AIP | The Journal of Chemical Physics

Kinetics of the Difluoromethylene—Nitric Oxide Reaction. I

A. P. Modica

Citation: The Journal of Chemical Physics **46**, 3663 (1967); doi: 10.1063/1.1841271
View online: http://dx.doi.org/10.1063/1.1841271
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/46/9?ver=pdfcov
Published by the AIP Publishing

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 46, NUMBER 9 1 MAY 1967

Kinetics of the Difluoromethylene–Nitric Oxide Reaction. I.

A. P. MODICA
Avco Corporation, Wilmington, Massachusetts

(Received 28 December 1966)

Evidence from mass spectra and ultraviolet-light absorption behind shock waves indicates a reversible reaction

$$CF_2+NO \underset{k_{1'}}{\overset{k_1}{\rightleftharpoons}} CF_2NO \qquad [1,1']$$

between difluoromethylene and nitric oxide. Above 2500°K the reaction proceeds further to equilibrium by

$$2CF_2NO \rightarrow 2CF_2O+N_2 \qquad [2]$$

and

$$CF_2NO+NO \rightarrow CF_2O+N_2O. \qquad [3]$$

In the temperature interval 1600°–2500°K, oscillogram records of CF_2 uv absorption are reduced in terms of [1,1′] by the rate law $-d[CF_2]/dt=k_1[CF_2][NO]-k_{1'}[CF_2NO]$ with

$$k_1=10^{13.951\pm0.338}\exp(-29200\pm3300/RT)\text{ cc/mole}\cdot\text{sec}$$

and

$$k_{1'}=10^{6.497\pm0.393}\exp(-20600\pm3600/RT)\text{ sec}^{-1}.$$

From the ratio $k_1/k_{1'}$, the heat of reaction [1] is found to be 4.6 kcal/mole, yielding a heat of formation of the CF_2NO radical equal to −15.7 kcal/mole.

INTRODUCTION

THE study of nitric oxide with methyl and ethyl radicals has recently been reviewed and extended by Heicklen to include the perfluoroalkyl reactions as well.[1–4] It has been shown from infrared[5] and mass-spectral analysis[6] that NO adds to CH_3 radicals to form the nitroso compound. Kinetic studies of this reaction at room temperature show a first-order dependence on both NO and the CH_3 radical.[6,7] When excess NO is present, the nitrosoalkane[8] reacts further to catalyze the conversion of NO to N_2 and NO_2. A number of studies by Christie and co-workers[9–11] show that the reaction is first order in CH_3NO and second order in NO. Heicklen[2] has observed the same reaction kinetics with CF_3NO, but notes[4] that with CH_3NO, N_2O also becomes an important product in the presence of excess NO.

Earlier the thermal decomposition of tetrafluoroethylene (C_2F_4) in shock waves[12] was reported and shown to be a convenient source of difluoromethylene (CF_2) radicals. Subsequently, this reaction was used to study the high-temperature kinetics of CF_2 with O_2 by means of a mass spectrometer and uv absorption technique. As part of a continuing investigation to understand the combustion kinetics of fluorocarbons, a similar experiment has been undertaken to study the oxidation of CF_2 with NO.

EXPERIMENTAL PROCEDURE

The shock-tube apparatus, optical, and mass-spectrometric diagnostic techniques used in the present investigation were identical to those described in previous papers.[12–14] Gas mixtures of C_2F_4 (99% purity) and NO (98% purity) in excess argon (99.999% purity) were prepared in mole ratios of 0.5:5:100, 1:5:100, and 1:2:100 C_2F_4–NO–Ar for study. The C_2F_4 was completely dissociated behind shock waves under pressure and temperature conditions such that the formation of CF_2 was virtually instantaneous compared to its reaction with NO. Temperatures and density ratio immediately behind the shock wave were computed from the Rankine–Hugoniot equations mak-

---

[1] J. P. Heicklen, "Reactions of NO($A\,^2\Sigma^+$) with H_2, CH_4, and C_2H_6: The Fate of RNO," Aerospace Corp. TDR-469 (5250-40)-9 (1965).

[2] J. P. Heicklen, J. Phys. Chem. **70**, 112 (1966).

[3] J. P. Heicklen, "Photolysis of C_2F_3I in the Presence of NO and O_2," Aerospace Corp. TDR-469 (5250-40)-13 (1965).

