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KINETICS OF C_2F_4 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)

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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 1.25×10^{-5} mole/cc. The rate of formation of CF_2 was observed spectrophotometrically and is reproduced by the rate law:

$$\frac{1/2 d[\text{CF}_2]}{dt} = k_f [\text{N}_2] [\text{C}_2\text{F}_4] - k_r [\text{N}_2] [\text{CF}_2] [\text{CF}_2]$$

with

$$k_f^{\text{N}_2} = (4.08 \pm 0.72) 10^{40} T^{-6.36 \pm 0.55} e^{\frac{-74900 \pm 3000}{RT}}$$

cc/mole-sec

and

$$k_r^{\text{N}_2} = (2.05 \pm 0.47) 10^{38} T^{-6.36 \pm 0.55} e^{\frac{-1840 \pm 263}{RT}}$$

cc²/mole² 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.¹ Equilibrium and second-order rate constants for the reversible reaction



were determined by employing a spectrophotometric technique to monitor the production of CF_2 radicals in absorption at 2536Å. A similar kinetic investigation of the C_2F_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 C_2F_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 C_2F_4 chemical relaxation would be about 100 to 1000 times faster than vibrational relaxation of pure N_2 . Hence, the measured C_2F_4 equilibrium constant was used to obtain the temperature behind the shock wave, after a known time, to estimate the 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 CF_2 radicals generated behind the shock wave was determined from Beer's law according to the expression

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

where I_0 and I are the incident and transmitted light intensity; ϵ is the molar extinction coefficient in cubic centimeter per mole-centimeter; $L = 3.91$ centimeters, the path length of light through the shock tube; α is the degree of C_2F_4 dissociation; ρ_{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 CF_2 radical UV absorption were made at 2536Å where ϵ was taken to be $(1.25 \pm 0.10)10^6$ cc/mole-cm over the temperature interval 1200° to 1600°K.² A general profile of the 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 CF_2 equilibrium absorption appears to overshoot slightly at first, and then to decay gradually later on. The effect here is attributed to the C_2F_4 equilibrium following the decrease in temperature behind the shock wave as the 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 C_2F_4 dissociation behind the shock wave.³ The dissociation energy of C_2F_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) C_2F_4 - N_2 mixtures used. For the same degree of dissociation, the difference in temperature between vibrationally unrelaxed and relaxed N_2 shocks was about 70°K. Attenuation of shock velocity under conditions of interest amounted to a decrease of 0.22 ± 0.08 percent per 20 cm length of tube, which introduced at most a 5°K uncertainty in the analyzed data.

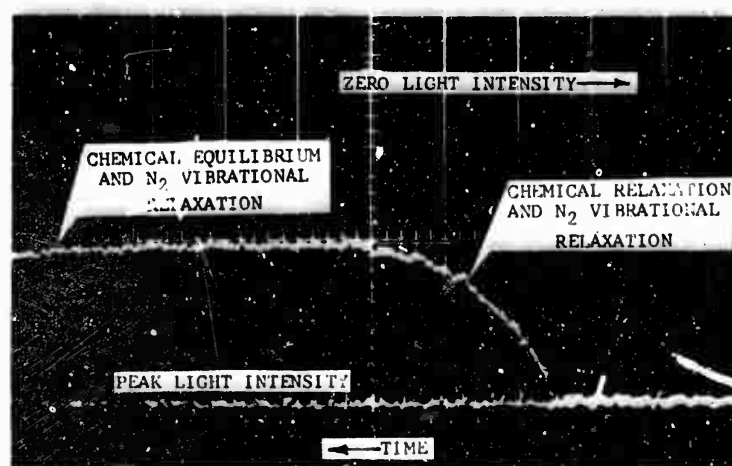


Figure 1 UV ABSORPTION PROFILE OF CF_2 RADICAL BEHIND INCIDENT SHOCK WAVE INTO 1:160 C_2F_4 - N_2 GAS MIXTURE. $P_1 = 5.0$ CM HG. $U_s = 1.472$ mm/ μ SEC. T_2 (UNRELAXED N_2) = 1290°K. WRITING SPEED = 20 μ SEC/CM

III. N₂ 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.⁴ 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.^{5, 6}

