sub> gas mixture, the vibrational relaxation time of C<sub>2</sub>F<sub>4</sub> (0.014 microsecond at 373°K and one atmosphere)<sup>4</sup> is about 10<sup>5</sup> times smaller than that of pure nitrogen. A comparison of the vibrational frequencies of the CF<sub>2</sub> radical<sup>7</sup> (668, 1102, 1222 cm<sup>-1</sup>) with that of N<sub>2</sub> (2330 cm<sup>-1</sup>) tends to suggest a shorter relaxation time for CF<sub>2</sub>. If it is assumed that behind a shock wave the C<sub>2</sub>F<sub>4</sub> and CF<sub>2</sub> molecules are in vibrational equilibrium at the local translational temperature and that N<sub>2</sub> is the slowest vibrationally relaxing component, the change in translational temperature due to N<sub>2</sub> vibrational excitation is approximately given by<sup>8</sup>

$$\frac{T - T_f}{T_o - T_f} = e^{-t/r_{eff}} \quad (2)$$

where subscripts o and f refer to the shocked translational temperature before vibrational relaxation and at equilibrium.  $r_{eff}$  is the effective N<sub>2</sub> relaxation time. The temperature dependences of the vibrational relaxation time of pure N<sub>2</sub> and the dissociation rate of C<sub>2</sub>F<sub>4</sub> indicate that chemical relaxation is between two and three orders-of-magnitude faster than pure N<sub>2</sub> vibrational relaxation for the temperature range of this study. Thus, in calculating the effective vibrational relaxation time, the initial and final translational temperatures are taken to be those of the chemically relaxed gas. A time corresponding to 0.98 chemical equilibrium of each run is used as a standard period at which to evaluate the equilibrium constant. With the measured C<sub>2</sub>F<sub>4</sub> equilibrium constant (Figure 2) and the equilibrium data of Reference 1, the translational temperature of the gas is determined. The experimental results are plotted in Figure 3 with the respective chemical relaxation times of the C<sub>2</sub>F<sub>4</sub> dissociation reaction, and are compared to N<sub>2</sub> relaxation times in pure nitrogen.<sup>5</sup>