[4] T. Johnston and J. Heicklen, "Photolysis of Methyl Iodide in the Presence of Nitric Oxide," Aerospace Corp. TR-669 (6250-40)-8 (1966).

[5] J. G. Calvert, S. J. Thomas, and P. L. Hanst, J. Am. Chem. Soc. **82**, 1 (1960).

[6] A. Maschke, B. S. Shapiro, and F. W. Lampe, J. Am. Chem. Soc. **85**, 1876 (1963).

[7] W. C. Sleppy and J. G. Calvert, J. Am. Chem. Soc. **81**, 769 (1959).

[8] J. F. Brown, J. Am. Chem. Soc. **79**, 2480 (1957).

[9] M. I. Christie, Proc. Roy. Soc. (London) **A249**, 258 (1958).

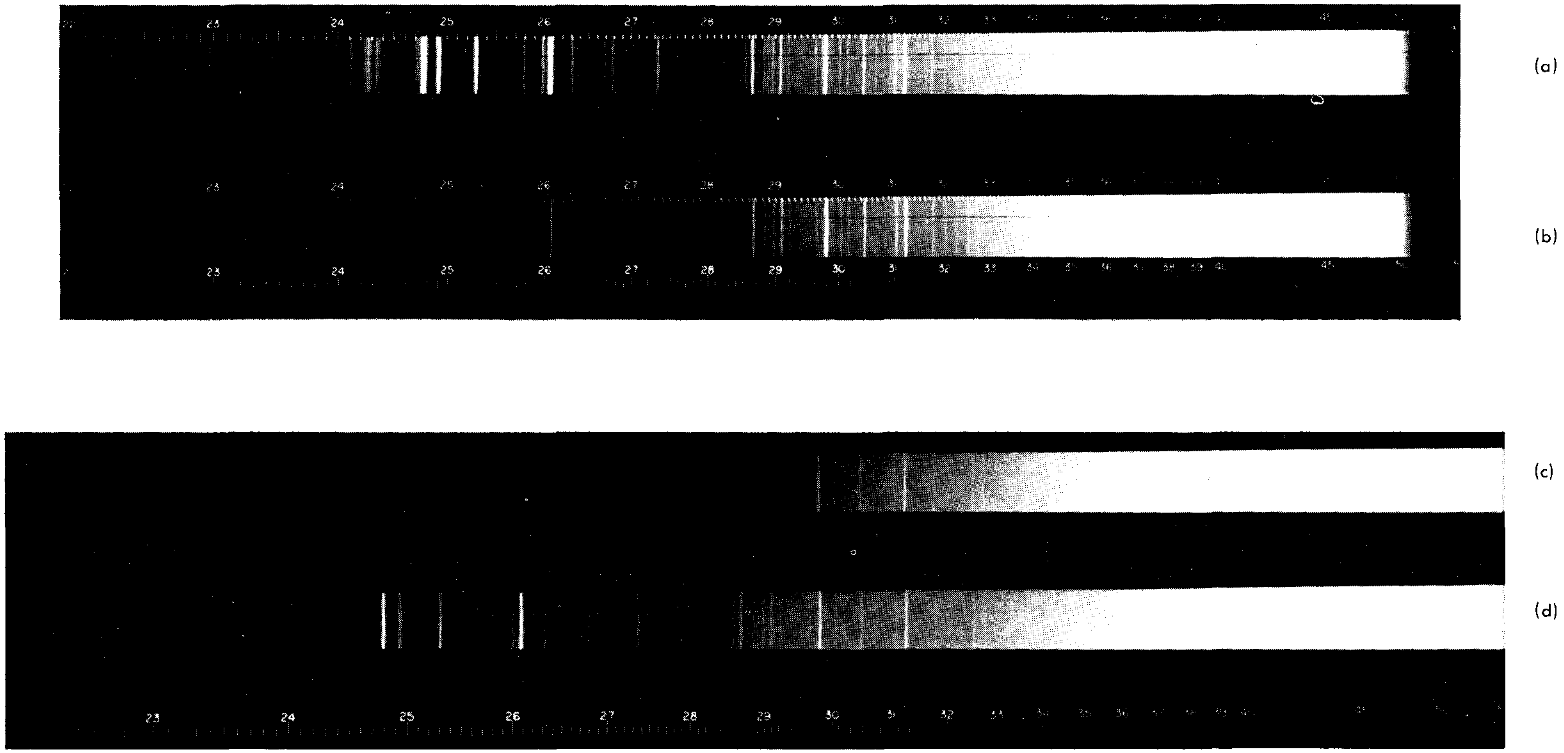
[10] M. I. Christie, J. S. Frost, and M. A. Voisey, Trans. Faraday Soc. **61**, 674 (1965).

