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SENSITIVITY STUDIES ON NF COMPOUNDS

by

T. E. Dergazarian and G. E. Vrieland

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The Dow Chemical Company
Midland, Michigan

FOREWORD

This report was prepared by The Dow Chemical Company, under USAF Contract Nr. AF 04(611)-9958. The contract was initiated under Air Force Program No. 750 G, AFSC Project No. 3148, "Sensitivity Studies of NF Compounds." The work was administered under the direction of the Rocket Propulsion Laboratory, Edwards Air Force Base, with Mr. G. Allen Beale acting as Air Force Project Officer.

This is the final report which covers the work conducted from 15 June 1964 through 15 July 1965.

The work was performed by Dr. G. E. Vrieland and Mr. T. E. Dergazarian, under the supervision of Dr. D. A. Rausch, Group Leader. Dr. R. G. Pearson, of Northwestern University, Evanston, Illinois, provided guidance and was consulted on the kinetics of decomposition of the NF materials. The Dow report number is NF-4Q-65.

This technical report has been reviewed and is approved.

George F. Babits, Lt. Colonel, USAF
Chief, Propellant Division

CLASSIFIED ABSTRACT

The decomposition of INFO-635P in the free amine and ammonium ion forms has been studied in dilute aqueous solution. Decomposition of the free amine of INFO-635P is rapid at room temperature and takes place unimolecularly to form ethylenimine. In the solid state, detonation occurs almost immediately in anhydrous ammonia gas. The tris(difluoroamino) group of INFO-635P in acid decomposes at 100°C. by homolytic C-N bond rupture into $\cdot NF_2$ radicals, and the final products containing nitrogen are N_2O and N_2. The ethanolamine formed seems to act as a reducing agent in acidic solutions and this should be tested conclusively for the solid decompositions as well. In general, the gaseous product distribution from solid phase decomposition is similar to that in acid solution.

The kinetics of decomposition of compound Delta is complex. At the high end of the temperature range studied, 140°-190°C., the dominant reaction is first order in Delta, and homogeneous. A second competing mechanism becomes more dominant at the intermediate temperatures where no distinct first order rate can be observed. The reaction at these lower temperatures is homogeneous, and possibly 3/2 order.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (Contd.)

I. INTRODUCTION

The purpose of this research has been to determine the kinetics and mechanism of the decomposition of Delta and INFO-635P under slow thermal conditions with the objective of using this knowledge to reduce their shock sensitivities. The first of these compounds, tetrakis(difluoroamino)methane (compound Delta), was studied in the gas phase at temperatures of 140°-200°C., whereas the second, 2-tris(difluoroamino)methoxyethylammonium perchlorate (INFO-635P), an ionic solid, was studied in aqueous solutions. Admittedly, slow thermal decomposition studies cannot lead to a detailed mechanism for the explosive reaction, but can yield a mechanism for the initial reaction and the intermediates which precede a chain or thermal explosion. With this information, it should be possible to make an intelligent choice of traps or inhibitors to prevent explosion. In this report the homogeneity of the gas phase decomposition of Delta was determined as well as evidence supporting the existence of competing reactions in the overall mechanism. The stoichiometric equations for the decomposition of Delta and INFO-635P in basic and acidic solution have been almost completely established. Kinetic studies on both compounds have resulted in tentative decomposition mechanisms.

II. DECOMPOSITION STUDIES OF INFO-635P

This section will report the work done on INFO-635P, whereas the following Section III will deal exclusively with Delta.

A. DISCUSSION AND RESULTS

1. Method of Study

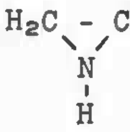
The decomposition of INFO-635P has been studied in solution in order to gain an understanding of the mode of decomposition of isolated molecules in environments of different acidity and polarity. Solution kinetic data are far easier to interpret than solid state data, and, furthermore, it is possible to study singly the various parts of the INFO-635P molecule. By analogy with other ammonium salts such as ammonium perchlorate or ammonium nitrate, it seemed reasonable to assume that the following equilibrium is established in solid INFO-635P, particularly on the surface:

$$(NF_2)_3COCH_2CH_2NH_3^+ClO_4^- \rightleftharpoons (NF_2)_3COCH_2CH_2NH_2 + HClO_4$$

This suggested a step by step consideration of the decomposition of INFO-635P: first, the organic part of INFO-635P, including the free amine, and ammonium ion in aqueous base and aqueous acid, respectively, and secondly, bringing in the inorganic group, the perchlorate ion, to study the ion pair in a slightly polar organic solvent. Since it is known that INFO-635P is unstable in base, the free amine was studied first because this would seem to have the greatest effect on the sensitivity of the solid.

2. The Free Amine Decomposition

a. Stoichiometry - The complete decomposition of dilute INFO-635P solution (10^{-2} M) in excess base at room temperature follows the equation:



$$(NF_2)_3COCH_2CH_2NH_2 + 9\ OH^- \rightarrow 5.68\ F^- + 1.19\ CO_3^= + 0.92\ \underset{\underset{H}{|}}{H_2C\overset{\ }{-}CH_2 \atop \diagdown N \diagup} + 0.28\ NO_2^- + 1.05\ N_2 + 0.1\ N_2O + 5\ H_2O + (NO_3^-\ ?) \quad (1)$$

Small amounts of ethylene, acetylene, and difluorodiazirine have also been detected; however, no ammonia, nitric oxide, nitrogen dioxide, or tetrafluorohydrazine have ever been observed.

The results of analysis of the decomposition products are recorded in Table I in terms of moles of product per mole of INFO-635P. Experiment 7045-20 was run in a closed glass volumetric flask in air, whereas Experiments 7045-32, 7045-36, and 7045-42 were run in vacuum, and the averages are calculated on the basis of the last three. The number of moles of base, N_{OH^-}, required per mole of INFO-635P for complete decomposition is given in the final column of Table I.

Table I

Results of Analyses of the Products from Basic Hydrolysis of INFO-635P

Experiment No.	Moles of Products per Mole of INFO-635P						
	F^-	Volatile C	Non-Volatile C	NO_2^-	N_2	N_2O	N_{OH^-}
7045-20 in air	6.0	1.04	1.86	0.311	--	--	9.57
7045-32	5.6	1.11	1.82	0.285	--	--	8.96
7045-36	5.7	1.275	1.85	0.275	1.1	0.11	9.23
7045-42	5.75	1.18	1.84	0.280	1.0	0.10	9.02
*Average	5.68	1.19	1.84	0.28	1.05	0.105	9.07

*This is the average based on the last three experiments.

The gaseous products were analyzed by mass spectroscopy and the results are given in Table II. It was necessary to consider the amount of gas dissolved in water in order to calculate the number of moles of N_2 and N_2O formed, particularly for N_2O, which is moderately water soluble. The gaseous distribution is different from that reported for HNF_2 decomposition in base[1,2,3,4].

The material balance for the decomposition equation (1) is given in Table III. The F^- content is 5% below that expected from

INFO-635P, and this cannot as yet be explained. The deficit in oxygen and hydrogen should come out in the ratio of 1:2 corresponding to water; however, the observed ratio is 1:1.78. If one assumes 5 moles of H_2O are formed, this ratio leaves an oxygen deficit of 0.6 atoms.

Table II

Mass Spectral Analysis of the Gaseous Decomposition Products of INFO-635P

	Component, Mole %[a]				
Run No.	N_2	N_2O	N_2F_2	C_2H_2	C_2H_4
7045-32	91.6	3.85	1.65	2.02	0.85
7045-36	94.4	4.08	0.20	0.38	0.78
7045-42	93.5	3.90	1.33	0.48	0.69
7045-54	93.6	4.47	0.53	0.69	0.55

[a] Excluding water.

Table III

Material Balance between INFO-635P + 9.07 OH^- and Analyzed Products

Element	INFO-635P + 9.07 OH^-	Products	Difference
N	4.0	3.50	- 0.50
F	6.0	5.7	- 0.30
C	3.0	3.02	+ 0.02
O	10.07	4.23	- 5.84
H	15.07	4.60	-10.40
Ions	9.07	8.30	- 0.67

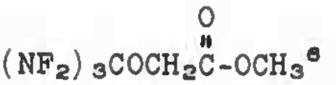
It was previously reported[5] that 0.68 moles of NO_3^- were formed. This has been found in error as a result of the effect of ethylenimine on the method of analysis. Two solutions were prepared which were both 0.15 N in base and 0.01 N in $Na^+NO_2^-$; one solution was also 0.01 M in ethylenimine. The nitrite analysis was unaffected by ethylenimine; however, by reduction with DeVarda's alloy to ammonia, the analysis gave apparently 0.0067M NO_3^-, indicating that ethylenimine behaved just like the ammonia. This indicates that the nitrate analysis using reduction to nitrogen ammonia is grossly in error, and if nitrate is present at all it is probably only 0.1-0.2 mole NO_3^- per mole of INFO-635P.

A simple oxidation-reduction balance indicates that one mole each of NO_2^- and N_2 could be formed, and this is also concluded from the material balance given above. The deficit in nitrogen and oxygen corresponds to NO_2^-. Experiments have shown that the NO_2^- is not appreciably attacked by air, ClO_4^-, or INFO-635P. Although it would be interesting to establish the stoichiometry more exactly, it was felt that it would not be worthy of further work.

From equation (1) it readily becomes apparent that the methoxy carbon-oxygen bond breaks with subsequent formation of carbonate ion.

Furthermore, of the three nitrogen atoms in this group in INFO-635P, two are found in N_2 and one in NO_2^- in the final products.

b. Kinetics of the Decomposition of the Free Amine - The initial step of the decomposition of the free amine of INFO-635P in basic solution could conceivably consist of a bimolecular reaction between the amine and a hydroxide ion. Since the three NF_2 groups on the methoxy carbon are strongly electronegative, one could expect a S_N2 displacement of the methoxy group by hydroxide ion similar to an ester hydrolysis, or hydroxide ion could attack the N-F bonds initially. The latter postulate seems improbable since Minnesota Mining and Manufacturing Company found that the compound



$(NF_2)_3COCH_2\overset{O}{\overset{\|}{C}}\text{-}OCH_3$[8] was completely hydrolyzed in 0.1 N NaOH at 25°C. in three days to the sodium salt of the acid without disturbing the $-NF_2$ groups on the methoxy carbon. In a striking comparison, INFO-635P decomposes in four hours under these same conditions. The compounds NF_3, N_2F_2, and N_2F_4 are also surprisingly resistant to hydrolysis[7].

The initial rate of decomposition of the amine of INFO-635P in base was followed in two ways: first, by using the change in pH with time, and secondly, by following pressure with time as indications of the extent of reaction.

Figure 1 shows the results of two experiments in which the initial INFO-635P concentration was varied at constant pH (11.5) to determine the order of initial reaction with respect to INFO-635P.

The equation,

$$\frac{d(OH^-)_i}{dt} = K(I)_i^{\alpha}(OH^-)_i^{\beta} \qquad (2)$$

where I = INFO-635P concentration and α and β are the order of reaction with respect to INFO-635P and hydroxide ion, respectively, can be rearranged into the form:

$$\log\left[\frac{d\log(OH^-)}{dt}\right]_i = \log\frac{K}{2.303} + \alpha\log(I)_i + (\beta-1)\log(OH^-)_i \qquad (3)$$

Plotting $\log\left[\frac{d\log(OH^-)}{dt}\right]_i$ vs. $\log(I)_i$ at constant initial pH gives a straight line with the slope being the order with respect to INFO-635P.

Figure 1 shows such a plot for two experiments with slopes of 0.87 and 1.29 (average of 1.07). Thus, the reaction is first order in INFO-635P, as expected.

Similarly, Figure 2 shows the same function, $\log\left[\frac{d\log(OH^-)}{dt}\right]_i$ vs. $\log(OH^-)_i$ with constant initial INFO-635P concentration. The results show that with increasing $(OH^-)_i$ the rate also increases up to pH ≅ 10. Thereafter, the slope changes sharply to a second

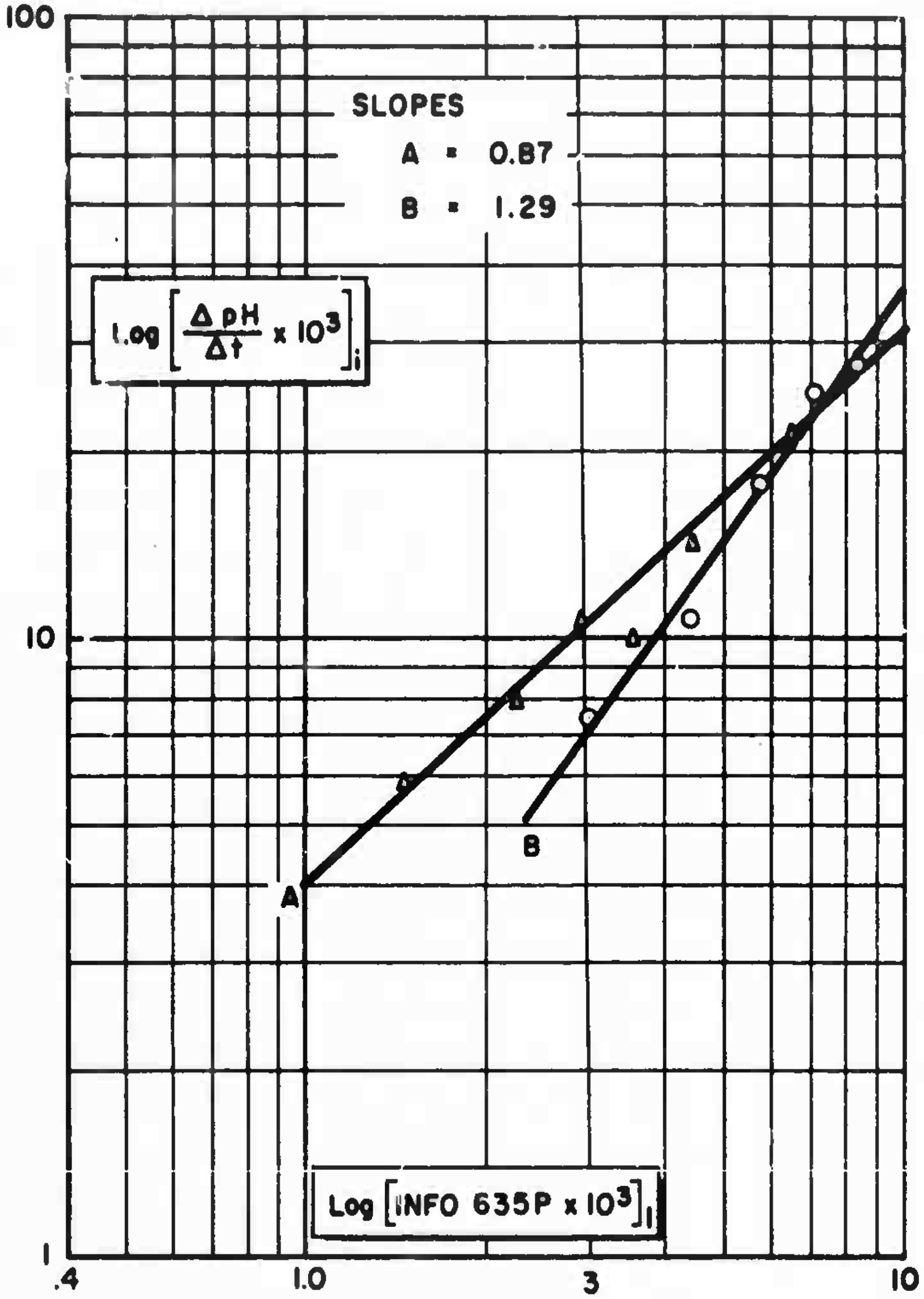


Fig. 1 - Determination of the Order of Decomposition with Respect to INFO-635P

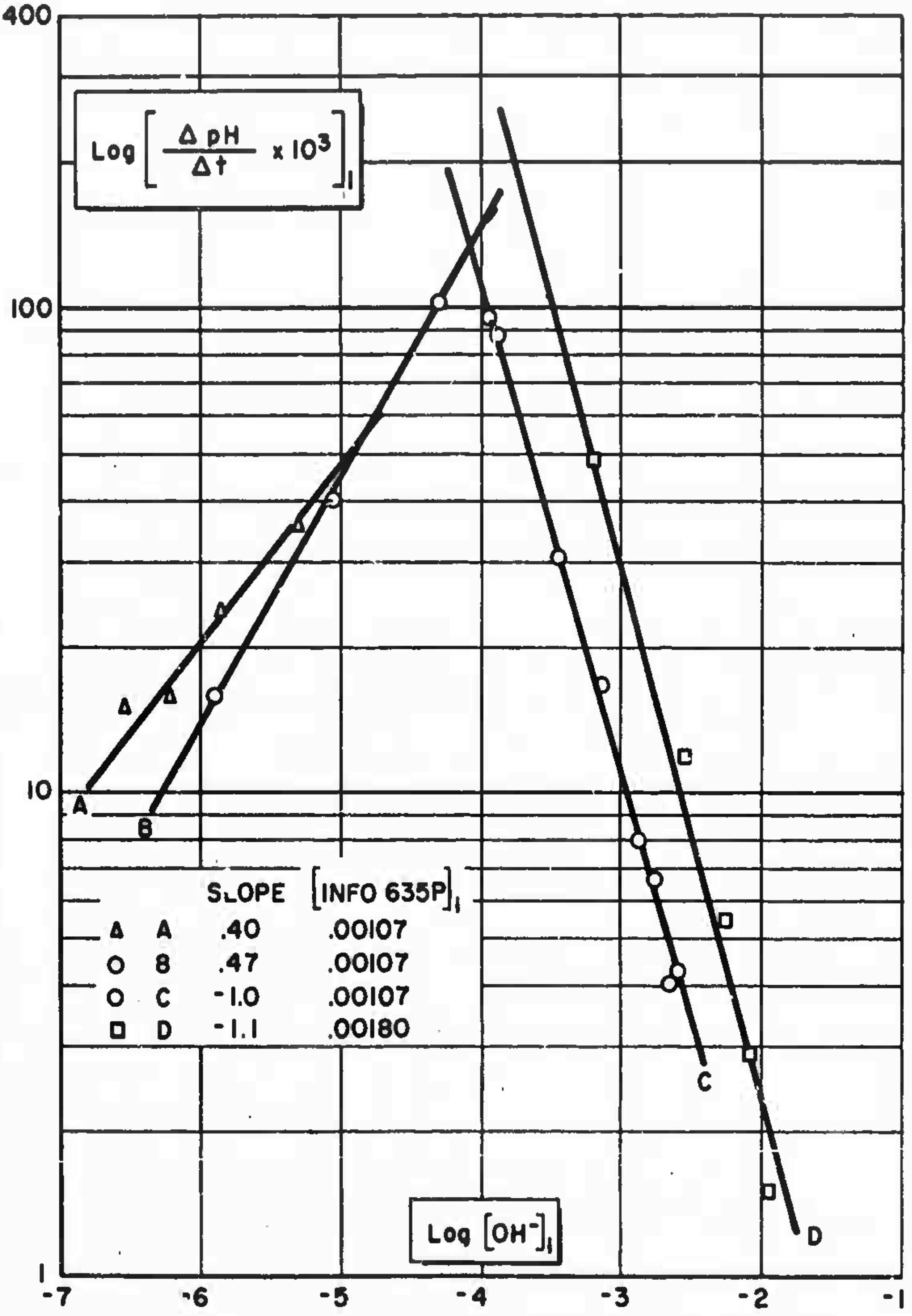


Fig. 2 .- Determination of the Order of Decomposition of INFO-635P with Respect to Hydroxide Ion

straight line. The initial slope is equal to 0.4-0.5, with a β equal to 1.4-1.5; the second slope is equal to -1, with β equal to 0. Line D is for a larger INFO-635P concentration, as indicated.

The pKa of ethanolamine[8] is 9.4, and, assuming that this is also the pKa of INFO-635P, it is observed that above a pH of 9.5 INFO-635P rapidly changes into the free amine. Unfortunately, near a pH of 9-10, a change in hydroxide concentration is accompanied by a substantial change in free amine concentration so that the true criterion for the extent of reaction is not $\left[\frac{d(OH^-)}{dt}\right]_i$ but $\left[\frac{d(OH^-)}{dt} + \frac{d(amine)}{dt}\right]_i$. This can be calculated using the pKa of 9.5 and in Figure 3 are plotted log $\left[\frac{d(OH^-)}{dt}\right]_i$, as well as log $\left[\frac{d(OH^-)}{dt} + \frac{d(amine)}{dt}\right]_i$ vs. log $(OH^-)_i$. The slope of the second plot is 1.1 rather than 1.5, but a mysterious maximum occurs in this plot before leveling off to zero slope above a pH of 10.

These results certainly indicate that the free amine is much more reactive than the ammonium salt. Furthermore, the free amine decomposes by a unimolecular mechanism independent of hydroxide ion. The hydroxide ion only serves to pull a proton from the ammonium ion and to hydrolyze intermediates after the rate-determining step for decomposition of the free amine.