In reference to the vibrational relaxation of a dissociated C₂F₄-N₂ gas mixture, the vibrational relaxation time of C₂F₄ (0.014 microsecond at 373°K and one atmosphere)⁴ is about 10⁵ times smaller than that of pure nitrogen. A comparison of the vibrational frequencies of the CF₂ radical⁷ (668, 1102, 1222 cm⁻¹) with that of N₂ (2330 cm⁻¹) tends to suggest a shorter relaxation time for CF₂. If it is assumed that behind a shock wave the C₂F₄ and CF₂ molecules are in vibrational equilibrium at the local translational temperature and that N₂ is the slowest vibrationally relaxing component, the change in translational temperature due to N₂ vibrational excitation is approximately given by⁸

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

where subscripts o and f refer to the shocked translational temperature before vibrational relaxation and at equilibrium. τ_{eff} is the effective N₂ relaxation time. The temperature dependences of the vibrational relaxation time of pure N₂ and the dissociation rate of C₂F₄ indicate that chemical relaxation is between two and three orders-of-magnitude faster than pure N₂ 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 C₂F₄ 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 C₂F₄ dissociation reaction, and are compared to N₂ relaxation times in pure nitrogen.⁵

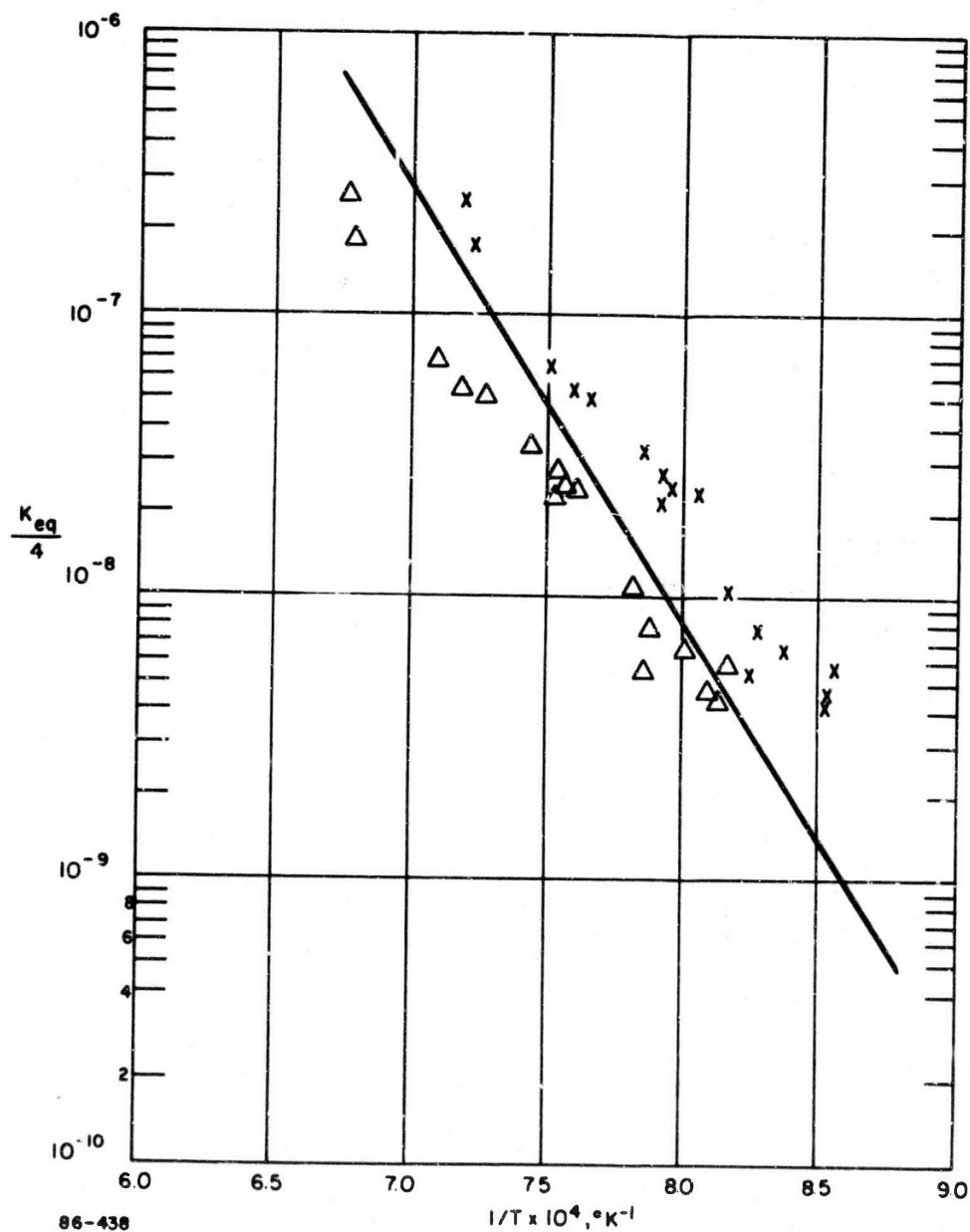
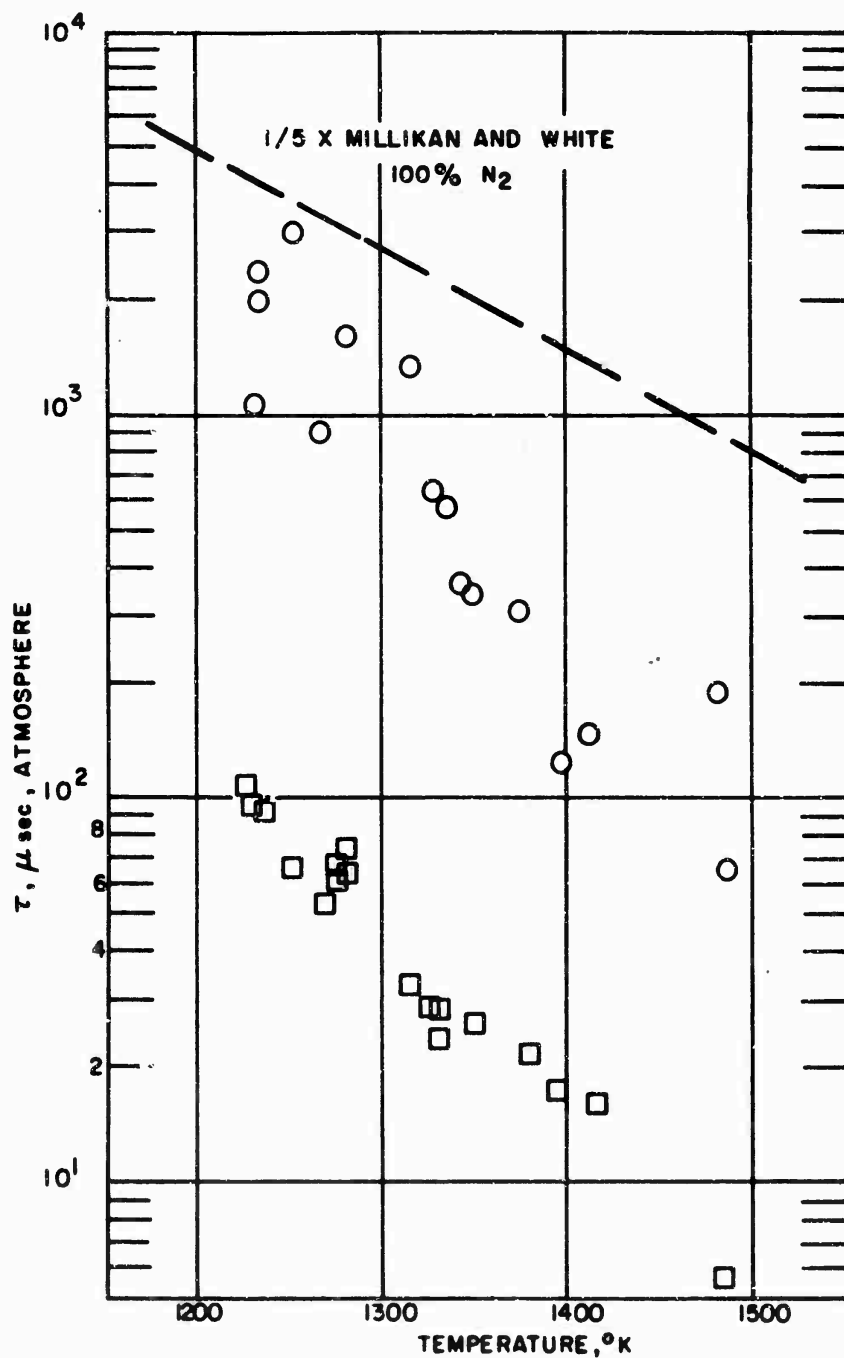


Figure 2 C_2F_4 THERMAL EQUILIBRIUM BEHIND N_2 SHOCK WAVES. Δ , VIBRATIONALLY UNRELAXED N_2 . x , RELAXED N_2 DATA. SOLID LINE IS $\log K_c = -69432/2.303RT + 4.62$ (K_c IN MOLE/CC) FROM LEAST-SQUARES FIT OF C_2F_4 EQUILIBRIUM CONSTANTS IN AR SHOCKS



26-2534

Figure 3 COMPARISON OF VIBRATIONAL RELAXATION TIME OF N₂ IN 1:100 C₂F₄-N₂ MIXTURE AND PURE N₂ AT A TOTAL PRESSURE OF ONE ATMOSPHERE.

