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:RPL - TR - 67 - 117

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KINETICS OF DECOMPOSITION OF SOLID OXIDIZERS

ANNUAL TECHNICAL SUMMARY REPORT AFRPL - TR - 67 - 117

(1 January 1966 to 31 March 1967)

15 APRIL 1967

**AIR FORCE ROCKET PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
EDWARDS AIR FORCE BASE, CALIFORNIA**

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(Prepared under Contract Nr. AF 04(611) - 11395 by
The Dow Chemical Company,
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QUARTERLY TECHNICAL REPORT NO. 5
(1 January - 31 March 1967)

KINETICS OF DECOMPOSITION
OF SOLID OXIDIZERS (U)

April 15, 1967

Dow Report NF-1Q-67

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THE DOW CHEMICAL COMPANY
MIDLAND, MICHIGAN 48640

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FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, on Air Force Contract Nr. AF 04(611)-11395, BPSN 623148, Project Number 3148, "Kinetics of Decomposition of Solid Oxidizers." This work was sponsored and administered by Air Force Rocket Propulsion Laboratory, Research and Technology Division, Edwards, California, Air Force Systems Command, United States Air Force, with Dr. William J. Leahy as Project Officer.

The report represents the work performed on this contract for the period of 1 January - 31 March 1967, and is being submitted as Quarterly Progress Report No. 5 as part of the contract commitment.

Management direction at Dow is under Dr. R. P. Ruh, Laboratory Director of the Scientific Projects Laboratory, and supervised by Dr. N. L. Madison, Group Leader. Mr. T. E. Dergazarian is the principal investigator. Dr. R. G. Pearson, Northwestern University, is a consultant to the project.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

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SECTION I

ABSTRACT

(U) Studies on the structural characterization of P-BEP and its unsaturated precursor PEP indicate that the structures of these compounds deviate from that previously proposed. This is based upon fluorine-19 and hydrogen-1 nmr analysis of the "as received" samples.

(U) Thermal studies in a static reactor indicate that P-BEP spatters during pyrolysis. Quantitative analysis of the product gases from the 160°C. pyrolysis indicates that hydrogen fluoride is one of the most abundant products. Mass spectrometric study of the pyrolytic decomposition has shown that spattering with gas evolution occurs at 50°C. to 55°C. Hydrogen fluoride is also the largest fragment observed at this low temperature.

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SECTION II

INTRODUCTION (U)

(C) It is the purpose of the present program to obtain new, basic information on the kinetics and mechanisms of decomposition of the energetic N-F compounds INFO-635P, BTU, poly FA-BDE, and the pre-polymer P-BEP.

(U) Each of these compounds is a sensitive, hence potentially hazardous, material. The data obtained during the course of this study should provide an understanding of the mechanisms of their decomposition and the relationship of these mechanisms to their sensitivity.

(C) The first three compounds are solid oxidizers. Work on these materials is complete and has been reported. P-BEP, however, is physically distinct from the solid oxidizers, since it is a very viscous liquid. P-BEP is used in solid propellants as an energetic binder.

(U) P-BEP is reported (1,2) to have inconsistent sensitivity and curing properties from batch to batch. Therefore, the objectives of this research relative to P-BEP must be prefaced with a structural determination of the polymer before the final kinetic and mechanistic objectives can be realized. To achieve these objectives, the research program includes concurrent studies on the structural characterization of P-BEP and on the determination of the kinetic parameters associated with the slow thermal decomposition.

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SECTION III

DISCUSSION AND RESULTS (U)

A. BACKGROUND (U)

(C) The energetic binder P-BEP, poly[1,2-bis(difluoroamino)-2,3-epoxypropane], and its precursor PEP, poly(2,3-epoxypropene) were prepared by the Shell Development Company in a process consisting of the polymerization of epichlorohydrin, alkaline dehydrochlorination of polyepichlorohydrin, and the addition of tetrafluorohydrazine to the unsaturated polymer.

(C) Impact testing of similar lots of P-BEP at different installations has shown a large variation in sensitivity ranging from 17 to 80 kg.-cm. (1). The hydroxyl functionality of the glycerol initiated polymer following each successive step in the synthesis has also shown some inconsistency (2), resulting ultimately in unsatisfactory properties upon curing (1).

B. STRUCTURAL ANALYSIS (U)

1. Theoretical Calculations (U)

(U) Some preliminary calculations were performed based upon the reported elemental analysis, molecular weights, and the suggested structures of the polymer P-BEP and its precursor PEP.

(C) Sample number 9557-82 of P-BEP and number 9557-93 of PEP were received from Shell Development Company (3) along with the data shown in Table I.