This observation is further substantiated by measuring the pressure over evacuated solutions having varying initial base concentration but constant INFO-635P concentration. These results are shown in Figure 4. The initial INFO-635P concentration was 1.8×10^{-3} M, whereas the initial hydroxide concentration varied from 0.56×10^{-3} M to 11.2×10^{-3} M and the rate of evolution of gas is unaffected. At the lowest concentration, the hydroxide ion is soon depleted. Addition of ethanolamine (0.01 M) to the base did not affect the rate of evolution of nitrogen. Of course, evolution of nitrogen is one of the final steps in this complex reaction. Nevertheless,

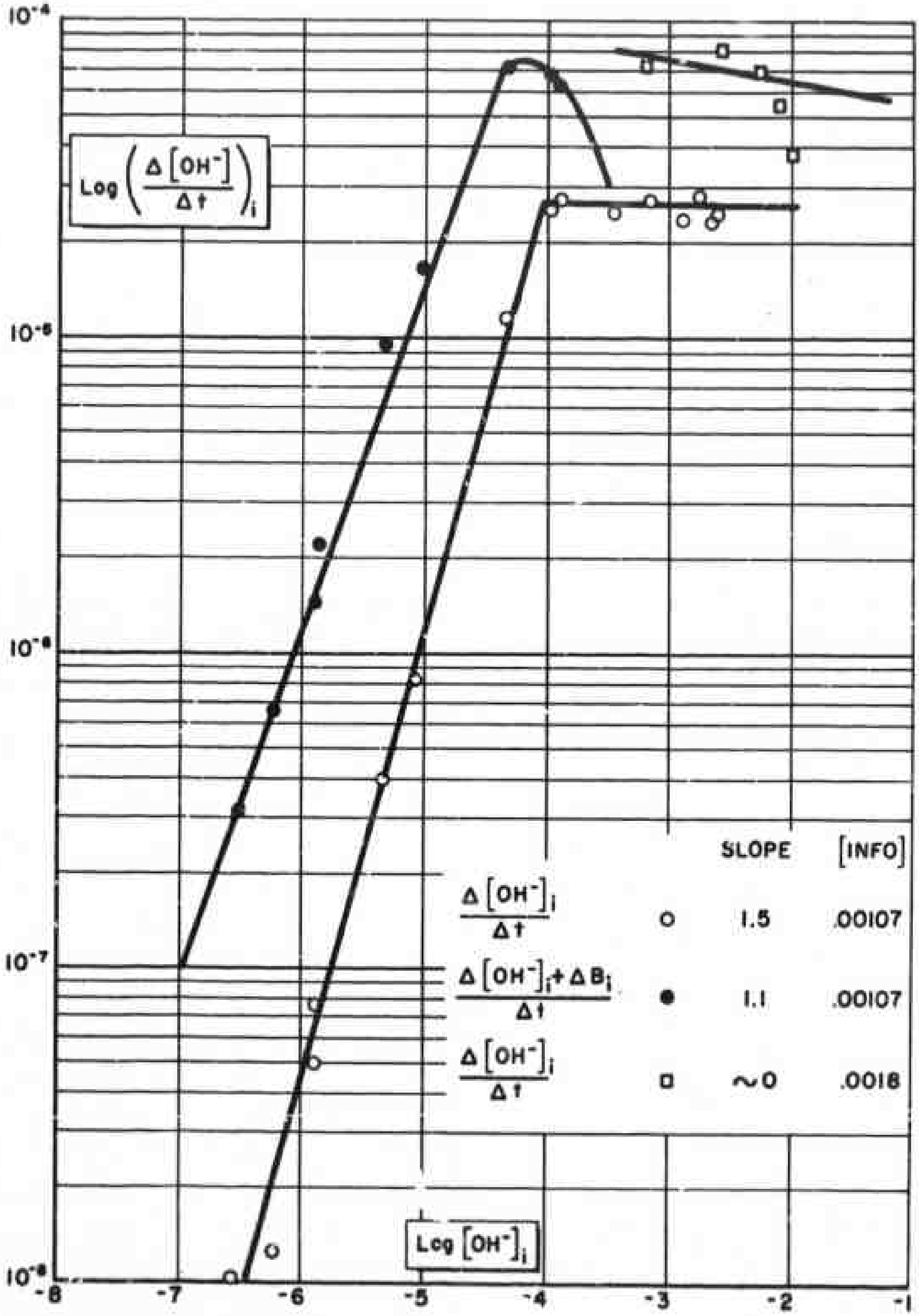


Fig. 3 - Log Rate vs. Log $(OH^-)_i$ at Constant INFO-635F Concentration

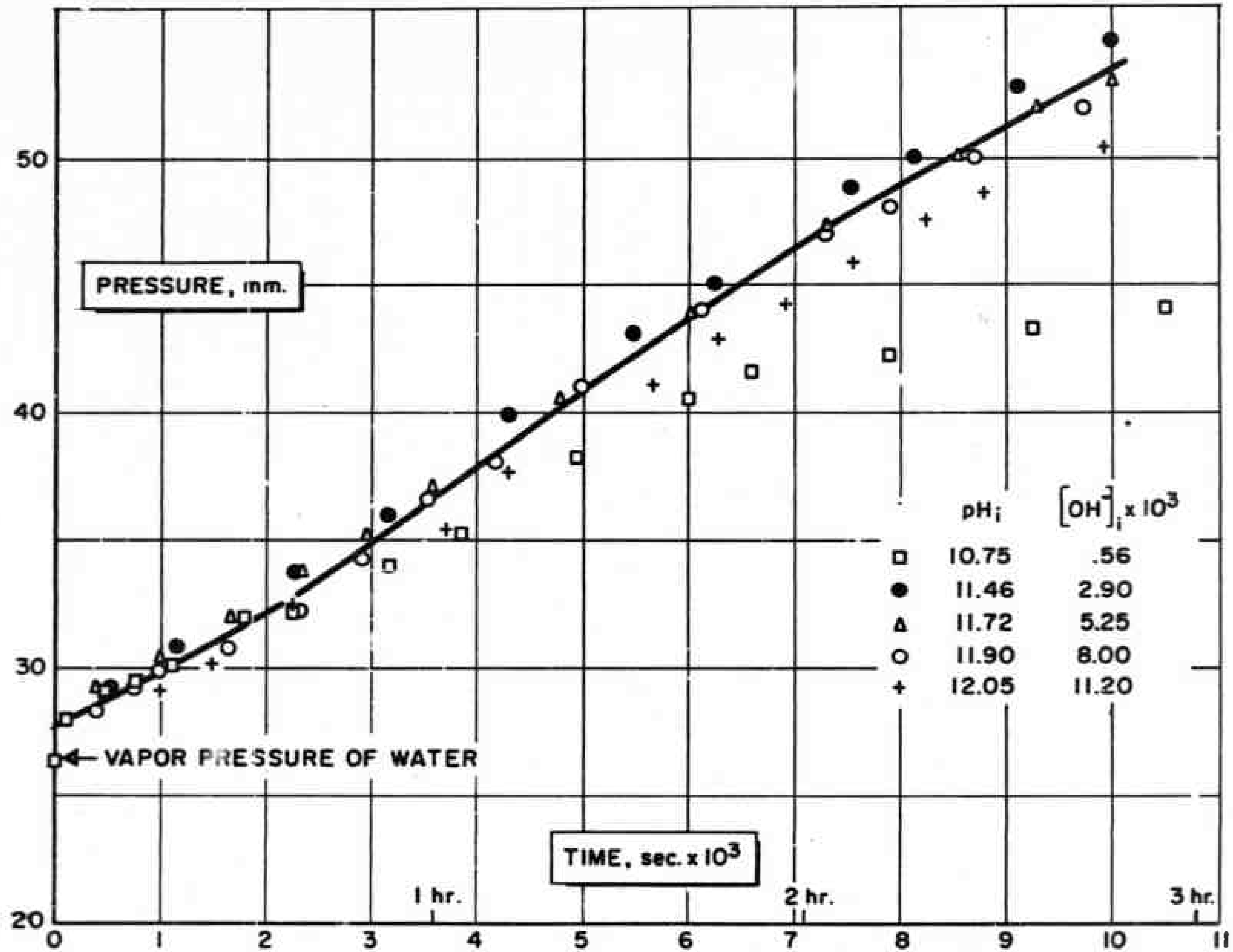
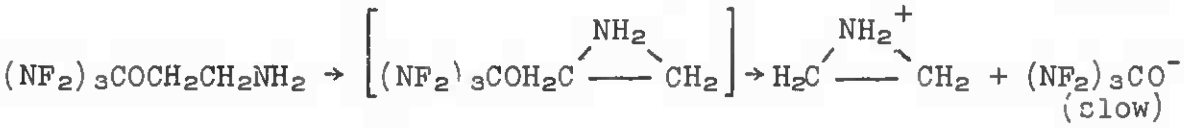


Fig. 4 - Pressure vs. Time at Various Initial Hydroxide Concentrations ($[INFO\text{-}635P]_i = 0.0018$ M)

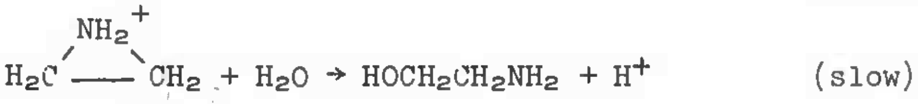
it indicates that the rate-determining step does not involve hydroxide ion.

c. Proposed Mechanism for Decomposition of the Free Amine - On the basis of the above experiments the following mechanism is proposed:

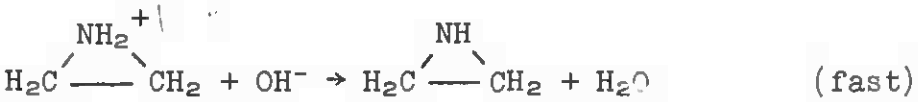
$$(NF_2)_3COCH_2CH_2NH_3^+ClO_4^- + OH^- \rightarrow (NF_2)_3COCH_2CH_2NH_2 + H_2O + ClO_4^- \quad \text{(fast)} \qquad (4)$$



$$(NF_2)_3COCH_2CH_2NH_2 \rightarrow \left[(NF_2)_3COH_2C\overset{NH_2}{\diagup\!\!-\!\!\diagdown}CH_2\right] \rightarrow H_2C\overset{NH_2^+}{\diagup\!\!-\!\!\diagdown}CH_2 + (NF_2)_3CO^- \quad \text{(slow)} \qquad (5)$$



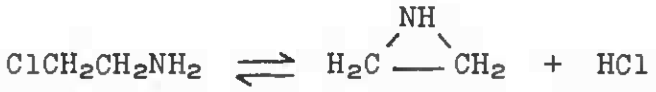
$$H_2C\overset{NH_2^+}{\diagup\!\!-\!\!\diagdown}CH_2 + H_2O \rightarrow HOCH_2CH_2NH_2 + H^+ \quad \text{(slow)} \qquad (6)$$



$$H_2C\overset{NH_2^+}{\diagup\!\!-\!\!\diagdown}CH_2 + OH^- \rightarrow H_2C\overset{NH}{\diagup\!\!-\!\!\diagdown}CH_2 + H_2O \quad \text{(fast)} \qquad (7)$$

$$(NF_2)_3CO^- + 8\ OH^- \rightarrow 6\ F^- + NO_2^- + N_2 + CO_3^= + 4\ H_2O + 0.1\ N_2O\ (+NO_3^-\ ?) \quad \text{(fast)} \qquad (8)$$

The three ring ethylenimine intermediate is rather common in β-substituted aliphatic amines[9,10]; for example, β-chloroethylamine cyclizes quantitatively to ethylenimine in alkaline solutions, but the ring hydrolyzes readily in neutral or acidic solutions to ethanolamine.



$$ClCH_2CH_2NH_2 \rightleftharpoons H_2C\overset{NH}{\diagup\!\!-\!\!\diagdown}CH_2 + HCl \qquad (9)$$

Once the tris(difluoroamino)methoxy group is liberated, it hydrolyzes rapidly. A crucial test for step (5) is the detection of ethylenimine because step (6) is irreversible. This has been accomplished by gas chromatography, which indicated that in 0.1 N NaOH solution only ethylenimine plus another higher boiling compound of about equal amount are formed with little or no ethanolamine. At the present time this second component is not identified.

d. Further Studies in an Open System - Up to this point the work described above has been carried out in a closed system. The results of analyses with time in an open system are shown in Figure 5. One of these experiments (7045-54) was carried out in a glass beaker in air, and a second in nitrogen atmosphere, while nitrogen was bubbled through it (Experiment 7045-61). Samples were periodically withdrawn and analyzed for fluoride ion and non-volatile carbon; the rate of nitrogen evolution was also followed in a closed system. The results indicate two conclusions: first that $(F^-)/5.7$ and N_2 initially increase at the same rate, but that the F^- levels off at a value of 4.6 moles/mole INFO-635P rather than 5.7 observed in a closed system. Apparently, some fluorine is lost in a volatile nitrogen or carbon-containing species. This is not likely to be N_2F_2, e.g., from NF_2^-, because N_2F_2 does not hydrolyze appreciably at room temperature[7].

Secondly, volatile carbon is formed much more rapidly than $(F^-)/5.7$ and reaches 1.5 mole/mole INFO-635P rather than 1.2 previously observed. This suggests that some of the "non-volatile carbon" is being lost. However, this is not likely in view of the high boiling point (177°C.) and solubility of ethanolamine. Rather, the possibility exists that ethylenimine forms and vaporizes (B.P. = 56°C.). All the evidence obtained points to an initial rate-determining step which is unimolecular and proceeds through a cyclic intermediate.

e. Effect of Solvent on Decomposition of Free Amine - The effect of using a basic non-aqueous solvent, ethanolamine, to form the free amine was investigated briefly. A small solid sample of INFO-635P was evacuated in a small pyrex vessel to which a Fisher-Porter valve was attached. The system, connected to a Wallace-Tiernan gauge, was closed and pure ethanolamine was added from the side arm. After a brief initial pause of around 30 seconds, gases were rapidly evolved for a few seconds until the reaction was completed. The only appreciable gaseous products were 92% N_2, 0.96% N_2O, and 3.66% N_2F_2. This is very similar to the aqueous basic

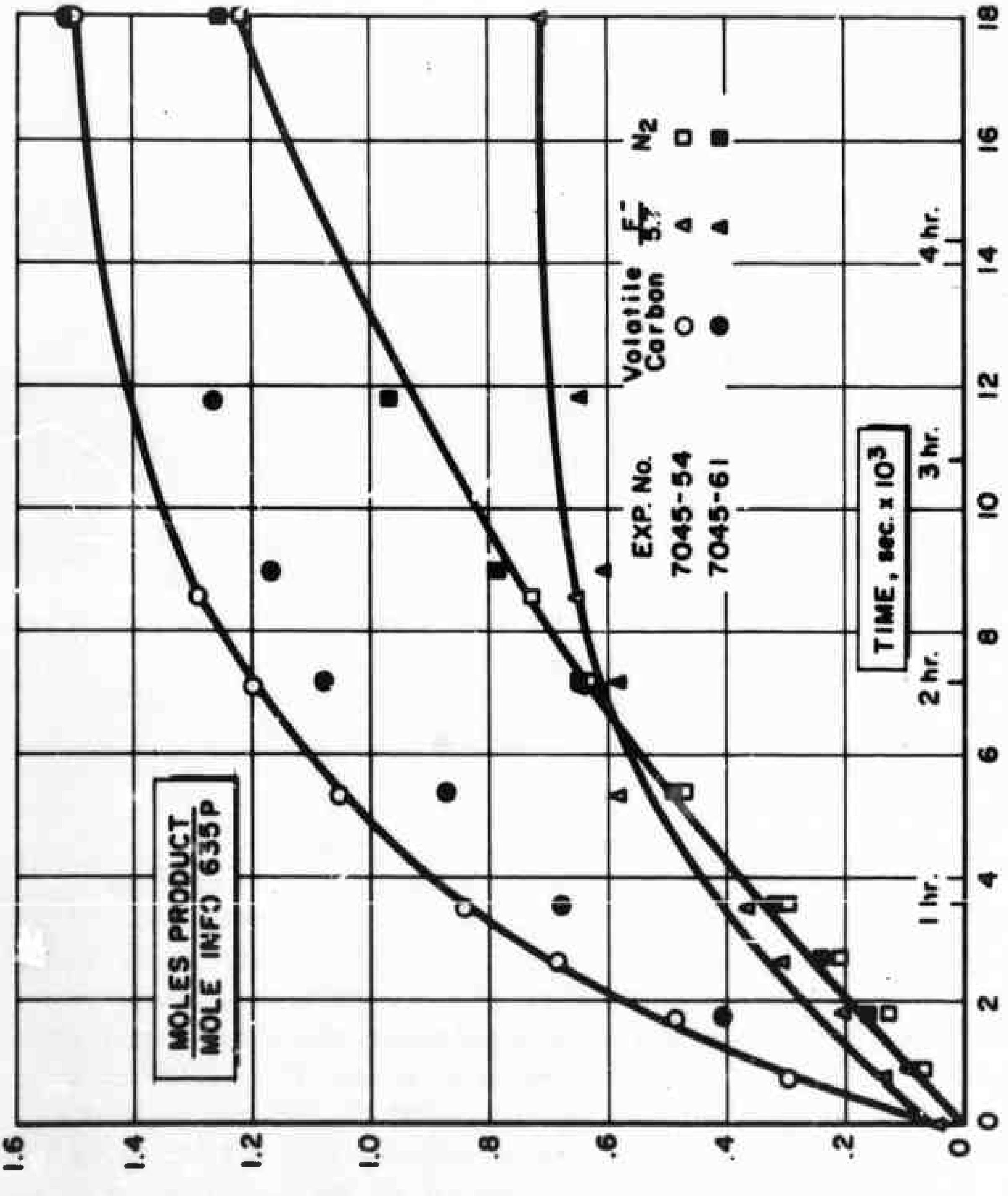


Fig. 5 - Moles of Various Products per Mole INFO-635P vs. Time

decomposition products, except that N_2F_2 is formed rather than N_2O in about the same amount. It is perhaps surprising that in ethanolamine the decomposition is so much more rapid than in aqueous base. One would expect the high dielectric constant of water to favor an ionic reaction. However, ethanolamine is a reducing agent which very likely complicates the comparison.

3. Decomposition of the Ammonium Ion of INFO-635P

The decomposition studies on the free amine of INFO-635P have not indicated the mechanism by which the tris(difluoroamino)methoxy group decomposition takes place, except that the tris(methoxide) ion rapidly decomposes, even at room temperature. In the ammonium ion form of INFO-635P, the ethylenimine would not form, and decomposition of the tris group would be expected to occur primarily.

a. Effect of pH on the Rate of Decomposition in Acid - The initial studies on the ammonium ion of INFO-635P were carried out to determine if the decomposition in acidic solutions proceeded by way of the small amount of amine present according to the mechanism already discussed, or if the ammonium ion has a unique mode of decomposition.

Solutions of INFO-635P with pH's varying from 1 to 3 were prepared and heated at constant temperatures for equal lengths of time. Typical fluoride analyses as a function of pH are shown in Table IV.

Beginning at a pH of 1, there seems to be little change in conversion until pH of 3, where it increases appreciably. This would indicate that the free amine does contribute to the decomposition rate and that acid catalysis is small or negligible.

However, a quantitative analysis of the data indicates that the ammonium ion must also contribute to the decomposition at these temperatures. If it is assumed that the reaction is first order in free amine and independent of ammonium ion, then,

$$\frac{d(\text{INFO})}{dt} = k(B) = \frac{k\,K_a(\text{INFO})}{(H^+)} \qquad (10)$$

where $K_a = \frac{(B)(H^+)}{(BH^+)}$

B = the free amine of INFO-635P
BH^+ = the ammonium ion of INFO-635P
($\cong$ INFO concentration at low pH) →

$$\log \frac{(\text{INFO})_\circ}{(\text{INFO})} = \frac{k\,K_a\,t}{(H^+)\;2.303} \qquad (11)$$

$$\left[\log \frac{(\text{INFO})_\circ}{(\text{INFO})}\right](H^+) = \frac{k\,K_a\,t}{2.303} \qquad (12)$$

Table IV

Effect of Hydrogen Ion Concentration on Conversion of INFO-635P

Experiment No.	Temp. °C.	Concentration Hydrogen Ion, moles	Concentration Fluoride Ion moles x 10^3	% Conversion
7045-83	90	0.10	4.16	7.33
		0.025	4.99	8.80
		0.005	4.58	8.07
		0.001	12.70	22.40
	100	0.10	5.95	10.50
		0.025	4.00	7.06
		0.005	6.90	12.20
		0.001	17.80	31.40
7045-97	110	0.1	--	35.10*
		0.025	--	39.0
		0.005	--	47.20
		0.001	--	57.40

*In this experiment conversions were based on CO_2 analysis.

Table V shows the values of $\frac{k\ K_a\ t}{2.303}$ calculated at pH of 1 and pH of 3 from conversion data based on fluoride concentration and CO_2 analysis. The observed fact that the rate constant at pH 1 is at least 30 times greater than can be accounted for by the amine only indicates that the ammonium ion is also contributing an appreciable amount to the overall conversion, and the rate equation should have the form:

$$\frac{d(\text{INFO})}{dt} = k_B(B) + k_{BH^+}(BH^+) \qquad (13)$$

$$2.303 \log \frac{(\text{INFO})_\circ}{(\text{INFO})} = \left[\frac{k_B K_a}{(H^+)} + k_{BH^+}\right] t \qquad (14)$$

Using equation (14), k_B has a value of approximately $10^7\ k_{BH^+}$ (see Appendix A). If the activation energy for k_{BH^+} were considerably larger than that of k_B, it could become the dominant mode of decomposition at much higher temperatures. However, these data are not sufficiently accurate or complete to determine these activation energies.

b. Stoichiometry - At the present time the stoichiometric equation for complete decomposition of INFO-635P in perchloric acid solution is incomplete, lacking the analysis of the water-soluble products. Quantitative analyses by mass spectroscopy were carried out on the gaseous products from dilute INFO-635P (0.01 M) solutions in 0.1 N $HClO_4$ at 110°C., which were heated a sufficient time for complete decomposition to occur. These results are shown in Table VI. Average values of each product in terms of moles per mole of INFO-635P were calculated on the basis of the last three experiments which were considered the most reliable. These indicate the following partial equation:

$$(NF_2)_3COCH_2CH_2NH_3^+ \rightarrow 5.8\ F^- + 1.1\ N_2 + 0.5\ N_2O + 0.8\ NH_3 + 0.7\ CO_2 + \ldots \qquad (15)$$

Table V

The Effect of Hydrogen Ion Concentration on the Apparent Rate Constant for Decomposition of INFO-635P in Acidic Solutions

Experiment No.	Hydrogen Ion Concentration moles	$\frac{(F^-)}{(INFO)} \times \frac{100\%}{6}$	$\frac{(CO_2)}{(INFO)} \times 100\%$	$\frac{k\ K_a\ t}{2.303} \times 10^3$	$\frac{kpH=1}{kpH=2}$
7045-79 (110°C.)	0.0834	44.5	--	21.2	--
	0.001	83.5	--	0.79	26.9
7045-83 (100°C.)	0.1	10.50	--	4.92	--
	0.001	31.40	--	0.16	30.0
7045-83 (90°C.)	0.1	7.33	--	3.34	--
	0.001	22.40	--	0.11	31.0
7045-83 (100°C.)	0.1	--	6.00	2.74	--
	0.001	--	15.10	0.07	39.20
7045-97 (110°C.)	0.1	--	32.7	17.32	--
	0.001	--	57.4	0.24	77.7

Table VI

Product Analysis for Complete Decomposition of INFO-635P in Perchloric Acid Solution at 110°C.

Time	Moles Product/Mole INFO-635P									
hrs.	N_2	NO	CO_2	N_2O	N_2F_2	N_2F_4	NH_3	NO_3^-	F/6	Total
22.7	0.774	0.299	0.490	0.270	0.003	0.008	1.0**	--	5.96	1.77
23.3	1.085	0.052	0.605	0.482	0.004	--	0.68	0.13	5.83	2.03
24.0	0.945	0.017	0.740	0.576	0.001	--	0.90	--	--	2.04
20.4	1.260	--	0.685	0.480	0.005	--	--	--	5.72	2.06
Avs.*	1.09	0.023	0.673	0.513	0.003	--	0.79	0.062	5.78	2.04

*These are based on the last three experiments only.

**This includes any NO_3^- which may be present as well as NH_3.

Mass balances for nitrogen, carbon, and fluorine are shown in Table VII.

Table VII

Mass Balance for Nitrogen, Fluorine, and Methoxy Carbon from INFO-635P Decomposition in Acid

Element	INFO-635P	Products	Difference
N	4	4.02	+0.02
F	6	5.78	-0.22
C	1 $[-O\underline{C}(NF_2)_3]$	0.67	-0.33

In some respects equation (15) is similar to that obtained in base. Slightly more than 2/3 of the nitrogen content from the tris group forms nitrogen gas; however, 1/2 mole of N_2O is formed rather than NO_2^- as in basic solutions. The CO_2 formed is close to one mole per mole INFO-635P and probably comes from the tris-methoxy carbon in the INFO molecule. The fact that it is 30% less than 1 mole suggests that some of the methoxy carbon is still in solution in some other form*. The presence of nearly one mole of ammonia is unexpected. Since the reduction of a $-NF_2$ group to ammonia is hardly expected in these solutions, this ammonia must come from the amino group originally present and, if so, oxidized products from ethanolamine would be expected from the ethylamine group in INFO-635P.

c. Kinetics - The kinetics of decomposition were studied by measuring gas pressure and composition as a function of time and temperature. This was accomplished by heating samples of solution in four Teflon-lined stainless steel reactors equipped with stainless steel valves. After a specific period of time the reactors were quickly cooled and the gases collected in a monel vacuum system.

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*This point is discussed further in the following Section, c.

Experiments were carried out on concentrated (0.3-1.0 M) and dilute (0.01 M) solutions of INFO-635P, which were 0.1 N in perchloric acid.