○, EXPERIMENTAL N₂ VIBRATIONAL RELAXATION TIME FROM C₂F₄ EQUILIBRIUM CONSTANTS. □, EXPERIMENTAL C₂F₄ CHEMICAL RELAXATION TIMES

IV. C_2F_4 DISSOCIATION KINETICS

The thermal dissociation of C_2F_4 in N_2 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_2 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 ± 3.0 kcal/mole. The forward rate constants in N_2 are found to be about 1.3 ± 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

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

cc²/mole² sec

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

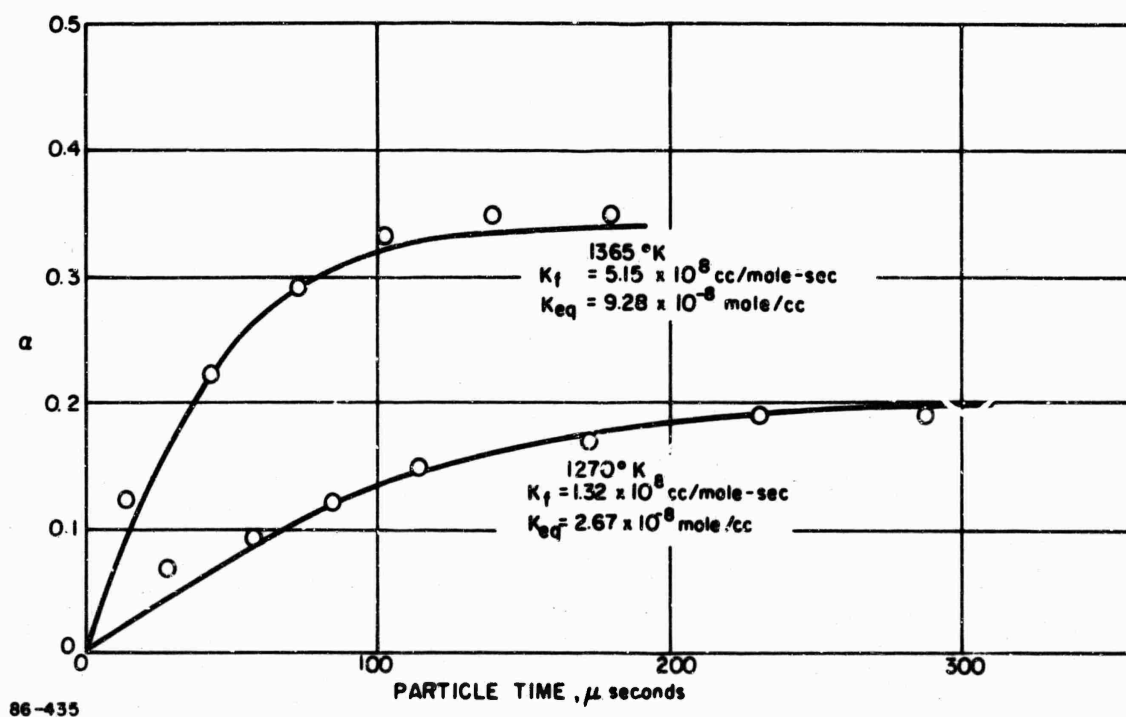
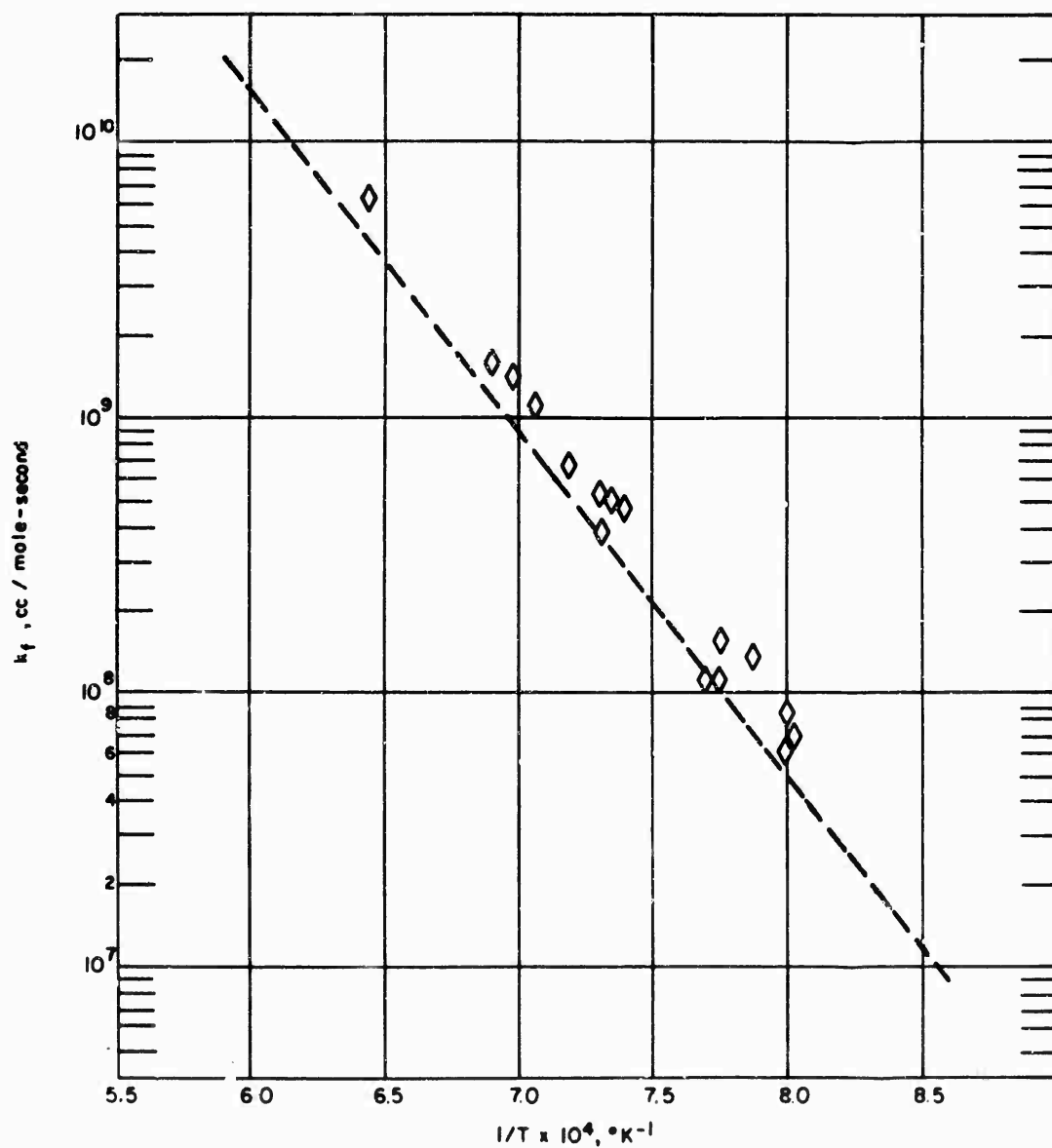


