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FINAL REPORT

A STUDY OF THE EXPLOSION LIMITS OF SIMPLE DIFLUORAMINO COMPOUNDS

Contract No. Nonr.-4065(00)

to

Office of Naval Research
Washington, D. C. 20360

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JUL 1 1969

from

Kinetics and Combustion Group
Atlantic Research Corporation
A Division of The Susquehanna Corporation

Chief Investigator: G. von Elbe
Consultant: J. B. Levy
Scientist: G. White

June, 1969

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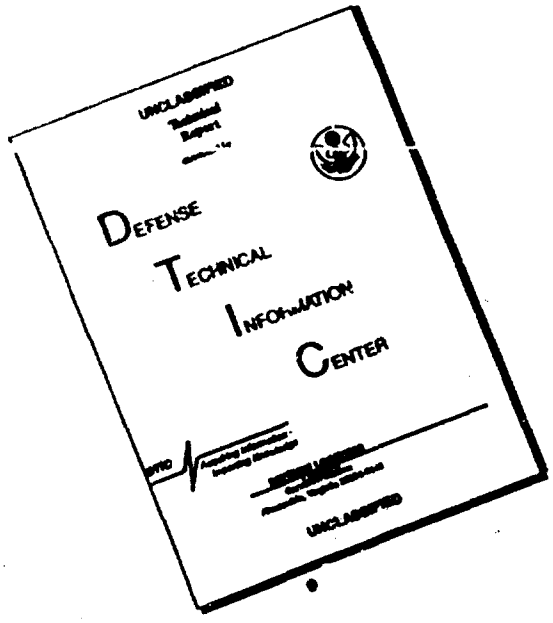

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I. ABSTRACT

Vapors of bis-difluoroamino propanes $C_3H_6(NF_2)_2$ (DP) and bis-difluoroamino butanes $C_4H_7(NF_2)_2$ (DB) were exploded either by raising the temperature or by adding fluorine. For the thermally induced explosion the experiments yielded explosion limits as functions of pressure p, temperature T and vessel diameter d. For the fluorine-induced explosion the experiments yielded explosion limits in terms of critical fluorine concentrations $[F_2]_{crit.}$. The data show prima facie that the reaction is of the branched-chain type and that at the explosion limits the relation Rate of Chain Branching = Rate of Chain Breaking is applicable. Using this relation in conjunction with chemical analysis of the reaction products and auxiliary data from photochemical experiments, the following reaction mechanism has been formulated for the DP isomers:

(1) $NF + DP = HCN + C_2H_2 + N_2 + 3HF + 2F$

(2) $NF + DP = HCN + C_2H_2 + N_2 + 3HF + F_2$

(3) $NF \xrightarrow{\text{surface}}$ destruction

(4) $R\ (=C_3H_5(NF_2)_2) = HCN + C_2H_2 + 2HF + NF + F$

(5) $R \xrightarrow{\text{surface}}$ destruction

(6) $F + DP + F_2 = HCN + C_2H_2 + 3HF + NF_2 + 2F$

(7) $F + DP = C_3H_6F(NF_2) + NF_2$

(8) $F + DP = HF + R$

(9) $R + F_2 = C_3H_5F(NF_2)_2 + F$

(10) $NF_2 \xrightarrow{\text{surface}}$ destruction

(11) $F + DP + O_2 \rightarrow$ inert products

The decomposition of the free radical $C_3H_5(NF_2)_2$ to yield NF + F rather than NF_2 is interpreted in terms of a sequential activation of the F-atoms in the two NF_2-groups of the radical R. Each group loses one F-atom in reactions with neighboring atoms H to form HF, so that the formation of the molecules HCN and C_2H_2 in the final break-up releases one radical NF and one atom F. This principle also applies to the ternary reaction F + DP + F_2 except that one NF_2-group is preserved because the

molecule F_2 furnishes an atom F to serve as reaction partner to one of the H-atoms in the carbon chain.

For the fluorine-induced explosion limit the mechanism yields the equation

$$[F_2]_{crit.} = \frac{k_7}{k_6} + \frac{k_{11}}{k_6} [O_2]$$

and for the thermally induced explosion limit

$$p^2d^2 = \frac{k_3/k_2}{\left[2\frac{k_1}{k_2} / \left(\frac{k_5}{k_4pd^2} + \frac{k_7}{k_8}\right)\right] - 1}$$

The coefficient k_7 is very small, being of the order of 10^{-6} of the gas-kinetic collision frequency for 1,2-DP and 2,2-DP and at least another order of magnitude smaller for 1,3-DP. Thus, for 1,3-DP the value of $[F_2]_{crit.}$ is so small that it cannot be determined experimentally with any certainty. Furthermore, whereas for 1,2-DP and 2,2-DP the ratio k_7/k_8 is substantially dominant over the competing ratio k_5/k_4pd^2 in the T, p, d - range of these experiments, the roles are reversed for 1,3-DP so that for this compound the thermally induced limit reduces substantially to the equation

$$pd^2 = \frac{k_5}{k_4} \quad \frac{k_2}{2k_1}$$

The fact that k_7 is smaller for 1,3-DP than for 1,2-DP and 2,2-DP indicates that an NF_2-group attached to an end atom of the carbon chain is relatively more resistant to displacement by an F-atom than an NF_2-group attached to the middle carbon atom. The displacement of NF_2 by F is seen to play a key role in positioning the explosion limits in the T,p,d - coordinate system, even though this reaction is a very rare molecular event and hence not detectable by chemical-analytical methods.

For the DB isomers the evidence indicates that in contrast to reaction (9) above the reaction of F_2 with free radicals $C_4H_7(NF_2)_2$ produces

more than one F atom or free radical and is thus a chain-branching reaction. For IBA the fluorine-induced explosion is described by the sequence of reactions

$$C_4H_8(NF_2)_2 \xrightarrow{F} \cdot HF + C_4H_7(NF_2)_2 \xrightarrow{F_2} HCN + C_2H_2 + 2HF + 2F$$

$$+ CH_2NF_2 \xrightarrow{C_4H_8(NF_2)_2} HCN + 2C_2H_2 + 2H_2 + N_2 + HF + 2F_2 + F$$

The high sensitivity of the DB isomers to initiation of explosion by fluorine is the probable cause of premature reaction on admitting DB vapor to a heated reaction vessel. For IBA, this premature reaction has prevented the determination of limits for the thermally induced explosion. For 2,3-DB and 1,2-DB a method has been found to obtain such data. They show that the reaction mechanism is analogous to the mechanism for the thermally induced explosion of 1,3-DP.

II. INTRODUCTION

This report concludes the study of the explosive reaction of bis-difluoroamino alkanes under the subject contract. Three propane isomers and three butane isomers of this group of alkanes were selected for this study. They are designated throughout this report by the abbreviations DP for difluoroamino propane and DB for difluoroamino butane and comprise

1,2-DP	$CH_2(NF_2) \cdot CH(NF_2) \cdot CH_3$
2,2-DP	$CH_3 \cdot C(NF_2)_2 \cdot CH_3$
1,3-DP	$CH(NF_2) \cdot CH_2 \cdot CH_2(NF_2)$
1,2-DB	$CH(NF_2) \cdot CH(NF_2) \cdot CH_2 \cdot CH_3$
2,3-DB	$CH_3 \cdot CH(NF_2) \cdot CH(NF_2) \cdot CH_3$
IBA (a code name)	$CH_2(NF_2) \cdot C(CH_3)(NF_2) \cdot CH_3$

These compounds are colorless liquids, stable at room temperature, and sufficiently volatile at room temperature (25°C) for admission of the vapors to a reaction vessel at 30 to 40 torr for DP and IBA, and at 20 to 30 torr for 1,2-DB and 2,3-DB. Explosive reaction was induced either by raising the temperature to the explosion threshold or by adding small quantities of fluorine to the vapor. The data on explosion limits show prima facie that the reaction is of the branched-chain type and that the relation Rate of Chain Branching = Rate of Chain Breaking is applicable to the limits. Using this relation in conjunction with chemical analysis of the reaction products and auxiliary data obtained from photochemical experiments, it has been possible to establish the reaction mechanism in considerable detail.

The mechanism represents a mode of degradation of DP and DB molecules that is governed by free-radical reactions and is therefore different from the modes of degradation observed in studies of molecular impingement of DP and DB on very hot surfaces[1] or in electron impact studies.[2] In these studies various molecular fragments have been obtained that do not occur in the chain reaction mechanism.

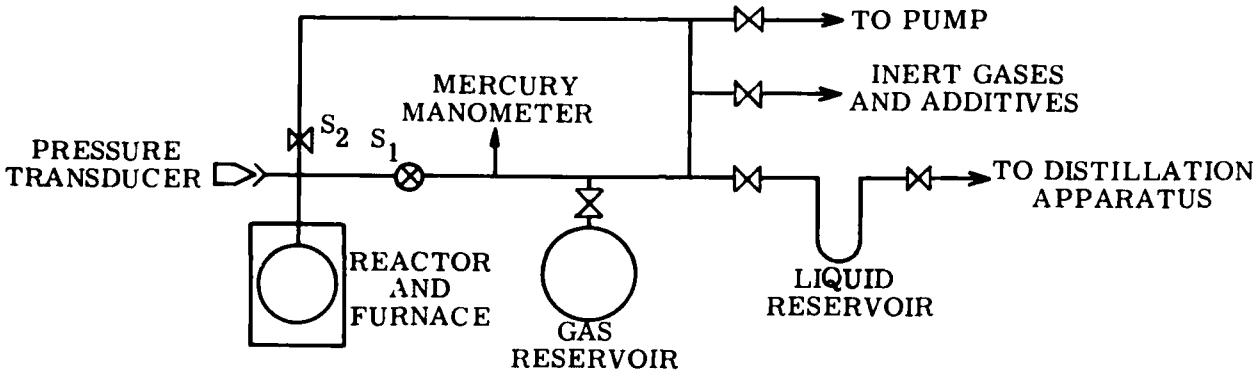
III. DIFLUOROAMINO PROPANES

1. Thermally Induced Explosions

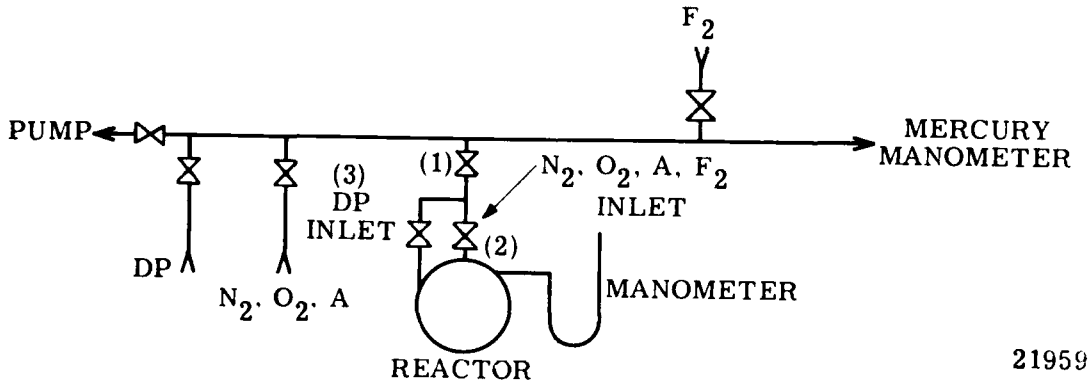
(a) Materials, Apparatus and Experimental Procedure.

A 100g quantity of 1,2-DP dispersed as a 20% solution in methylene chloride was received from the duPont Eastern Laboratories; 110g of 2,2-DP dissolved in 990g of sym-tetrachlorethane were received from the Rohm and Haas Redstone Arsenal Laboratory; and 60g of 1,3-DP dissolved in 350 grams of methylene chloride were received from Aerojet Laboratories in Azusa, California. From these solutions small samples were prepared by stripping the solvent in a micro-distillation apparatus equipped with a 20 cm vacuum-jacketed Vigreaux column. Purity as determined by gas chromatography was 99%+ for 1,2-DP and 2,2-DP. Samples of 1,3-DP contained about 16% of a residual diluent which apparently was a fluorocarbon material of approximately the same boiling point as 1,3-DP.

Experiments up to about 50 torr of DP vapor pressure were performed in an apparatus shown schematically in Figure 1. About 1 cc of distilled DP was condensed at the bottom of a U-tube. From this liquid reservoir DP-vapor at pressures up to the vapor pressure at the ambient room temperature could be admitted through a previously evacuated manifold to a vapor reservoir and diluted with inert gas as desired. The manifold was connected to the reactor by the large-bore stopcock S_1 which could be opened and closed by a 180° turn in a time of about 80 milliseconds. This time was substantially smaller than the induction period of the reaction in the range of the reported data. The reactors used in these experiments were spherical pyrex bulbs ranging in volume from 100cc to 2,000cc. They were mounted in an air furnace consisting of an aluminum cubicle heated by nichrome wire and insulated with expanded magnesia and transite. The furnace could operate at temperatures up to 450 C. The temperature was monitored by a thermocouple in contact with the reaction vessel. The pressure was monitored by a transducer whose



Apparatus for Thermally Induced Explosion

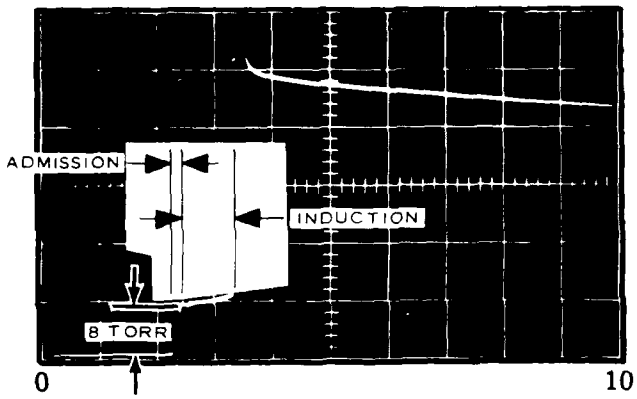


Apparatus for Fluorine-Induced Explosion

Figure 1. Apparatus for Explosion Limit Studies.