Table I

Physical Data as Reported by Shell
on Samples of P-BEP and PEP (C)

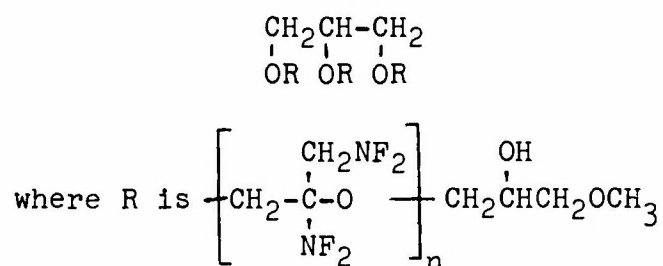
	<u>P-BEP(9557-82)</u>	<u>PEP(9557-93)</u>
Molecular Wt.	3670	1670
Thermal Stability, cc./g./100 hrs.	4.6	--
Impact Sensitivity, kg.-cm.	18	--
Unsaturation Value, moles/ 100 g.	--	1.35
Chlorine, wt. %	--	0.09

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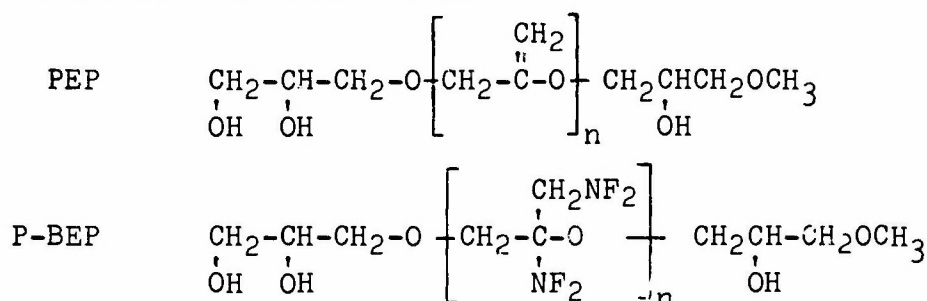
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(C) Shell (4) has very recently informed us that the structure of P-BEP may be:



However, under the experimental conditions of polymerization of the starting materials, it is believed that the most predominant structure is that shown below:



(C) Based upon the molecular weights and the assigned structures, a degree of polymerization of 26 and 22, respectively, is derived for the unsaturated and saturated polymers. Elemental analysis of these two polymers has been determined and is shown in Table II.

Table II

Elemental Analysis of PEP and P-BEP in Mole Percent (U)

Element	PEP		P-BEP		Theory n=26
	Experimental	Theory	Experimental Shell ^a	Dow ^b	
C	61.4	62.3	26.5	26.8	23.6
H	6.87	7.3	3.3	3.26	2.8
O	31.73	30.3	13.2	14.35	11.68
N	--	--	15.7	15.28	16.6
F	--	--	41.3	40.09	45.2

^aSample No. 9557-82 (3).

^bSimilar Shell sample (4).

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(U) An immediate hypothesis is that the proposed structure for P-BEP is incorrect, whether a degree of polymerization of 26 or 22 is used in the calculation. One tentative solution is to assume that there is some residual unsaturation, about one out of four monomer units, which is reasonable considering the large discrepancy in the fluorine analysis. Calculations were repeated on this basis, and the theoretical and experimental values are compared in Table III.

(U) There are many mathematical manipulations that can be performed to bring the theoretical and experimental elemental analysis into agreement. However, it would not be of any more utility than the present calculation in emphasizing the obvious discrepancy of the N-F content in the structure. Further experimental analysis using various analytical techniques will hopefully resolve the structural problem.

Table III

Elemental Analysis of P-BEP Assuming
Residual Unsaturation in Mole Percent (U)

<u>Element</u>	<u>Experiment</u>	<u>Theory</u> <u>(n=26)</u>
C	26.8	27.4
H	3.26	3.2
O	14.35	13.3
N	15.28	15.07
F	40.09	40.9

2. Poly(2,3-epoxypropene), PEP (C)

(C) Two samples of poly(2,3-epoxypropene) were purified and submitted for analysis. Hydroxyl functionality was determined by two different methods shown in Table IV.

(U) The unsaturation value, Table IV, on these same two samples of PEP indicate a large discrepancy. The particular experimental techniques, i.e., the addition of bromine and iodine and titration of the excess, suggest that a substitution reaction as well as addition to the carbon-carbon double bond in the polymer is possibly occurring. Catalytic hydrogenation of the unsaturated polymer yields results consistent with the Shell report (3).