The results on the decomposition of dilute INFO-635P at 90°C., 100°C., and 110°C. are shown in Figures 6 and 7 in terms of moles of product per mole of INFO-635P. It is immediately apparent that there is a considerable amount of scatter in the data, and, in general, it was extremely difficult to obtain reproducible results from these studies. Increasing the temperature from room temperature to 110°C. multiplies the problems of obtaining gas samples free from impurities and of avoiding contamination of the solutions due to contact with the vessel. Furthermore, many side reactions and reactions between products readily occur in the acid solution or in the gas phase above it.

Although these problems limit the quantitative interpretation of the data, several qualitative conclusions can be obtained. First, there is no apparent induction period. All the major products except NO are evolved at a constantly decreasing rate with time and the reaction is not autocatalytic.

Secondly, the major products, N_2 and CO_2, at 100°C. and 110°C., are evolved at equal rates for around two-thirds of the reaction, after which the CO_2 levels off at around 60-70 mole %. At 90°C. the CO_2 is always about one-half the N_2 produced. In Figure 8 are plotted total nitrogen and carbon dioxide in the gas phase as a function of time and the same relationship is obtained. A real possibility exists that the solutions are supersaturated with CO_2 and the questions are whether this could amount to the 30% discrepancy in CO_2 analysis, and whether the analysis should disagree with that for N_2 over only part of the range and not as, at 90°C., over all the range. The data at 90°C. particularly favor the explanation that some intermediates or products containing the methoxy carbon are still present in solution.

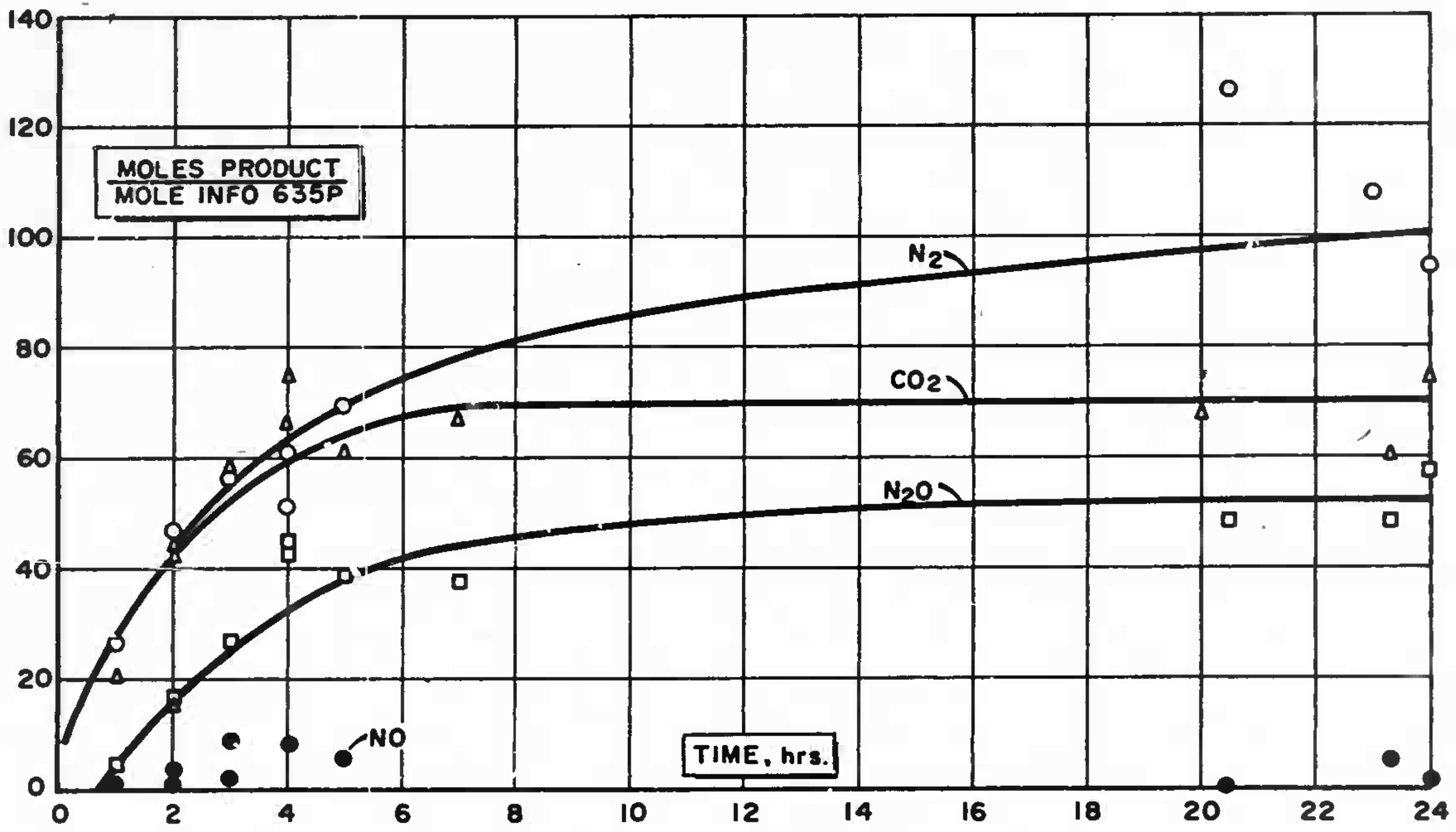


Fig. 6 - Gaseous Products Formed from the Decomposition of 0.01 M INFO-635P in 0.1 M Perchloric Acid at 110°C.

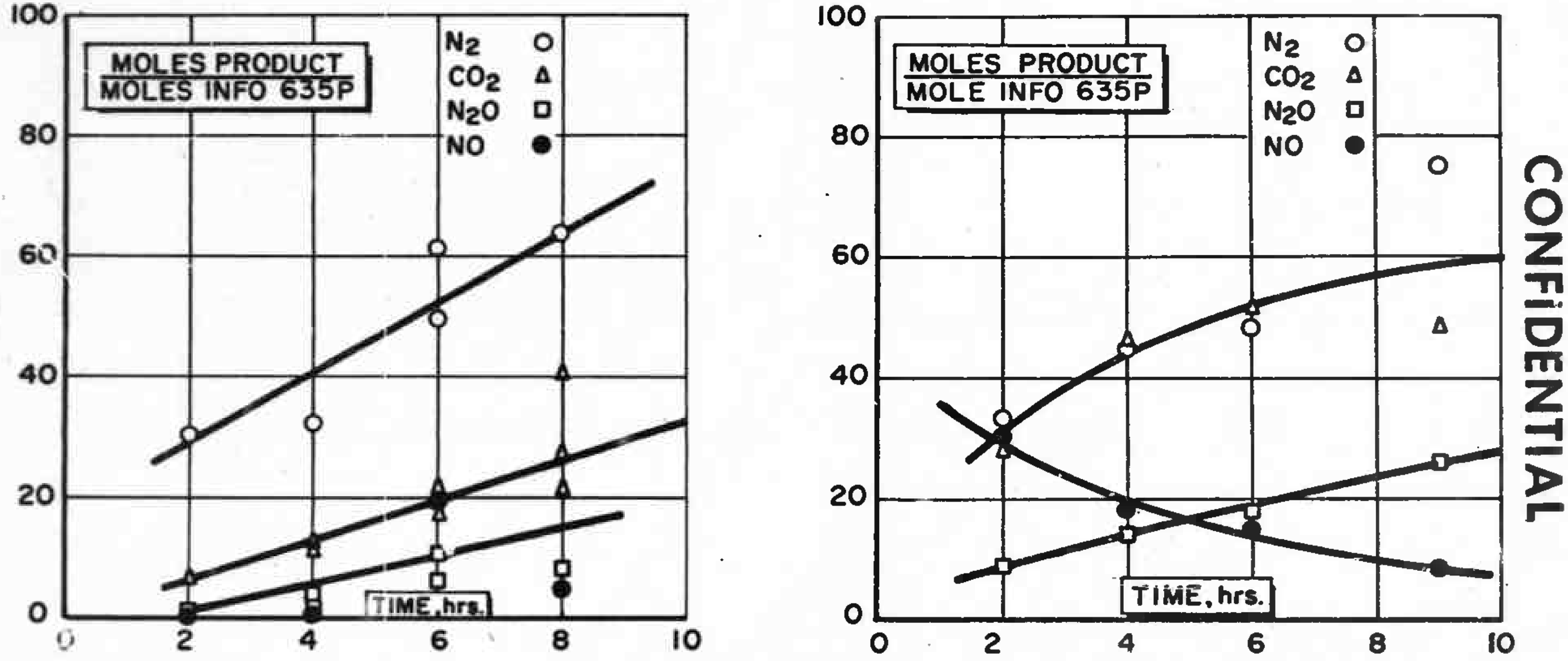


Fig. 7. - Gaseous Products Formed from Decomposition of 0.01 M INFO-635P in 0.1 M Perchloric Acid at 100°C. and 90°C.

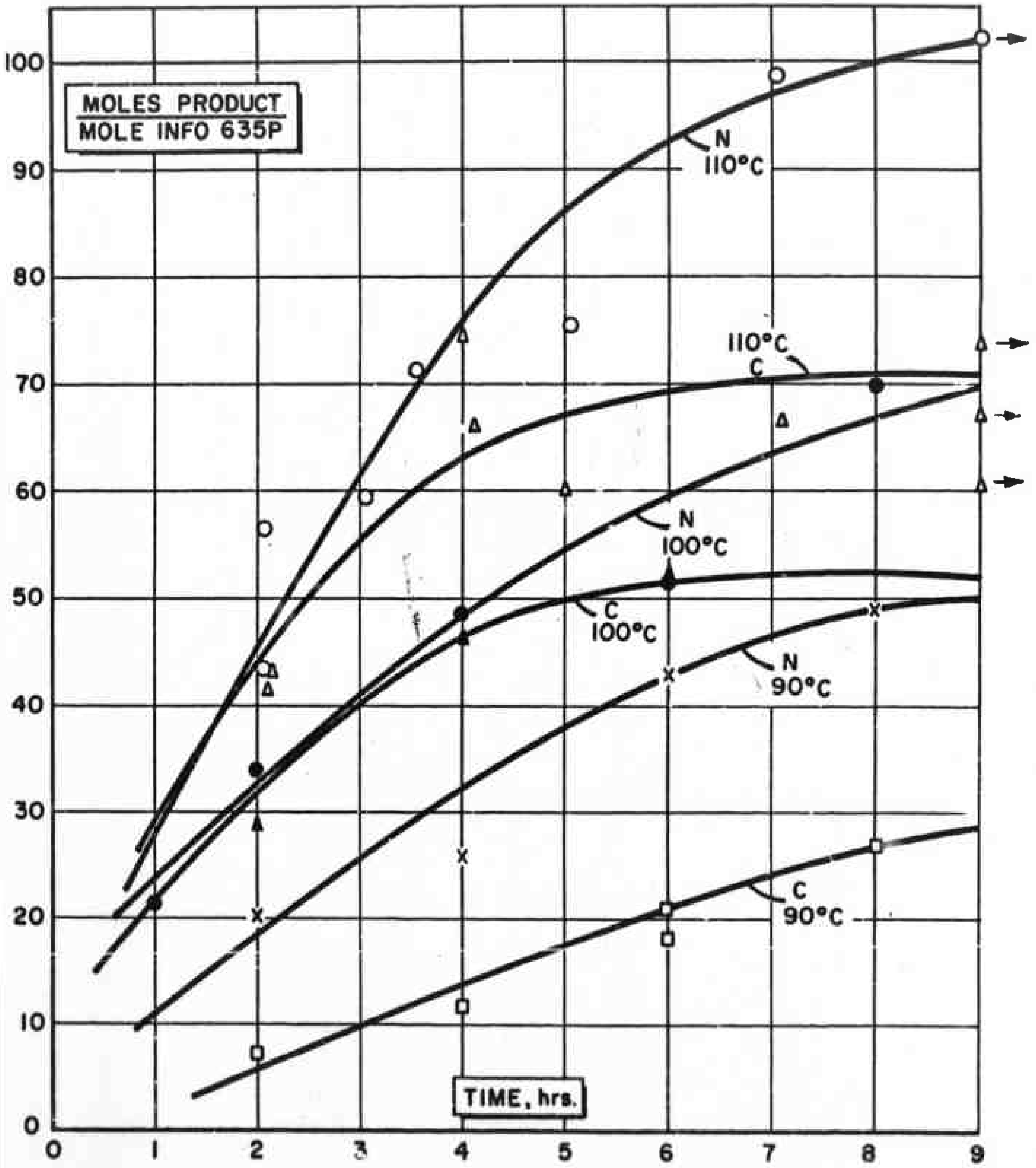


Fig. 8 - Total Nitrogen and Carbon in the Gaseous Products from the Decomposition of 0.01 M INFO-635P in 0.1 N Perchloric Acid

The third conclusion is that the amount of NO produced is erratic and varies from 0-30%. It is not a final product and does not always yield a smooth curve containing a maximum, although occasionally its concentration did reach high values between 2 to 7 hours. Oxygen was also obtained in many samples in varying amounts. This could not always be attributed to an air leak, because there was insufficient N_2 in the samples. The reactor could also hold gases at low pressures for several hours with no pressure increase. Therefore, it is believed that in some cases oxygen is formed as a product and it would react with the NO to form nitric acid.

In Figure 9 and Table VIII are shown the results of the decomposition in concentrated solutions of INFO-635P (approximately 10% by weight) at 100°C. and are slightly different than the results of the dilute solutions. Carbon dioxide is by far the major product with approximately half as much N_2. Tetrafluorohydrazine is almost certainly formed from $\cdot NF_2$ free radicals, indicating that the decomposition occurs at least partially by way of a free radical mechanism. In the dilute acidic solutions it probably hydrolyzes rapidly before it can be detected. Difluoroamine is also formed in small amounts and probably is formed from NF_2^- in an ionic mechanism. The curve for NO is smoother than from dilute solution and appears to be dropping off relative to the other components. No O_2 was observed in any of these samples; therefore, there must be some other route to the disappearance of NO.

d. Solution Analysis - Gas analysis at best can give only a limited amount of information on the rate determining step in the decomposition of the ammonium ion of INFO-635P, simply because the real intermediates probably exist only in solution and the gases observed may be a result of many previous steps. Attempts were made to determine soluble intermediates and products. Generally, this is best performed by an in situ measurement such as infrared or N.M.R. However, vapor phase chromatography was also carried out with some interesting results.

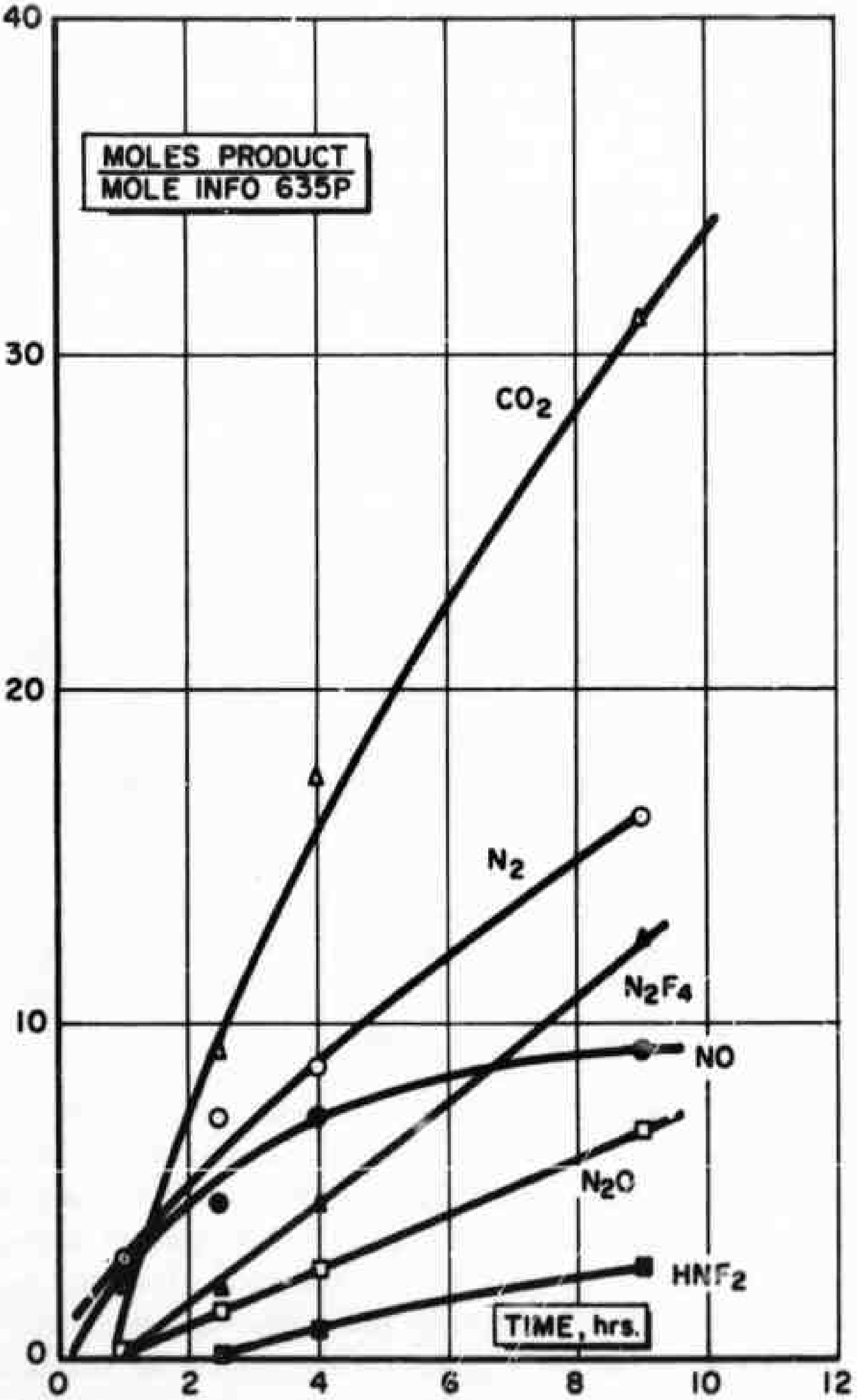


Fig. 9 - Gaseous Products Formed from the Decomposition of 0.3 M INFO-635P in 0.1 N Perchloric Acid at 100°C.

Table VIII

Gaseous Products Formed from Decomposition of Concentrated INFO-635P in 0.1 N $HClO_4$

Temp. °C.	[INFO]	Time hrs.	$\frac{\text{Mole Product}}{\text{Mole INFO-635P}} \times 100\%$						
			N_2	NO	CO_2	N_2O	N_2F_2	HNF_2	N_2F_4
100	0.314	1	2.98	2.59	2.06	0.29	0.12	0	0.28
		2.5	7.15	4.66	9.04	1.46	0.29	0.15	2.09
		4	8.82	7.40	17.50	2.55	0.72	0.90	4.56
		9	16.15	9.14	31.90	6.61	0.66	2.88	12.45
110	0.969	2.5	7.95	2.20	19.40	1.55	0.15	6.51	4.20
		16.0	10.45	2.18	17.85	2.15	0.88	0.62	8.24

(1) Vapor Phase Chromatography - In order to obtain a chromatograph of the products, it was necessary to make the solution basic and quickly chromatograph it on a basic column. Since decomposition of the amine of INFO-635P occurs rapidly at 70°C., the experiment consisted of a comparison of the chromatograph of a solution of pure INFO-635P and one which had been heated for several hours in acid and then chromatographed.

The results are shown in Figures 10 and 11. The chromatographs of both heated and unheated INFO-635P solution give at least 7 peaks which differ appreciably in relative magnitudes. The peak at E is ethylenimine (by comparison with the retention times for a known ethylenimine sample) and it is closely followed by peak F which is definitely a product of the acidic decomposition. At present the identity of this peak is unknown, except that it probably has a boiling point and polarity roughly similar to ethylenimine. In addition, there are some lower boiling compounds which include ammonia and perhaps ethanol. Ethanolamine would not appear on the chromatograph under these conditions. It was originally hoped that mass spectra could be obtained on each of these peaks using a Bendix time-of-flight spectrometer, but for some reason spectra were not obtainable.

(2) Nuclear Magnetic Resonance - The fluorine N.M.R. was carried out on concentrated INFO-635P solution decomposed in acid. Nine values of ϕ relative to $CFCl_3$ are shown in Table IX. Peaks A and B at -24 ϕ and 20.0 ϕ correspond to INFO-635P and the adduct of ethanolammonium perchlorate, respectively. Peaks D and E were also occasionally observed as impurities in the decomposed INFO-635P samples. The interesting peaks representing products or intermediates have ϕ values of 5.9, 128, 144, 148 and 155. Of these peaks, G was only obtained once and is probably not significant.

Figure 12 shows the results of one experiment in which two samples were heated 4 and 6 hours, respectively, at 110°C. The samples were completely enclosed in Teflon, except for a small Viton rubber

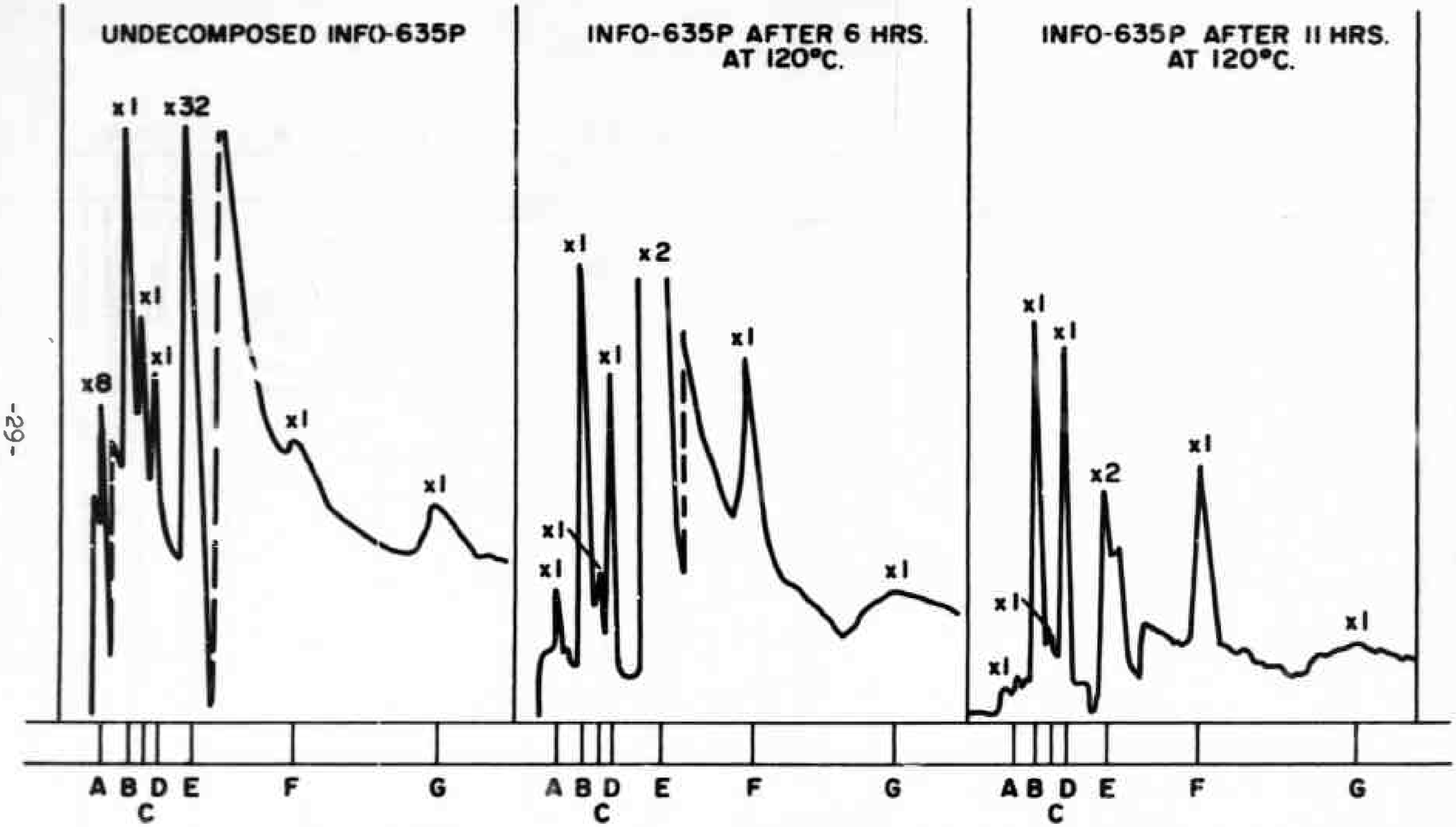


Fig. 10 - Gas Chromatography of INFO-635P Solution Before and After Heating at 120°C. in 0.1 N Perchloric Acid. (The Peak at E is Ethylenimine).