[11] M. I. Christie, C. Gilbert, and M. A. Voisey, J. Chem. Soc. **1964**, 3147.

[12] A. P. Modica and J. E. LaGraff, J. Chem. Phys. **43**, 3383 (1965).

[13] A. P. Modica, J. Chem. Phys. **44**, 1585 (1966).

[14] A. P. Modica and J. E. LaGraff, J. Chem. Phys. **44**, 3375 (1966).



. 1. Flash absorption spectrograms behind incident shock waves. (a) Xenon flash lamp. (b) Shocked 1:2:100 C_2F_4–NO–Ar gas mixture. (c) Shocked 1:100 CF_4–Ar gas mixture. (d) Xenon flash lamp.

ing use of the measured incident shock velocity and the enthalpy values of C_2F_4, CF_2, NO, and argon taken from the *JANAF Tables*.[15] Calculations were based on total dissociation of C_2F_4 ($C_2F_4=2CF_2$) with a heat of reaction of 74.9 kcal/mole.[12]

In order to check for absorption by species other than CF_2 in the C_2F_4–NO reaction mixture, spectra of 1:2:100 C_2F_4–NO–Ar gas mixtures shock heated to 1600°–2000°K at 2.7 atm pressure were recorded on 103-F plates using a Hilger medium quartz spectrograph with 200-μ slitwidth. Superimposed exposures totaling 600 μsec were taken by synchronizing a xenon flash lamp with the shock front. A comparison of spectrograms (Fig. 1) from the shocked C_2F_4–NO reaction mixture and that from shocked CF_4 demonstrated only ultraviolet-light absorption in the region characteristic of the CF_2 radical.[16] A more sensitive search for absorption spectra in the wavelength interval from 3000 to 5500 Å was performed spectrophotometrically using the monochromator light absorption station. The measurements showed that the species in the C_2F_4–NO reaction mixture were nonabsorbing in this wavelength region.

Kinetics of the CF_2 reaction with NO were studied in incident shocks by following photometrically the decrease in absorption of the CF_2 radical at 2660 Å (Fig. 2). As given in Ref. 13, the fraction α of CF_2 molecules reacted behind the shock wave is related to the absorbance by the expression

$$\alpha=1-\frac{\ln[H/(H-h)]}{\ln[H/(H-h_{in})]}, \qquad (1)$$

where H is the deflection height for 100% absorption generated by a light chopper immediately after the run. The absorption caused by CF_2 radicals immediately behind the shock produces the deflection h_{in} and during reaction h.

In addition to the optical measurements, similar experiments were performed in reflected shock waves using a shock-tube/TOF mass-spectrometer apparatus to characterize qualitatively the reaction products.

REACTION MECHANISM

Mass spectra (Fig. 3) of reflected-shock-heated mixtures of C_2F_4 and NO in excess argon at 2600°K indicate mass peaks for $CF_2NO(80)$, $COF_2(66)$, $CF_2(50)$, COF(47), $N_2O(44)$, Ar(40), Ar(38), Ar(36), CF(31), NO(30), $N_2(28)$. Also observed are traces of H_2O at mass peak 18. It is seen that immediately behind the shock the CF_2 and NO peaks dominate and with time decrease in intensity. The first reaction product detected is CF_2NO, with COF_2 and N_2 later appearing. The COF peak is believed to result from the electron cracking pattern of COF_2 since its thermal decomposition under these shock conditions has been found to be negligible.[17] Interestingly, just above the background noise of the Ar(40) peak, a mass peak indicating the presence of N_2O is observed. An analysis of the time-dependent mass spectra shows that the rate ratio CF_2/NO for disappearance of CF_2 and NO is about 1/1.2. A reaction mechanism, consistent with the above chemistry and rate ratio, is suggested by