(U) There is a possibility that the difference in the hydroxyl functionality and the unsaturation value between the two samples of PEP may be real because the samples were prepared on different days by slightly different methods.

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Table IVHydroxyl Functionality and Unsaturation Value of PEP (U)

Sample No.	Hydroxyl Functionality		Unsaturation	
	OH/Mole	Method	eq./100 g. ^a	Method
9557-93-1	2.6	Acetic anhydride	1.68	Excess ICl titration
9557-93-2	1.8	Phthalic anhydride	2.49	Br ₂ coulometric titration
			1.34	Catalytic hydrogenation
Theory (n=26)	3.0	--	1.55	--

^aEq. Wt. = 24.

(U) Analysis of the infrared absorption spectrum of the epoxy-propene PEP polymer supports the main structural assignment. The analysis as determined by the Chemical Physics Research Laboratory of The Dow Chemical Company is reported in Table V.

Table VInfrared Absorption Analysis of PEP (U)

Band, cm. ⁻¹	Assignment
820	CH ₂ wag of -C=CH ₂ group
~1671	C=C stretch
~1627	First overtone of C=CH ₂ wag in Fermi resonance
~1251	From C-O stretch of C=C-O group
~1121	From C-O stretch of CH ₂ -O group
~1720	Result from C=O impurities
~1740	
~1765	

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3. Poly[1,2-bis(difluoroamino)2,3-epoxypropane], P-BEP (C)

(C) The infrared absorption spectrum of P-BEP was relatively weak, most likely due to a poor film cast of the sample. However, examination of the spectrum did show that there was no residual unsaturation and that a broad band near 1730 cm^{-1} could result from a -C=O group, amounting to 5 to 10%.

(U) The lack of any residual unsaturation is in contradiction to the earlier conclusions about the structure; however, the structural discrepancy may be rationalized in another manner which seems to be consistent with the data (see Section V).

(U) Nuclear magnetic resonance spectroscopy of P-BEP in methylene chloride and in chloroform shows essentially the same spectrum. The proton spectrum (^1H) generally supports the assigned structure, shown in Table VI; however, some extraneous hydrocarbon structure is also indicated. The fluorine spectrum (^{19}F) does not entirely support the proposed general structure. There is an unexpected third NF_2 group in this sample of P-BEP.

(C) The possibility that the hydrocarbon and the third -NF_2 structure may be associated with an impurity or with particular molecular weight fractions was examined. A sample of P-BEP, 800 mg., was purified by repeated solvent stripping and redissolving in triple distilled THF and submitted to gel permeation chromatography. Five different molecular weight fractions were collected (Table VII). The molecular weights reported are based on a polystyrene calibration. The chromatogram gave a very symmetrical peak of a narrow molecular weight range. No low or high molecular weight fractions were observed chromatographically. These five fractions were then examined by nmr spectroscopy, after stripping the THF and redissolving the P-BEP fractions in distilled chloroform. Except for the relative intensity of the peaks, the ^1H and ^{19}F spectra were the same as before. The only observed difference between these samples and the "as received" material is that the hydrocarbon structure has disappeared.

(C) It was hoped that the proton spectra of the primary and secondary hydroxy groups could be distinguished and that some insight as to their specific structure and number could be obtained; however, no spectral shift was observed.

(C) In a recent article (6), functional group characterization and classification by nmr spectroscopy of alcohols by ^{19}F spectra of trifluoroacetates was reported. Primary, secondary, and tertiary alcohols were successfully characterized by study of the ^{19}F nmr spectra of the trifluoroacetate (TFA) esters. This technique was applied to P-BEP after the TFA ester of P-BEP was synthesized. The proton spectrum was consistent with the earlier spectrum of the "as received" material. The ^{19}F spectrum of the NF_2 groups was also the same. However, two new sharp peaks at 76.136 and 75.732 ppm were

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observed, which were assigned to the primary and secondary structures, respectively. An integral was also obtained, from which the ratio of primary to secondary hydroxyl functionality was calculated to be 1:1.65.

Table VI

NMR Spectrum of P-BEP (as received) (C)

<u>Shift, ppm</u>	<u>Structural Assignment</u>	<u>Comment</u>
¹ H spectrum		
4.6	F ₂ N-CH ₂ -C-	Backbone
4.1	-C-CH ₂ -O-	Backbone
3.9	-CH ₂ -C-O-	Secondary structure
3.6	-C-CH ₂ -O-CH ₃	Secondary structure
3.4	-OCH ₃ (broad)	Secondary structure
3.3	-OCH ₃ (sharp)	End group
1.6	-C-CH ₂ -C-	Hydrocarbon impurity
0.8	-CCH ₃	Hydrocarbon impurity
¹⁹ F spectrum		
-63	-CH ₂ NF ₂	Backbone
-20.55	-C-NF ₂	Backbone
-19.38	-C-NF ₂	Secondary structure

4. Secondary Reactions (U)

(U) There are a number of possible secondary reactions which can conceivably give inconsistent hydroxyl functionalities for P-BEP.