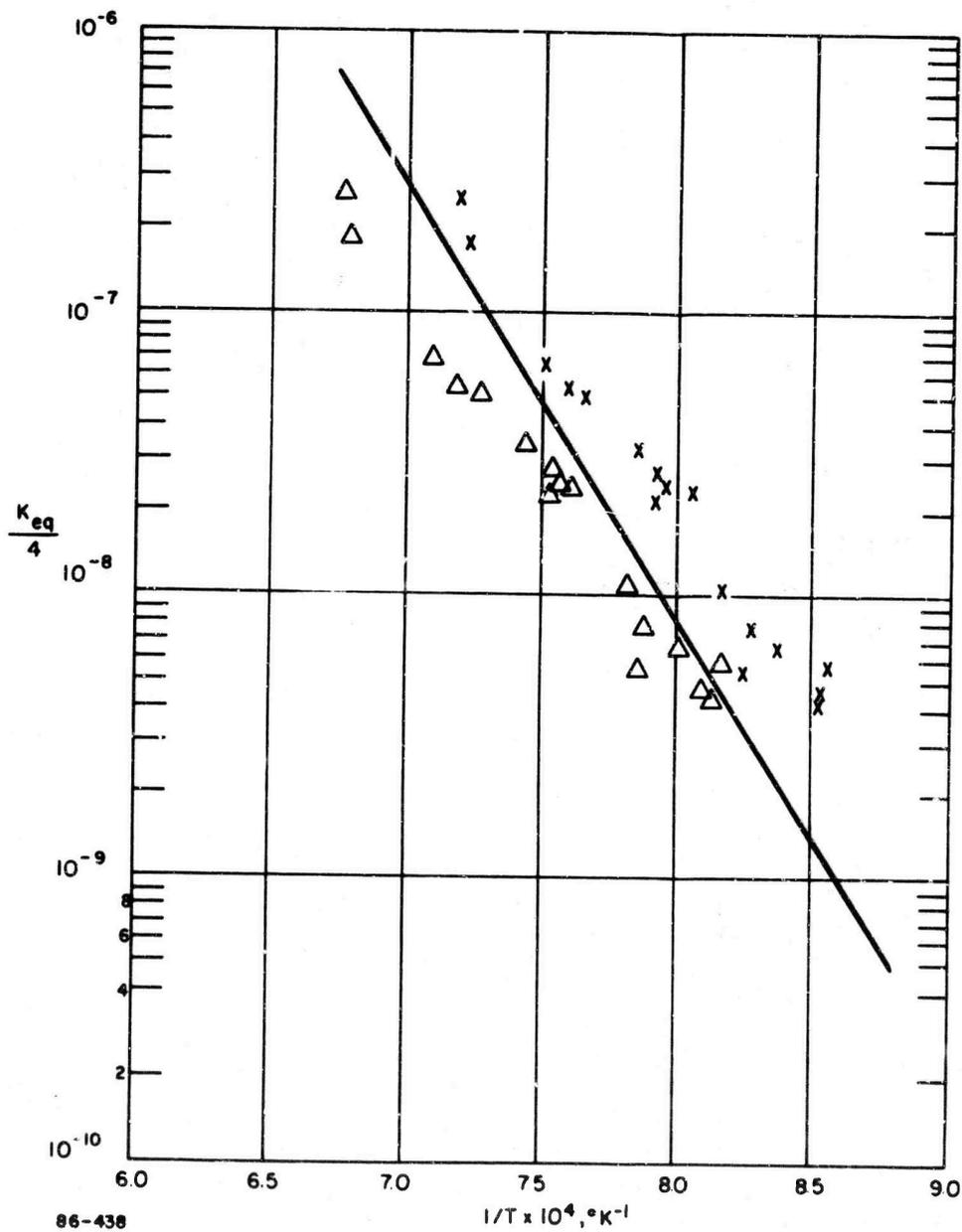
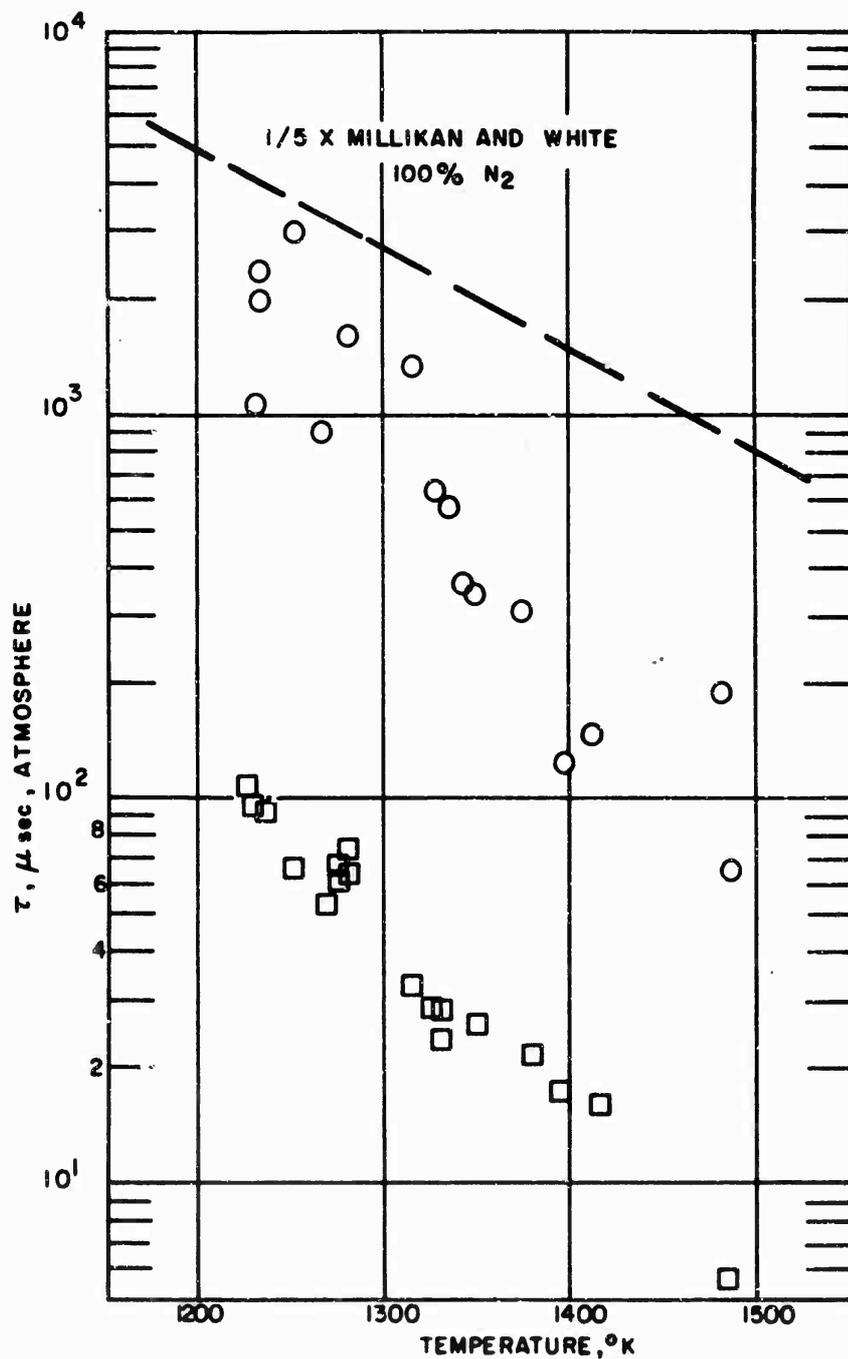