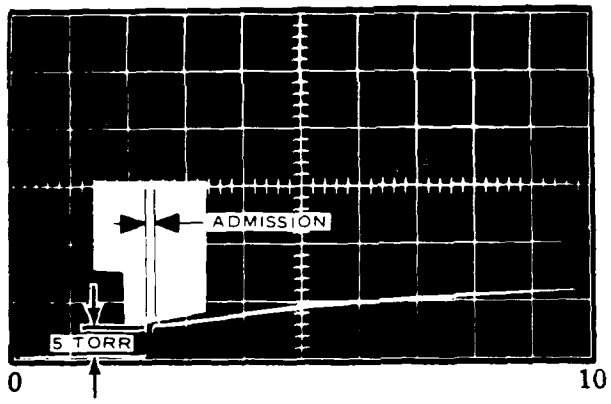
signal was displayed on a Tektronic 535A oscilloscope. The oscilloscope trace was photographed by means of a Polaroid camera. In earlier experiments the transducer was an SLM pressure indicator (Kistler Instrument Co.) which has a quartz sensing element. In later experiments a carrier-demodulator instrument manufactured by Pace Engineering Company was used, which has a transducer comprising a variable reluctance coil in contact with a stainless-steel diaphragm.

At the start of an experiment the temperature was adjusted to the desired level and the system was evacuated to about 0.1 torr. Then, with stopcock S_2 closed and the vapor reservoir open to the manifold, the vapor was admitted by a turn of stopcock S_1 and a pressure-time record was obtained. The recorded initial pressure at the end of the admission period was found to agree closely with the residual pressure in the reservoir and manifold. Typical records, one for non-explosive reaction and the other for explosion, are shown in Figure 2. Explosion was usually accompanied by a click and a flash that was visible in the reactor inlet tube outside the furnace. Explosion limits were determined in repeated tests by varying the pressure of the admitted gas while the temperature was kept constant. The explosion limits were found to be insensitive to the vacuum level prior to gas admission, so that evacuation to 0.1 torr was amply sufficient. The reaction produces HF and free carbon, so that the internal surfaces of the pyrex glass reactors were etched by HF and became covered with carbon deposits. The condition of the reactor surface was found to have no effect on the explosion limits of the various DP isomers. In contrast, it was found to be critical in experiments with the DB isomers $C_4H_8(NF_2)_2$. Depending on surface conditions the DB isomers tend to decompose vigorously during the 80 millisecond period of admission to the reactor before the stopcock S_1 is closed. This premature reaction sometimes causes flash-back of flame into the manifold. Generally, its occurrence is indicated by an anomaly in the pressure trace, i.e., the recorded final pressure is below the normal pressure expected from the number of moles of decomposition products because at the instant of closing



Time (sec)

EXPLOSION



Time (sec)

NONEXPLOSION

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Figure 2. Pressure-Time Traces for 1, 2 DP in 1,000 cc Bulb at 413°C.

of the stopcock S_1 the reactor does not contain undiluted DB vapor but a mixture of DB and decomposition products. With 2,3-DB and 1,2-DB the effect could be eliminated by burn-out of the carbon deposit with air or oxygen, whereas with IBA the effect could not be eliminated and, hence, no meaningful explosion limits could be obtained. With the DP isomers no surface treatment was required because identical data were obtained with fresh and aged vessels and the ratio of the final to the initial pressure was always between 4 and 5, in close agreement with theoretical estimates of product yields.

It was found necessary to extend the limit data to DP-pressures of 100 torr and higher. In order to avoid the breakage hazards of exploding large pressures of DP in a glass manifold, the following procedure was used for these explosion studies: A small volume of liquid DP is measured into a small glass vial using a micro-syringe and the vial is inserted into the pyrex reaction bulb. The liquid volume is calculated to attain the target pressure in the reactor at the temperature of the experiment, using the measured density of 1.3 g/cc for liquid DP. The DP-sample is frozen in the bulb by immersing the bulb in liquid nitrogen; in this state the bulb is evacuated and sealed, and after warming and evaporation of the liquid it is plunged into a large heated salt bath. The desired temperature of the salt bath is maintained by several immersion heaters, a thermo-regulator and a stirrer. In case of explosion one observes a flash of light, a clearly audible click and instant deposition of carbon on the reactor wall. In case of no explosion one observes merely a slow deposition of carbon. In explosions near the limit the temperature equalization between bath and vessel is assured by an induction period of the order of 10 seconds or more. Explosion raises the pressure by a factor of 4 to 5 due to increase of the number of moles, and by another factor of the same order due to heat release. At an initial pressure of 200 torr the reactor wall is thus suddenly exposed to a pressure of six atmospheres or more and additionally stressed by shock waves. The reactor was therefore occasionally shattered in these experiments and safety precautions were necessary.

By attaching a Toepler pump to the apparatus shown in Figure 1 it was possible to sample the gaseous explosion products for analysis. As described below, the products were fractionated by cold traps at approximately -45°C and -196°C, and the fractions were analyzed by mass and infrared spectroscopy, and other methods.

(b) Explosion Limits of 1,2-DP, 2,2-DP and 1,3-DP Vapors.

Data on explosion limits of DP vapors without addition of other gases are listed in Table 1. Each pair of p,T-values represents the median between closely spaced experimental p,T-values for explosion and no explosion in a spherical reaction vessel of the indicated diameter d.

In figures 3, 4 and 5 the products pd and pd^2 in units of torr x cm and torr x cm^2 are plotted versus 1/T in units of 1000/°K. It is seen that for 1,2-DP (Figure 3) the pd-data are closely represented by a common non-linear curve which approaches "infinity" at 1.528×10^{-3} °K^{-1} or 382 C, whereas the pd^2-data show no correlation. For 2,2-DP (Figure 4) the pd-data for large vessels are also correlated by a common non-linear curve. The pd-data for small vessels show substantial discrepancies but for all vessels the pressure p or product pd approaches "infinity" at 1.758×10^{-3} °K^{-1} or 296°C. Again, the pd^2-data show no correlation. For 1,3-DP (Figure 5) the pd-data show no correlation whereas the pd^2-data fall on a common linear curve except for data obtained at high pressure by the salt-bath method. The slope of the curve corresponds to an activation energy of 42.5 kcal/mole.

Figure 6 shows explosion limits of mixtures of 1,2-DP and xenon. It is seen that xenon decreases the pressure of DP at the explosion limit but has no substantial effect on the temperature of 382°C below which 1,2-DP does not explode at any pressure. Similar data have been obtained with argon and nitrogen.

A reverse effect on the DP-pressure at the explosion limit was found with isobutane. In experiments at 419°C, using a reaction vessel of 7.5 cm diameter, the limit pressure of undiluted 1,2-DP was found to

TABLE 1 - Explosion Limits of DP-Vapors

d = Diameter of Spherical Reaction Vessel, cm
p = DP-pressure at Explosion Limit, torr

1,2-DP

d	6.0	7.3	7.3	7.3	7.3	7.3	7.3
p	200	42	27	22	11.5	8.5	6.6
°C	383	393	401	405	421	437	452
$10^3/°K$	1.524	1.497	1.484	1.475	1.441	1.408	1.380

d	16	16	16	16
p	30	15	9	6
°C	385	391	400	412
$10^3/°K$	1.520	1.506	1.486	1.460

2,2-DP

d	4.6	4.6	4.6	4.6	4.6	7.5	7.5
p	200	150	22	15	7	100	54
°C	296	296	322	329	353	296	297
$10^3/°K$	1.757	1.757	1.681	1.661	1.597	1.757	1.754

d	7.5	7.5	7.5	7.5	7.5	12.5	12.5
p	43	23	19	9.5	5.5	93	20
°C	299	305	314	324	334	296	297
$10^3/°K$	1.748	1.730	1.704	1.675	1.674	1.757	1.754

d	12.5	12.5	12.5	15.8	15.8	15.8
p	15	7.5	4.5	17	7	3
°C	302	316	325	297	309	322
$10^3/°K$	1.739	1.707	1.672	1.754	1.718	1.680

1,3-DP

d	5.75	5.75	7.5	7.5	7.5	7.5	7.5
p	150	100	39	32	24	19	15
°C	398	405	395	401	408	414	420
$10^3/°K$	1.490	1.475	1.497	1.484	1.468	1.455	1.443

d	7.5	7.5	12.4	12.4	12.4	12.4	12.4
p	14	7	-	16	14	9	5
°C	426	432	-	392	398	405	421
$10^3/°K$	1.430	1.418	-	1.504	1.490	1.475	1.441

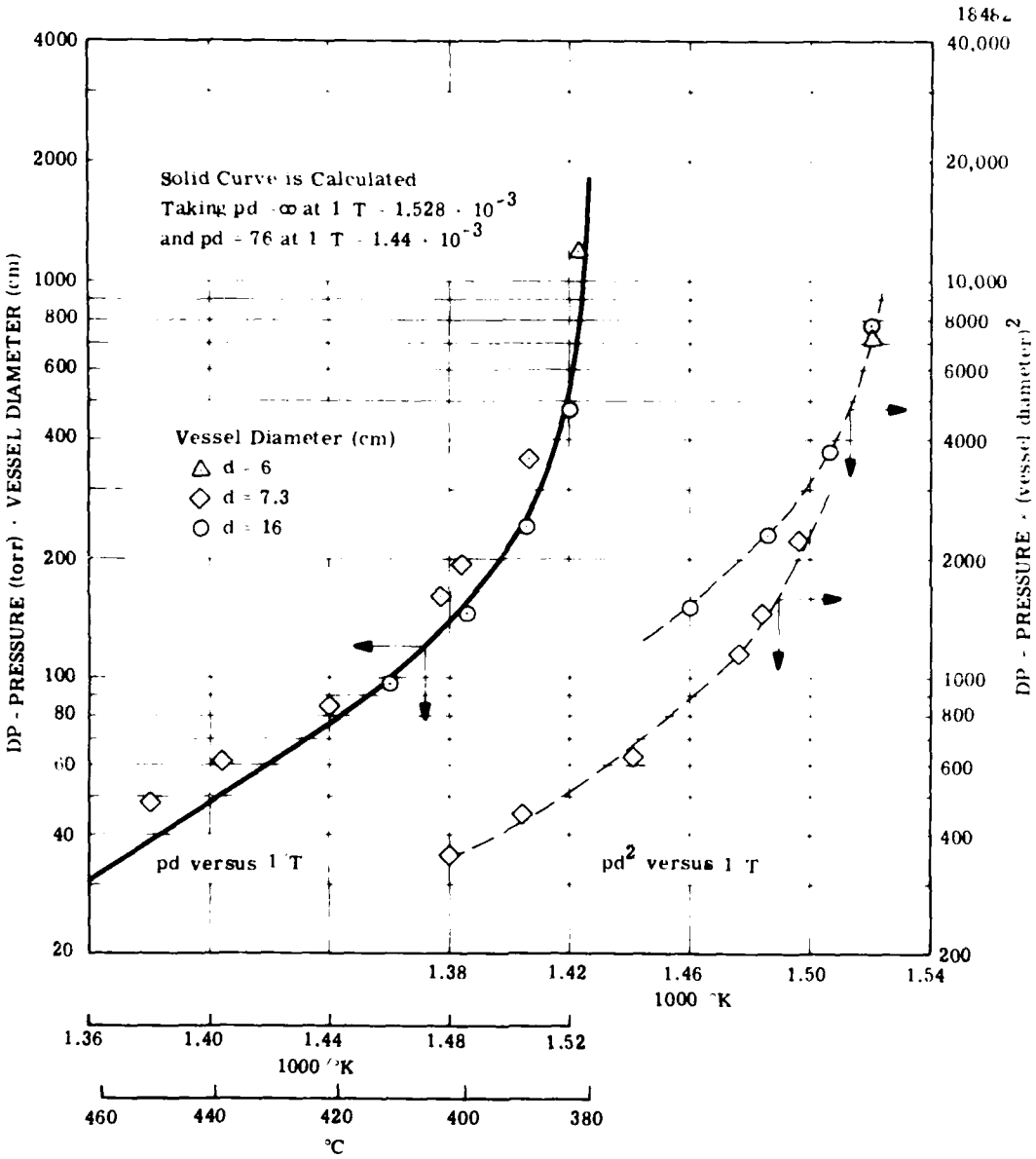


Figure 3. Explosion Limit of 1, 2 - DP Vapor.