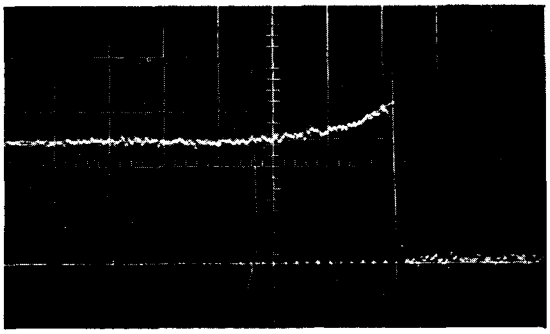


FIG. 2. Oscillogram record of CF_2 uv absorption behind incident shock wave into 1:2:100 C_2F_4–NO–Ar gas mixture at 5.0 cm Hg initial pressure (Expt. No. 8). Shock temperature = 2080°K. Writing speed = 5 μsec between vertical markers.

$$\mathrm{CF_2+NO}\underset{k_{1'}}{\overset{k_1}{\rightleftharpoons}}\mathrm{CF_2NO}, \qquad [1, 1']$$

$$2\mathrm{CF_2NO}\xrightarrow{k_2}2\mathrm{COF_2}+\mathrm{N_2}, \qquad [2]$$

and

$$\mathrm{CF_2NO}+\mathrm{NO}\xrightarrow{k_3}\mathrm{COF_2}+\mathrm{N_2O}. \qquad [3]$$

In view of the observed CF_2/NO rate ratio and relatively large N_2 content in the reaction mixture, [3] would appear to be less important than [2].

KINETICS

At temperatures between 1600° and 2500°K, it was noticed from the experimental oscillogram records that the CF_2 radicals were not completely reacted after chemical relaxation, but rather reach a steady-state concentration dependent on temperature. For temperatures above 2500°K, the decrease in CF_2 absorption was found to proceed rapidly to a quasisteady level, and then to relax further slowly in time. According to these observations, it is believed that above 2500°K, Reactions [2] and [3] may be occurring, whereas at lower temperatures a reversible reaction between NO and CF_2 dominates.

In the interpretation of the kinetic data for which the steady-state condition is observed, [1] is considered. The rate law for NO addition to CF_2 is taken

---

[15] *JANAF Tables* (Dow Chemical Co., Midland, Mich., 1963).

[16] D. E. Milligan, D. E. Mann, and M. E. Jacox, J. Chem. Phys. **41**, 1199 (1964).

[17] A. P. Modica and J. E. LaGraff, "Shock Tube Kinetic Studies of the Tetrafluoroethylene–Oxygen System," AVCO Report RAD-TM-65-29 (1965), Avco Corp., Wilmington, Mass.

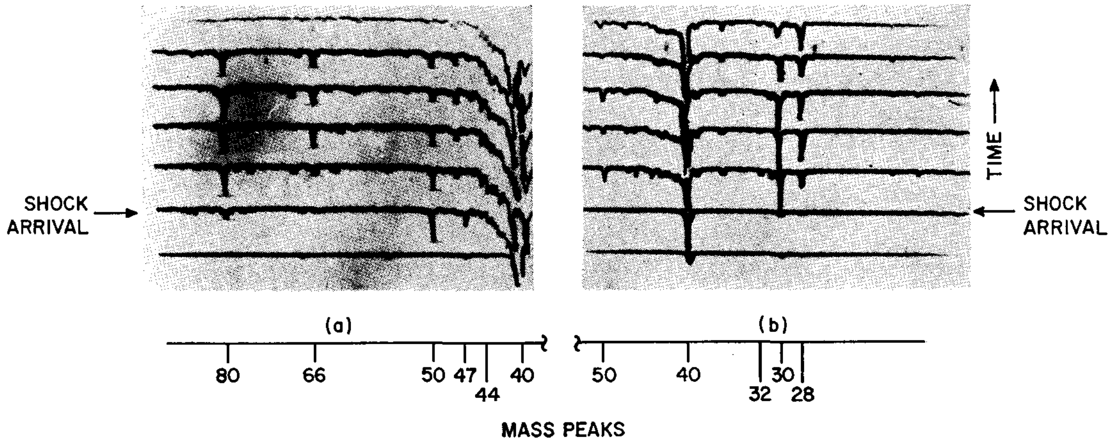


FIG. 3. Mass spectrogram of reflected-shock-heated 1:5:100 C_2F_4–NO–Ar gas mixture. Analysis is performed at 25-μsec intervals. Initial pressure = 0.4 cm Hg. Reflected shock temperature≃2600°K.