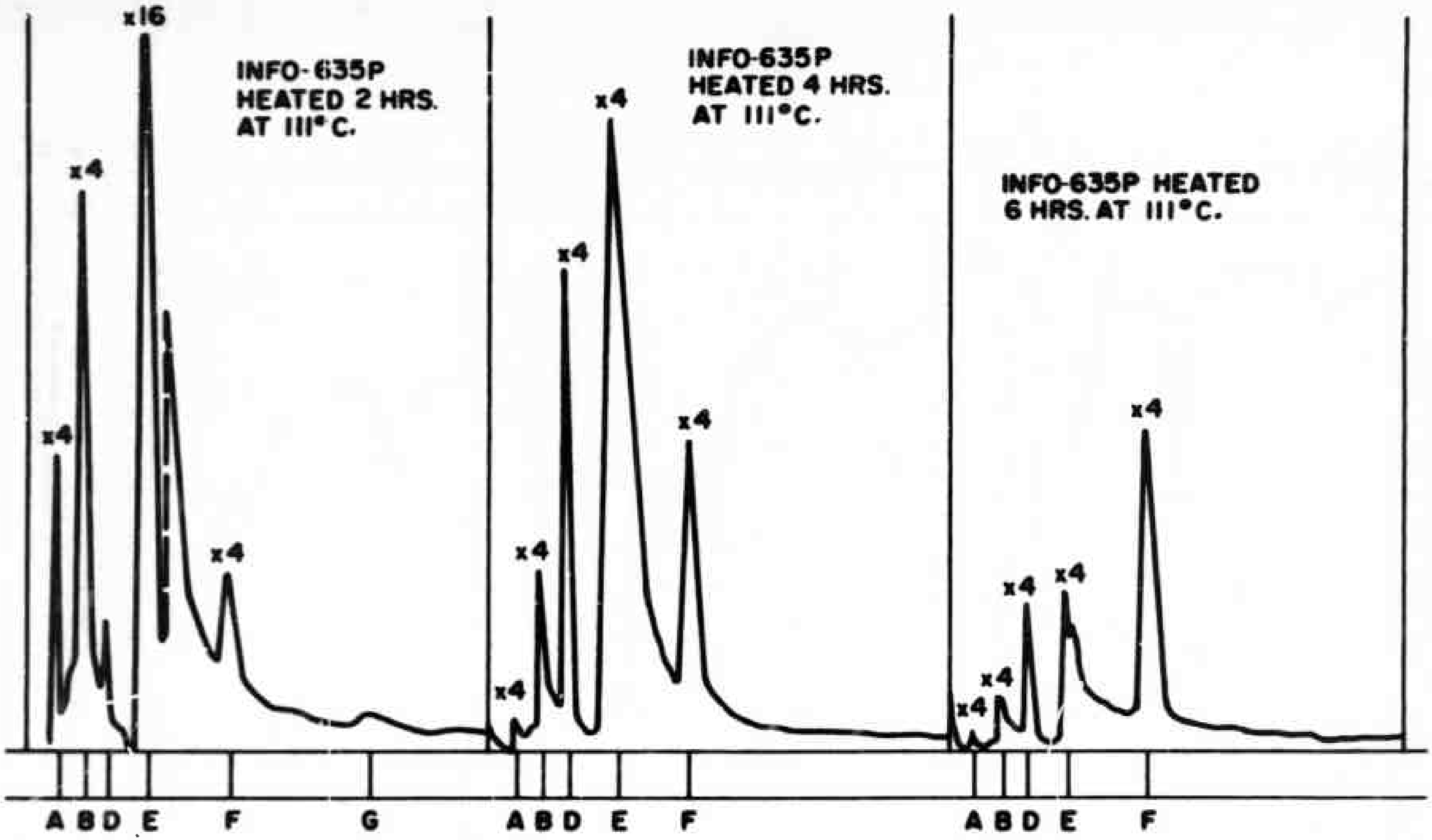
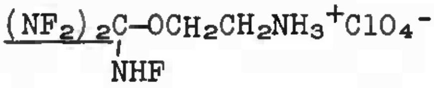
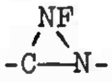
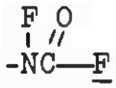
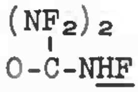


Fig. 11 - Gas Chromatography of INFO-635P Solution After Heating at 111°C. in 0.1 N Perchloric Acid. (The Peak at E is Ethylenimine).

gasket. The liquid samples were frozen at -78°C. immediately after being heated. The major peak at 155 Ø was almost comparable in height to the original INFO-635P and was only moderately stable. In previous experiments in which the samples were not stored on dry ice, this large peak never appeared, and, indeed, in this case upon standing in the NMR tube, it disappeared. In addition to this peak there existed a small peak at 5.85 Ø which disappeared slowly from 4 to 6 hours, one at 148 Ø which increased with time, and one at 128 Ø which also appeared to increase.

Table IX

NMR Peaks Observed in Partially Decomposed Concentrated Aqueous INFO-635P Solutions in 0.1 N Perchloric Acid

Peak Letter	Ø (Shift from $CFCl_3$)	Possible Assignments
A	- 24.0	$\underline{(NF_2)_3}COCH_2CH_2NH_3^+ClO_4^-$
B	- 20.6	 $\underline{(NF_2)_2}\underset{\substack{\vert\\ NHF}}{C}-OCH_2CH_2NH_3^+ClO_4^-$
C	+ 5.9	 or  $-\overset{F\ \ O}{\overset{\vert\ \ \Vert}{NC}}-\underline{F}$
D	+ 85.2	C—F or $C=N\underline{F}$
E	+ 116.5	C—F
F	+ 128.3	HF
G	+ 144.1	Doublet (7 cps). Possibly  $O-\overset{\substack{(NF_2)_2\\ \vert}}{C}-N\underline{HF}$
H	+ 148.8	Doublet (5 cps). + quadruplet (1.3 cps)
I	+ 155.0	

Both samples at 4 and 6 hours were allowed to stand briefly at room temperature and the NMR repeated as shown in Figure 12. Under these conditions, the peak I at 155 Ø completely disappeared and

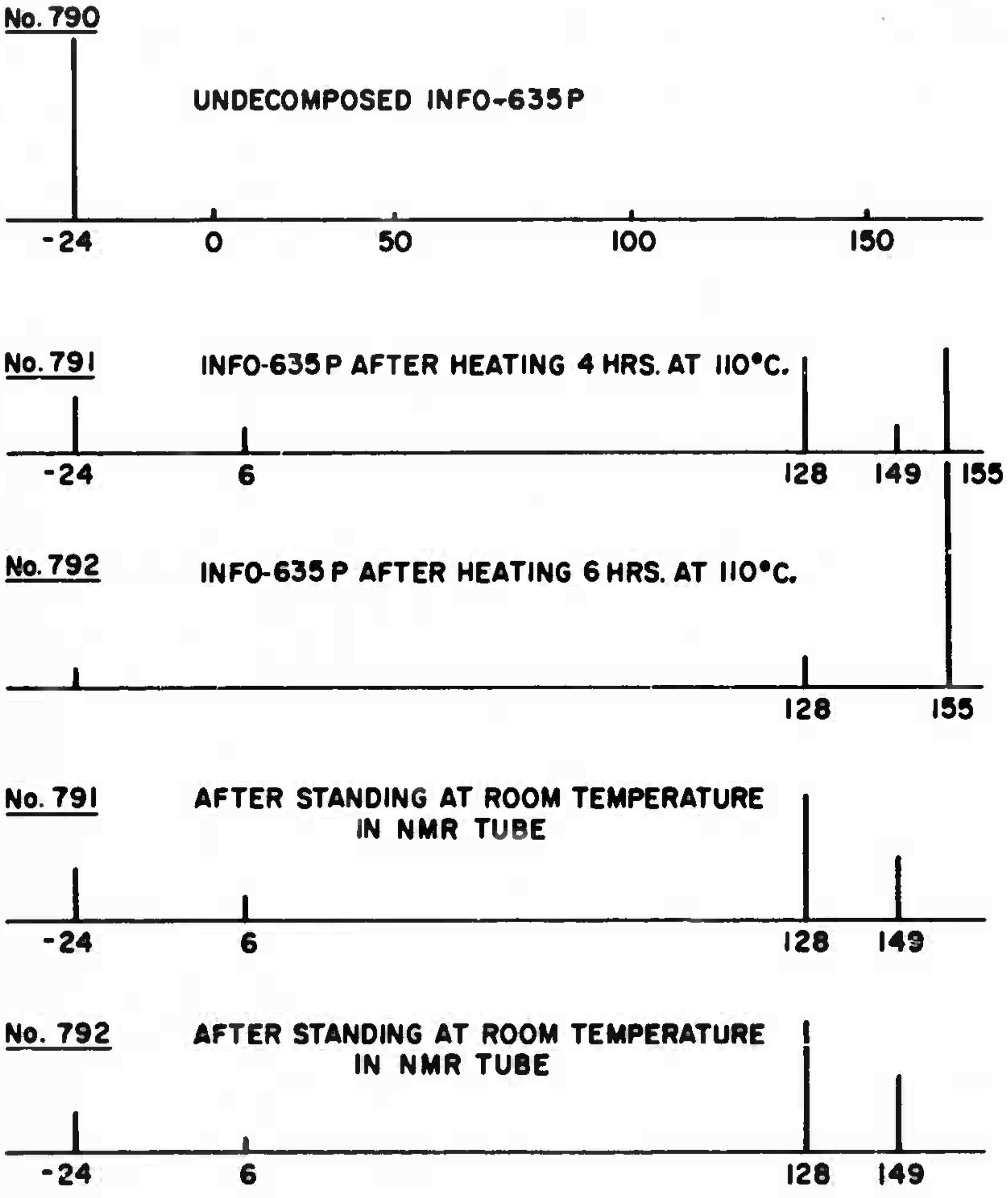
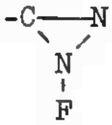
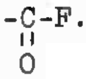
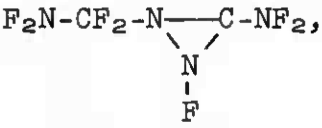
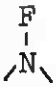
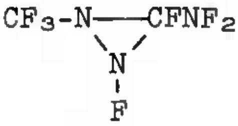
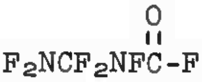
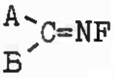
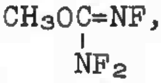


Fig. 12 - NMR Spectra of 0.3 M INFO-635P Solutions Immediately After Heating at 110°C. and After Standing Briefly at Room Temperature in an NMR Tube

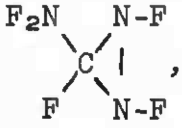
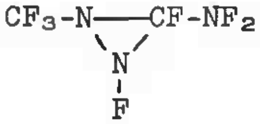
both F and H have considerably increased, whereas C was the same or less. Therefore F and H are products of 155 ϕ and C is not. Furthermore, C and H or I are not derived from the same molecule.

The important question is the identification of these compounds or the kind of fluorines which give resonance at these values. This identification is difficult because these are probably new compounds with no recorded NMR spectra, so tentative assignments only can be made by comparison with similar known compounds. The peak at 128 ϕ is almost certainly fluoride ion, because a known KF solution gave a large peak at 122 ϕ. There are very few compounds which resonate around +6 ϕ and give a broad peak (30 cps wide) with no fine structure. The possibilities seem to be  or  $-\underset{O}{\underset{\|}{C}}-F$.

For example, in compound E,  the  group absorbs at +11.2 ϕ and in  at +8.3 ϕ[11]. In  $F_2NCF_2NF\overset{O}{\overset{\|}{C}}-F$, the C-F is assigned to +8.5 ϕ[11]. Although the fluorine resonance in  can vary tremendously depending on the nature of A and B, in the compound  $CH_3O\underset{NF_2}{\underset{|}{C}}=NF$, this fluorine absorbs at +45.3 ϕ[10], so very likely the peak of +6 ϕ does not correspond to this configuration.

The peak of 149 ϕ has the rather strange fine structure shown in Figure 13 consisting of four close peaks of equal height, and spacing on the right side of a broad doublet. This structure was determined at both 56 and 93 megacycles and gave splittings of

Fig. 13 - Fine Structure of Fluorine NMR Peak at 149 0

1.3 cps between the quadruplet peaks and 5 cps between the doublets. These small J values would indicate that whatever nuclei are responsible for splitting the fluorine are relatively far removed in the molecule. The fine structure of the peak at 155 φ has not been determined. Compounds containing certain C-F groups absorb in the 150 φ region, namely, Compound E at 150.4 φ, Compound G,  , at 159.2 φ,  at + 154.2 φ, and many complex ions containing fluorine. In general, to absorb in this region the fluorine must be fairly well shielded by a partial minus charge or donation of electron into its p orbitals. In the examples cited, however, the couplings are much larger than those observed here and these cannot be applied directly to our spectra.

4. Decomposition Studies on Solid INFO-635P

The thermal decomposition of solid INFO-635 has been studied briefly in a single experiment carried out at 150°C. in Vycor in order to determine whether the products were similar to those obtained from aqueous decomposition. The results of pressure measurement and analysis of the gases are shown in Figure 14 and Table X.

Table X

Gas Analysis of Products Over Solid INFO-635P at 154°C.

Product	Sample No. 1	Sample No. 2	Moles Product/ Mole INFO-635P from No. 2
CO	3.74	6.69	0.253
NO	3.53	4.04	0.155
N_2	27.20	21.0	0.805
N_2O	11.30	12.40	0.476
CO_2	29.60	28.60	1.10
SiF_4	22.30	23.30	0.895
N_2F_4	0.76	1.06	0.041

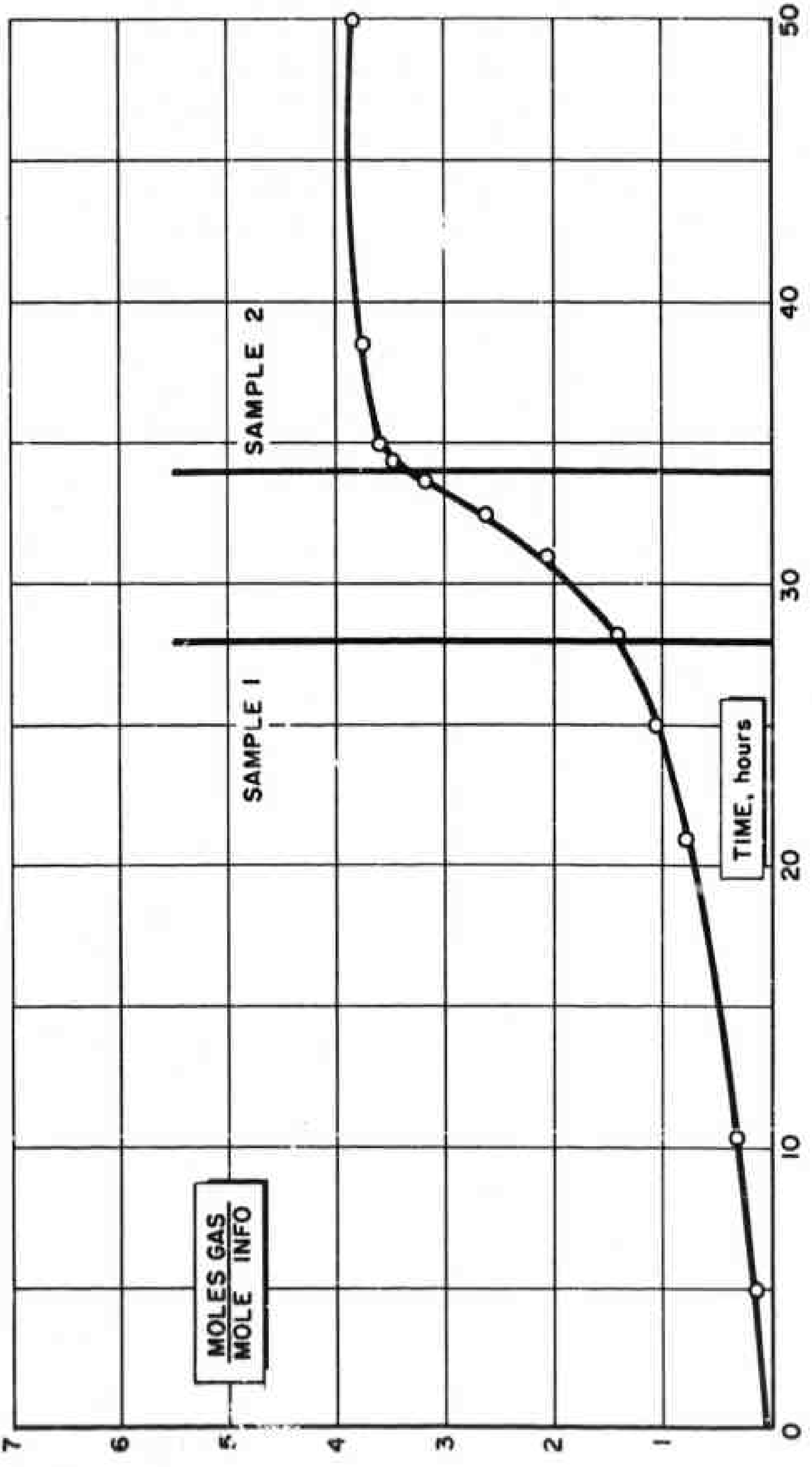


Fig. 14 - Moles of Gas Produced over Solid INFO-635P at 154°C. with Time

The pressure-time curve is a typical sigmoid. However, it should be noted that the pressure increased abruptly after withdrawal of the first sample and least rapidly after withdrawal of the second sample. The amounts of N_2 and CO_2 are surprisingly similar to those found in both acidic and basic solution decompositions, namely about one mole per mole of INFO-635P. The amount of N_2O formed is equal to that obtained from decomposition of the ammonium ion of INFO-635P in solution. Nitric oxide, NO, is also an important product in solid as well as in the acidic solutions, although in acid solutions it apparently reacts further and does not appear in the final products. Some of the fluorine must have remained in the residue or on the Vycor. The residue was brown and soluble only in polar solvents such as water and acetone. The similarity of product distribution, particularly of the nitrogen, points to a similarity between solid and aqueous decomposition of INFO-635P.

Considering the rapid rate of decomposition of the free amine of INFO-635P, it must be concluded that the formation of the free amine must be inhibited if INFO-635P is to be stabilized. This has been demonstrated by several solid state experiments. When a sample of INFO-635P was evacuated and then exposed to ammonia vapor, the sample exploded almost immediately.

Ammonia removes a proton from INFO-635P, causing increased sensitivity. In the next experiment, the effect of acid was tested by dissolving INFO-635P in nitromethane, adding acid, evaporating most of the nitromethane, and co-precipitating with chloroform. Water, HCl, and $HClO_4$ had little effect on the sensitivity of pure INFO-635P; in fact, HCl, $HClO_4$ and H_2O appeared to increase it slightly (590 g. cm. compared to 740 g. cm. for pure INFO-635P). However, sulfuric acid decreased the sensitivity from around 740 g. cm. to 1300 g. cm. There is a positive correlation between volatility of the acid and the sensitivity, HCl being the least effective and H_2SO_4 the most effective in desensitizing INFO-635P. The results, particularly with ammonia, confirm the prediction that the free amine of INFO-635P contributes to the sensitivity; however, since the fact that acids have so little effect indicates that the tris group on the ammonium ion is in itself capable of rapid decomposition.

5. The Mechanism of Decomposition of the tris(Difluoroamino)-methoxy Group

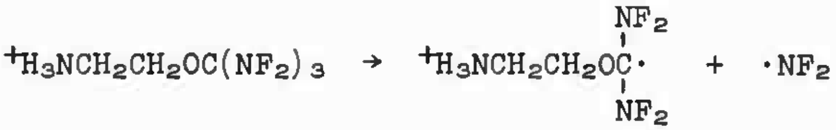
The decomposition of INFO-635P has been studied under widely different conditions ranging from aqueous and non-aqueous base and aqueous acid to the pure solid state. Although there are differences in rates and products, several unifying factors emerge which suggest that the mechanisms may be similar. Of these, the most important are that the methoxy carbon appears as CO_2 in the products and two of the three nitrogens in the tris(difluoroamino)methoxy group appear as nitrogen in the products.

In the tris group there are no N-N bonds; therefore, the formation of nitrogen could conceivably occur in two ways. First, primary decomposition ions or radicals such as NF_2^- or $\cdot NF_2$ could eventually combine to form an N-N bond and be reduced to N_2 gas. Secondly, an N-N bond could form in an intramolecular reaction before the C-N bonds are broken.

Considering first the intramolecular hypothesis, if NF_2^- were formed by heterolytic cleavage, it has been shown[4] to decompose to N_2F_2 and F^-. The N_2F_2 is very stable under the conditions of these experiments[7], and it would have been observed in appreciable amounts rather than N_2. If $\cdot NF_2$ were formed by homolytic cleavage, it would form N_2F_4 which hydrolyzes rather rapidly at 100°C. to NO and HF or F^- with smaller amounts of N_2. Solid $AlCl_3$, however, reduces[7] N_2F_4 to N_2 and Cl_2; therefore, if mild reducing agents are present it can form N_2. This reduction does not seem likely in the present work in rather dilute solutions and particularly not in basic solutions.

The second hypothesis, the intramolecular decomposition mechanism, is believed to adequately explain the formation of one mole of N_2.

The general type of mechanism appears to be the loss of one of the nitrogens initially, followed by formation of an N-N bond between the remaining two nitrogens. In acid solutions the first reaction is C-N bond rupture:



$$^{+}H_3NCH_2CH_2OC(NF_2)_3 \rightarrow {}^{+}H_3NCH_2CH_2O\overset{NF_2}{\underset{NF_2}{C}}\cdot + \cdot NF_2 \qquad (16)$$

I

This much is fairly certain, since N_2F_4 is formed in such large quantities in concentrated solutions as shown in Figure 12, and the only reasonable source of N_2F_4 is from $\cdot NF_2$ radicals. In dilute solutions, N_2F_4 appears only in minute quantities, if at all, because $\cdot NF_2$ radicals are probably hydrolyzed before they can combine according to the reaction:

$$\cdot NF_2 + H_2O \rightarrow \cdot NO + 2\,HF \qquad (17)$$

The resulting radical I in equation (16) is similar to the tris free radical observed in Delta decomposition.