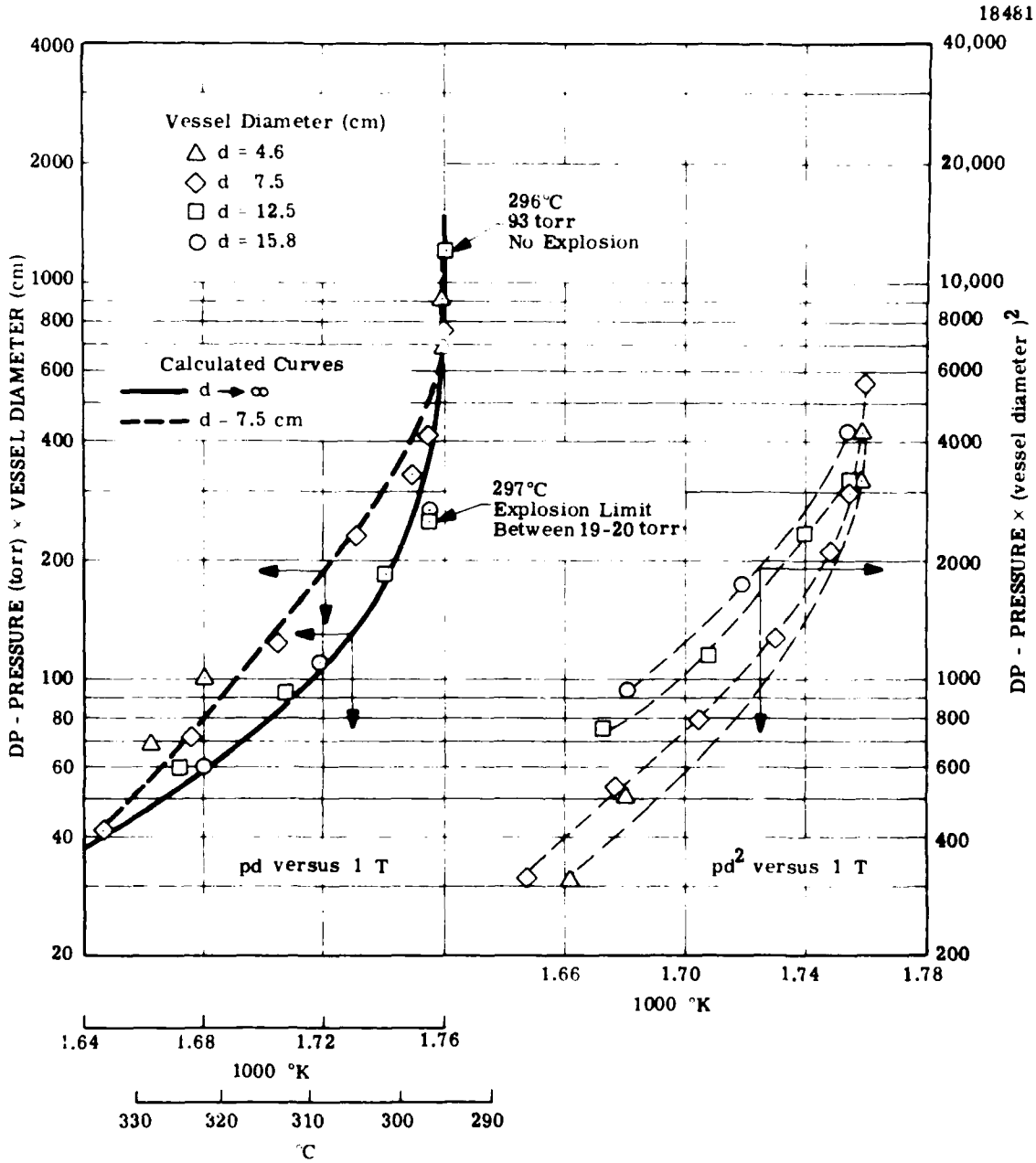


Figure 4. Explosion Limit of 2, 2 - DP Vapor.

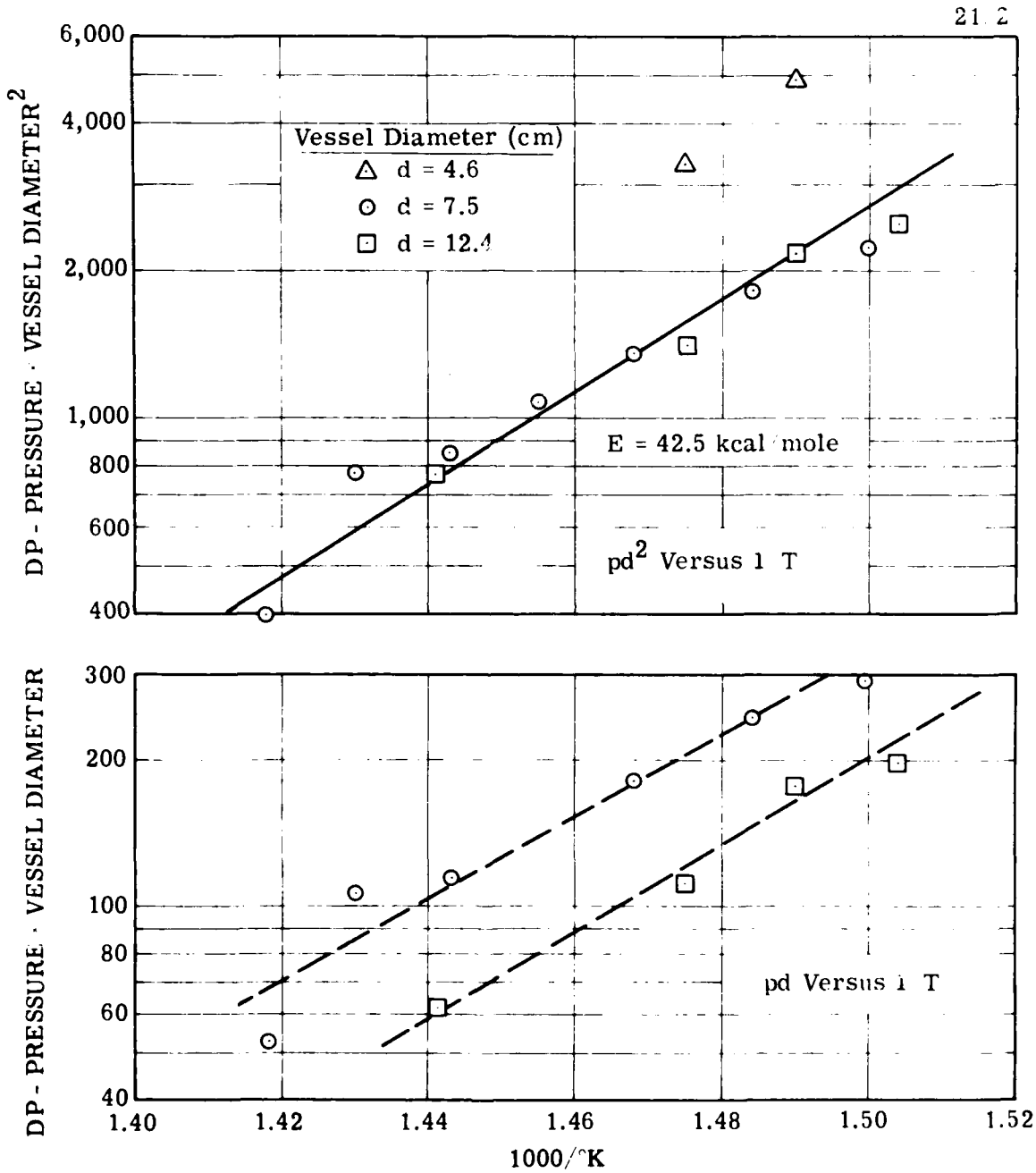


Figure 5. Explosion Limit of 1, 3 - DP Vapor.

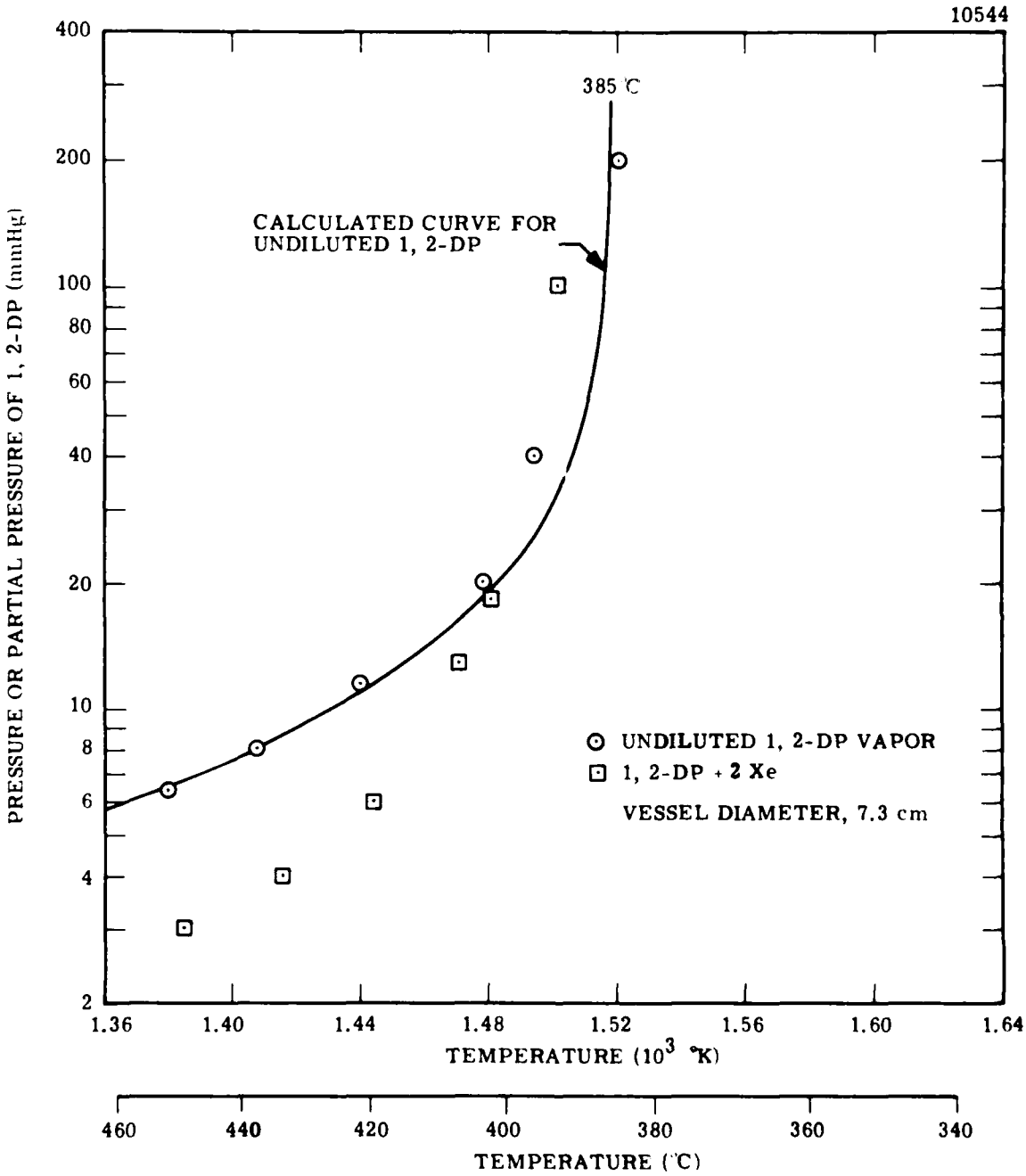


Figure 6. Explosion Limits of 1, 2 - DP Vapor with and Without Addition of Xenon.

be 13 torr. On adding isobutane in 1:1 molar ratio the partial limit pressure was increased to 18 torr. Experiments of this type were carried out with other additives in the expectation of finding an effective chemical inhibitor. The search included propene, acetylene, methyl acetylene, 1,1-difluoroethylene, CH_4, HBr, H_2 and SF_6. None of these compounds proved to be more effective than isobutane.

It is possible that the unidentified residual diluent in liquid 1,3-DP is an inhibitor comparable to isobutane. In low-pressure experiments where the apparatus shown in Figure 1 was used, vapor was obtained from the liquid sample at room temperature and the percentage of contaminant in the vapor was therefore probably much smaller than in the liquid. In high pressure experiments by the salt-bath method the liquid including the contaminant was vaporized completely and the percentage of contaminant was therefore unchanged. The anomaly of the high-pressure data points in Figure 5 may thus be attributable to inhibition of the reaction by the contaminant. As will be seen later, similar difficulties with the available 1,3-DP material were encountered in experiments on fluorine-induced explosions. It is also apparent from the later discussion of the mechanism of the explosive reaction that the explosion limit of 1,3-DP is more sensitive to inhibitors such as isobutane than the 1,2-DP or 2,2-DP limit, and, hence, the rather large displacement of the salt-bath method data from the other data in Figure 5 does not indicate that the contaminant is more effective than isobutane. Unfortunately, no experiments on the effect of isobutane on the 1,3-DP explosion limit were performed.