to be

$$-d[CF_2]/dt = k_1[CF_2][NO] - k_{1'}[CF_2NO] \qquad (2)$$

or alternately in integral form

$$\int \frac{d\alpha}{k_1[CF_2]_0(1-\alpha)(n-\alpha) - k_{1'}\alpha} = t, \qquad (3)$$

where α is the fraction of CF_2 reacted, n is the mole ratio of $[NO]_0$ to $[CF_2]_0$ concentration initially present, t is time. Evaluation of the integral was done numerically on an IBM 7094 computer, using k_1 measured from the initial slope of the CF_2 absorption record and $k_{1'}$ determined from the steady-state condition. The agreement between the computed kinetic profiles and the experimental points (Fig. 4) for the three gas mixtures at various temperatures is regarded as evidence in support of [1] and the rate law expressed by Eq. (2).

Forward and reverse rate constants for the addition of nitric oxide to difluoromethylene were determined between 1600° and 2500°K at total shocked gas pressures around 0.8–1.4 atm. Reactant concentrations ranged between $(0.39\text{–}2.0)10^{-7}$ mole/cc for CF_2 and $(1.2\text{–}5.0)10^{-7}$ mole/cc for NO. Table I summarizes the shock-tube experiments of the present study. A least-squares fit (Figs. 5 and 6) with the Arrhenius equation for the rate constant gives

$$k_1 = 10^{13.951\pm0.338}\exp(-29\,200\pm3300/RT)\text{ cc/mole}\cdot\text{sec} \qquad (4)$$

and

$$k_{1'} = 10^{6.497\pm0.393}\exp(-20\,600\pm3600/RT)\text{ sec}^{-1}. \qquad (5)$$

According to the "law of mass action," the difference in activation energies of k_1 and $k_{1'}$ gives the change in energy for [1], $\Delta E_r = 8.6$ kcal/mole, or the heat of reaction, $\Delta H_r = 4.6$ kcal/mole, by subtracting $RT(2000°K)$.

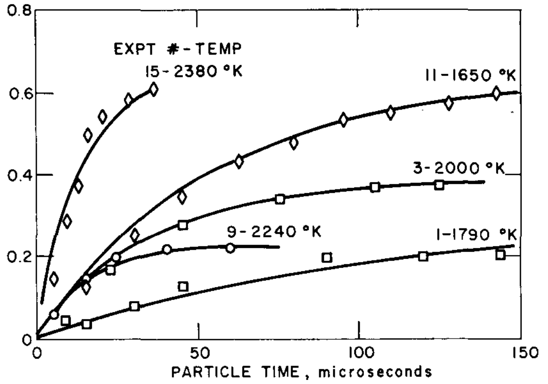


FIG. 4. Kinetic profiles of the difluoromethylene–nitric oxide reaction. Symbols are experimental points; □, 0.5:5:100 C_2F_4–NO–Ar data; ○, 1:2:100 C_2F_4–NO–Ar data; ◇, 1:5:100 C_2F_4–NO–Ar data. Solid lines are calculated curves.

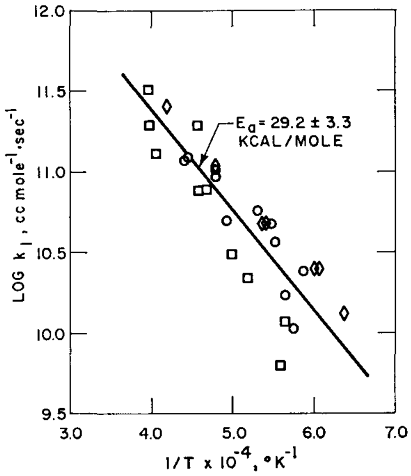


FIG. 5. Bimolecular rate constants for the difluoromethylene–nitric oxide reaction. □, 0.5:5:100 C_2F_4–NO–Ar data; ○, 1:2:100 C_2F_4–NO–Ar data; ◇, 1:5:100 C_2F_4–NO–Ar data. Solid line is least-squares fit of the data. The uncertainty in the activation energy is the standard deviation of fit.