Figure 15 is a diagram of a possible mechanism which could explain some of the products formed, particularly N_2. Radical I rearranges by means of a fluorine shift into the more stable radical II. This radical undergoes reduction by water to a C-NHF group which terminates the free radical mechanism. Then, by analogy with the known rearrangement of PFG and PFF in RbF solution[12], this species cyclizes to the difluorodiaziridine ring compound. In acid solution the ring opens via protonation of the nitrogen, HF is eliminated, and the diazonium fluoride rapidly decomposes to CO_2, N_2 and HF. The acid hydrolysis of a diaziridine ring containing only hydrogens is known to yield hydrazine and ketones or aldehydes[13].

The formation of the considerable amount of N_2O must then be derived from reduction of N_2F_4, $\cdot NF_2$ or $\cdot NO$. The $\cdot NF_2$ originally formed

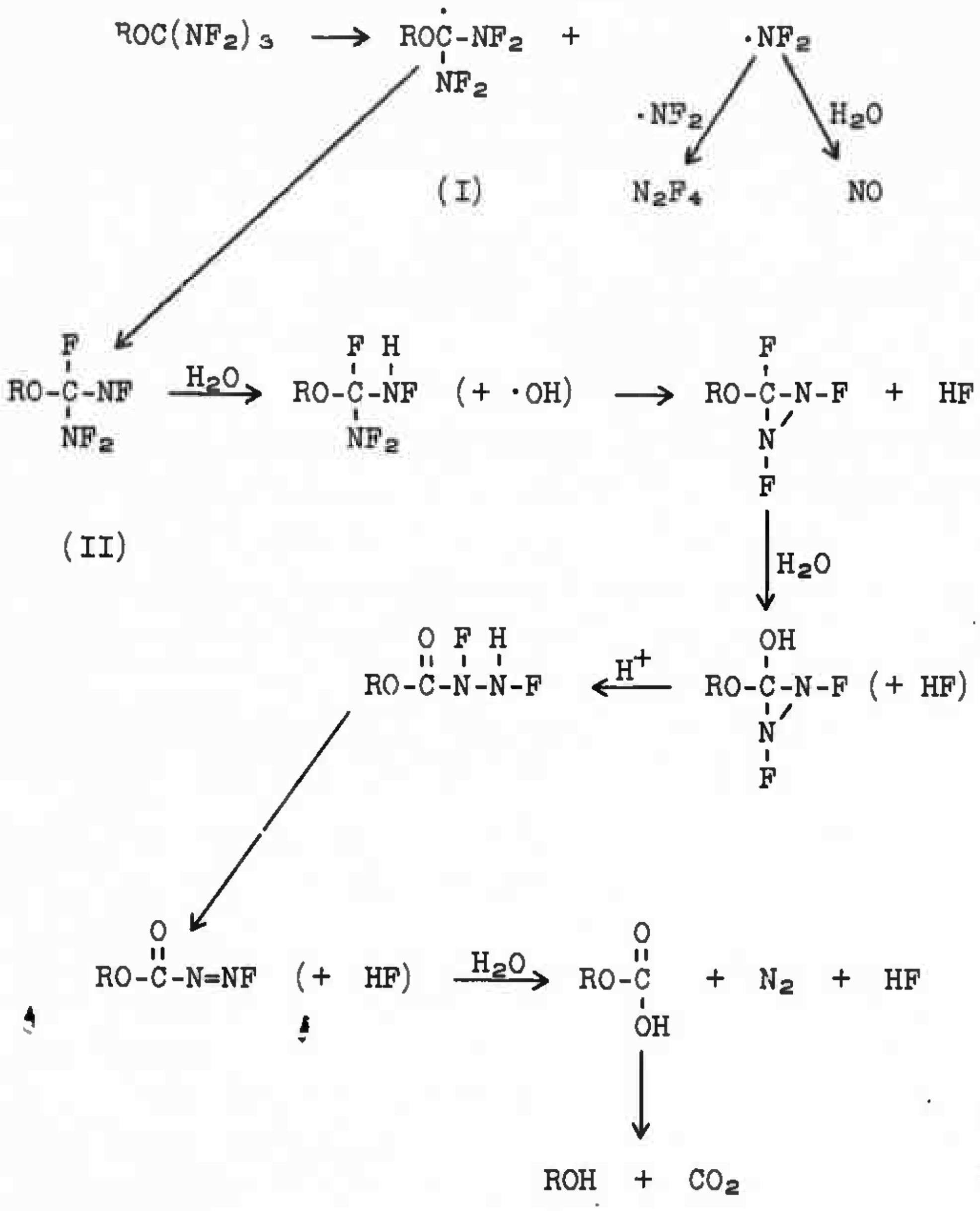


Fig. 15 - Proposed Mechanism for Decomposition of the Ammonium Ion of INFO-635P

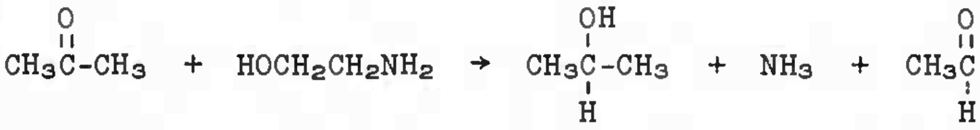
probably combines rapidly with ·OH according to the equations:

$$\cdot NF_2 + \cdot OH \rightarrow HONF_2 \rightarrow HF + FN{=}O \qquad (18)$$

$$FN{=}O + H_2O \rightarrow HF + HNO_2 \qquad (19)$$

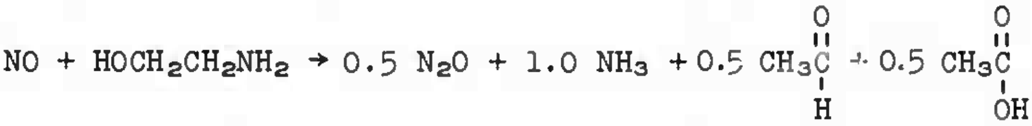
$$3\ HNO_2 \rightarrow H^+ + NO_3^- + H_2O + 2\ NO \qquad (20)$$

The data suggest that NO is formed as an intermediate which disappears with time, and the presence of ammonia indicates that the ethanolamine group is being attacked. It has long been known that ethanolamine is a mild reducing agent. For example, acetone is reduced to isopropyl alcohol by monoethanolamine according to the reaction[14,15,16]:



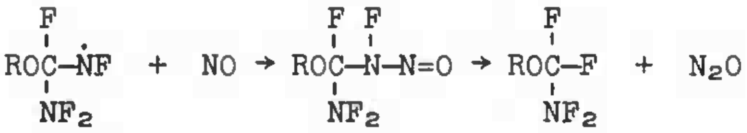
$$CH_3\overset{O}{\overset{\|}{C}}-CH_3 + HOCH_2CH_2NH_2 \rightarrow CH_3\underset{H}{\overset{OH}{C}}-CH_3 + NH_3 + CH_3\underset{H}{\overset{\overset{O}{\|}}{C}} \qquad (21)$$

Then N_2F_4 or NO may be sufficiently potent oxidizers to promote the following reaction:



$$NO + HOCH_2CH_2NH_2 \rightarrow 0.5\ N_2O + 1.0\ NH_3 + 0.5\ CH_3\underset{H}{\overset{\overset{O}{\|}}{C}} + 0.5\ CH_3\underset{OH}{\overset{\overset{O}{\|}}{C}} \qquad (22)$$

The test for this reaction would consist of analysis for ethanol and acetic acid. The formation of N_2O is difficult to explain by any other path. The literature contains no indication of hydrolysis of NO to N_2O and NO_3^-. A possibility might be the reaction:



$$RO\underset{NF_2}{\overset{F}{C}}-\dot{N}F + NO \rightarrow RO\underset{NF_2}{\overset{F}{C}}-\overset{F}{N}-N{=}O \rightarrow RO\underset{NF_2}{\overset{F}{C}}-F + N_2O \qquad (23)$$

However, this would be expected to lead to considerable amounts of products such as N_2F_4 or F_2CO, which are not observed, and would reduce the amount of N_2 formed.

These reactions, proposed only as possible steps in the decomposition, explain some but not all of the observed data, and no doubt other possibilities exist. It is difficult to relate the N.M.R. absorptions at 148 ϕ and 155 ϕ to any of the intermediates in the mechanism because these are expected to be short-lived and would require other absorptions which are not observed. However, this mechanism is valuable, giving direction to further research. As the chemical and N.M.R. analyses become more nearly complete, the mechanism may be altered.

Although it would be possible to write a mechanism for the decomposition of the $(NF_2)_3CO^-$ group, in basic solution, there is not enough data to warrant it. It may bear some similarity to the decomposition of the ammonium form of INFO-635P; and, if product distribution is any indication of mechanism, the solid phase decomposition is similar to that for the acidic solutions of INFO-635P. However, in the solid phase, water could not enter the mechanism as has been proposed for acidic solution decompositions of INFO-635P. Possibly, the ammonium ion hydrogens of INFO-635P could enter the reaction instead of water.

B. EXPERIMENTAL METHODS

1. Procedures for Studying the Free Amine

a. Product Analyses - In these experiments the carbon analyses were carried out by completely oxidizing the total carbon content to CO_2 and analyzing by means of an infrared analyzer[17]. The non-volatile carbon was obtained by the same method, preceded by acidifying the solution and blowing out the CO_2 at room temperature. The volatile carbon, CO_2, was obtained as the difference between the total and non-volatile carbon. The fluoride analysis was done spectrophotometrically with the alizarin complex[18]. The nitrite analysis was also done spectrophotometrically with the use of sulfanilic acid[19].

The decomposition in vacuum and collection of gaseous products for mass spectral analysis were carried out in the reactor shown in Figure 16. This flask was initially evacuated and either helium or nitrogen was bubbled through the burets containing basic and INFO-635P solutions. The system was then closed and either base or INFO-635P solution was added and zero pressure recorded. The second solution was added and the pressure was followed with time on a Wallace-Tiernan gauge. After about 16 hours, the gas was collected and analyzed. In the kinetic experiments in which pressure was recorded versus time, nitrogen gas was used to flush air from the solutions and to saturate the solutions with nitrogen. Thus, there is no induction period during which the solution becomes saturated. In most of the experiments, the bulb temperature was held at 23°C. in a constant temperature bath.

b. pH Measurements - The pH of samples versus time was determined with a Leeds and Northrup pH meter, Model 7401. The output was recorded directly on a Brown recorder. The kinetic experiments were run by adding 0.1 N base from a buret to a stirred solution of INFO-635P until the desired pH was attained. This took approximately a half minute. Then, beaker and electrode assembly were enclosed under a bell jar and this was flushed continually with carbon dioxide-free air.

c. Open System Experiments - One of the experiments recorded in Figure 8 was run in a beaker with a Teflon stirring bar. This was enclosed in the bell jar flushed with air. The second reaction occurred in a three-neck flask. Nitrogen, previously saturated with water, bubbled through the solution. In both experiments samples were withdrawn periodically by pipette, acidified to pH ~3 and stored in closed polyethylene bottles. One of the two samples was flushed with nitrogen to eliminate CO_2 and was analyzed for carbon. The other was analyzed for fluoride ion.

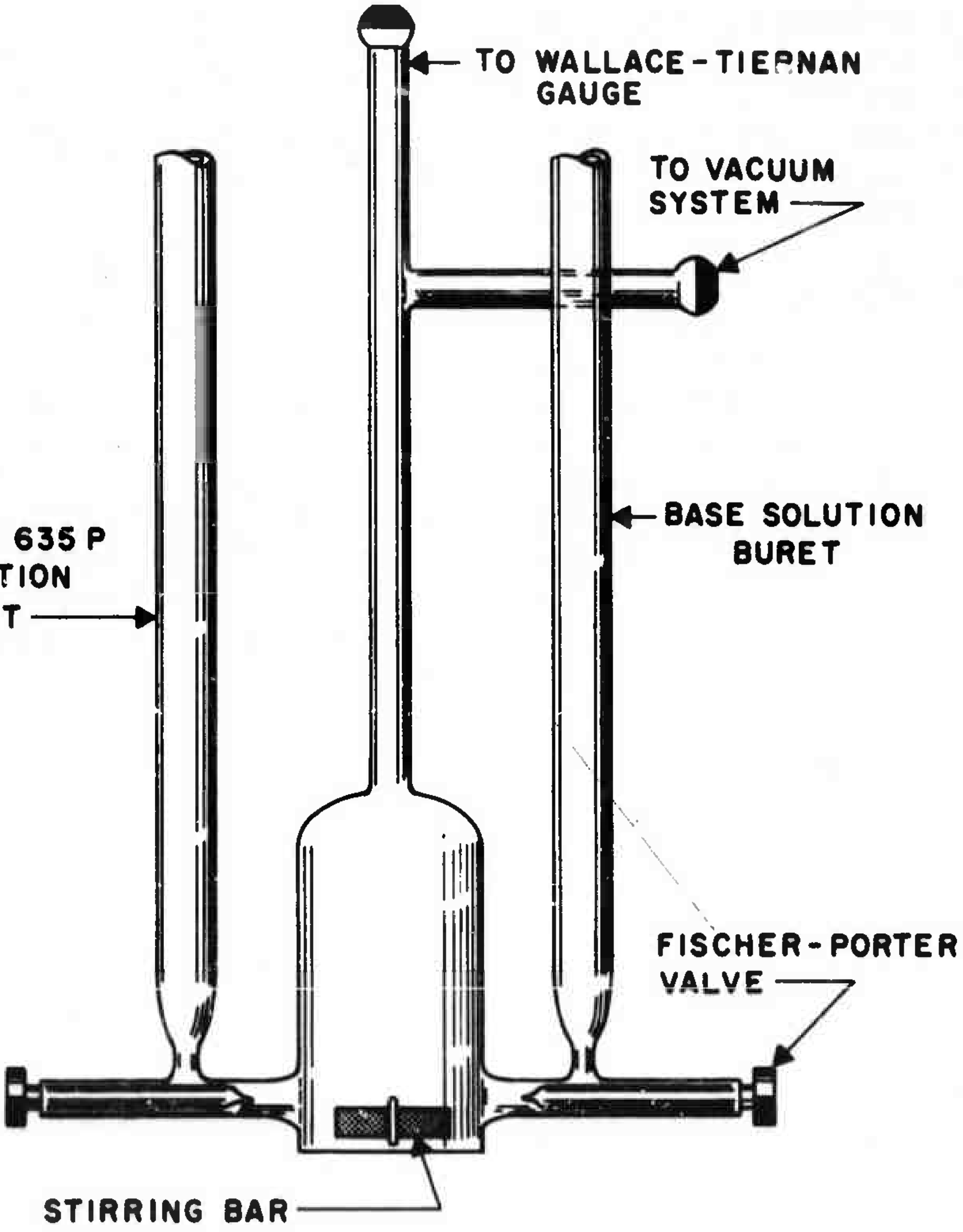


Fig. 16 - Reaction Vessel for Pressure Measurements over Solutions

2. Procedure for Studying the Ammonium Ion

a. Reactor - The reactor used in these experiments is shown in Figure 17. It consists of a steel cylinder equipped with a cap and stainless steel valve. The sample was contained in a machined Teflon liner which was sealed to the stainless steel flask with a Viton gasket. Originally, a Teflon seal was planned, but this leaked consistently with heating and cooling. Even the small exposure to stainless steel resulted in some dissolution of iron, nickel, chromium, and manganese. The reactor was evacuated at room temperature to the vapor pressure of water and then immersed in a constant temperature oil bath up to the middle of the cap. At the desired time it was quenched in cool water, attached to a small-volume monel vacuum line, and held at room temperature in a water bath. The gases were expanded into the Wallace-Tiernan gauge and collected in a glass mass spectrometer tube. The measured pressure would remain constant for at least one hour.

The analysis of the solution for F^- was carried out in most cases by a titration method[20] rather than spectrophotometrically, because there was less chance of interference by the cation impurities.

b. Vapor Chromatography - Vapor chromatographic analysis for ethylenimine in concentrations down to 0.06% was obtained on a 6.5 foot stainless steel column packed with 8.3% Carbowax 20M, 8.3% KOH on Chromasorb P, 60-80 mesh. The same results were obtained if the sample was injected directly unto the basic packing or if it was made basic and quickly chromatographed. The results shown in Figures 13 and 14 were obtained in an Aerograph Hy-Fi A600B, F.I.D., instrument with a column temperature of 90°C. and 1 μl. sample, using a flame ionization detector.

c. N.M.R. Analysis - For N.M.R. analysis, the concentrated solutions were stored in polyethylene bottles for periods of time ranging from overnight to several days at room temperature, except in the last experiment when they were stored in dry ice. Just before a measurement, they were introduced into thin-walled glass

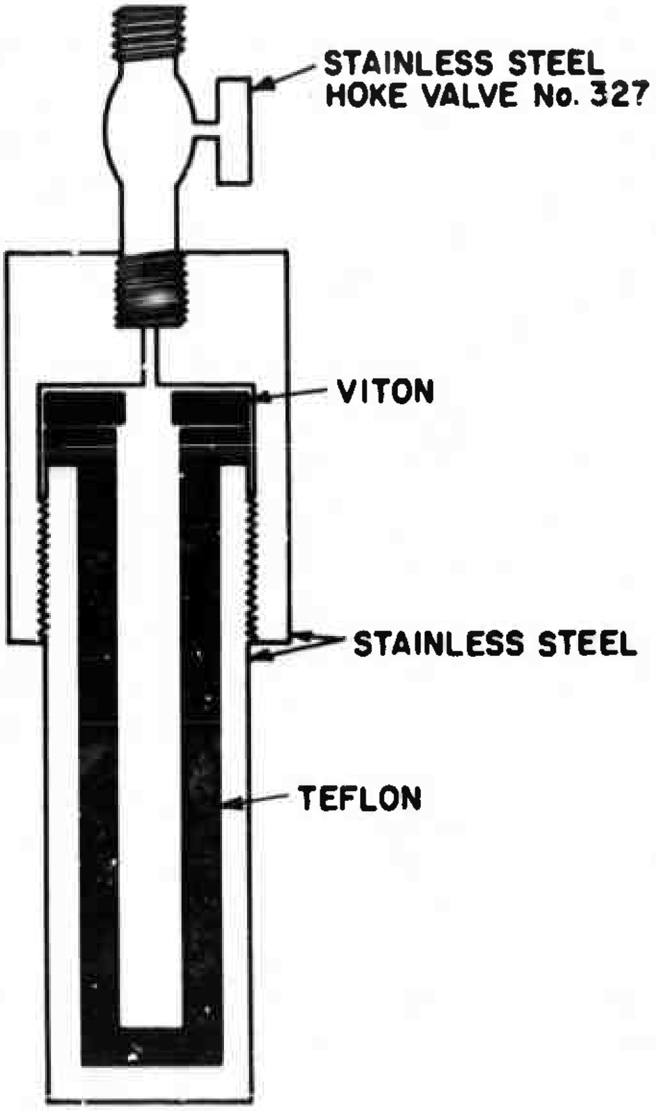


Fig. 17 - Schematic of Apparatus for Decomposition Studies in a Static System

N.M.R. tubes. All of the samples were run on a 94.1 Mc. instrument, except for the last few which were run at 56.5 Mc.

3. Procedure for Solid State Decomposition

Pressure versus time measurements were carried out on 83.4 mg. of solid INFO-635P in a Vycor tube connected to the Wallace-Tiernan gauge and the vacuum system. The sample was first dissolved in methanol and later deposited evenly on the Vycor as the methanol was pumped off. Sample No. 1 was taken at 28 hours and then the INFO-635P tube was cooled overnight. After heating was resumed, the decomposition proceeded much more rapidly. Sample No. 2 was taken at 34 hours, and thereafter the decomposition increased only slightly.

The sensitivity of solid INFO-635P was determined by placing it between a small anvil and a 1/4 in. diameter cylindrical hammer. A 37 g. weight was dropped onto this hammer from various measured heights.

C. SUMMARY AND CONCLUSIONS

The slow thermal decomposition of INFO-635P has been studied in aqueous base and acid and briefly in the solid state. The free amine of INFO-635P decomposes rapidly at room temperature by forming a three-membered intermediate involving the amino group. Ultimately ethylenimine is formed in this initial step. The mechanism of the tris group decomposition in acidic solution is extremely complicated; however, a mechanism has been proposed to account for its decomposition. There is no doubt that $\cdot NF_2$ radicals are produced and it is believed this is the initial step which is followed by cyclization of the remaining two $-NF_2$ groups.

Particularly in acid solution the work is far from complete. The solution to this problem lies in the analysis of the aqueous solutions for the oxidation products of the ethylamine group and the interpretation of the N M R spectra. The reducing action of ethanolamine could prove very important in the solid state as well as in solutions. The gaseous product distribution from solid decomposition closely resembles that from acidic decomposition, which indicates a similar mechanism.

If the initial step is the homolytic C-N bond rupture, this could make desensitization virtually impossible by an external additive. Stabilization can then be brought about only by introducing another group into the molecule itself to stabilize the C-N bond and prevent or retard its homolytic rupture. However, the presence of even small amounts of free amine of INFO-635P in the solid state may be the source of initiation of a detonation, even though it may not actively participate further in the propagation and detonation steps. This was definitely indicated by the explosions which occurred upon exposure to ammonia. The experiments in which acids were added to the solid were crude and inconclusive. A real possibility still exists and ought to be pursued; if the free amine form was effectively suppressed, e.g., by forming the quaternary ammonium salt, sensitivity might be greatly reduced.

III. DECOMPOSITION STUDIES OF GASEOUS DELTA

The second high-energy NF compound studied under this program was tetrakis(difluoroamino)methane, $(NF_2)_4C$, commonly called Delta.

A. DISCUSSION AND RESULTS

1. Method of Study

The initial attempts were to determine the stoichiometry of the complete decomposition, the intermediate products of decomposition, some idea as to the rate of decomposition, and possible mechanisms.

The gas phase decomposition of Delta was studied by the method of sampling which involves the withdrawal of small samples from the reaction chamber, a rapid quench, and analysis.

The early kinetic data on Delta suggested that the decomposition was first order, and allowed the calculation of tentative rate constants and an activation energy. Although the results as reported were correct, there were some experimental drawbacks. Specifically, Delta was introduced into a cold reactor and then immersed in a hot bath. The time required to reach the desired temperature was relatively long, and although decomposition was taking place at the lower temperature, no sample was removed for analysis until ambient temperature was reached. Thus, the analysis was not of a reaction under isothermal control. The sample volume also was large, 1.6% of the reactor volume, which could cause, after repeated samplings, a change in the mechanism.

Subsequent modifications of the vacuum-reactor system, in particular the reduction of the sampling volume and the addition of a pressure tranducer[5], and development of a technique of loading Delta into a hot bomb and of almost immediate sampling, have corrected the drawbacks mentioned above. More importantly, it has revealed that there may be more than one mechanism for the decomposition of Delta.