(c) Analysis of Reaction Products

The gaseous products of DP explosions were found to contain no significant amounts of fluorine compounds other than SiF_4, which is formed by reaction of HF with the glass vessel according to $4HF + SiO_2 = SiF_4 + 2H_2O$. H_2O is correspondingly present in copious quantity. Other products are HCN, C_2H_2, N_2, CO and H_2. CO and H_2 are present in about equal amounts and may therefore have been formed by reaction of H_2O with the carbon

deposit at the vessel wall. Table 2 shows the results of an analysis of the gaseous products of an 1,2-DP explosion. In this experiment the products were transferred from the hot vessel through a glass coil trap at -45°C and another trap at liquid-nitrogen temperature to a reservoir, using a Toepler pump. In order to increase the yield of products the evacuated reaction vessel was recharged with the same amount of DP vapor that was used for the previous explosion and the experiment was repeated identically. The total number of moles of non-condensible products from the two explosions were determined and the products were analyzed by infrared and mass spectroscopy. The reservoir was then evacuated and the contents of the liquid nitrogen trap were similarly collected, measured and analyzed. The procedure was repeated for the contents of the -45°C trap. Similar data were obtained from explosions of 2,2-DP. No nitrogen compounds other than HCN and N_2 and no fluorocarbons in more than trace amounts were detected by mass-spectroscopic scanning of the collected product fractions of either DP isomer.

In later work it was observed that near the explosion limit a substantial fraction of DP survives the explosive reaction. This may be due to flow of DP from the reactor into the inlet tube where the reaction is quenched, and is also due to quenching of the reaction near the vessel wall where the temperature and chain carrier concentration is relatively low. A remark on this quenching mechanism is included in the later discussion. From the available data the unreacted fraction of DP is conservatively estimated to be of the order of 10 percent. Other sources of loss by reaction products are shown by the data in Table 2. Thus, about 6.3×10^{-4} moles corresponding to about 20% of the gas contents of the reaction vessel were lost in the Toepler pumping operation. Later observations have confirmed that gases are entrapped by the mercury of this pump. Presumably, the entrapment involved chiefly the compounds that have a relatively low vapor pressure, i.e., unreacted DP, H_2O and HCN (B.P. 26°C), whereas the other products including SiF_4 (180 torr vapor pressure at -65°C) were not entrapped significantly. In addition, about 10 percent of the contents of the non-condensible fraction and the condensate in the liquid-

TABLE 2

Analysis of Products of 1,2-DP Explosion at 394°C and 56 torr DP vapor in a 5.9 cm Pyrex bulb. Data are listed in units of 10^{-4} moles.

1,2-DP before Explosion	7.6*
Total Vessel Contents before Evacuation with Toepler Pump	30.3
Total Contents of Fractions	
-45°C Trap	5.98
Liquid-N_2 Trap	14.2
Non-Condensible	3.76
Sum of Fractions	24.0

Analysis of Fractions

-45°C Trap	Liq. N_2 Trap		Non-Condens.	
Mainly H_2O (nothing else identified by mass spectr. analysis)	HCN	7.52	N_2	1.61
	C_2H_2	1.28	H_2	0.89
	SiF_4	4.00	CO	0.82
	Sum	12.80	Sum	3.32

Atoms in DP molecule	F	N	C	H
7.6×10^{-4} moles DP contain	30.4	15.2	22.8	45.6×10^{-4} moles
Identified in Liq. N_2 Trap and Non-Condensible Fraction	16.0	10.7	10.9	11.9×10^{-4} moles

* Total of two experiments.

nitrogen trap were lost in the procedure of analyzing the fractions.

Assuming that 10 percent DP are unreacted one accounts for $10.7 + 1.5 = 12.2 \times 10^{-4}$ moles of N out of a total of 15.2×10^{-4} moles. On this basis, the overall loss of HCN in the Toepler pump operation and product analysis becomes 3×10^{-4} moles. Subtracting this quantity, plus 14.2×10^{-4} moles of the liquid-nitrogen condensate, plus 3.76×10^{-4} moles of non-condensibles, from 30.3×10^{-4} moles in the vessel before evacuation, one obtains 10.3×10^{-4} moles of H_2O + unreacted DP, or about 9.5×10^{-4} moles H_2O and 0.76 moles DP. This yields the following balance of atomic species in units of 10^{-4} moles:

	F	N	C	H
From Table 2	16.0	10.7	10.9	11.9
10% Unreacted DP, 0.76×10^{-4} moles	3.0	1.5	2.3	4.6
HCN-loss, 3×10^{-4} moles		3.0	3.0	3.0
H_2O, 9.5×10^{-4} moles				19.0
Sum	19.0	15.2	15.2	38.5
In gas phase before explosion	30.4	15.2	22.8	45.6
Not accounted	11.4	0	7.6	7.1

From this summation it appears that not only carbon but also fluorine and some hydrogen are retained in the reaction vessel, the former presumably by reaction with sodium and other metallic ions in the pyrex glass and the latter by adsorption of H_2O at the vessel wall. Some small quantities of F and H are probably also contained in the carbon deposit. However, the details of the F and H balance are of minor interest compared to the balance of C and N. Except for traces of fluorocarbons these elements are present only in the form of HCN, C_2H_2, C_{solid} and N_2. HCN and C_2H_2 cannot be generated spontaneously from C_{solid}, N_2 and H_2 for thermodynamic reasons and represent therefore primary molecular fragments of DP molecules. Hence, there are two reaction paths which the DP-decomposition may take, viz.,

(a) $C_3H_6(NF_2)_2 \rightarrow HCN + .5C_2H_2 + .5N_2 + C_{solid} + 4HF$

(b) $C_3H_6(NF_2)_2 \rightarrow 2HCN + C_{solid} + 4HF$

and the presence of C_2H_2 among the reaction products shows that path (a) is followed by at least a part of the DP molecules in the system. The yield of C_2H_2 is found to be approximately equal to the yield of N_2, which agrees with the stoichiometry of reaction path (a). This fact, plus the fact that the yields of H_2 and CO are approximately equal and that therefore the presence of H_2 is attributable to the secondary reaction $H_2O + C_{solid} = H_2 + CO$, leads to the conclusion that little or no C_2H_2 and HCN is lost in these experiments by decomposition; that is, the reactions $C_2H_2 \rightarrow 2C_{solid} + H_2$ and $HCN \rightarrow .5H_2 + .5C_{solid} + .5N_2$ are negligible in these experiments. The experimentally determined ratio HCN/C_2H_2 is much larger than the ratio $HCN/C_2H_2 = 2$ obtained from reaction (a). This shows that the larger part of the decomposition occurs by reaction (b).

Studies have been made of the non-explosive decomposition of 1,2- and 2,2-DP at temperatures and pressures much below the explosion limits. Under these conditions HCN was obtained in large yield but virtually no C_2H_2 was found. This leads to the conclusion that reaction (a) is associated with the chain-branching mechanism of the explosive reaction and that no chain-branching occurs via reaction (b).

2. Fluorine-Induced Explosions

(a) Preliminary Observations

The existence of a critical fluorine concentration above which a DP-F_2 mixture explodes spontaneously even at low temperature was noted in attempts of preparing a 1,2DP-F_2 mixture at room temperature. For this purpose fluorine was gradually added in small increments to 1,2-DP vapor. The vessel was a 500 cc Pyrex bulb and the Pyrex inlet tube was provided with two stopcocks in series, so as to leave a space of 3 cc between the stopcocks. Fluorine was admitted to this space at a pressure exceeding

the 1,2-DP pressure in the vessel; in this way it was possible to admit a small amount of fluorine to the reactor by closing the upper stopcock and opening the lower stopcock. Table 3 summarizes the data and observations.

TABLE 3

Fluorine-Induced Explosion of 1,2-DP Vapor at Room Temperature

Experiment	Pressure, torr		Comments
	1,2-DP	1,2-DP + F_2	
1	20	20.9	F_2 added in increments of app. 0.25 torr. No detectable reaction after standing 2 hrs.
2	22	22.9	F_2 added in increments of 0.45 torr. No reaction.
		23.5	Addition of 0.6 torr more of F_2 produced an explosion (click and flash). Final pressure 61 torr.
3	18.5	19.7	1.2 torr of F_2 added in a single increment. No reaction.
		20.15	0.45 torr more F_2 added - explosion. Final pressure, 51 torr.
		51 + .66	0.66 torr more F_2 added - another smaller explosion.
4	19.5	21.0	1.5 torr F_2 added in a single increment - small flame in bore of stopcock but no explosion. Final pressure 21.0 torr.
		21.3	0.3 torr more of F_2 added in two 0.15 torr increments. No detectable reaction.

According to the data in experiments 1 to 3, no detectable reaction takes place between F_2 and 1,2-DP vapor if the partial pressure of F_2 is less than about 1.5 torr, whereas an increase of the F_2-pressure to 1.5 torr or more produces explosive reaction characterized by a click, a luminous flash and a sharp pressure rise. In experiment 4, a near-critical quantity of F_2 produced a

reaction which was detectable by luminosity but did not cause a noticeable increase of pressure, and no further reaction was observed on subsequent addition of small quantities of F_2. On the other hand, experiment 3 shows that even after an explosion it is possible to induce further rapid reaction by adding a comparatively large amount of F_2. The ratio of the final pressure after explosion to the initial pressure is about 2.5 to 3, which is considerably below the pressure ratio in thermally induced explosions.

An infrared analysis of the gas after explosion showed the presence of HCN, C_2H_2 and SiF_4. Carbon was deposited at the vessel wall and some fluorocarbon identified as CF_4 was detected.

(b) Critical Fluorine Concentrations for 1,2-DP, 2,2-DP and 1,3-DP.

It appears from the foregoing that the fluorine-induced explosive reaction is self-inhibiting, and from experiment 4 in Table 3 it appears that under some conditions a rather vigorous reaction may occur which does not increase the number of moles in the vessel - that is, which does not fragment the carbon skeleton of the DP molecule - but generates a product which significantly inhibits the reaction and thus increases the critical fluorine concentration. It is therefore understandable that data on critical fluorine concentrations tend to be somewhat erratic.

A series of such data were obtained using the apparatus shown schematically in Figure 1. The manifold line was made from teflon tubing, fittings and valves. Inlets were provided for DP, fluorine and other gases. A glass-capillary mercury manometer with a constant-level bulb was used to measure the pressure in the line. The bulb was coated with Kel-F wax and the mercury was covered with Kel-F oil. The pyrex glass reactor was provided with stopcocks S_2 and S_3, one being used for admitting DP-vapor, oxygen and inert gases, and the other for fluorine. This was done in order to avoid any reaction of fluorine with DP in the bore of the stopcock where the two gases might momentarily be in contact at the high inlet pressure of fluorine. Pressures in the reactor were measured by a mercury manometer. After the system was

completely evacuated DP vapor at pressure p_{DP} was admitted to the reactor with stopcocks S_1 and S_2 open and S_3 closed. S_2 was closed, the line was evacuated, and fluorine at a predetermined pressure $p_{1,F_2} - p_{DP}$ was admitted to the line. S_1 was closed and the experiment was performed by a rapid turn of stopcock S_3. In other experiments oxygen, inert gas and fluorine were admitted successively to the volume between stopcocks S_1, S_2 and S_3 at partial pressures p_{1,O_2}, p_{1,F_2},... p_{DP} and admitted to the reactor through stopcock S_3. Since the gas expansion in this system is substantially isothermal the partial pressures p_{F_2}, etc., of the admitted gases are obtained from the equation $p_{F_2} = (p_{1,F_2} - p_{DP})/(1 + V/v)$, etc., where V is the reactor volume and v is the volume between stopcocks S_1, S_2 and S_3. The data are summarized in Table 4 and the effect of oxygen is illustrated in Figure 7.

The reaction-kinetic aspects of these data are discussed below. Here we mention that in experiments with 1,3-DP a critical fluorine pressure of 0.4 torr was obtained from one sample of the material, whereas with another sample the limit pressure was so small that it could not be measured. As stated previously, the contaminant in this material appears to have an inhibiting effect and, hence, the discrepancy in the data reflects the purity of the vapor obtained from the reservoir of liquid 1,3-DP.

(c) Photochemical Experiments on Mixtures of 1,2-DP and 2,2-DP with F_2 and Cl_2.

As may be seen from the data in Tables 3 and 4, the critical concentration of fluorine for 1,2-DP and 2,2-DP is sufficiently high to permit the preparation and study of mixtures of these DP isomers with fluorine at subcritical concentration. With 1,3-DP this is not feasible because of the extremely low limit concentration.

The objective of these experiments was a study of the effect of photochemically generated F-atoms and Cl-atoms on DP. It was found that DP can be mixed with Cl_2 at room temperature in any proportion without detectable dark reaction.