Figure 2  $C_2F_4$  THERMAL EQUILIBRIUM BEHIND  $N_2$  SHOCK WAVES.  $\Delta$ , VIBRATIONALLY UNRELAXED  $N_2$ . X, RELAXED  $N_2$  DATA. SOLID LINE IS  $\text{LOG } K_c = -69432/2.303RT + 4.62$  ( $K_c$  IN MOLE/CC) FROM LEAST-SQUARES FIT OF  $C_2F_4$  EQUILIBRIUM CONSTANTS IN AR SHOCKS



26-2534

Figure 3 COMPARISON OF VIBRATIONAL RELAXATION TIME OF N<sub>2</sub> IN 1:100 C<sub>2</sub>F<sub>4</sub>-N<sub>2</sub> MIXTURE AND PURE N<sub>2</sub> AT A TOTAL PRESSURE OF ONE ATMOSPHERE.  
 O, EXPERIMENTAL N<sub>2</sub> VIBRATIONAL RELAXATION TIME FROM C<sub>2</sub>F<sub>4</sub> EQUILIBRIUM CONSTANTS. □, EXPERIMENTAL C<sub>2</sub>F<sub>4</sub> CHEMICAL RELAXATION TIMES

#### IV. C<sub>2</sub>F<sub>4</sub> DISSOCIATION KINETICS

The thermal dissociation of C<sub>2</sub>F<sub>4</sub> in N<sub>2</sub> is described by the rate expression for the forward and reverse processes

$$\frac{-d[C_2F_4]}{dt} = \frac{1}{2} \frac{d[CF_2]}{dt} = k_f [N_2] [C_2F_4] - k_r [N_2] [CF_2] [CF_2] \quad (3)$$

or in terms of the degree of dissociation

$$\frac{da}{dt} = k_f [N_2] (1 - a) - 4k_f/K_{eq} ([N_2] [C_2F_4]_0 a^2) \quad (4)$$

where the reverse rate constant  $k_r$  has been replaced by the ratio  $k_f/K_{eq}$  and  $[C_2F_4]_0$  is the concentration behind the shock wave prior to dissociation.

The experimental values of  $a$  were determined from the oscillogram records by means of Equation (1) and the shock-tube performance data. An analysis of the initial slope yielded  $k_f$ , and the CF<sub>2</sub> equilibrium absorption gave  $K_{eq}$ . To compute the kinetic profile of  $a$  behind the shock wave, Equation (6) was integrated and solved on an IBM 7094 machine with the empirical values of  $k_f$  and  $K_{eq}$ . The coincidence between the experimental values of  $a$  and the calculated profile (Figure 4) is considered to be further evidence in support of the proposed rate law and dissociation mechanism.