Figure 4 DETAILED ANALYSIS OF C_2F_4 DISSOCIATION BEHIND SHOCK WAVES.
 ○, EXPERIMENTAL POINTS. SOLID LINE IS CALCULATED CURVE



86-436

Figure 5 SECOND-ORDER RATE CONSTANTS FOR C_2F_4 DISSOCIATION
IN EXCESS N_2 . BROKEN LINE IS

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

cc/mole-sec

FROM ARGON KINETIC DATA

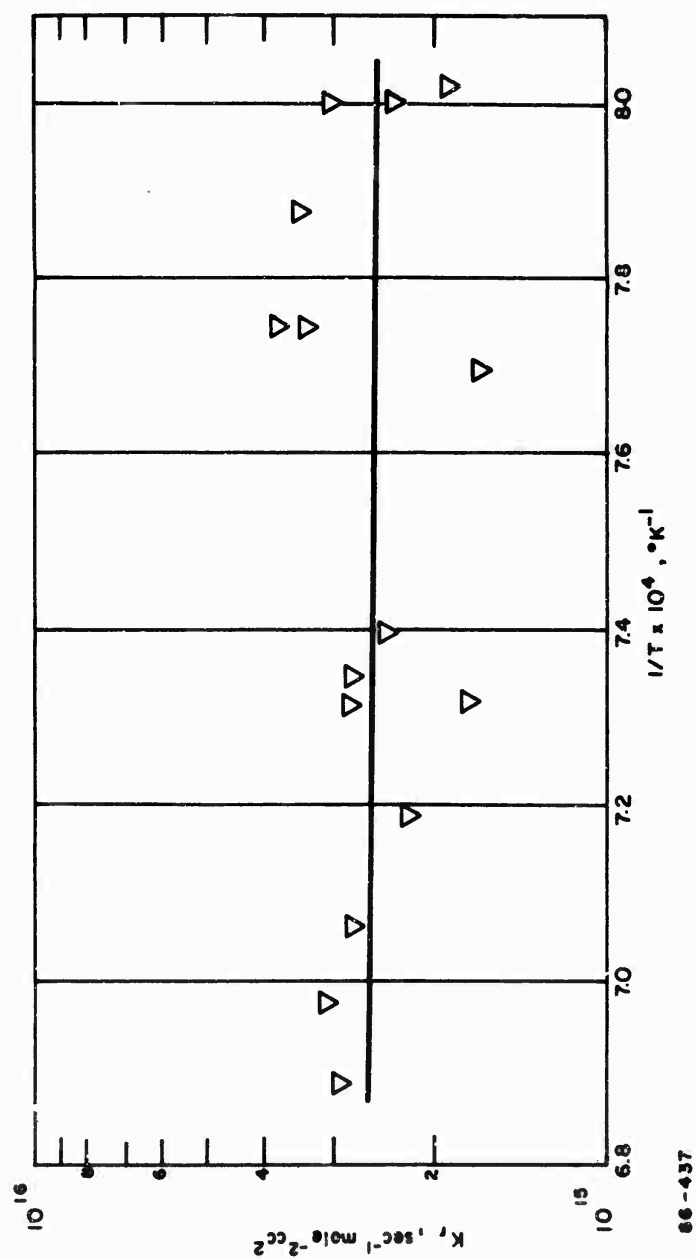


Figure 6 CF₂ RADICAL RECOMBINATION RATE CONSTANTS IN EXCESS N₂

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TABLE 1
C₂F₄ DISSOCIATION IN 1:100 C₂F₄-N₂ GAS MIXTURES BEHIND INCIDENT SHOCK WAVES*

Run No.	U_s (mm/ μ sec)	T_2 (°K)	ρ_{21}	Total Shocked Gas Conc'n (mole/cc) 10^5	N ₂ k _f (cc/mole sec)
1	1.435	1245	4.77	1.29	6.94 $\times 10^7$
2	1.440	1250	4.78	1.28	8.02 $\times 10^7$
3	1.441	1250	4.78	1.29	6.05 $\times 10^7$
4	1.455	1270	4.80	1.29	1.32 $\times 10^8$
5	1.468	1290	4.82	1.29	1.53 $\times 10^8$
6	1.472	1290	4.83	1.30	1.07 $\times 10^8$
7	1.481	1300	4.84	1.30	1.07 $\times 10^8$
8	1.511	1350	4.88	1.31	4.66 $\times 10^8$
9	1.521	1360	4.90	1.32	4.90 $\times 10^8$
10	1.527	1365	4.90	1.32	3.74 $\times 10^8$
11	1.527	1365	4.90	1.32	5.15 $\times 10^8$
12	1.539	1390	4.92	1.20	6.50 $\times 10^8$
13	1.562	1415	4.94	1.07	1.07 $\times 10^9$
14	1.573	1430	4.95	1.07	1.32 $\times 10^9$
15	1.588	1455	4.98	1.08	1.54 $\times 10^9$
16	1.650	1550	5.04	0.815	6.33 $\times 10^9$

*Vibrationally unrelaxed N₂.

TABLE II
C₂F₄-CF₂ THERMAL EQUILIBRIUM
BEHIND N₂ SHOCK WAVES*

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

*Vibrationally unrelaxed N₂.

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 experiments, 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 frequency⁹ at 1872 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 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 (≈ 0.5 dissociated) and N_2 is calculated to be 4.28×10^{-5} at 1350°K as compared to 5.86×10^{-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 ± 0.1 which may be compared to the value 1.49 ± 0.07 found by Volpe and Johnston¹⁰ for the unimolecular decomposition of NO_2Cl , and the value 1.7 given by Johnston¹¹ 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,¹² 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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II. Nitrogen Shocks						
III. N_2 Vibrational Relaxation						

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