The photochemical experiments were carried out in a cylindrical cell with monel walls and sapphire windows. The cell was 10 cm long and 4.41 cm in

TABLE 4

Critical Pressures for Fluorine-Induced Explosions of DP

	DP Pressure torr	Temp. °C	Volume cc	Pressure O_2 torr	Pressure N_2 torr	Pressure A torr	Pressure F_2 at limit torr
1,2-DP	8	25	200	-	-	-	2.3,2.5-2.8,2.3
	20	25	200	-	-	-	2.0
	8	55	200	-	-	-	2.5
	8	1	200	-	-	-	3.5
	8	8	200	-	-	-	3.0
	8	100	200	-	-	-	1.24
	8	25	1000	-	-	-	1.40
	8	25	200	2.2	-	-	6.6-6.9,4.8
	8	25	200	2.2	-	9.8	7.0-7.3
	8	25	200	-	2.3	-	2.3
	8	25	200	1.1	-	-	3.5
	8	25	200	3.6	-	-	8.0
2,2-DP	8	25	200	-	-	-	2.8-3.4
1,3-DP	8	25	200	-	-	-	0.2
	8	25	200	2.2	-	-	3.0-3.3,4.6
	8	25	200	2.2	-	9.2	4.1
	8	25	200	2.2	2.1	-	3.9
	8	25	200	1.1	-	-	1.0

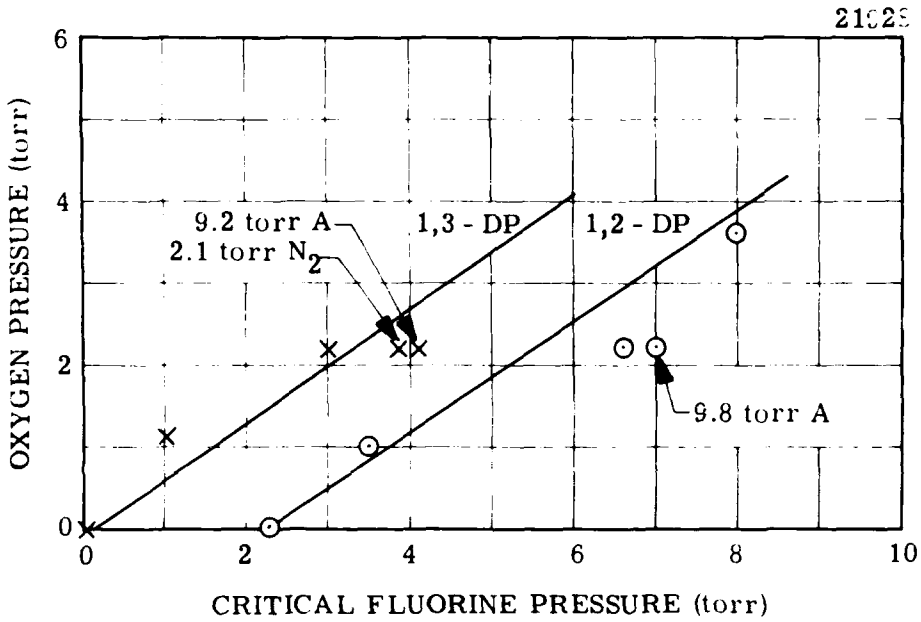


Figure 7. Effect of Oxygen on Critical Fluorine Pressure. DP - Pressure = 8 torr; Temperature, 25°C.

diameter. The cell was equipped with copper coils through which glycerin from a heating bath was cirulated. It had a mercury U-tube manometer which could be closed off to prevent reaction of halogen with the mercury. The light source was a high pressure mercury-arc lamp equipped with a monochromator. The cell was placed on an optical bench which also contained focusing lenses and a photo-tube to measure the light transmittance.

It was desired in particular to monitor the yields of HF and HCl in the photochemical reaction. A series of preliminary experiments were performed to calibrate IR spectra for various pressures of HF. This calibration proved rather unreliable at low HF pressures. However, the data did provide a semi-quantitative estimate of the HF present in a mixture. HCl concentrations could not be determined by IR analysis because of the opaqueness of the sapphire windows; however, data were obtained by mass-spectroscopic analysis.

Experiments were performed using light at 3300 Å for DP-Cl_2 mixtures and light at 3130 Å for DP-F_2 mixtures. DP transmits fully at these wavelengths. The number of absorbed quanta was determined from the known absorption coefficients of Cl_2 and F_2, the partial pressure, cell length, exposure time and total quantum flux which had been previously determined for the source in the present spectral range.

In the first experiment a mixture of 10 torr 2,2-DP + 30 torr Cl_2 was irradiated at room temperature for a period of 160 minutes corresponding to absorption of quanta in excess of the number of DP-molecules in the vessel. This resulted in the formation of HCl and essentially chlorinated DP with no pressure change. The experiment was repeated with a shorter period of irradiation (10 minutes). The quantum yield was found to be larger than 2 and of the order of 10; there was much unreacted DP and no pressure change.

Experiments at 100°C yielded some HF but the significance of this result is uncertain because small amounts of HF appear when DP is heated to this temperature in the dark.

Another series of experiments was performed at much lower Cl_2 pressure (about 2 torr) and higher DP pressure (about 40 torr). When this mixture was irradiated at room temperature for about 10 minutes (corresponding to absorption of quanta about equal to the number of molecules Cl_2

present) about 1 torr of HF appeared. Irradiation for 10 minutes with only about 0.2 torr Cl_2 also produced detectable amounts of HF, though it was not possible to determine the yield. There was no pressure change in these runs.

Experiments with F_2 at sub-critical concentration and room temperature were made using both 2,2-DP and 1,2-DP vapor. The results were identical for both compounds. There was no change of pressure in these runs. Forty torr DP + 2 torr F_2 yielded about 2 torr HF; the irradiation time was 10 minutes corresponding to admittance of quanta to the vessel in excess of the molecules F_2 present. Forty torr DP + 0.2 torr F_2 yielded a barely detectable amount of HF over an irradiation time of 10 minutes; this amount seemed to increase slightly during an additional hour of irradiation. Some HF was also formed in the dark reaction at 2 torr F_2 over a period of the order of ten hours.

(d) Products of Decomposition of 1,3-DP by F_2

In this experiment a sample of 1,3-DP vapor at about 8 torr was exploded with F_2 at room temperature, using a fairly large quantity of F_2 to insure complete decomposition. The reaction products were identified by mass-spectroscopic scanning and the relative yields were determined. The data (excluding SiF_4 and H_2O) are shown in Table 5.

TABLE 5. Products of Decomposition of 1,3-DP by F_2

Products (excluding SiF_4 and H_2O)	C_2H_2	HCN	H_2	N_2	CH_3CN	CH_4
Relative Yields	.33	1	0	.5	.33	trace

The relative yields show an overall ratio C/N ≈ 1 instead of the ratio 1.5 corresponding to the formula $C_3H_6(NF_2)_2$. Presumably, the loss of carbon is caused by reaction of C_2H_2 with fluorine, to yield HF and solid carbon. If the data are corrected for such loss one obtains about equal yields of HCN and C_2H_2 in this reaction. The product CH_3CN which appears here in small yield has not been found among the products of thermally induced 1,2-DP and 2,2-DP explosions.

3. Chemistry and Kinetics of the Chain Reaction

In the reaction paths (a) and (b) (see III,1,c) two steps are discernible: DP molecules are fragmented by elementary molecular reactions into HCN, C_2H_2, HF and products comprising nitrogen and fluorine; and carbon is precipitated by reaction of C_2H_2 with excess fluorine. The literature on acetylene reactions shows that C_2H_2 as such does not decompose significantly at temperatures of the order of the temperatures in these experiments - in fact, C_2H_2 is recoverable from flame gases - but it reacts readily with fluorine to yield HF and solid carbon. These products are thermochemically favored over stoichiometrically equivalent products comprising fluorocarbons and hydrogen, so that the virtual absence of fluorocarbons is not surprising. Because the reaction involves polymerization to yield solid carbon it becomes significant only after the primary DP decomposition is far advanced and C_2H_2 and fluorine have accumulated in substantial concentrations. The two reaction paths (a) and (b) represent therefore sequences of primary and secondary processes which are schematically represented by

(a) $C_3H_6(NF_2)_2 \rightarrow HCN + C_2H_2 + .5N_2 + 3HF + .5\ F_2$

$$\rightarrow HCN + .5C_2H_2 + .5N_2 + .5C_{solid} + 4HF$$

(b) $C_3H_6(NF_2)_2 \rightarrow 2HCN + C_2H_2 + 2HF + F_2 \rightarrow 2HCN + C_{solid} + 4HF.$

From general kinetic experience as well as from the characteristics of the DP-decomposition reactions it is certain that each of these sequential processes comprises a free-radical chain mechanism. Fluorine atoms are certainly present and according to the photochemical data (see III,2,c) they react with DP to form HF, as is known to occur with hydrocarbons in general. Thus, free radicals $C_3H_5(NF_2)_2$ are formed, and since it has been found that the pressure in the reaction vessel does not change, the radicals are shown to be rather stable at room temperature; they are not decomposed into smaller molecular products. However, at higher temperatures they may be expected to react in several ways, as for example,

$$C_3H_5(NF_2)_2 + C_3H_6(NF_2)_2 = 4HCN + C_2H_2 + 5HF + F_2 + F ,$$

followed by

$$F + C_3H_6(NF_2)_2 = HF + C_3H_5(NF_2)_2$$

This chain reaction corresponds to the primary process in reaction path (b) and is unbranched; it therefore meets the specifications for the non-explosive decomposition of DP (see III,1,c) and appears to be the correct choice of mechanism for this reaction because no plausible alternative is discoverable.

The theory of the explosive decomposition requires the development of a system of elementary free-radical reactions which involves no more than one DP molecule or DP free radical in each reaction and is consistent with the experimentally determined explosion limits and other data, as well as with thermochemical requirements and reaction-kinetic theory. In order to simplify this task we present in Table 6 a complete system of reactions that has been developed in the course of this work and meets these specifications.

TABLE 6. Mechanism of Explosive Reaction of DP

(1)	$NF + DP = HCN + C_2H_2 + N_2 + 3HF + 2F$	+ 94 kcal/mole
(2)	$NF + DP = HCN + C_2H_2 + N_2 + 3HF + F_2$	+ 130
(3)	$NF \xrightarrow{\text{surface}}$ destruction	
(4)	$R = [C_3H_5(NF_2)_2] = HCN + C_2H_2 + 2HF + NF + F$	- 34 (-25?)
(5)	$R \xrightarrow{\text{surface}}$ destruction	
(6)	$F + DP + F_2 = HCN + C_2H_2 + 3HF + NF_2 + 2F$	+ 31
(7)	$F + DP = C_3H_6(NF_2) + NF_2$	+ 36
(8)	$F + DP = HF + R$	+ 35
(9)	$R + F_2 = C_3H_5F(NF_2)_2 + F$	+ 70
(10)	$NF_2 \xrightarrow{\text{surface}}$ destruction	
(11)	$F + DP + O_2 \cdot$ inert products	

Heats of reaction are based on the heats of formation listed in Table 7. The plus and minus signs correspond to chemical usage in the sense that the positive sign denotes an exothermic reaction and the negative sign an endothermic reaction. The heat of formation is $-\Delta H_f$; the enthalpy of formation conventionally used in thermodynamic calculations is ΔH_f.

TABLE 7. Heats of Formation

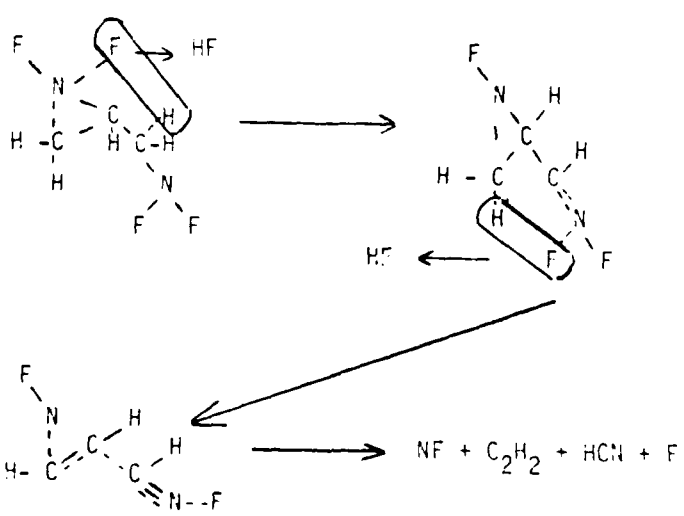
Compound	Heat of formation, kcal/mole
$C_3H_6(NF_2)_2$ = DP	+ 41
$C_3H_5(NF_2)_2$ = R	- 6
NF	- 65
NF_2	- 17
F	- 17.8
HCN	- 31.3
C_2H_2	- 54.2
HF	+ 64.2

In Table 7, the values for DP, R, NF and NF_2 are estimated from bond energies and are therefore uncertain. This is relevant in particular to reaction 4 above, R → 2HF + NF + F, which according to activation energy estimates given below should be endothermic by no more than about -25 kcal mole.