TABLE I. Examples of the difluoromethylene–nitric oxide shock-tube experiments.

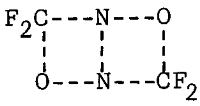
Expt No.	U_s (mm/μsec)	T_2[a] (°K)	ρ_{21}	$[CF_2]_0$ (mole/cc) 10^7	$[NO]_0$ (mole/cc) 10^7	$\log k_1$ (cc/mole·sec)	$\log k_{1'}$ sec^{-1}
			0.5:5:100 C_2F_4–NO–Ar data				
1	1.37	1790	3.765	0.955	4.78	9.796	3.860
2	1.405	1925	3.785	0.768	3.84	10.350	4.173
3	1.435	2000	3.800	0.775	3.87	10.497	4.274
4	1.503	2170	3.835	0.586	2.93	10.894	4.453
5	1.62	2485	3.888	0.394	1.97	11.294	4.803
			1:2:100 C_2F_4–NO–Ar data				
6	1.364	1810	3.935	1.64	1.64	10.569	4.258
7	1.450	2025	3.96	1.65	1.65	10.713	4.534
8	1.472	2080	3.97	2.08	2.08	10.993	4.458
9	1.534	2240	3.99	1.25	1.25	11.090	4.630
10	1.544	2270	3.99	1.67	1.67	11.076	4.593
			1:5:100 C_2F_4–NO–Ar data				
11	1.308	1650	3.96	2.00	5.00	10.415	3.736
12	1.394	1850	4.00	1.62	4.05	10.682	3.732
13	1.485	2075	4.035	1.23	3.08	11.045	3.978
14	1.592	2360	4.07	0.828	2.07	11.413	4.310
15	1.598	2380	4.07	0.828	2.07	11.410	4.346

[a] Temperature behind incident shock wave.

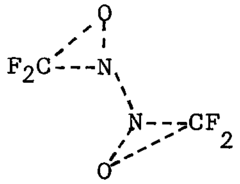
DISCUSSION

Structure of the $CF_2(NO)$ Molecule

In the mass spectra of $CF_2(NO)$, it is seen that electron-cracking-pattern ions having fluorine atoms attached to nitrogen or oxygen are absent. On the other hand, the presence of only carbon–fluorine ions leads one to conclude that both fluorine atoms are attached to the carbon atom. The addition of nitric oxide to the difluoromethylene radical may result in two structures, the nitroso configuration (F_2C–NO) or the oxyimide configuration (F_2C–ON). Kinetic evidence supports the oxyimide structure. Consider [2] and [3], for N_2 to be formed from the nitroso structure, a six-center activation complex



or a highly strained complex



would be required. Because of the large steric factors associated with these excited states, [3] would seem to dominate over [2], with the rate ratio CF_2/NO being more nearly 1/2 and a larger yield of N_2O being observed instead of N_2. However, it was found that the rate ratio was close to 1/1 and that N_2 was more abundant in the system than N_2O.

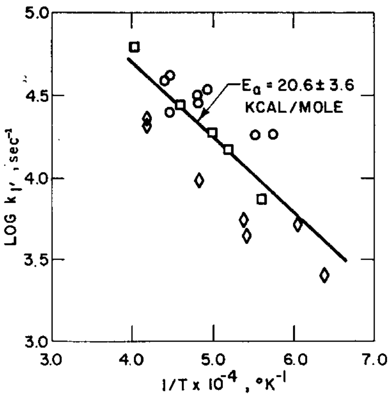


FIG. 6. Rate constants for the unimolecular dissociation of the $CF_2(NO)$ reaction complex. □, 0.5:5:100 C_2F_4–NO–Ar data; ○, 1:2:100 C_2F_4–NO–Ar data; ◇, 1:5:100 C_2F_4–NO–Ar data. Solid line is least-squares fit of the data. The uncertainty in the activation energy is the standard deviation of fit.

Heat of Formation of the $CF_2(NO)$ Molecule

At 2000°K (average temperature of the present study) taking $\Delta H_f(CF_2)^{12}$ equal to −41.9 kcal/mole and $\Delta H_f(\text{NO})$[15] equal to 21.6 kcal/mole, with the experimental heat of reaction of 4.6 kcal/mole, the heat of formation for $CF_2(NO)$ is calculated to be -15.7 kcal/mole.