The results of the equilibrium and forward rate constants from the present experiments are compiled in Tables I and II. The forward rate constants are plotted against reciprocal temperature in Figure 5 and are least squares fitted by the function

$$k_f^{N_2} = (4.08 \pm 0.72) 10^{40} T^{-6.36 \pm 0.55} e^{\frac{-74900 \pm 3000}{RT}} \quad (5)$$

cc/mole sec,

taking the minimum dissociation energy to be  $74.9 \pm 3.0$  kcal/mole. The forward rate constants in N<sub>2</sub> are found to be about  $1.3 \pm 0.1$  times higher than the ones in Ar. A least-squares fit of  $k_f/K_{eq} = k_r$  (Figure 6), with the collisional temperature dependence  $T^{-6.36 \pm 0.55}$  of Equation (5) gives

$$k_r^{N_2} = (2.05 \pm 0.47) 10^{38} T^{-6.36 \pm 0.55} e^{\frac{-1840 \pm 263}{RT}} \quad (6)$$

cc<sup>2</sup>/mole<sup>2</sup> sec

for the reverse rate constant. The standard deviation of the pre-term indicates the scatter of experimental points from the fit values.

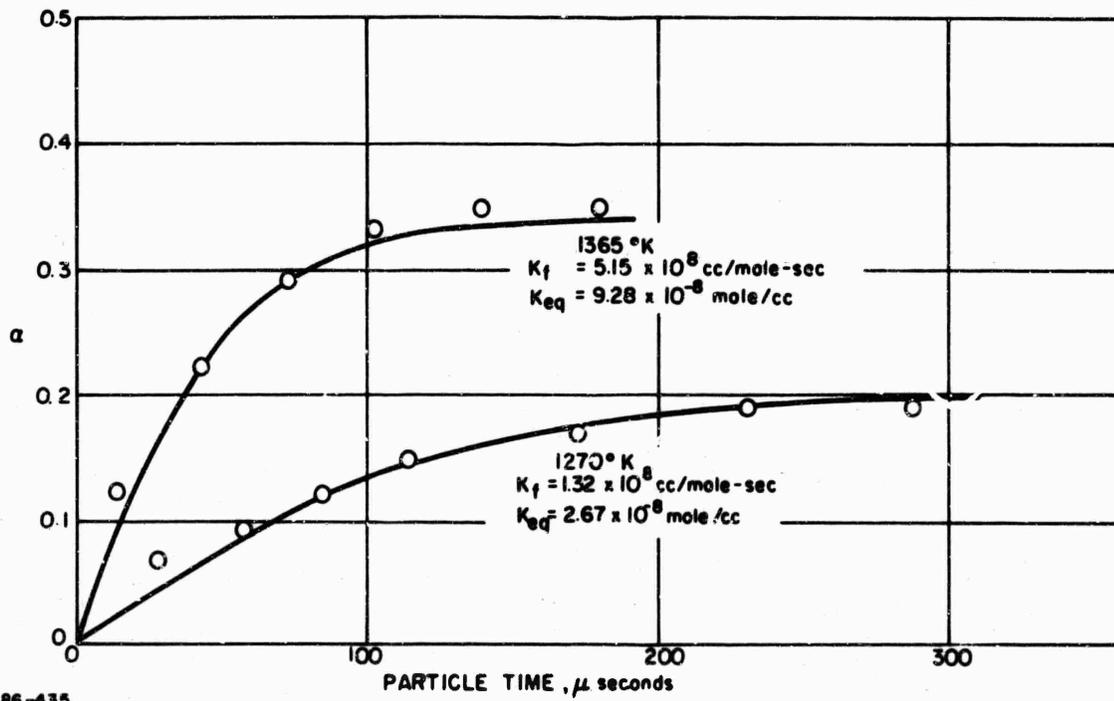
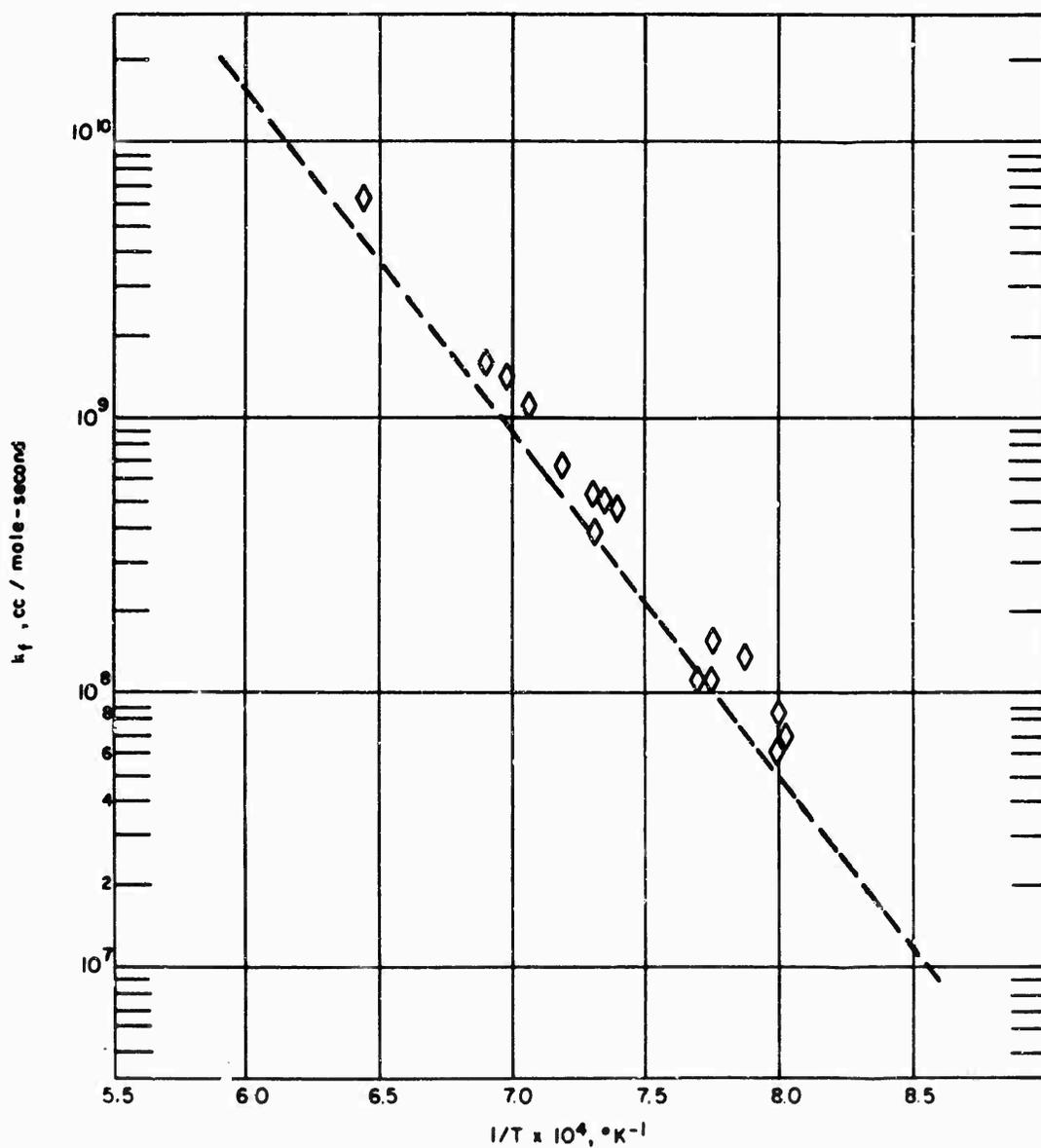


Figure 4 DETAILED ANALYSIS OF  $C_2F_4$  DISSOCIATION BEHIND SHOCK WAVES.  
 ○, EXPERIMENTAL POINTS. SOLID LINE IS CALCULATED CURVE