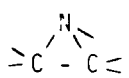
In the low-temperature regime reactions 1, 2, and 4 are negligible because of their high activation energies. In most collisions of F and DP the DP-molecule loses a hydrogen atom and becomes the free radical R according to reaction 8. In very rare collisions, presumably governed by a specific attitude of the colliding species and a specific distribution of intramolecular rotation and vibrations of the DP-molecule, the F-atom

may also displace an NF_2-group from its bond to a carbon atom according to reaction 7. The probability of this reaction in collisions F + DP is thought to be very small and to be not or only mildly dependent on temperature. If F_2 is present in sufficiently high concentration, R does not go to the vessel wall (reaction 5) but reacts with F_2 and regenerates an F-atom (reaction 9). Evidence for the analogous reaction with Cl_2 instead of F_2 is obtained in the photochemical experiments on Cl_2 and DP, which at high Cl_2-concentration were found to produce HCl and chlorinated DP. We have not attempted to verify the corresponding fluorination of DP because the photochemical reaction can only be studied at very low F_2-concentration; however, it is reasonable to assume that the reaction $R + F_2 = RF + F$ takes place at least as readily as $R + Cl_2 = RCl + Cl$.

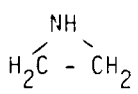
Concerning the unimolecular decomposition of the free radical $R = C_3H_5(NF_2)_2$, the thermochemically most stable products that can be formed from the available atomic species are HCN, C_2H_2, 2HF and NF_2. However, one may envisage a mechanism of break-up which yields NF + F instead of NF_2, as illustrated below. According to this concept, the various bonds in the



radical R = $C_3H_5(NF_2)_2$ as well as the molecule DP - $C_3H_6(NF_2)_2$ are so strong (C-H ≈ 99, C-C ≈ 83, C-N ≈ 70, N-F ≈ 66 kcal/mole) that thermal bond-breaking does not occur significantly in the temperature range of the present experiments (up to 450°C). Instead, the free radical R decomposes due to successive stripping of H-atoms from the carbon skeleton by reaction between N-bonded F and C-bonded H to form HF. In the neutral DP-molecule this is not possible energetically because the sum of the bond energies N-F and C-H is larger than the bond energy H-F, which is 134 kcal/mole. On the other hand, in the free radical R the free valence on one of the C-atoms tends to bond with the N-atom of one of the two NF_2-groups, to form a double bond >C = N- or a ring structure such as



which is found in aziridine



and related compounds. In this way one of the F-atoms in one of the NF_2-groups is loosened and may become sufficiently activated to react with an H-atom to form HF. This reduces the group $-NF_2$ to =NF and generates another free carbon valence which in turn activates an F-atom in the other NF_2-group, stripping another H off the carbon skeleton and reducing the remaining group $-NF_2$ to = NF. In the final break-up one atom N is triple-bonded to C to form HCN, so that one atom F and one free radical NF are liberated.

Concerning the course of reaction 6 in ternary collisions F + DP + F_2 one may envisage that the F-atom strips one H as in reaction 8 and that the rather weak F-F bond (35.6 kcal/mole) in the collision partner F_2 is sufficiently activated by the energy released in this process to cause one of its F-atoms to react with another H instead of bonding to carbon as in reaction 9. The other F-atom is thus liberated and the energized remainder of the original DP-molecule reacts according to the previous scheme. However, there is now only one more H-atom available to combine with F because the three other

H-atoms enter into the stable products HCN and C_2H_2 and thus one NF_2-group remains intact while the other yields one atom F to form HF and an atom N to form HCN. In this way the intact NF_2-group becomes a free radical and the remaining F-atom of the other NF_2-group becomes a free atom in addition to the free atom furnished by the F_2-molecule.

At the explosion limit the rate of formation of each chain carrier equals the rate of destruction. For the fluorine-induced explosion this corresponds to the equations

$$(k_6[DP][F] + k_9[R])\ [F_2]_{crit.} = (k_7 + k_8)[DP][F] + k_{11}[DP][O_2][F] \qquad (1)$$

$$k_8[DP][F] = k_9[F_2]_{crit.}\ [R] \qquad (2)$$

so that

$$[F_2]_{crit.} = \frac{k_7}{k_6} + \frac{k_{11}}{k_6}\ [O_2] \qquad (3)$$

Equation (3) states that the critical fluorine concentration is independent of the partial pressures of DP and inert gases and independent of vessel diameter. This is consistent with the data in Table 4 if differences such as p_{F_2} = 2.3 torr at p_{DP} = 8 torr, and p_{F_2} = 2.0 torr at p_{DP} = 20 torr in a 200 cc vessel, and p_{F_2} = 1.4 torr at p_{DP} = 8 torr in a 1000 cc vessel are attributed to erratic effects, as explained in III,2,a. Oxygen increases the critical concentration and the relation between $[O_2]$ and $[F_2]_{crit.}$ is linear, which appears to be consistent with the data in figure 7. The ratio k_{11}/k_6 is of the order of 2, which is an acceptable ratio for the rate coefficients of two ternary collision reactions in which the collision diameters are nearly identical and activation energies are very small.

The choice of reaction (7), followed by reaction (10) by which radicals NF_2 are destroyed at the vessel wall without undergoing any gas-phase reaction with DP is dictated by the fact that 1,2-DP and 2,2-DP would not be miscible even with traces of F_2 without undergoing vigorous reaction,

if there were no reaction by which F-atoms are removed from the system; and furthermore, this reaction can only be a gas-phase reaction and not a surface reaction involving diffusion of F-atoms to the vessel wall, because in the latter case $[F_2]_{crit.}$ would be strongly dependent on the pressure of DP and inert gases and on the vessel diameter; whereas the data in Table 4 show that no such dependence exists. We have been unable to discover an acceptable alternative to the reaction sequence (7) and (10). Reaction (7) is bimolecular and reaction (6) is trimolecular. If reaction (7) had an activation energy larger than reaction (6), $[F_2]_{crit.}$ would increase with increasing temperature. The data in Table 4 show that the opposite is the case, and hence, reaction (7) has a slightly smaller activation energy than (6). The ratio k_7/k_6 is therefore substantially the ratio of the pre-exponential factors of the rate coefficients. Typical "ball park" values of pre-exponential factors are 10^{-11} cm^3 $molecule^{-1}$ sec^{-1} for bimolecular reactions and 10^{-34} cm^6 $molecule^{-1}$ sec^{-1} for trimolecular reactions. On this basis one would obtain $[F_2]_{crit.} \approx 10^{23}$ molecules per cm^3, whereas data in Table 4 such as $p_{F_2} \approx 2$ torr correspond to $[F_2]_{crit.} \approx 10^{-17}$ molecules per cm^3. k_7 is thus smaller than a normal bimolecular rate coefficient by a factor of about 10^{-6}. We propose therefore that the reaction (7) $F + DP = C_3H_5F(NF_2) + NF_2$, is about 10^{-6} times less probable than the reaction (8) $F + DP = HF + R$; that neither has a significantly large activation energy, and that reaction (7) occurs therefore only in very rare collisions, as mentioned above.

Because there is no gas phase reaction of NF_2 that competes with reaction (10), the latter does not enter into the explosion limit equation. However, the surface chain-breaking reactions (3) and (5) play a determining role in competition with reactions 1 and 2, and reaction (4). The rate coefficients of these surface reactions are obtained from diffusion theory. Generally, if the fraction of destructive collisions with the vessel surface is large compared with the ratio of the mean free path to the vessel diameter, the rate of destruction of a species X at the surface, per unit volume of the reaction vessel, becomes $(4^2/d^2)\, D_x[X]$.[3] D_x is the diffusion coefficient of species X; it is inversely proportional to the total pressure $p + p_i$ (p_i being the partial pressure of any gas added to the DP-vapor) and proportional

approximately to $T^{3/2}$, T being the absolute temperature. Introducing $k_x = 4.^2 D_x(p + p_i)$ one may write the rate of destruction of X at the surface in the form $k_x (p + p_i) d^2 [X]$. We introduce coefficients k_3, k_5 for reactions 3 and 5 corresponding to k_x; they are thus independent of pressure and vessel diameter and increase with temperature at the order $T^{3/2}$.

For the thermally-induced explosion limit one obtains by a series of algebraic operations and setting $k_1/k_2 << 1$, $k_7/k_8 << 1$ and $k_5pd^2/k_4 << 1$ the equation

$$p^2d^2 = \frac{k_3/k_2}{\left[2\frac{k_1}{k_2} / \left(\frac{k_5}{k_4pd^2} + \frac{k_7}{k_8}\right)\right] - 1} \tag{4}$$

where p and d correspond to DP-pressures and vessel diameters, as listed in Table 1. The coefficients k are the rate coefficients of the reactions indicated by the subscript.

When k_7/k_8 is small compared to k_5/k_4pd^2 equation (4) reduces to

$$p^2d^2 = \frac{k_3}{k_2} \frac{1}{2\frac{k_8}{k_7}\frac{k_1}{k_2} - 1} \tag{5}$$

which yields limit curves corresponding to the data for 1,2-DP and 2,2-DP in large vessels, as shown in figures 3 and 4. When k_7/k_8 is small compared to k_5/k_4pd^2 one obtains by cross-multiplication and transposing

$$pd^2 = \frac{k_5}{k_4}\frac{k_2}{2k_1}\left(1 + \frac{k_3}{k_2p^2d^2}\right) \tag{6}$$

which yields a limit curve corresponding to the data for 1,3-DP in figure 5, if $k_3/k_2p^2d^2$ is small compared to 1. When k_7/k_8 and k_5/k_4pd^2 are of comparable

magnitude one obtains curves such as shown by the data for 2,2-DP in small vessels. This change-over of the limit equation from the form (5) for 1,2-DP and 2,2-DP to the form (6) for 1,3-DP is consistent with the fact that $[F_2]_{crit}$ is smaller for 1,3-DP than for 1,2-DP and 2,2-DP by at least an order of magnitude (see table 4) and that k_7 is correspondingly smaller by at least an order of magnitude.

From equation (5) one obtains p^2d^2 or $pd \to \infty$ when $(2k_8/k_7)(k_1/k_2) = 1$. This occurs at 382°C = 655°K with 1,2-DP and at 296°C = 569°K with 2,2-DP. Since the pre-exponential factors of the coefficients k_1 and k_2 are identical the ratio k_1/k_2 is

$$k_1/k_2 = e^{-(E_1 - E_2)/RT} \tag{7}$$

and therefore

$$T(pd \to \infty) = \frac{E_1 - E_2}{R} \Big/ \ln 2 \frac{k_8}{k_7} \quad °K \tag{8}$$

If $2k_8/k_7$ is taken to be of the order of 10^6 one obtains $E_1 - E_2 \approx 18.0$ kcal/mole for 1,2-DP and 15.7 kcal/mole for 2,2-DP.

From kinetic theory one obtains for the diffusion coefficient D_x of a species X diffusing through DP-vapor

$$D_x = \frac{\bar{v}_X}{3\,\sigma^2_{X,DP}\sqrt{\frac{m_X}{m_{DP}} + 1}\,[DP]} \quad cm^2\ sec^{-1} \tag{9}$$

where $\sigma_{X,DP}$ is the average diameter of the molecules X and DP in units of cm, m_X and m_{DP} are the molecular weights, and $\bar{v}_X$ is the average molecular velocity corresponding to

$$\bar{v}_X = \sqrt{\frac{8}{\pi}\frac{RT}{m_X}} \quad cm\ sec^{-1} \tag{10}$$

with $R = 8.31 \times 10^7$ erg mole^{-1}°C^{-1}; and

$$[DP] = 2.7 \times 10^{19} \times \frac{273}{T} \times \frac{p}{760} \text{ molecule cm}^{-3} \tag{11}$$

p being the pressure in torr and T the temperature in °K.

The rate coefficient of a bimolecular reaction is

$$k = f \left(2\sigma^2_{X,DP} \sqrt{\frac{2\,RT}{m_X}} \sqrt{\frac{m_X}{m_{DP}} + 1} \right) e^{-E/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \tag{12}$$

where f is the "steric" factor and E the activation energy. The diameter of a DP molecule is about 8×10^{-8} cm and the diameter of NF is about 2.5×10^{-8} cm. The average diameter $\sigma_{NF,DP}$ is therefore about 5.3×10^{-8} cm. From the molecular weights of NF and DP and writing

$$k_3 = 4\sigma^2 D_{NF} \times [DP] \text{ molecule cm}^{-1} \text{ sec}^{-1} \tag{13}$$

one obtains with $f \approx 1$

$$k_3/k_2 = 2.8 \times 10^{29}\, e^{E_2/RT} \text{ (molecule/cm}^3)^2 \text{ cm}^2 \tag{14}$$

or in units of torr

$$k_3/k_2 = 3.0 \times 10^{-9}\, T^2\, e^{E_2/RT} \text{ torr}^2 \text{ cm}^2 \tag{15}$$

Using equations (8) and (15) and taking $2k_8/k_7 \approx 10^6$ the limit equation (5) becomes

$$p^2 d^2 = \frac{3.0 \times 10^{-9}\, T^2\, e^{E_2/RT}}{e^{2.3 \times 6(1 - T_{(p \to \infty)}/T)} - 1} \tag{16}$$

where $T_{(p \to \infty)}$ is 655°K for 1,2-DP and 569°K for 2,2-DP. Equation (16) is fitted to the data in figures 3 and 4, using E_2 = 21.8 kcal/mole for 1,2-DP and E_2 = 17.3 kcal/mole for 2,2-DP. The corresponding values for E_1 are 39.9 and 33.0 kcal/mole, respectively.