2. Stoichiometry

The stoichiometry of the complete decomposition of Delta apparently follows the equation[21]:

$$C(NF_2)_4 \rightarrow CF_4 + 4/3\ NF_3 + 4/3\ N_2 \qquad (24)$$

This is based on a decomposition of 170.8 mg. of Delta for 16 hours at 175°C. and on the mass spectral findings for NF_3, as compared to the theoretically expected percentages for equations (24) and (25).

$$C(NF_2)_4 \rightarrow CF_4 + NF_3 + 4/3\ N_2 + 1/2\ F_2 \qquad (25)$$

3. Decomposition Intermediates and Products

Delta was expected to be similar in its decomposition kinetics to compound R, $(NF_2)_3CF$, with C-N homolytic cleavage to form $\cdot NF_2$ radicals and activation energies of the order of magnitude as reported for R. Compound H, $(NF_2)_2CF_2$, and CF_3NF_2 were found in appreciable amounts in the decomposition of R[22,23]. The appearance of compound H and CF_3NF_2 as decomposition products may be predicted for R, based on the assumption that the relative abundance of the cations listed in the mass spectrum of R by American Cyanamid[24] and Minnesota Mining[24] are an indication of the comparative ease in breaking and forming bonds.

The same assumption about the mass spectra for Delta would tend to indicate that among the decomposition products R, PFF, $NF_2C{=}(NF)F$, or PFG, $(NF_2)_2C{=}NF$, CF_3NF_2, as well as N_2, CF_4, and NF_3, are expected to be found, but relatively little or no compound H. At present, the products N_2F_4, CF_3NF_2, PFF, PFG, CF_4, NF_3, N_2 and, under special conditions, H have been identified.

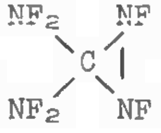
4. Kinetics

a. Constant Temperatures - The results of each run will be presented in order of decreasing temperature, and unless otherwise noted, the technique of expanding Delta into the hot reactor was used. In addition, the pressure-time results indicate that the reaction proceeds almost instantaneously with the exposure of Delta to the hot reactor[5].

The rate constants for the final reaction period as calculated by the method of least squares are given in Table XI.

Since the half life of Delta at 200°C. is very short, no kinetic data on the decomposition of Delta was possible, and only a single point relative to the amount of Delta was obtained. Analysis of subsequent samples indicated that the concentrations of PFF, PFG, and an unknown were increasing with time while that of Delta had almost reached zero. The original Delta sample for this run was condensed into the reactor, warmed to room temperature, and then immersed in a hot oil bath.

A second decomposition at 200°C. was made in an attempt to duplicate the earlier run. No correspondence was obtained, the primary reason being the difference in the technique of introducing Delta into the reactor. Again, no kinetic data on the decomposition of Delta were possible.

The unknown intermediate observed in the decomposition at 200°C., using a 25-foot dual FX 45* column was not definitely identified[5]. However, the infrared spectrum, Figure 18, of a small sample collected from a reaction at 190°C. using a 43-foot dual FX 45 column suggests that the compound may be diaziridine. The conclusion is based primarily upon a comparison of the spectra reported for compounds "E" and "G", and for the corresponding unsaturated compounds (diazirines)[5]. It is believed that the unknown compound may be bis(difluoroamino)diaziridine,  . Mass spectral analysis

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[*] A fluorocarbon obtained from Minnesota Mining and Manufacturing Company.

Table XI

First Order Rate Constant Versus Temperature for Delta

Temp. °C.	Type Reaction	k x 10^{-4}, seconds^{-1}	$t_{1/2}$ minute	P_i mm.
190	Neat	7.69	15.0	150.0
190	Neat	7.61	15.1	132.2
180	Neat	2.98	38.8	154.8
180	N_2F_4(5%)	2.89	39.98	158.5
180	Neat	2.43	47.44	94.9
179	Neat	2.68	43.1	154.0
178	Packed	1.73	66.6	127.2
175	Neat	1.27	90.6	87.9
175	Neat	1.37	84.6	123.4
170	Neat	1.05	110.5	152.5
170	Neat	0.954	121.1	104.0
169	Neat	1.01	114.3	156.1
168	Neat	0.683	169.1	103.9
160	Neat	0.295	391.4	153.5
150	Neat	0.151	766.6	131.3
150	Neat	0.186	622.4	151.8
150	N_2F_4(5%)	0.105	1098.1	100.4
150	N_2F_4(5%)	0.098	1176.4	92.5
150	Packed	0.148	779.8	133.0
140	Neat	0.064	1796.5	130.5
140	Neat	0.074	1563.2	148.0

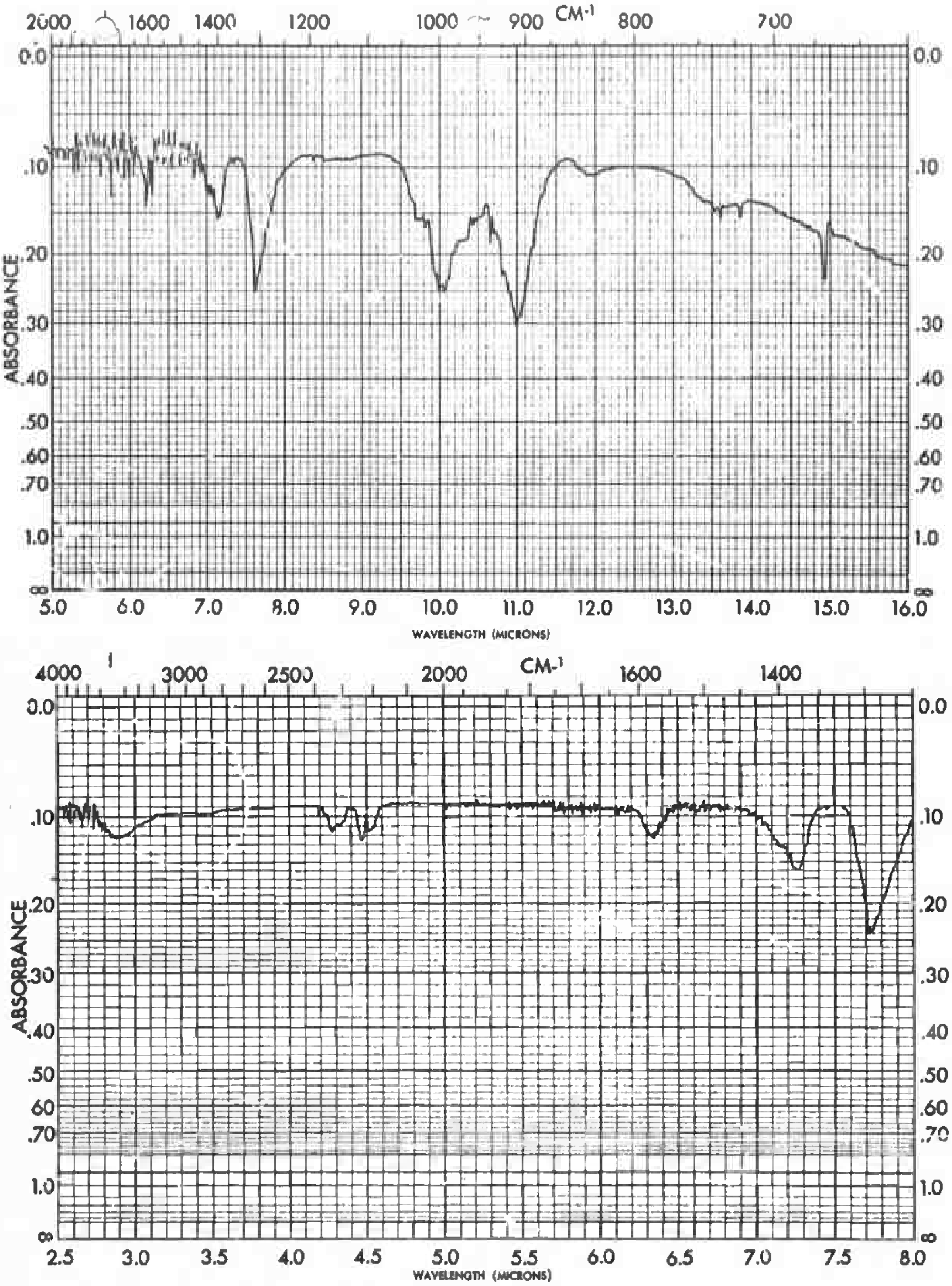


Fig. 18 - Infrared Spectra of Unknown Intermediates

of the sample could not give a definite answer, since the cracking patterns of all these NF materials are similar.

Two decompositions at 190°C. gave similar results. Little or no PFF or PFG was observed chromatographically. A plot of log of the concentration of Delta (mg.) versus time (10^3 sec.), Figure 19, gave a linear relationship indicating that the disappearance of Delta at this temperature was first order. There was some N_2F_4; however, the amount could not be determined using thermal conductivity detectors on the dual column chromatograph, because as the N_2F_4 passes over the filaments some of it dissociates endothermically causing a negative deflection of the recorder pen. The remainder of the products at this temperature was identified as N_2, CF_4, and NF_3.

Examination of the data from the several 180°C. runs indicates the existence of an initial reaction period during which about 30% to 40% of the starting amount of Delta disappears. This part of the reaction will be discussed more fully later. After this initial period of about 15 minutes, the reaction appears to follow a first order law with respect to Delta, Figure 20.

A 5% mixture of N_2F_4 and Delta was decomposed. The results, Figures 20, 21, and 22, indicate that the N_2F_4 increases the initial rate of Delta, then as the N_2F_4 concentration passes through a maximum and begins to decrease, the rate of disappearance of Delta approaches that of the neat reaction. Further evidence that N_2F_4 increases the reaction rate of Delta is the fact that PFF and PFG reach their maximum concentration about 15 minutes sooner than in the neat reaction.

A reaction was run at 179°C., and considering the temperature difference, the results are in agreement with the data reported for 180°C.

Another monel reactor was packed with monel wire. The surface to volume ratio was changed from 0.83:1 to 4.67:1. The reactor was charged with Delta and the decomposition at 178°C. followed

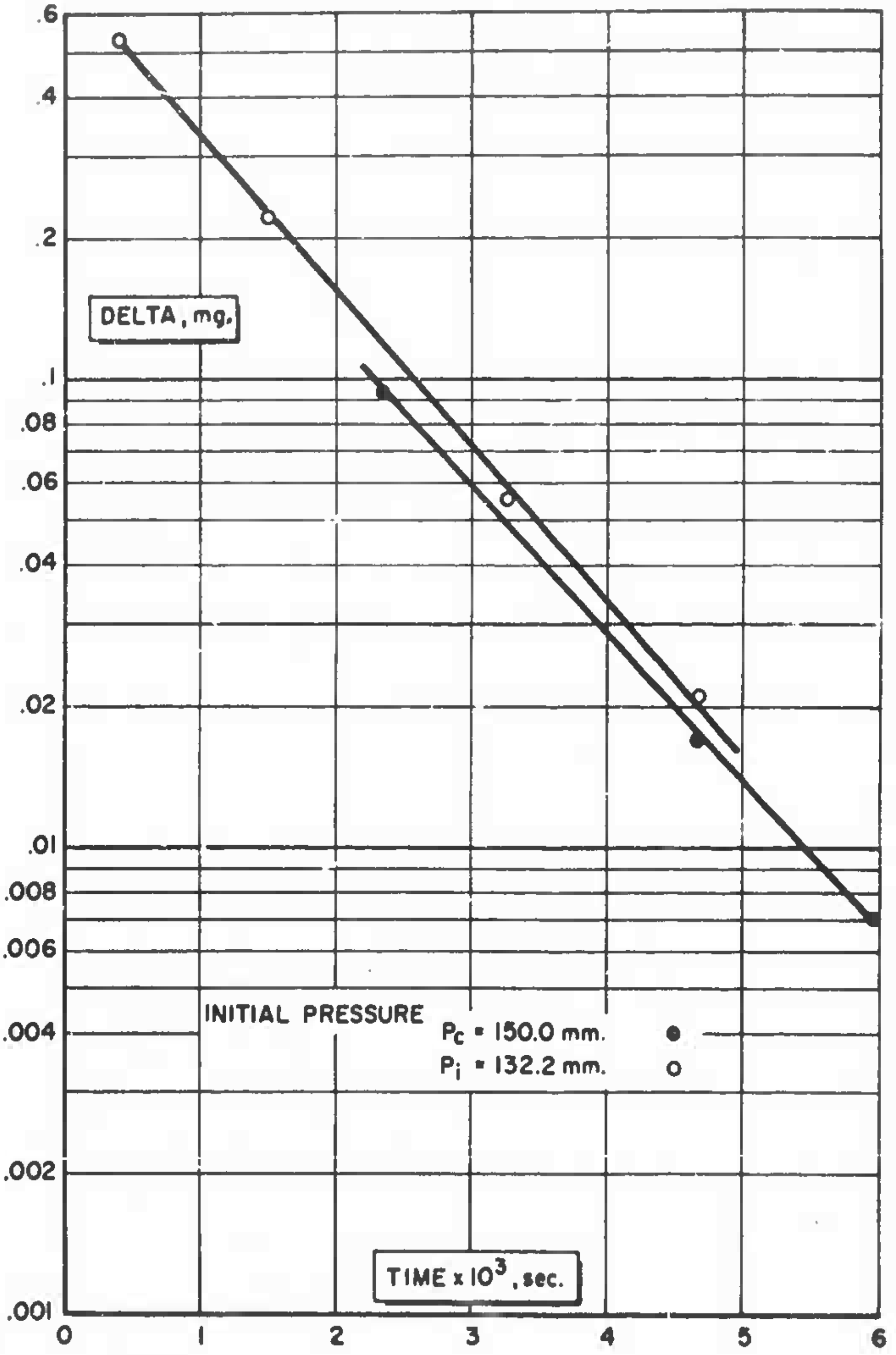


Fig. 19 - First Order Kinetic Plot at 190°C. for Delta

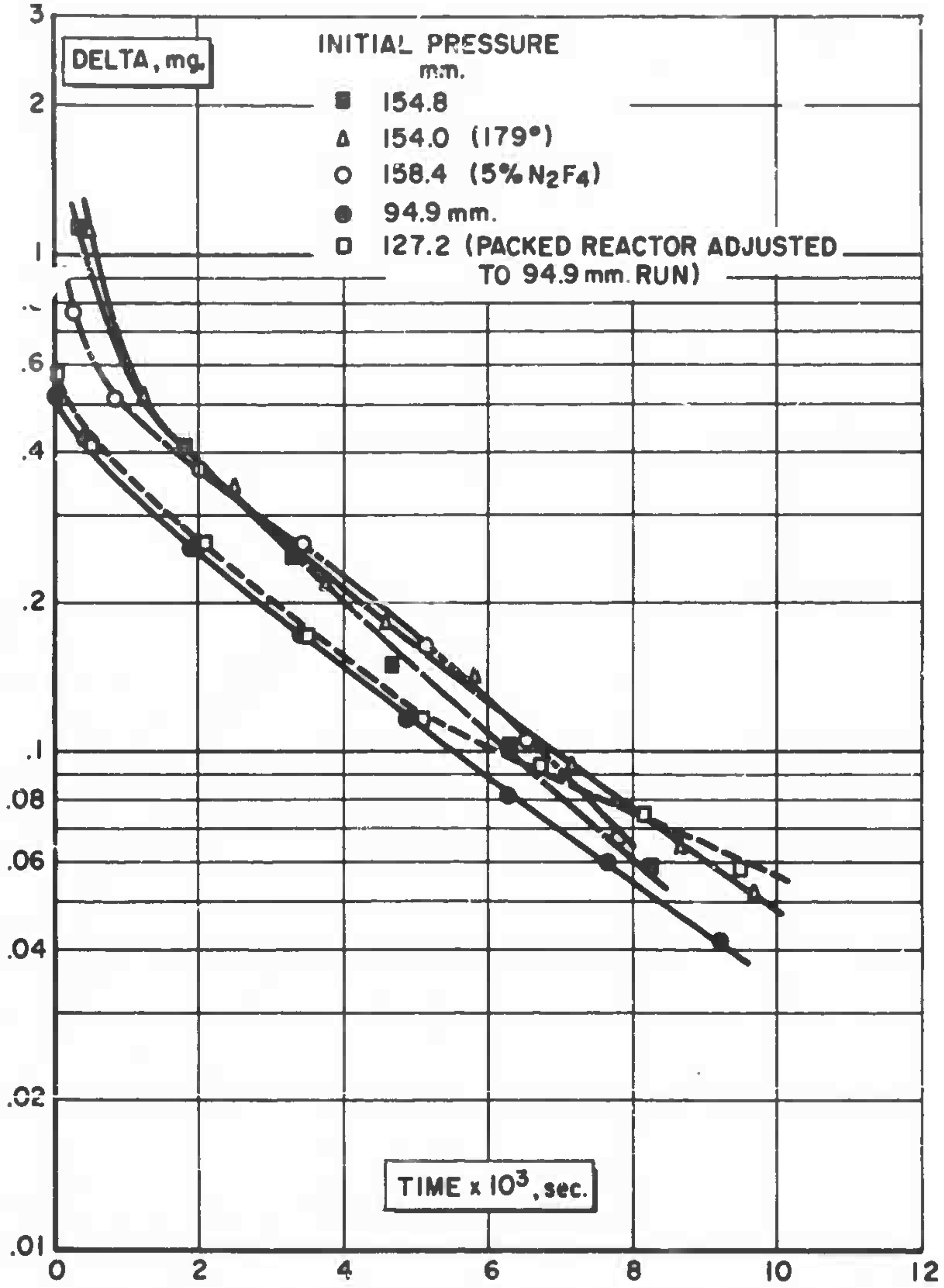


Fig. 20 - First Order Kinetic Plot at 180°C. for Delta

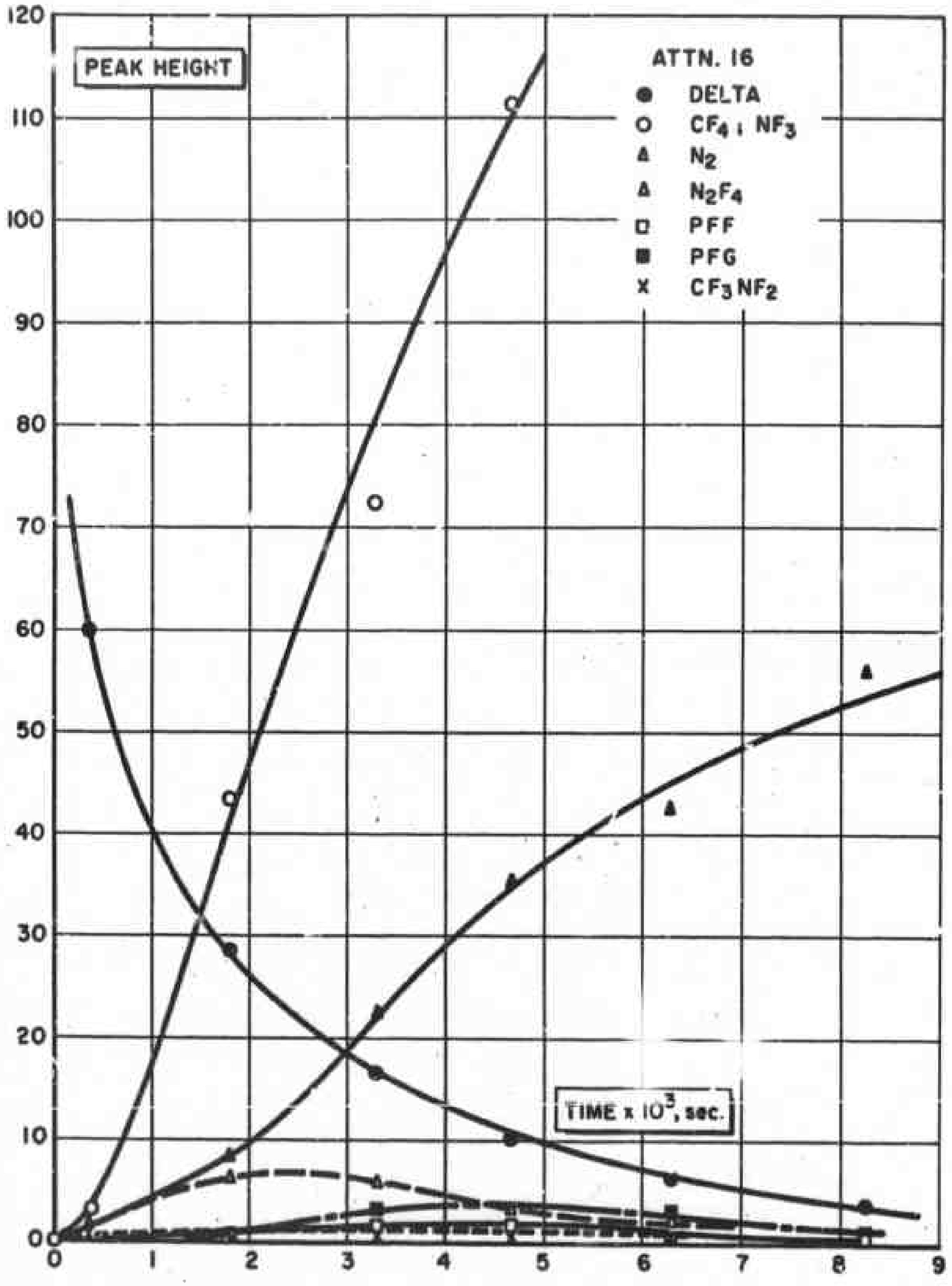


Fig. 21 - Peak Height vs. Time for Gas Phase Decomposition of Delta at 180°C. and Pi=154.8 mm.

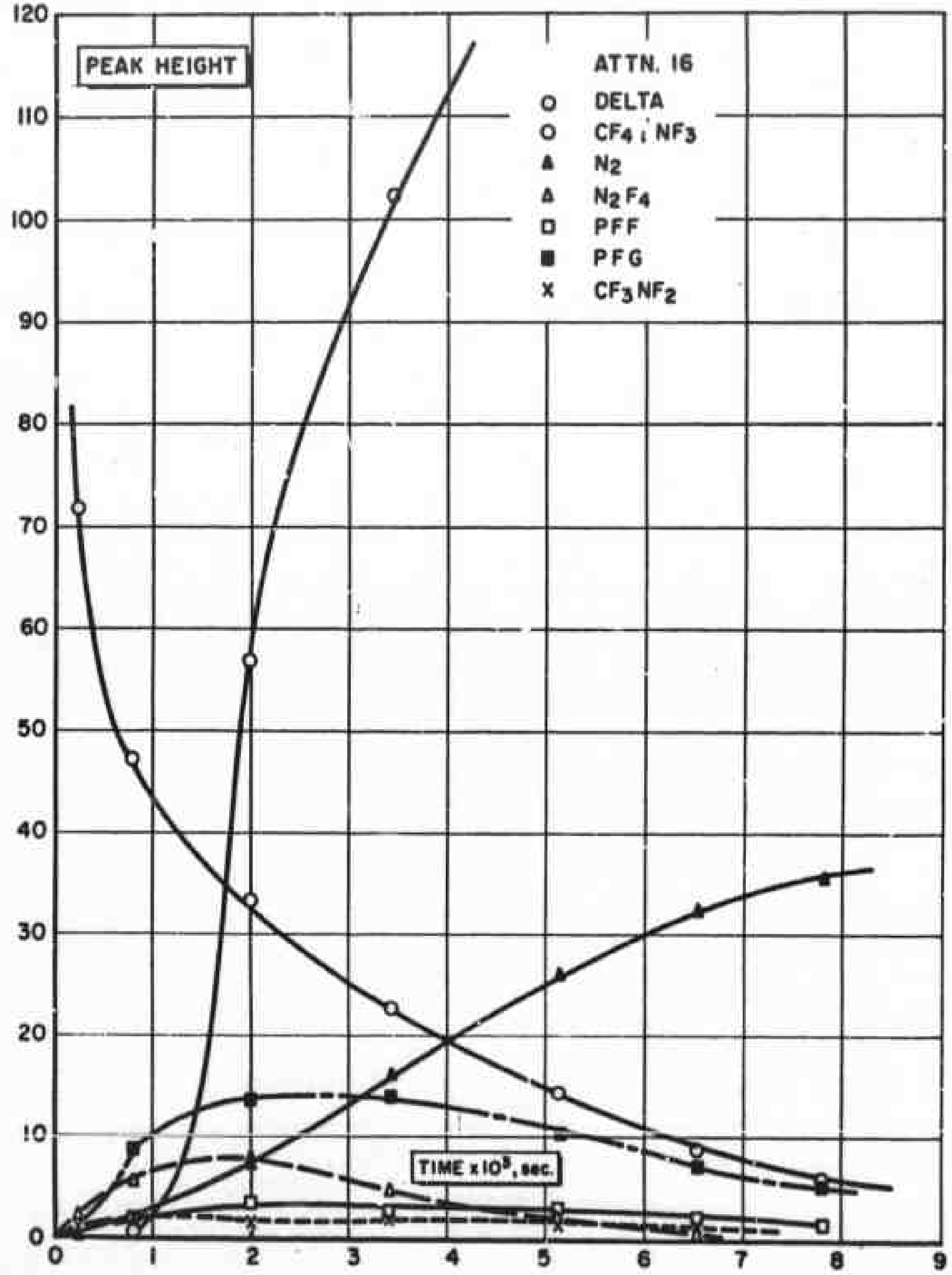


Fig. 22 - Peak Height vs. Time for the Gas Phase Decomposition of Delta at Pi=158.5 (5% Tetrafluorohydrazine)

chromatographically. These data, Figure 20, indicate, just as in previous runs, that there is an initial reaction period of possibly higher order. Comparison of these data, after correcting to the operating conditions of the neat reaction at 180°C., P_1=94.9 mm., suggests that the reaction is quite complex.