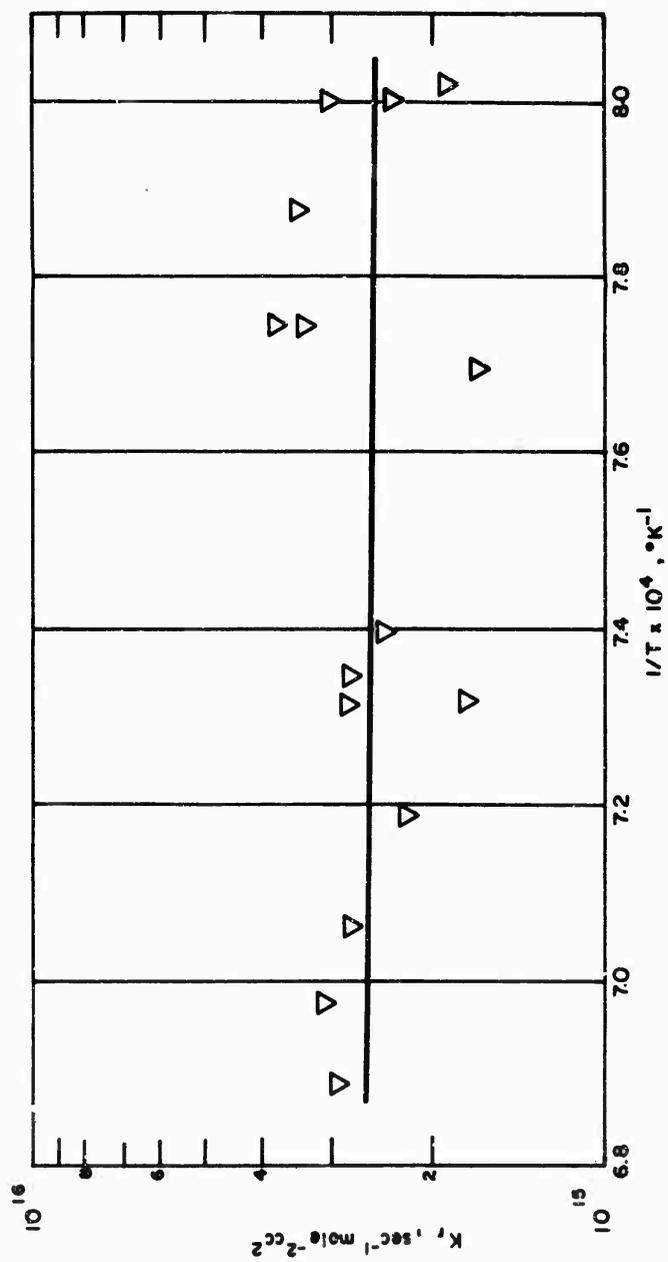
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Figure 5 SECOND-ORDER RATE CONSTANTS FOR  $\text{C}_2\text{F}_4$  DISSOCIATION IN EXCESS  $\text{N}_2$ . BROKEN LINE IS

$$k_f^{\text{Ar}} = 3.96 \times 10^{39} T^{-6.08} \exp(-74900/RT)$$

cc/mole-sec

FROM ARGON KINETIC DATA



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Figure 6 CF<sub>2</sub> RADICAL RECOMBINATION RATE CONSTANTS IN EXCESS N<sub>2</sub>

TABLE 1

C<sub>2</sub>F<sub>4</sub> DISSOCIATION IN 1:1.00 C<sub>2</sub>F<sub>4</sub>-N<sub>2</sub> GAS MIXTURES BEHIND INCIDENT SHOCK WAVES\*

Run No.	U <sub>s</sub> (mm/μsec)	T <sub>2</sub> (°K)	p <sub>21</sub>	Total Shocked Gas Conc'n (mole/cc)10 <sup>5</sup>	N <sub>2</sub> k <sub>f</sub> (cc/mole sec)
1	1.435	1245	4.77	1.29	6.94x10 <sup>7</sup>
2	1.440	1250	4.78	1.28	8.02x10 <sup>7</sup>
3	1.441	1250	4.78	1.29	6.05x10 <sup>7</sup>
4	1.455	1270	4.80	1.29	1.32x10 <sup>8</sup>
5	1.468	1290	4.82	1.29	1.53x10 <sup>8</sup>
6	1.472	1290	4.83	1.30	1.07x10 <sup>8</sup>
7	1.481	1300	4.84	1.30	1.07x10 <sup>8</sup>
8	1.511	1350	4.88	1.31	4.66x10 <sup>8</sup>
9	1.521	1360	4.90	1.32	4.90x10 <sup>8</sup>
10	1.527	1365	4.90	1.32	3.74x10 <sup>8</sup>
11	1.527	1365	4.90	1.32	5.15x10 <sup>8</sup>
12	1.539	1390	4.92	1.20	6.50x10 <sup>8</sup>
13	1.562	1415	4.94	1.07	1.07x10 <sup>9</sup>
14	1.573	1430	4.95	1.07	1.32x10 <sup>9</sup>
15	1.588	1455	4.98	1.08	1.54x10 <sup>9</sup>
16	1.650	1550	5.04	0.815	6.33x10 <sup>9</sup>