The rate coefficient for the unimolecular reaction (4) may be written in the form

$$k_4 = A_4 e^{-E_4/RT} \tag{17}$$

and neglecting the term $k_3/k_2 p^2 d^2$ the limit equation (6) for 1,3-DP becomes

$$pd^2 = \frac{1}{2} \frac{k_5}{A_4} e^{-(E_4 + E_1 - E_2) / RT} \tag{18}$$

From the data in figure 5 one obtains $E_4 + E_1 - E_2$ = 42.5 kcal/mole, and calculating k_5 analogous to k_3 from equation (13), A_4 is found to be of the order of 10^{13} sec^{-1}, which is the correct order for the pre-exponential factor of a monomolecular rate coefficient. Taking $E_1 - E_2 \approx 18$ kcal/mole as suggested by the data for 1,2-DP, E_4 is found to be $\approx$25 kcal/mole.

IV. DIFLUOROAMINO BUTANES

1. Thermally Induced Explosions

(a) Materials

A quantity of IBA was received from Rohm and Haas Redstone Arsenal Laboratory, and 1,2-DB and 2,3-DB were made available by Stanford Research Institute. The materials were shipped as 10% solutions in methylene chloride. From these solutions small samples were prepared by stripping the solvent, as described in Section III, 1, a. The purity of the samples was 99%+.

(b) Explosion Limits

The difficulty of determining meaningful explosion limits of the DB isomers has already been mentioned in Section III, 1, a. The difficulty is illustrated by data on 2,3-DB explosion limits in a 200 cc vessel (7.3 cm diameter). The data points are plotted in Figure 8 and are numbered according to the sequence of runs. In run 1 there was an instant explosion in the act of admitting the vapor, causing flashback through the line. At a somewhat higher pressure the result was negative and at a still higher pressure an explosion with the usual short induction period was obtained. Run 2 yielded a well-defined data point at an unexpectedly high pressure in relation to the former point, and the negative results in subsequent runs, particularly 4 and 6, are equally inconsistent with the data of run 1.

Figure 9 shows pressure traces obtained in the latter runs. The initial rapid pressure rise represents the admission of the gas to the vessel. In run 4, the subsequent slow but steady pressure rise indicates that the gas is reacting at a steady rate. In run 6 the pressure is seen to become constant soon after admission at a level which is only about 1.6 times larger than the admission pressure, and hence smaller than the ratio of about 3 to 4 obtained in the normal DB reaction. Since DB cannot cease to decompose at this temperature (406°C), it must be concluded that the gas is spent at the constant pressure level and that therefore less DB had entered the vessel than is indicated by the admission pressure of 20 torr. This signifies that a large fraction of the DB vapor was decomposed during

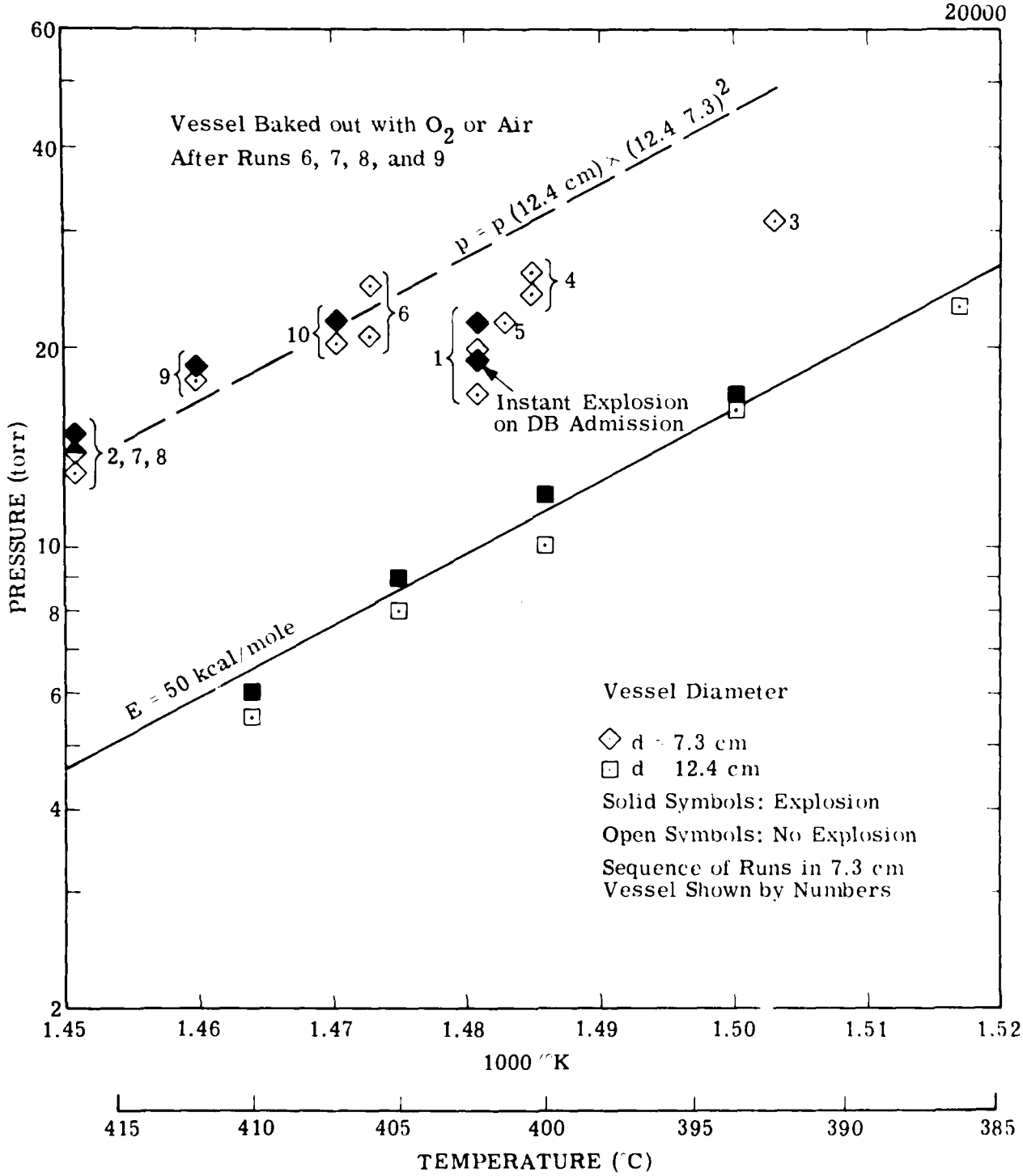
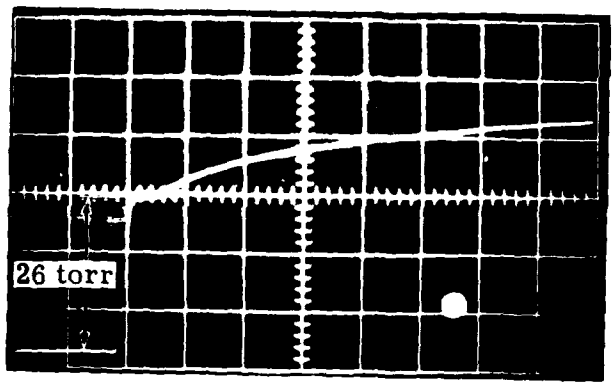
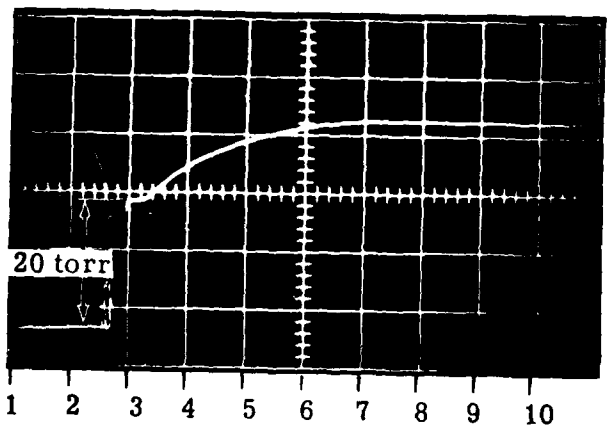


Figure 8. Explosion Limit of 2,3 - DB Vapor.



Fourth Run (400°C)



Sixth Run (400°C)

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Figure 9. Pressure Traces of Successive Runs with 2,3-DB in 200 cc (7.3 cm Diameter).

the period of admission to the vessel, building up a pressure of spent reaction products which substantially decreased the amount of unreacted DB in the vessel at the end of the admission period.

After run 6 oxygen was admitted to the vessel and the temperature was maintained at about 400°C for several days. This treatment removed the carbon that had been deposited on the surface during the previous runs, showing the surface to be etched white-opaque due to exposure to HF. Run 2 at 416°C was now repeated twice (runs 7 and 8) and data points identical with run 2 were obtained. The vessel was again baked out with oxygen and other well-defined data points were obtained at lower temperatures (runs 9 and 10).

With a 1000 cc vessel it proved to be unnecessary to remove the carbon deposit at the vessel surface. Normal pressure traces of the type shown in Figure 2 and reproducible, well-defined explosion limits (Figure 8) were obtained in a random sequence of runs during which the carbon deposit was building up. It appears that the effect of premature reaction of 2,3-DB vapor is sensitive not only to the nature of the vessel surface but also to vessel dimensions.

With IBA, an intensive effort comprising large numbers of runs failed to produce a single pressure trace in either large or small vessels that did not show the occurrence of premature reaction. The IBA data are therefore useless for the purpose of kinetic interpretation and are omitted from this report. It may be mentioned that with a 1,000 cc vessel a smooth, self-consistent curve of explosion limits was obtained, but the temperatures and pressures along this curve were substantially above the p,T range of the 2,3-DB and 1,2-DB limits or of the 1,3-DP limit (which is in the same range as 2,3-DB and 1,2-DB); whereas with a 200 cc vessel and a 2,000 cc vessel the IBA data were erratic. With 1,2-DB the experimental effort has not been carried far enough to establish complete limit curves, but a few data points have been obtained which place the 1,2-DB limit close to the 2,3-DB limit.

It is shown below that the butane homologues differ from the propane homologues by their high sensitivity to traces of fluorine, and it is therefore very probable that the occurrence of premature reaction involves the generation of traces of fluorine by catalytic decomposition of IBA or DB at the vessel surface. Inasmuch as the phenomenon occurs during the act of admission of the vapor to the evacuated vessel, it appears that this surface-catalyzed reaction generates a high concentration of chain carriers over a period of milliseconds in the early stage of the vapor flow into the vessel when the pressure is still very low, and that the reaction is rendered ineffective as the pressure rises. The carbon deposit at the surface appears to be implicated by the apparent suppression of the phenomenon when the vessel is baked out with oxygen. Thus, perhaps F_2 reacts with solid carbon to form carbon fluorides and F, causing free atoms as well as F_2 to escape from the surface. Depending on circumstances the quantities of F and F_2 may suffice to initiate instant explosion, as in run 1 of the small vessel series in Figure 8, or the reaction is quenched in time so that only a fraction of the entering vapor is decomposed. It is understandable that the effects should increase with increasing surface-to-volume ratio, and hence should be more prominent in the smaller vessel; however, it is difficult to understand that in the runs with 2,3-DB the effect should have been substantially inhibited by increasing the diameter from 7.3 cm to only 12.4 cm, that is, by decreasing the surface-to-volume ratio by a factor of only about 0.6.

According to the data in Figure 8 the limit pressures for 2,3-DB, and hence presumably also for 1,2-DB are approximately in the ratio $(12.4/7.2)^2 \approx 3$; that is, the product pd^2 appears to be reasonably constant. The limit mechanism appears therefore to be analogous to the mechanism for 1,3-DP which is described by equation (18). The line drawn in Figure 8 through the data points for the 12.4 cm vessel corresponds to an activation energy of 50 kcal/mole. Writing equation (18) in the form

$$[DB]\, d^2 = \frac{k_5}{A_4}\, e^{(E_4 + E_1 - E_2)/RT} \qquad (19)$$

computing k_5 as outlined in previous reports and setting $E_4 + E_1 - E_2 =$ 50 kcal/mole, one finds about 10^{16} sec^{-1} for the value of the pre-exponential factor A_4 of the coefficient k_4, the rate coefficient for the unimolecular decomposition of the DB radical $C_4H_7(NF_2)_2$. This value appears to be high compared to the usual value of 10^{12} to 10^{13} sec^{-1} for the pre-exponential factor of a unimolecular reaction. However, by a slight adjustment of the slope of the line in Figure 8, E may be reduced to the range of 40 kcal/mole corresponding to A 10^{13} sec^{-1}, and such adjustment may be rationalized by modifying the scheme of DP reactions in Table 6 to allow for the difference between $C_4H_8(NF_2)_2$ and $C_3H_6(NF_2)_2$. Thus, the chain-branching reaction (1) might be replaced by the reactions

(1a) $NF + DB = CH_3CN + C_2H_2 + N_2 + 3\ HF + 2F$

(1b) $NF + DB = HCN + C_2H_2 + CH_2 + 3\ HF + 2F$

which would have different activation energies. The radical CH_2 might react with DB to yield neutral products, as for example,

$CH_2 + DB = HCN + CH_3CN + C_2H_2 + 4\ HF.$

Reaction (2) would be replaced by analogous reactions (2a) and (2b), writing F_2 instead of 2F. The free radical $R = C_4H_7(NF_2)_2$ might decompose either via (4) $R = CH_3CN + C_2H_2 + 2\ HF + NF + F$ or $R = 2\ HCN + C_2H_2 + 3\ HF + F$, the latter reaction being inconsequential in the branched chain mechanism because it constitutes an unbranched chain as F reacts with DB to yield HF + R. With these assumptions the explosion limit becomes

$$pd^2 = \frac{k_5}{k_4}\ \frac{k_{2a} + k_{2b}}{2(k_{1a} + k_{1b})} \qquad (20)$$

and the slope of log p versus 1/T changes with temperature according to the change of the coefficients k_{1a}, k_{1b}, etc., relative to each other.