Examination of the curves indicates that under these operating conditions the decomposition is homogeneous; at least the rate of reaction is not greater in the packed reactor.

Early in the program two kinetic runs were made at 175°C. The bomb was charged by condensing Delta into the reactor, which was immersed into the hot oil bath. The data, Figure 23, indicate only that the reaction could be first order and that one mechanism is observed.

The two runs at 170°C. and one at 169°C. indicate that there is an initial reaction period of probably higher order, in which a large portion of the Delta has apparently decomposed (Figure 24).

An early decomposition at 168°C., using the method of loading the bomb then immersing in the hot oil, gave data that were consistent with a previous report[5].

The single study at 160°C.[5] was the first to show that there was a possibility of either a heterogeneous reaction occurring initially or two mechanisms being involved in the decomposition (Figure 24). Consequently, it was stated that the lower temperature reactions would not be studied, but further work at 180°C. and 170°C. (see above) showed this same apparent high order in the initial period. It was then decided to study the decomposition at 150°C. and 140°C.

Five runs were made at 150°C., two neat reactions, two with 5% N_2F_4, and one with the packed reactor (Figure 25); and two runs were also made at 140°C. (Figure 26). By going to these lower temperatures, it was hoped that the initial reaction period would sufficiently increase in time to allow the determination of the initial order.

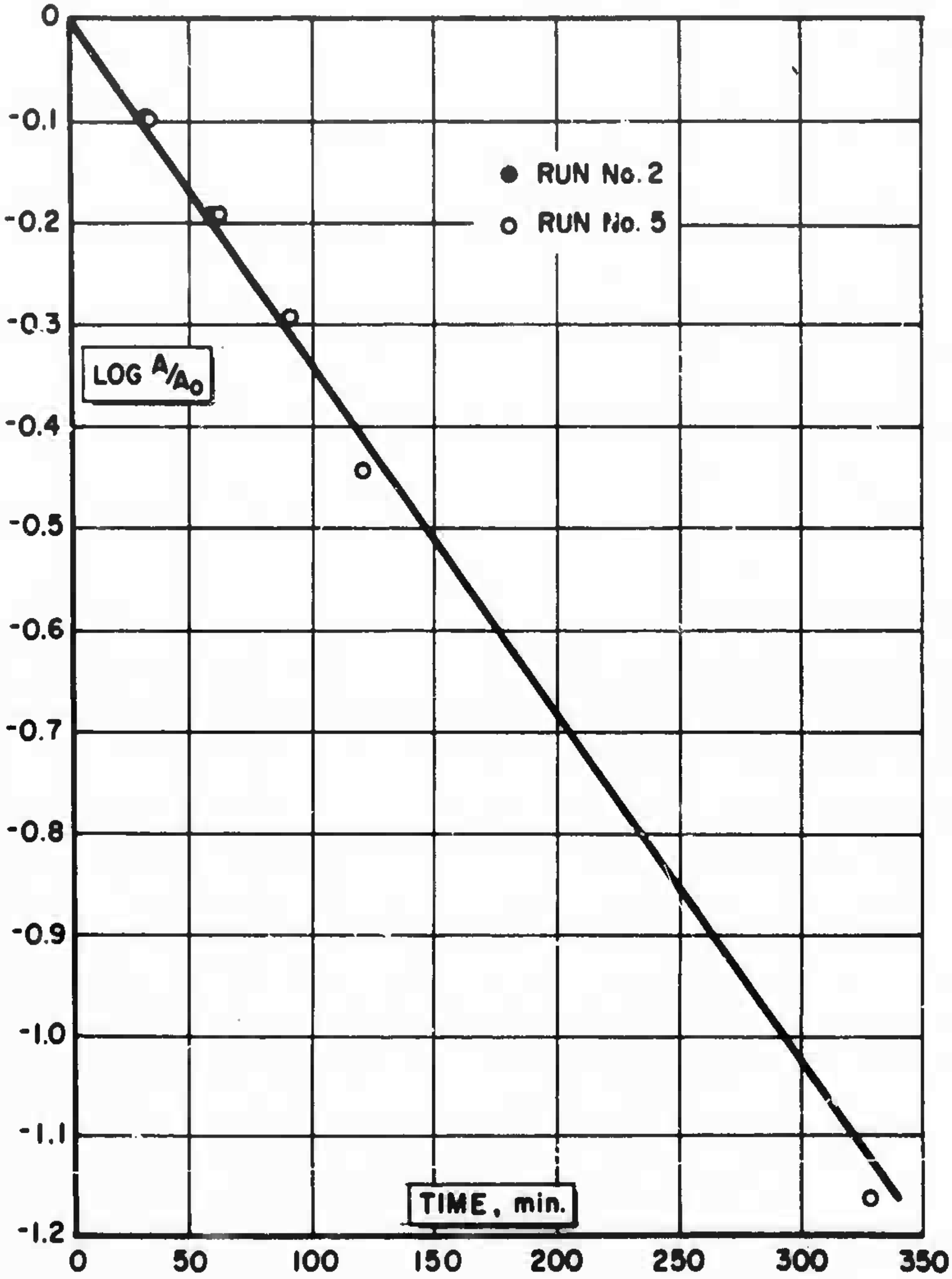


Fig. 23 - Graphical Representation of Disappearance of Delta

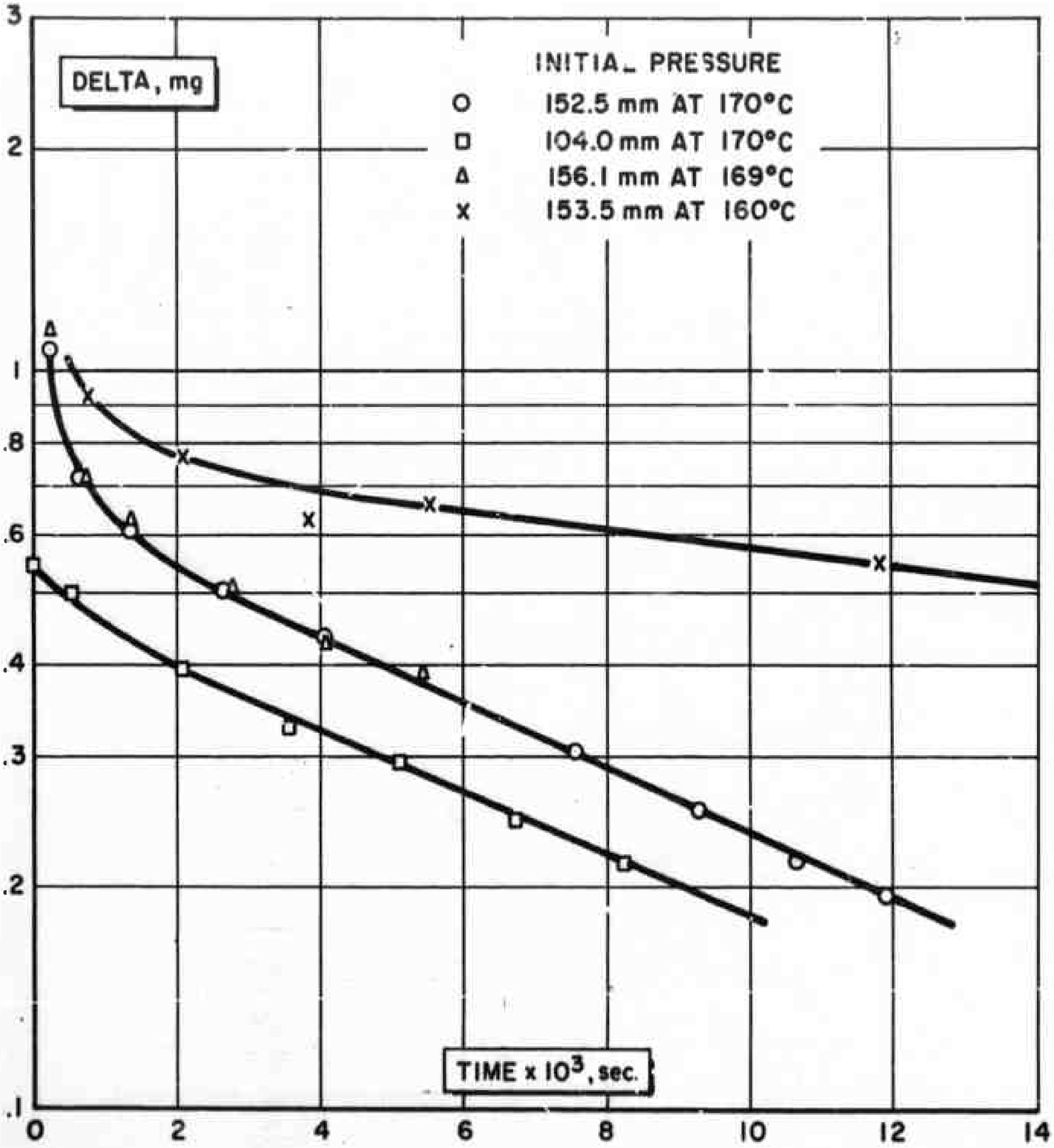


Fig. 24 - First Order Kinetic Plot for the Decomposition of Delta at 170°C. and 160°C.

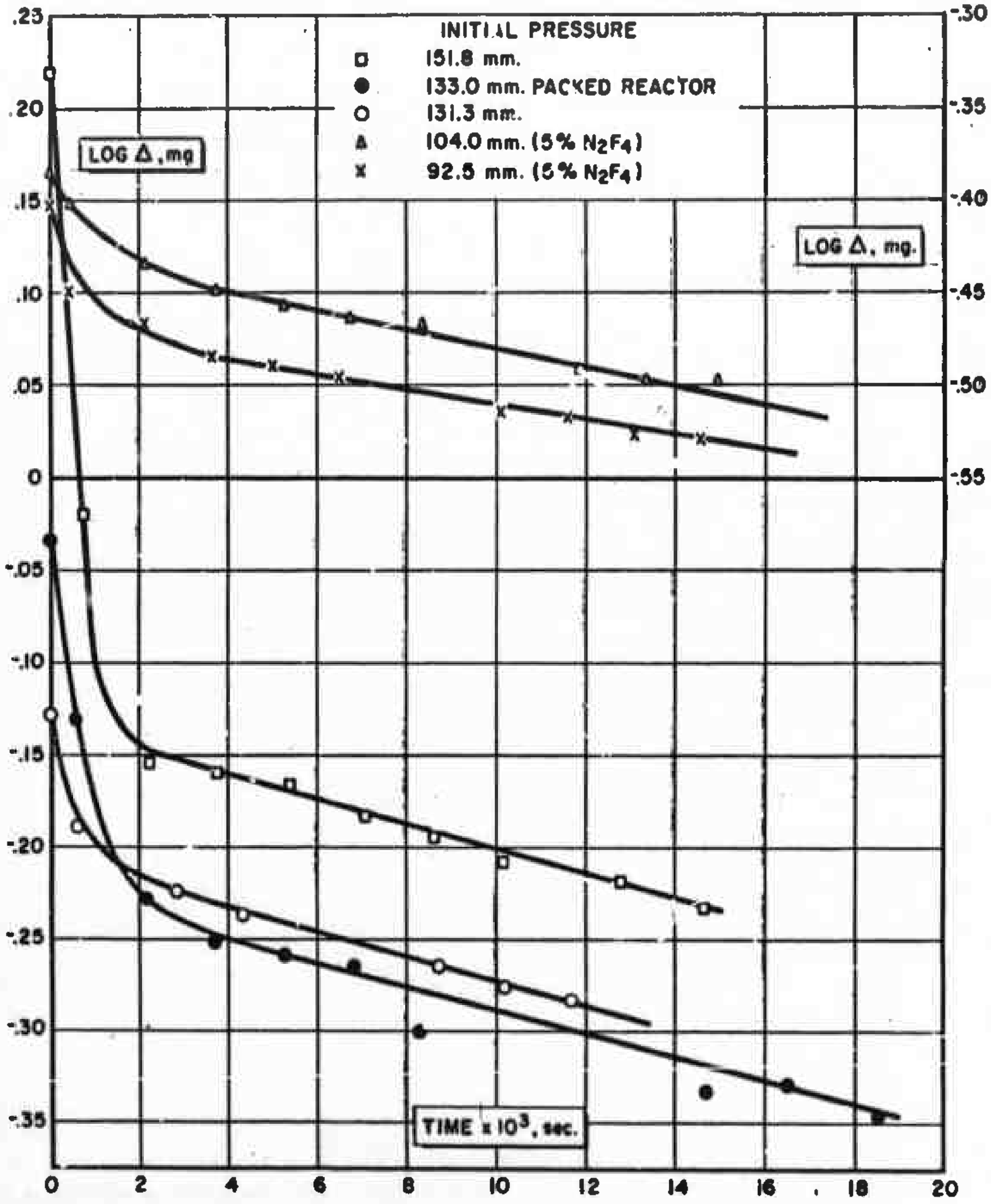


Fig. 25 - First Order Kinetic Plot of the Decomposition of Delta at 150°C.

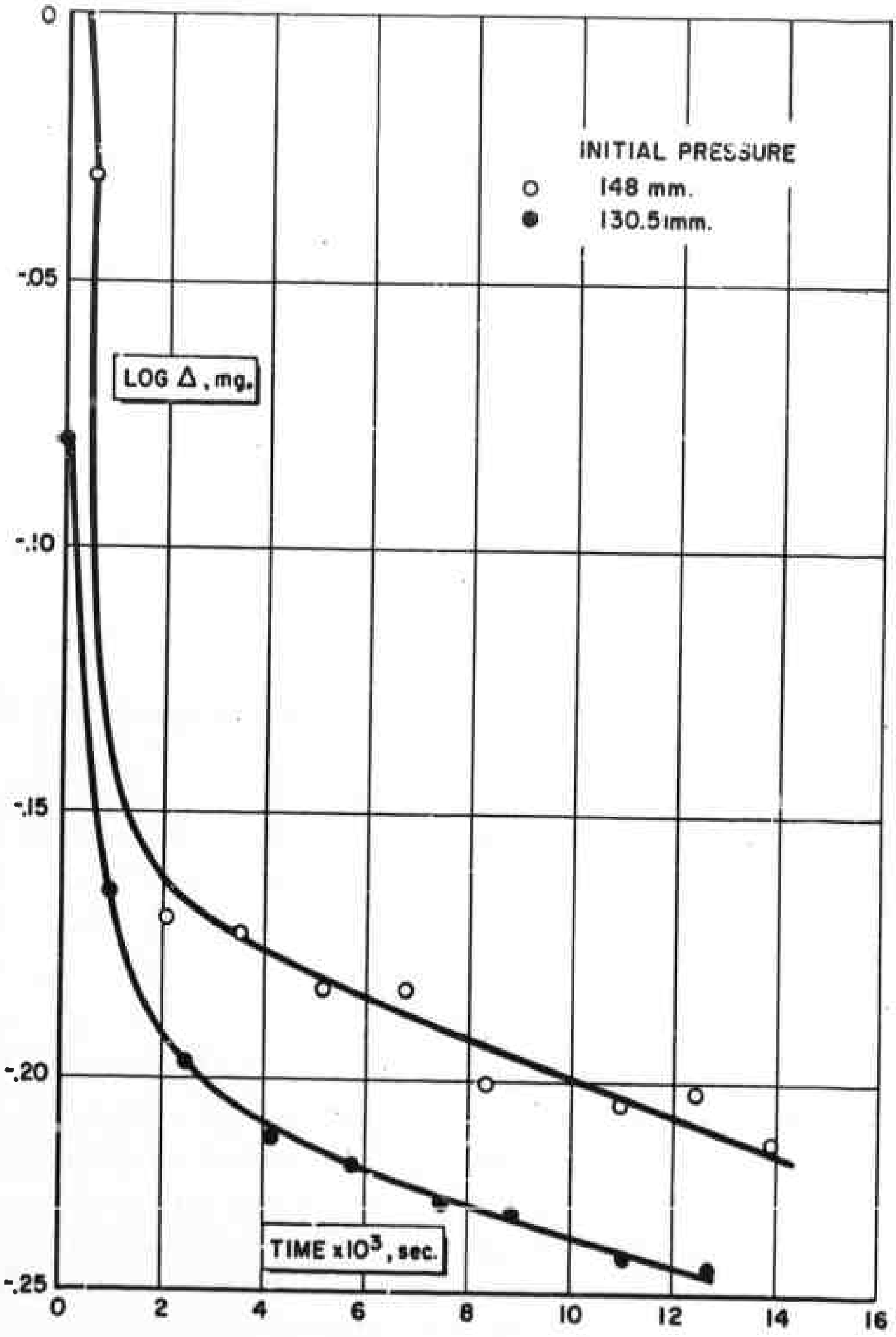


Fig. 26 - First Order Kinetic Plot of the Decomposition of Delta at 140°C.

b. Initial Reaction - During the initial reaction period, the rate of reaction is effected by the change in initial pressure of Delta and by the addition of N_2F_4. Calculation of the initial orders (n), by the method of initial rates give n=2 for the reactions at 140°C. and 150°C. This same calculation at 170°C. and 180°C. gives n=3 and 1, respectively, and at 190°C. the initial reaction is too fast to observe. The packed vessel reactions at 178°C. and 150°C. showed that the rate of reaction had increased in the initial period due possibly to the increase in the surface to volume ratio. The conclusions, therefore, are that the reaction in this initial period is of higher order, and thus pressure (concentration) dependent, and that the reaction may in part be heterogeneous during this initial period.

c. Final Reaction - The final reaction period is considered to be homogeneous, mostly first order in Delta,and complex. The effect of pressure can be seen on the first order specific rate constants (Table XI and Figure 27). The rate constants appear to be dependent on the initial pressure of Delta, the higher the pressure the greater the rate constant, except at high temperature where the deviation between the high and low pressure rate constants is less. It may be expected that at constant temperature a high pressure and a low pressure limit may exist for the first order specific rate constant, which, of course, is not probable for first order reactions. The observed pressure effect is more likely due to a competing higher order reaction.

The Arrhenius plot of the first order specific rate constants, Figure 27, indicates that at 150°C. and 140°C., the slope of the line may be changing in such a manner as to suggest a change in the mechanism. A review of the data from the packed vessel decomposition at 150°C. (Figures 26 and 27) indicates that the reaction is independent of the surface area, and therefore not heterogeneous. A competing higher order reaction with a lower activation energy would have a similar effect on an Arrhenius plot if the rate constants were calculated erroneously on the basis of a purely first order mechanism.

Therefore, at about 150°C. the duration of the initial reaction has effectively been increased, with the dominant reaction having an order (n) greater than one. As the ambient temperature of the decomposition is increased, the first order competing reaction with a higher activation energy, becomes more dominant until at 190°C. it is the primary reaction. However, the decomposition is still not totally first order.

The activation energy derived by the method of least squares in the temperature interval 190°-170°C. is 42.5 kcal./mole, log A = 16.94 seconds^{-1}, which has been related to the homolytic rupture of the C-N bond in Delta. However, the average frequency factor for most first order unimolecular reactions is 10^{13} to 10^{14} seconds^{-1}. The calculated value of 10^{16} seconds^{-1} also suggests that the mechanism may be complex.

5. Mechanism

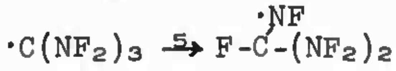
a. Equations - The possible mechanism is described in the following statements. Free radicals are initiated by splitting the molecule at its weakest link. A chain is propagated when one of these radicals (or both) abstracts F from the parent compound to form a stable intermediate and a new free radical. The free radical may stabilize itself by splitting off NF_2. Chain termination then occurs through association or disproportionation of the radicals.

Estimated $\Delta H_{r\ 298}$ kcal./mole

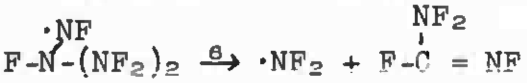
$$C(NF_2)_4 \underset{2}{\overset{1}{\rightleftarrows}} \cdot C(NF_2)_3 + \cdot NF_2 \qquad +52 \qquad (26)$$

$$\cdot NF_2 + C(NF_2)_4 \xrightarrow{3} NF_3 + F\dot{N}C(NF_2)_3 \qquad +8 \qquad (27)$$

$$F\dot{N}C(NF_2)_3 \xrightarrow{4} \cdot NF_2 + FN{=}C(NF_2)_2 \qquad -71.7 \qquad (28)$$



$$\cdot C(NF_2)_3 \xrightarrow{5} F-\overset{\cdot NF}{C}-(NF_2)_2 \qquad -6.0 \qquad (29)$$



$$F-\overset{\cdot NF}{N}-(NF_2)_2 \xrightarrow{6} \cdot NF_2 + F-\overset{NF_2}{C}=NF \qquad -66.4 \qquad (30)$$

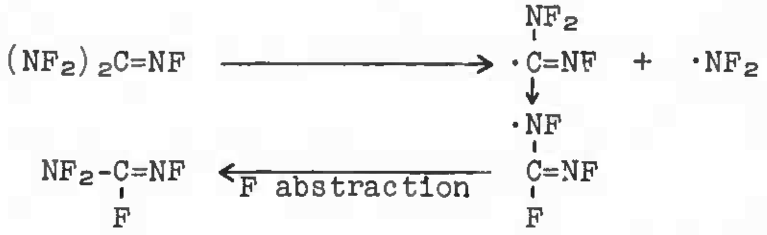
$$\cdot NF_2 \underset{8}{\overset{7}{\rightleftarrows}} 1/2\ N_2F_4 \qquad -11.1 \qquad (31)$$

The reaction of the tris-NF_2 free radical with the parent molecule is given below. The heat of reaction is estimated to be -61 kcal./mole.

$$C(NF_2)_4 + \cdot C(NF_2)_3 \rightarrow F-C(NF_2)_3 + F\dot{N}C(NF_2)_3 \qquad (32)$$

However, no compound R was observed. The unimolecular stabilization of the tris-NF_2 free radical, thus, seems more likely to occur, equations (29) and (30), then the bimolecular reaction, equation (32).