Kinetic Parameters

The collision efficiency for reaction between CF_2 and NO is found to be 0.26, taking $Z=\sigma^2(8\pi RT/\mu)^{1/2}$ as the collision frequency and the collision cross section σ to be 3.49 Å, the mean diameter of NO (3.53 Å)[18] and CF_2(3.44 Å).[13] From Eq. (5) the mean lifetime ($\tau=1/k_{1'}$) of the $CF_2(NO)$ radical at 2000°K is 5.61×10^{-5} sec. A comparison with the time between collision of a $CF_2(NO)$ radical with argon, $1/Z=2.6\times10^{-10}$ sec, shows that the $CF_2(NO)$ dissociation would be unimolecular and independent of pressure under the present experimental conditions.

ACKNOWLEDGMENTS

The author gratefully acknowledges the support of the Ballistic Systems Division/U.S. Air Force under contract AFO4(694)-890, part of ABRES Program, and the Advanced Research Projects Agency/U.S. Army under Contract DA-01-021-AMC-12005(2), part of Project DEFENDER.

---

[18] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 1111.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 46, NUMBER 9 1 MAY 1967

Crystallization of Diamond and Graphite

H. M. Strong and R. E. Hanneman

General Electric Research and Development Center, Schenectady, New York

(Received 26 October 1966)

The key features of the complete, stable nickel–carbon phase diagram have been established at pressures up to 54 kbar, and these features have been directly related to the nucleation and growth characteristics of diamonds in this system. At pressures in excess of 52.5 kbar, a liquid+graphite+diamond eutectic is formed at approximately 0.3 at. % nickel which results in an effective displacement of the diamond–graphite equilibrium line. This displacement is shown to be of considerable importance in the nucleation and growth of diamonds in this system. Under low and moderate driving forces, the rate-controlling mechanism in the growth on a speed diamond is the diffusion of carbon across the molten metal film surrounding the diamond. The observed diffusion coefficients at 54 kbar and $1660° < T < 1800°$K lie in the range: $2\times10^{-5} < D < 4\times10^{-5}$ cm^2/sec.

INTRODUCTION

SINCE the first successful synthesis of diamond, a great deal of interest and activity has centered around the effects of pressure, temperature, and composition on the nucleation and growth of diamonds. Quantitative experiments aimed at determining the mechanisms controlling diamond synthesis have been particularly challenging and difficult because of the extreme conditions required for the formation of diamonds. In addition, progress in understanding has been hampered by a serious lack of phase-diagram data and other thermodynamic and kinetic information on the carbon-rich side of most metal- or alloy-vs-carbon systems. The purpose of this study is threefold: (1) to establish the fundamental aspects of phase equilibria for the formation of diamonds from graphite in catalyst metal systems, (2) to investigate the effects of pressure, temperature, and composition on the nucleation and growth characteristics of diamonds and large graphite crystals in the metal–carbon system, and (3) to establish the controlling mechanism for the growth of synthetic diamonds.

There are two methods for synthesis of diamonds: direct and indirect (or catalytic). The direct conversion by static pressure involves only carbon and requires conditions in excess of ~130 kbar[1]; shock wave, direct conversion may also be attained at pressures of the order of 400 kbar and temperatures of the order of 1000°K.[2] The indirect or catalytic conversion process which is treated here can be carried out with pressure–temperature conditions as low as ~45 kbar and ~1400°K through the use of certain liquid metals or alloys.

The temperature–pressure conditions for equilibrium coexistence of pure graphite and diamond have been calculated based upon thermodynamic grounds.[3] Initial experiments in this calculated diamond stable region were unsuccessful in directly forming diamond from

---

[1] F. P. Bundy, J. Chem. Phys. **38,** 618 (1963); R. H. Wentorf, Jr., J. Phys. Chem. **69,** 3063 (1965).

[2] P. S. DeCarli and J. C. Jamieson, Science **133,** 1821 (1961); B. J. Alder and R. H. Christian, Phys. Rev. Letters **7,** 367 (1961).

[3] R. Berman and F. Simon, Z. Electrochem. **59,** 333 (1955); R. Berman, *Physical Properties of Diamond* (Clarendon Press, Oxford, England, 1965), pp. 371–393.