2. Fluorine-Induced Explosions

The initiation of explosive reaction of the DB isomers by fluorine has been tested using the apparatus and procedure described in Section III, 2,b. The experiments were performed at room temperature. In most runs the pressure of the DB vapor was 8 torr, and with 2,3-DB several runs were also made at 2 torr.

Very small quantities of fluorine proved to be sufficient to produce the flash and click characteristic of explosive reaction. With 1,2-DB and 2,3-DB it was possible to add trace amounts of fluorine, too small to be measured in these experiments, to the vapor without initiating explosive reaction. With IBA this was found to be not possible, and furthermore, with IBA the initial light flash and pressure surge was frequently followed by a series of intermittent flashes and surges.

No inhibition of the reaction by oxygen was found for any of the three DB isomers. This is in contrast to the marked inhibiting effect of oxygen on DP explosions, as illustrated in Figure 7. Another difference between DP and DB explosions is the fact that with DP, including 1,3-DP, the reaction ceases after the first flash, leaving a substantial residue of unreacted DP unless fluorine is added to excess. The mechanism in Table 6 accounts for this effect by the reaction (9) $C_3H_5(NF_2)_2 + F = C_3H_5F(NF_2)_2 + F$, which removes F_2 from the system and thus terminates the chain-branching process before the reaction is complete. Reaction (9) thus accounts for the self-inhibition of the DP - F_2 reaction as well as for the fact that photodissociation of F_2 in DP vapor at subcritical concentration causes the disappearance of F_2 and generation of an equal amount of HF with no change of the total pressure of the system. The DB - F_2 reaction should be analogously self-inhibiting if radicals $C_4H_7(NF_2)_2$ would similarly react with F_2, i. e., destroying F_2 and generating only one chain carrier such as F. Since this is not the case, it may be concluded that reactions between $C_4H_7(NF_2)_2$ and F_2 are chain-branching reactions generating more than one chain carrier. This means that in a DB - F_2 system chain-branching occurs in binary reactions and that ternary reaction analogous to reaction (6) are insignificant. On this basis it may be suggested that the inhibiting effect of O_2 in a DP - F_2

system is due to the ternary character of the chain-breaking reaction (11), which permits association of F and O_2 to yield the relatively inert free radical FO_2, and that oxygen correspondingly has no inhibiting effect in a DB - F_2 system. Concerning possible binary reactions of O_2 with free radicals $C_3H_5(NF_2)_2$ or $C_4H_7(NF_2)_2$ it may be suggested that any such reaction produces one free radical OH, as occurs generally in reactions of O_2 with hydrocarbon free radicals. This would cause neither chain breaking nor chain branching; that is, neither inhibition nor promotion, but merely continuation of the chain inasmuch as OH radical reacts with DP or DB to yield H_2O and the corresponding free radical R.

In the case of IBA the extreme sensitivity to fluorine and periodic recurrence of flashes and surges indicate a sequence of reactions which generates not only F atoms and free radicals but also F_2 molecules, whose supply is thus not exhausted but replenished at periodically changing rates. Additional information on the chemical mechanism is obtained from mass-spectroscopic data on the nature and yields of the products of the fluorine-induced IBA explosion. These data are shown in Table 8.

TABLE 8

Products of Decomposition of IBA by F_2

Products (excluding SiF_4 and H_2O)	Relative Yields
C_2H_2	3
HCN	2.5
H_2	2
N_2	1
CH_3CN	0.1
CH_4	0.1

According to Table 8, the principal carbon-containing products are HCN and C_2H_2. If the four carbon atoms of a single IBA molecule would form HCN and C_2H_2 only, the break-up would yield either 2HCN + C_2H_2 or $2C_2H_2$, which is inconsistent with the product ratio in Table 8. On the other hand,

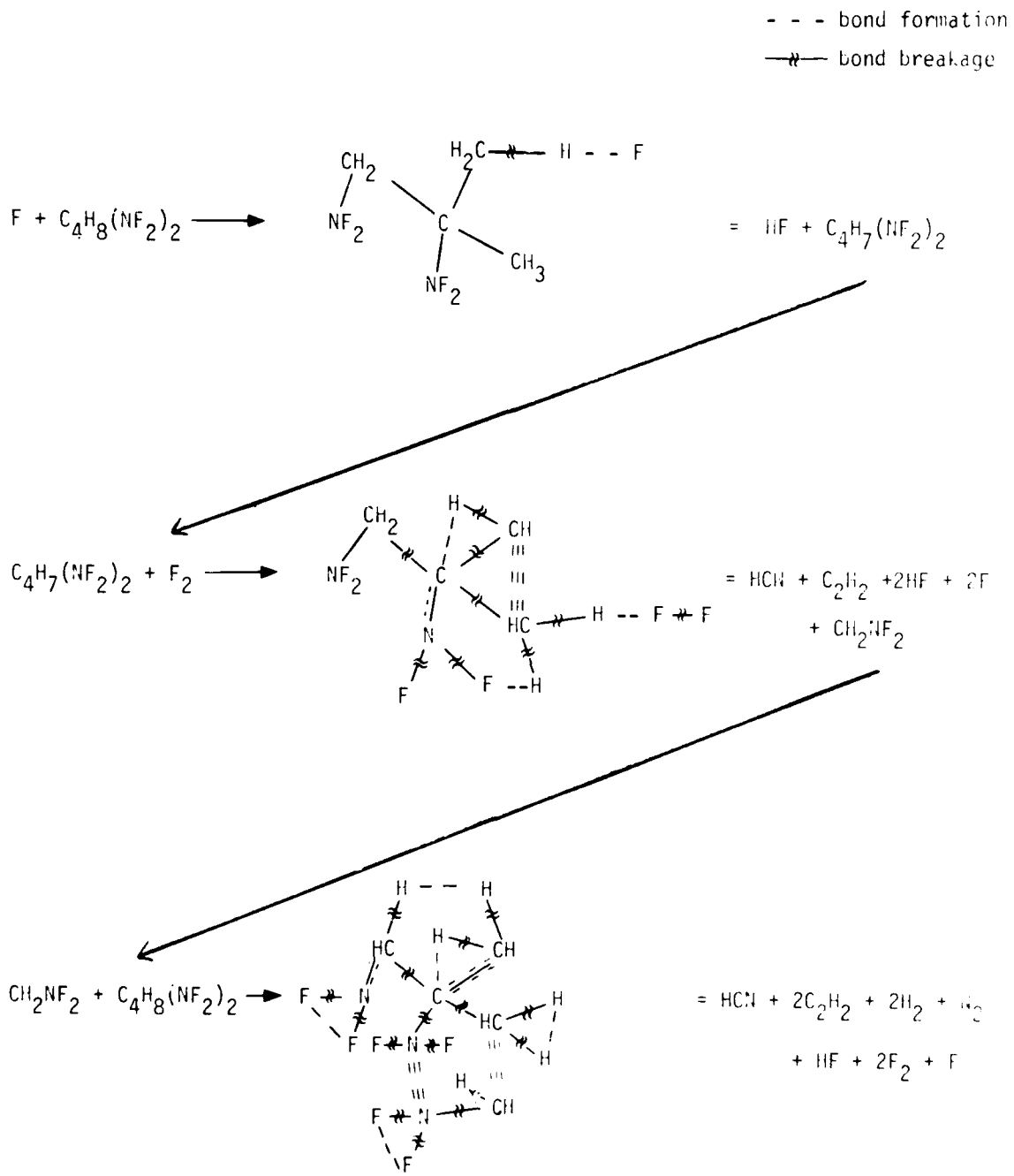
a reaction sequence involving two IBA molecules might yield $3C_2H_2$ + 2HCN + N_2 + ·· and thus be consistent with the experimentally determined C and N balance in close approximation. Such sequence would necessarily comprise the generation of an IBA free radical as a first step; reaction of the free radical with F_2 as a second step; and as a third step, reaction of an IBA molecule with one of the second-step products so that overall more species F and F_2 are produced than consumed. It is also to be demanded that each step of the sequence should be exothermic or at least approximately thermoneutral. The total of these constraints sharply limits the options available for postulating a reaction mechanism. We have discovered only one such mechanism that satisfies the various requirements. This mechanism is illustrated in Figure 10 as far as this can be done without the aid of three-dimensional molecular models. In three-dimensional configurations the interatomic distances are found to be realistically small and no steric hindrances are apparent. Heats of reaction are estimated from bond energies listed in Section III, 3, plus minor corrections obtained from the heat of formation of the products which apply mainly to the heat balance in the formation of C_2H_2. The estimates yield about 35 kcal/mole for the first reaction (F + IBA = HF + IBA radical) and about 17 kcal/mole and 21 kcal/mole respectively, for the two subsequent reactions. Although inexact, these estimates support the view that the indicated reaction steps are exothermic or at least thermoneutral. The product ratio, 2HCN + $3C_2H_2$ + $2H_2$ + N_2 , is reasonably consistent with the data in Table 8. The scheme is considered to represent the main reaction sequence. Additional reactions might be introduced to account for the formation of CH_3CN and CH_4 in small yields.

The scheme represents a run-away reaction that is triggered by trace amounts of F_2. Denoting the second and third step by a and b, respectively, introducing the symbol R for the IBA radical and Y for the radical CH_2NF_2, and assuming that F reacts instantly to generate a radical R, one may write:

$$d[F_2]/dt = 2k_b[Y]\,[DB] - k_a[R]\,[F_2] \tag{21}$$

$$d[Y]/dt = k_a[R]\,[F_2] - k_b[Y]\,[DB] \tag{22}$$

$$d[R]/dt = 2k_a[R]\,[F_2] + k_b[Y]\,[DB] \tag{23}$$



Summary of Reaction Sequence:

$$F + F_2 + 2\ C_4H_8(NF_2)_2 = 2\ HCN + 3\ C_2H_2 + 2\ H_2 + N_2 + 4\ HF + 2\ F_2 + 3F$$

Fig. 10 Scheme of Branched-Chain Reaction of IBA and F_2.

It is apparent that the kinetics of the scheme admits periodic fluctuations of the free-radical and F_2 concentrations and is thus consistent with the observed phenomenon of intermittent flashes and surges.

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13. ABSTRACT

Limits of vapor phase explosions of DP isomers $C_3H_6(NF_2)_2$, induced thermally or by F_2 addition, depend on pressure p, vessel diameter d, and rate coefficients k according to

$$\frac{k_3/k_2}{p^2d^2} = [2\frac{k_1}{k_2}/(\frac{k_5}{k_4pd^2} + \frac{k_7}{k_8})]-1 \quad \text{and} \quad [F_2]_{crit.} = \frac{k_7}{k_6} + \frac{k_{11}}{k_6}[O_2],$$

which corresponds to the chain-branching mechanism

(1) $NF + DP = N_2 + 3HF + 2F + HCN + C_2H_2$
(2) $NF + DP = N_2 + 3HF + F_2 + HCN + C_2H_2$
(3) NF (surface) · destruction
(4) $R = 2HF + NF + F + HCN + C_2H_2$
(5) R (surface) · destruction
(6) $F + DP + F_2 \cdot 3HF + NF_2 + 2F$
(7) $F + DP = C_3H_6(NF_2) + NF_2$
(8) $F + DP = HF + R\ (= C_3H_5(NF_2)_2)$
(9) $R + F_2 = C_3H_5F(NF_2)_2 + F$
(10) NF_2 (surface) · destruction
(11) $F + DP + O_2$ · inert products

DB isomers $C_4H_8(NF_2)_2$ are much more sensitive to F_2 because chain branching occurs in reaction (9). Thus, for "IBA", $CH_2(NF_2) \cdot C(CH_3)NF_2 \cdot CH_2 \cdot CH_3$, $IBA \xrightarrow{F} HF + C_4H_7(NF_2)_2 \xrightarrow{F_2} HCN + C_2H_2 + 2HF + 2F + CH_2NF_2 \xrightarrow{IBA} HCN + 2C_2H_2 + H_2 + N_2 + HF + 2F_2 + F$.

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Security Classification

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14 KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
bisdifluoraminopropane						
explosion limits						
chain reaction						
fluorine compounds						
difluoramines						
kinetics						

INSTRUCTIONS

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