\*Vibrationally unrelaxed N<sub>2</sub>.

TABLE II  
 $C_2F_4-CF_2$  THERMAL EQUILIBRIUM  
 BEHIND  $N_2$  SHOCK WAVES\*

Run No.	$T_{2eq}$ (°K)	$a_{eq}$	$(C_2F_4)_{eq}$ (mole/cc) $10^7$	$K_{eq}/4$ (mole/cc)
1	1225	0.193	1.30	$5.96 \times 10^{-9}$
2	1230	0.171	1.29	$4.57 \times 10^{-9}$
3	1235	0.175	1.30	$4.81 \times 10^{-9}$
4	1250	0.204	1.30	$6.62 \times 10^{-9}$
5	1270	0.220	1.30	$8.10 \times 10^{-9}$
6	1275	0.197	1.31	$5.55 \times 10^{-9}$
7	1280	0.252	1.31	$1.12 \times 10^{-8}$
8	1315	0.349	1.34	$2.54 \times 10^{-8}$
9	1325	1.352	1.34	$2.63 \times 10^{-8}$
10	1330	0.367	1.34	$2.89 \times 10^{-8}$
11	1330	0.341	1.34	$2.32 \times 10^{-8}$
12	1350	0.413	1.23	$3.55 \times 10^{-8}$
13	1380	0.472	1.10	$5.45 \times 10^{-8}$
14	1395	0.506	1.11	$5.76 \times 10^{-8}$
15	1415	0.544	1.11	$7.20 \times 10^{-8}$
16	1480	0.750	0.855	$1.93 \times 10^{-7}$
17	1485	0.804	0.855	$2.82 \times 10^{-7}$

\*Vibrationally unrelaxed  $N_2$ .

## V. DISCUSSION

The presence of a small quantity of  $C_2F_4$  in excess  $N_2$  appears to enhance the vibrational relaxation of  $N_2$  molecules. The apparent  $N_2$  vibrational relaxation time was obtained on the assumption that the  $C_2F_4$  and  $CF_2$  molecules were in vibrational equilibrium with the translational gas temperature so that the measured chemical equilibrium constant could be used as a temperature indicator during  $N_2$  vibrational relaxation. Since the vibrational histories of  $C_2F_4$  and  $CF_2$  were not measured in the experiment, the present data does not permit an estimation of the relative importance of the translational-vibrational and vibrational-vibrational exchange processes between  $N_2$  molecules and  $C_2F_4$  or  $CF_2$ . However, it may be pointed out that near-resonance vibrational-vibrational exchange between  $N_2$  and  $C_2F_4$  may be possible because of the  $C_2F_4$  vibrational frequency<sup>9</sup> at  $1872\text{ cm}^{-1}$ . This behavior suggests itself in view of the near-resonance vibrational-vibrational coupling exhibited by  $N_2$  and  $NO$  whose fundamental frequency is  $1876\text{ cm}^{-1}$ . More importantly, it is noticed from Figure 3 that the apparent  $N_2$  relaxation time appears to have nearly the same temperature dependence as the chemical relaxation time for  $CF_2$  formation. This observation tends to suggest near-resonance vibrational coupling between  $CF_2$  and  $N_2$  in which exchange a 2-quantum jump process would be required. For the mixture, the apparent probability per collision of vibrational energy transfer between  $C_2F_4$  ( $\approx 0.5$  dissociated) and  $N_2$  is calculated to be  $4.28 \times 10^{-5}$  at  $1350^\circ\text{K}$  as compared to  $5.86 \times 10^{-8}$  for pure  $N_2$ . The collision frequency of  $N_2$  with both  $C_2F_4$  and  $CF_2$  was taken to be the same.