The mechanism above predicts the increase in concentration of NF_3 and PFG upon the addition of NF_2 in the form of N_2F_4 in the reaction zone, but not that of PFF. Since an increase in the PFF concentration was also observed, equation (33) is written purely as speculation to account for the increased yield in PFF.



The initial products given by this mechanism are NF_3 and PFG [equations (27) and (28)].

However, at 190°C. very little PFG or PFF is observed. Decreasing the reaction temperature to 180°C. increases the amount of observed PFG. Observations at temperatures below 180°C. again show a decrease in the amount of PFG produced, which is expected. The implication is that the rate of decomposition of PFG under these experimental conditions is similar to the rate of decomposition for Delta at 190°C. and 180°C., and is greater than the rate for Delta at temperatures less than 180°C.

b. <u>Mathematical Treatment</u> - The decomposition system is too complicated for an exact mathematical treatment at this time. However, some reasonable limiting cases can be considered.

The stationary-state solution to a first approximation is obtained by letting $Z\cdot$* equal any free radical. Then initially,

$$\frac{d(Z\cdot)}{dt} = k_1[C(NF_2)_4] - k(Z\cdot)^2$$

---

*Most of $Z\cdot$ are $\cdot NF_2$.

where k is a composite term and $k(Z\cdot)^2$ implies that free radicals disappear in pairs. Then,

$$\frac{d(Z\cdot)}{dt} = 0 \text{ gives } (Z\cdot)_{ss} = \left[\frac{k_1[C(NF_2)_4]}{k}\right]^{1/2}$$

for the steady state approximation. For long chains,

$$\frac{d[C(NF_2)_4]}{dt} = k_3[C(NF_2)_4](Z\cdot) = k_3\left[\frac{k_1}{k}\right]^{1/2}[C(NF_2)_4]^{3/2}$$

suggesting that the initial rate may be 3/2 order in Delta.

The steady state solution for $\cdot NF_2$ gives the result that $(NF_2)_{ss}$ = constant, where the constant is a function of all the many rate constants. The result, valid at long time, is:

$$\frac{d[C(NF_2)_4]}{dt} = k_3[C(NF_2)_4](NF_2\cdot)_{ss} = k'[C(NF_2)_4] \quad \text{first order.}$$

The equilibrium constant for equation (31) also controls $(\cdot NF_2)_{ss}$ at long times,

$$(\cdot NF_2)_{ss} = K_{eq}^{1/2}(N_2F_4)^{1/2}$$

but N_2F_4 will come to the same steady state value regardless of whether it is added initially or not. Therefore, only the initial rate is affected by adding N_2F_4, which should be proportional to $(N_2F_4)^{1/2}$ added.

c. Estimated Thermodynamics - The estimated heats of reaction were calculated from the tabulated heats of formation given in the JANAF Thermochemical Tables[26] and the JANAF Propellant Ingredient Tables[27]. The heat of formation of $\cdot C(NF_2)_3$ was calculated from the heat of reaction of equation (26) which was assumed to be the average C-N bond energy in Delta, and "R".

The heat of formation of the free radical $F\dot{N}-C(NF_2)_3$ was simply estimated as that of the calculated ΔH_r for the reaction:

$$\cdot NF_2 \rightarrow \cdot NF + \cdot F \qquad (33)$$

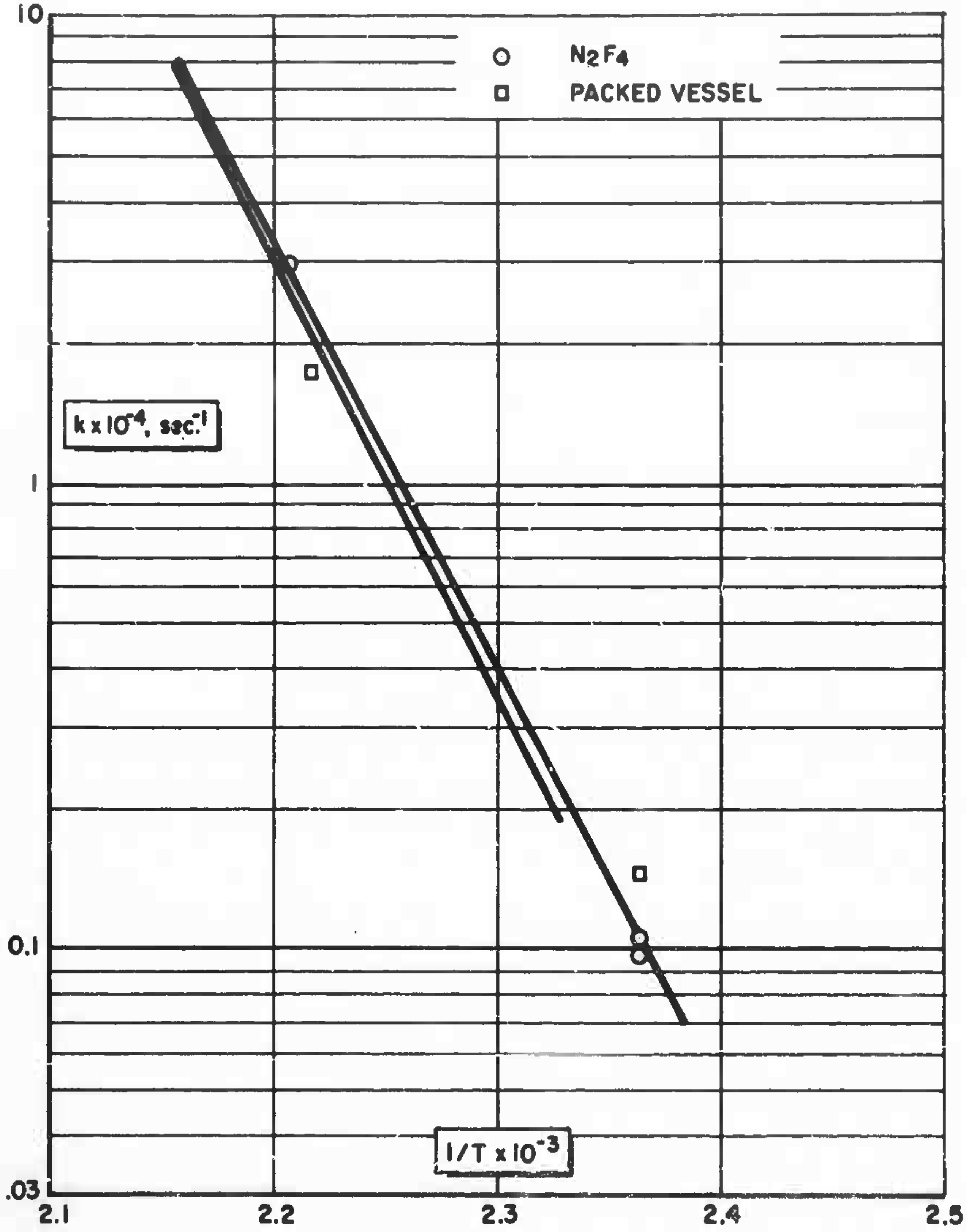
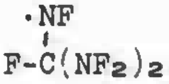


Fig. 27 - Arrhenius Plot of the Thermal Decomposition of Delta

The value for ΔH_f for the free radical  $F\text{-}\overset{\cdot NF}{\overset{|}{C}}(NF_2)_2$ was based upon the estimate for $\cdot C(NF_2)_3$ and the calculated heat of reaction for equation (10) and the $\Delta H_f(CF)$.

B. EXPERIMENTAL METHOD

The experimental vacuum system is shown schematically in Figure 28. The experimental procedure to manipulate the sample in this system is as follows: The complete system, glass and monel, is evacuated to 0.5μ up to the Hoke valves 6, 3, and 2. The bath is raised to a point where the oil level is just below valve 8, and the bath heated to the selected temperature. Prepurified Delta is introduced by expansion through the glass system valve b, up to the monel valve 6 and monel "T", valve 5, with glass valves a and c being closed. The pressure is noted on the Heise vacuum gauge, valve 5 is opened, allowing Delta to expand into the 155 cc. high pressure Hoke monel cylinder, then valve 8 is closed, and the pressure noted again.

To quench the decomposition, the sampling volume is water-cooled by several windings of 1/8" tubing. Sampling of the gaseous products is accomplished by trapping a sample between valves 7 and 8, then expanding to the volume between valves 6 and 4. Valve 5 is then closed. Valve 1 is closed, valve 2 opened to allow helium to enter, and then closed. This is done to prevent the reverse surge of helium from the detector column. Valves 3, 4, and 6 are then opened in succession, and the sample passed through to the chromatograph.

The system is then prepared for the next sample by closing valves 6 and 3. Valve 1 is opened and the system is evacuated up to the "T" valve. The remaining entrapped gases between valves 5 and 8 are condensed into a trap at b. The system to valve 8 is evacuated again in preparation for the next sample.

Two different packings in 25-foot dual columns were used in the analysis of the decomposition products. The first column was

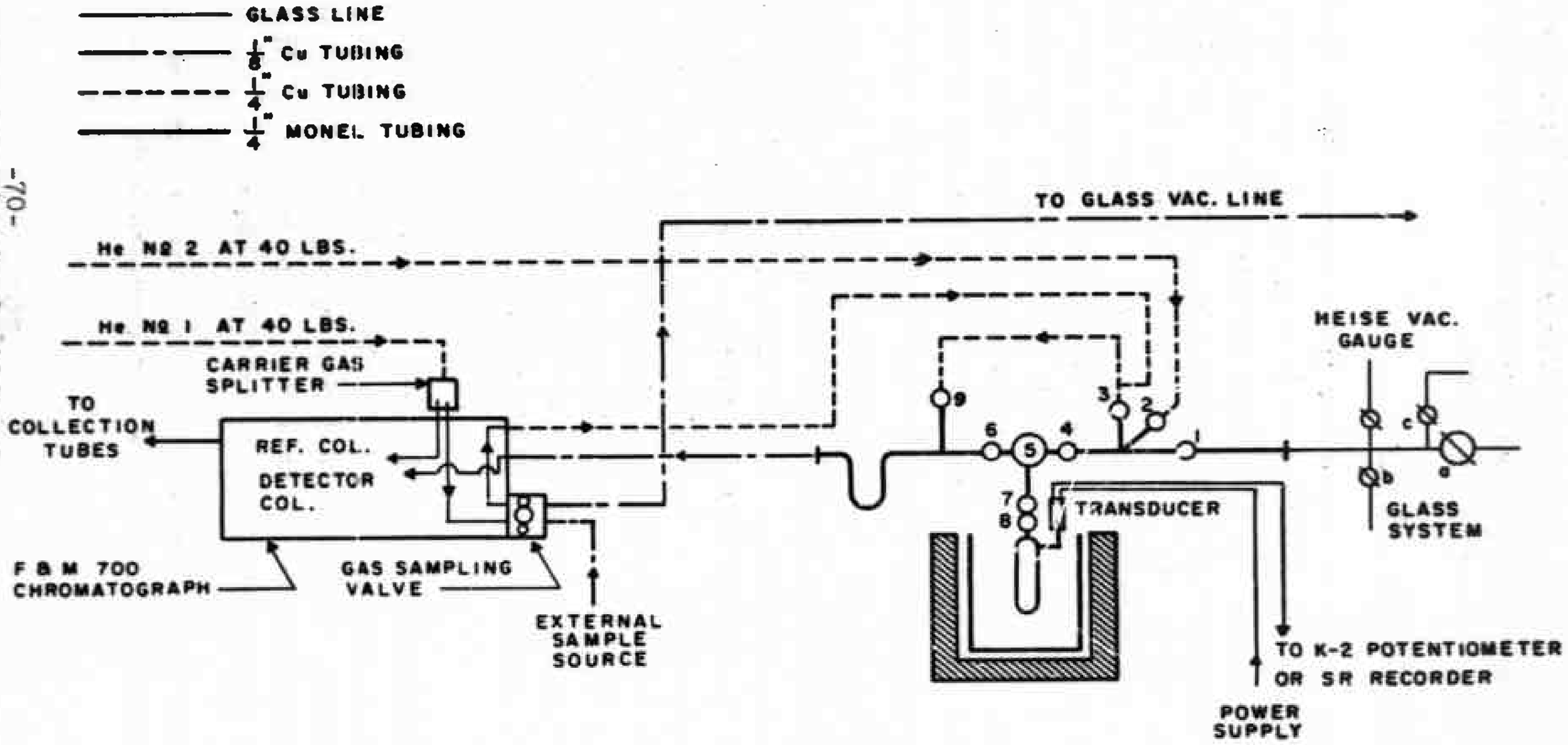


Fig. 28 - Experimental Reactor and Vacuum System

packed with 30% F-45* on Chromasorb W. Although good separations could be obtained by operating at or near room temperature, the retention time and dragging effect on Delta was increased, which was a disadvantage in obtaining data points relatively close to one another. For this reason, the change was made to a second VPC column packed with 30% Dow Corning Fluorosilane fluid, FS 1265, on Chromasorb W, which gave comparable resolution of reaction products, as well as a decrease in retention time of Delta.

C. PREPARATION OF DELTA

Compound Delta, tetrakis(difluoroamino)methane, has been synthesized by two different reaction processes. One, developed by the Minnesota Mining and Manufacturing Company,** involves the reaction of ammonia and perfluoroguanidine (PFG) followed by the direct fluorination of the adduct.[28] The other process, developed by the American Cyanamid Company,[29] is similar and involves the reaction of isocyanic acid (HNCO) and PFG to form the adduct followed by direct fluorination to Delta. Scale-up by Cyanamid to the pound-quantity level is in progress. Dow selected the latter approach and installed a gram-scale unit to produce sufficient quantities of Delta for use in the kinetic study.

1. Process Description

Isocyanic acid, prepared by the depolymerization of cyanuric acid, and perfluoroguanidine were charged to a clean, dry reactor containing catalyst, potassium thiocyanate, and solvent, sulfur dioxide. The reactants were condensed into the reactor, a small, glass flask equipped with a magnetically driven stirrer, at -90°C. and slowly warmed to the reaction temperature of -30°C. After the reaction was complete, unreacted starting materials and solvent were removed by vacuum stripping at -25°C. The adduct was stripped from the reactor at ambient temperature and collected in a modified centrifuge tube at -78°C.

---

*A fluorocarbon obtained from Minnesota Mining and Manufacturing Co.

**3M designation for $(F_2N)_4C$ is "Compound T."

Gaseous nitrogen was slowly bubbled through the liquid at ambient temperature to sweep the adduct into a copper coil fluorination reactor. Addition of a dilute fluorine stream resulted in the vapor phase fluorination to tris-isocyanate. Further fluorination in the presence of NaF converted the tris-I to Delta. The product was collected in a U-tube at -100°C.

2. Results

Results were extremely erratic with 32 of 40 runs failing to yield adduct. The remaining 8 runs, summarized in Table XII, produced 35 grams of Delta with a purity in excess of 98%. Yields, based on the isocyanic acid, were low in the early runs but increased to 40% to 50% in later runs. Seven runs were terminated by explosion Most of these explosions occurred during addition of the PFG to the reactor and were related to its sensitivity. Remaining explosions occurred after the adduct was stripped from the reactor and were apparently initiated by the reactor residue.

Reaction conditions were varied considerably as a result of the low yields and unreactivity. Excess PFG was used in all runs with the molar ratio varying from 1.01 to 2.15. Catalyst ratio was varied from 1.14 to 3.75 mg. KSCN per mmol. PFG. Most of the runs, however, were between 1.5 and 2.0. Two time-temperature relations were used: (1) 2 hours at -30°C., and (2) 18 hours at -70°C. followed by 45-60 minutes at -30°C. A 25 volume percent mixture of fluorine in nitrogen was used in all fluorinations. These variations were attempts to improve the yield or initiate the reaction and included no process parameter studies.

3. Discussion

The major problem encountered in the preparation effort was inconsistent results. Lack of reaction between the PFG and isocyanic acid was apparent in a number of runs. Early runs were plagued by isocyanic acid decomposition and polymerization in addition to inadequate agitation. Modifications in handling technique and

Table XII

Summary of Delta Synthesis Runs[a]

	Reactor Charge				Ratios		Temp.	Time	Yield of Delta	
Run No.	KSCN g.	SO_2 cc.	HOCN g.	PFG g.	m. PFG / m. HNCO	mg. KSCN / mmole PFG	°C.	Hrs.	g.	%
1	0.0487	30	1.19	4.78	1.16	1.52	-30	1.5	1	16.5
10	0.0487	30	1.29	4.92	1.10	1.48	-70	18.0		
							-30	1.0	1	15.1
11	0.0487	30	1.50	5.3	1.03	1.35	-30	3.0	1.1	14.3
15	0.112	30	2.15	11.2	1.50	1.50	-30	2.3	5.25	47.8
17	0.112	33	2.15	10.6	1.42	1.58	-30	3.0	1.5	13.6
38	0.120	10	2.5	9.0	1.20	2.00	-40/-25	2.0	7	63.6
39	0.240	20	4.3	18.0	1.20	2.00	-35	2.0	10	45.5
40	0.240	20	4.0	17.0	1.23	2.10	-35/-25	2.2	8	39.1

---

[a] Flow rate for F_2 and N_2 was 80 cc./min. and 240 cc./min., respectively.

reactor design solved these problems. PFG quality became the principal problem in later runs and will be discussed in detail. Fluorination to tris-I and Delta proceeded as planned.

Reaction between the PFG and isocyanic acid did not occur as shown by the recovery of approximately 80% of the PFG in one run. Infrared analysis of the vent gases indicated similar results in several other runs. This lack of reactivity appeared to be deactivation of the catalyst. Analytical analysis of the solvent and reactants failed to yield any clues. Inspection of the reaction system and manifold reveals no deposits or other sources of contamination. After considerable effort, the problem was finally isolated and found to be related to some impurity or impurities in the PFG.

The PFG used in this work was prepared by the aqueous fluorination of guanidine hydrofluoride and purified by vacuum stripping until the PFG content was in excess of 95%. Small scale, laboratory work revealed that chromatographically pure PFG always produced adduct while the vacuum stripped material did not. Further purification by vacuum stripping was unsuccessful and usually resulted in an explosion. Chromatography was not economical and distillation not practical because of the relatively high purity of the stripped sample.

Since PFG purity was critical and catalyst deactivation was the apparent problem, an attempt was made to remove the deactivating impurity from the PFG by passing it through a bed of vacuum dried KSCN at ambient temperature. The bed turned yellow on the influent side, indicating a reaction, and the treated PFG resulted in the desired adduct. Delta yields, based on the HNCO, averaged 40% to 50% in runs where the treated PFG was used.

Chromatographic studies of treated and untreated PFG using electron capture techniques showed that no single impurity of measurable quantity was removed. Concentration of several impurities, however, were significantly reduced. Therefore, either the reduction in concentration or the removal of some very low concentration impurity was responsible for the lack of reactivity. No further attempts were made to elucidate the effect of the KSCN treatment.

D. SUMMARY AND CONCLUSIONS

The kinetics of decomposition of Delta are considered to be primarily first order at 190°C. and 180°C. The reaction appears homogeneous. The specific rate constant at each 10° interval from 190°C. to 140°C., derived on the assumption that the reaction is first order in Delta shows a dependence on the initial pressure of Delta. At lower temperatures the distinction of the exact order of the decomposition is difficult since the data of the final reaction period is a result of competing reactions. The Arrhenius plot of the derived first order constants suggests a change in mechanism at 150°C. The results from a reaction run at 150°C. in the packed reactor indicate a homogeneous reaction. The implication, therefore, is that at 150°C. the reaction is not totally first order, rather it appears to be of higher order, possibly 3/2.

It is believed that there are two competing reactions occurring in the decomposition of Delta. At high temperatures, the higher order reaction is surpressed, but becomes more dominant as the reaction temperature is lowered.

The existence of competing reactions leads to a situation where, in a given range of temperatures and pressures, a series of radical reactions yields a variety of products. This multiplicity of products complicates the task of unraveling the reaction mechanism. In such cases the method usually consists of determining quantitatively the stable products during the course of the process; the order in which the various products appear; the effect of each intermediate and final product on the reaction; the rates of formation and disappearance of the intermediate products; the rate of formation of the final products; and the effect of pressure on the overal reaction. Therefore, considerably more research is required to complete the kinetics of decomposition of Delta.

The proposed mechanism of decomposition of INFO 635 in the solid phase and in acidic solution compares in certain respects with that of Delta in the gas phase. If the initial step is the homolytic rupture of the C-N bond then, similarly, the use of an external additive to desensitize Delta is impossible.

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V. APPENDIX

Calculation of ratio $\frac{k_B}{k_{BH^+}}$

$$\frac{d[\mathrm{INFO}]}{dt} = \frac{k_B\, K_a [\mathrm{INFO}]}{[H^+]} + k_{BH^+}[\mathrm{INFO}] \qquad (1a)$$

where

$[BH^+] \cong [\mathrm{INFO}]$

k_B = rate constant for amine

k_{BH^+} = rate constant for ammonium ion

$$\frac{d[\mathrm{INFO}]}{[\mathrm{INFO}]} = \left[\frac{k_B\, K_a}{[H^+]} + k_{BH^+}\right] dt = k_{ov}\, dt \qquad (2a)$$

where

k_{ov} = overall first order rate constant

$$\log \frac{[\mathrm{INFO}]^\circ}{[\mathrm{INFO}]} = \frac{k_{ov}}{2.303}\, t \qquad (3a)$$

$$\left[\log \frac{[\mathrm{INFO}]^\circ}{[\mathrm{INFO}]}\right] [H^+] = \frac{k_{ov}\, [H^+]\, t}{2.303} \qquad (4a)$$

$$\frac{k_{ov}[H^+] \text{ at pH} = 1}{k_{ov}[H^+] \text{ at pH} = 3} = \frac{30}{1} \qquad (5a)$$

$$\begin{array}{l} k_B\, K_a + k_{BH^+}\,(0.1) = 30 \\ \underline{k_B\, K_a + k_{BH^+}\,(0.001) = 1} \end{array} \qquad (6a)$$

$$\begin{array}{l} k_{BH^+} = 293.0 \\ k_B = 2.31 \times 10^8 \end{array} \qquad (7a)$$

$$\frac{k_B}{k_{BH^+}} \cong 10^7 \qquad (8a)$$

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The decomposition of INFO-635P in various forms has been studied in dilute aqueous solution. Decomposition of the A form of INFO-635P is rapid at room temperature and takes place unimolecularly. In the solid state, detonation occurs almost immediately in anhydrous ammonia gas. The tris- group of INFO-635P in acid decomposes at 100°C. by homolytic rupture into free radicals, and the final products. One of these final products seems to act as a reducing agent in acidic solutions and this should be tested conclusively for the solid decompositions as well. In general, the gaseous product distribution from solid phase decomposition is similar to that in acid solution.

The kinetics of decomposition of compound Delta is complex. At the high end of the temperature range studied, 140°-190°C., the dominant reaction is first order in Delta, and homogeneous. A second competing mechanism becomes more dominant at the intermediate temperatures where no distinct first order rate can be observed. The reaction at these lower temperatures is homogeneous, and possibly 3/2 order.

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