In regard to the  $C_2F_4$  dissociation kinetics, the average of the ratio of the forward rate constants in  $N_2$  and Ar diluent  $k_{f,N_2}/k_{f,Ar}$  is  $1.3 \pm 0.1$  which may be compared to the value  $1.49 \pm 0.07$  found by Volpe and Johnston<sup>10</sup> for the unimolecular decomposition of  $NO_2Cl$ , and the value 1.7 given by Johnston<sup>11</sup> for the decomposition of  $N_2O_5$ . The ratio of the relative velocities of approach of  $N_2$  and Ar in the  $C_2F_4$  dissociation is calculated to be 1.23. Analysis of the pre-exponential coefficients in terms of classical collision theory,<sup>12</sup> shows that the steric factor for Ar ( $P_{Ar} = 0.62$ ) is slightly higher than that for  $N_2$  ( $P_{N_2} = 0.47$ ). The collision diameter of  $C_2F_4$  was taken to be  $5.8\text{\AA}$  (Reference 1) and those of  $N_2$  and Ar,  $3.75\text{\AA}$  and  $3.4\text{\AA}$  respectively.

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DOCUMENT CONTROL DATA - R&D		
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1. ORIGINATING ACTIVITY (Corporate author) Avco Corporation Avco Space Systems Division Research and Technology Laboratories Wilmington, Massachusetts		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP
3. REPORT TITLE Kinetics of C <sub>2</sub> F <sub>4</sub> Dissociation in Nitrogen Shocks		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Research Report		
5. AUTHOR(S) (Last name, first name, initial) Modica, A. P. LaGraff, J. E.		
6. REPORT DATE 1 September 1966	7a. TOTAL NO. OF PAGES 21	7b. NO. OF REFS 12
8a. CONTRACT OR GRANT NO. DA-01-021-AMC-12005 (Z)	8b. ORIGINATOR'S REPORT NUMBER(S) AVSSD-0185-66-CR	
a. PROJECT NO. DEFENDER		
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.		
10. AVAILABILITY/LIMITATION NOTICES Qualified requesters may obtain copies of this report from DDC		
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY ARPA
13. ABSTRACT		
ABSTRACT		
<p>A kinetic study of the tetrafluoroethylene-difluorocarbene radical reaction was conducted in excess nitrogen behind incident shock waves over the temperature range from 1200 to 1600° K at total gas concentration around 1.25 x 10<sup>-5</sup> mole/cc. The rate of formation of CF<sub>2</sub> was observed spectrophotometrically and is reproduced by the rate law:</p> $\frac{1}{2} \frac{d[CF_2]}{dt} = k_f [N_2] [C_2F_4] - k_r [N_2] [CF_2] [C_2F_4]$ <p>with</p> $k_f^{N_2} = (4.08 \pm 0.72) 10^{10} T^{-6.36 \pm 0.55} e^{-\frac{7400 \pm 3000}{RT}}$ <p>cc mole-sec</p> <p>and</p> $k_r^{N_2} = (2.05 \pm 0.47) 10^{14} T^{-6.36 \pm 0.55} e^{-\frac{1840 \pm 263}{RT}}$ <p>cc<sup>2</sup> mole<sup>2</sup> sec</p> <p>Comparisons between the tetrafluoroethylene-difluorocarbene thermal equilibrium constants in N<sub>2</sub> and Ar shocks indicate that N<sub>2</sub> is vibrationally unrelaxed during chemical relaxation. The temperature determined from the chemical equilibrium constant and the time to reach 0.98 chemical equilibrium after shock compression are used to calculate the N<sub>2</sub> relaxation time. The results show that N<sub>2</sub> vibrational relaxation in the 1.00 tetrafluoroethylene-nitrogen mixture is about 10 to 50 times faster than in pure nitrogen.</p>		

DD FORM 1 JAN 64 1473

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1c. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
I. Kinetics of $C_2F_4$						
II. Nitrogen Shocks						
III. $N_2$ Vibrational Relaxation						

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