(C) The infrared analysis as discussed above for PEP and P-BEP clearly indicates the presence of carbonyl in both materials. This could arise as follows:

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- (i) Under the acidic conditions of the glycerol initiated polymerization of epichlorohydrin, a pinacol type reaction could occur to give aldehydes or ketones which would reduce the hydroxyl content.
- (ii) The epoxide end group before dehydrochlorination of polyepichlorohydrin could isomerize under acidic conditions to a carbonyl group, leaving it unavailable to form hydroxyl in later reactions.

Table VII

Gel Permeation Chromatograph of P-BEP
Molecular Weight Fractions (U)

<u>Sample</u>	<u>Cut No.</u>	<u>Molecular Wt.^a</u>
1 ^b	29, 30	5800-4600
2	31	3500
3	32	2700
4	33	2000
5 ^b	34-35	1500-1000

^aBased on polystyrene calibration.

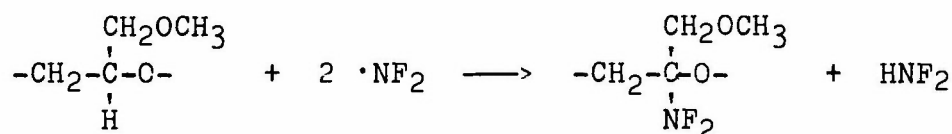
^bTwo molecular weight fractions combined because concentration was too low for reasonable nmr analysis.

(C) The proton-1 and fluorine-19 nmr spectral analysis of P-BEP suggest the following reactions.

(C) In the dehydrochlorination reaction of the polyepichlorohydrin, substitution of the chloride by the methoxide would result in a decrease in the unsaturation value. This is suggested by the presence of more than one type of -OCH₃ and -C-CH₂O-.

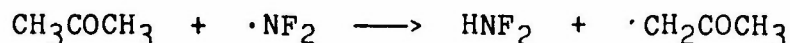
(C) The addition of N₂F₄ to the PEP polymer could result in several side reactions.

(i) The reaction of ·NF₂ can occur with the tertiary hydrogen from the product of the substitution reaction discussed above, i.e.:



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(11) The reaction of $\cdot\text{NF}_2$ radical with the solvent acetone has been reported (7).



Thus, solvent interaction with the unsaturated polymer is possible via the products of the above reaction.

(U) Based upon the present study the backbone structure of P-BEP is not certain, and could be the cause of variation in shock sensitivity. The end-group structure is also suspect resulting in variable hydroxyl functionalities.

C. THERMAL DECOMPOSITIONS (U)

1. Mass Thermal Analysis (U)

(U) It is believed that the method of mass thermal analysis (MTA) will provide substantial aid in the identification of first fragments and intermediates from the thermal decomposition of the solids under study. In this method a sample of approximately one milligram is introduced into a very small furnace located within two millimeters of the ionizing beam of a Bendix time-of-flight (TOF) mass spectrometer. The temperature of the furnace can be heated at a constant rate or can be run isothermally. Since the sample is located at such close proximity to the ionizing beam and at a pressure of 10^{-6} to 10^{-7} Torr in the spectrometer chamber, the probability of recombination of the gaseous decomposition products is small. For example, it can be shown by calculation from the kinetic theory of gases that the mean free path of difluoroamino radical at a pressure of 10^{-6} Torr is 10^{-4} cm. Also, at a most probable velocity of 3×10^4 cm./sec. such a radical would be in the ionizing beam in less than 10^{-5} sec.

(U) Samples of PEP and P-BEP were loaded into glass capillaries and each in turn was placed on the probe of a TOF mass spectrometer. The sample was heated slowly and the mass spectrum scanned at various intervals to 110°C . with PEP and to 250°C . with P-BEP.

(C) Preliminary analysis of the mass spectrum of the PEP sample suggests the possible presence of propylene oxide, ethylene oxide, and ethylene. The spectra are presently being examined for unexpected products that would cause variations in the hydroxyl functionality and in the addition of N_2F_4 . Decomposition of PEP begins at 38°C . and appears to be rapid at about 70°C . The PEP sample apparently popped out of the capillary tube at 110°C .

(U) Two MTA runs were made on P-BEP. The first run, 28°C . to 280°C ., showed the presence of large amounts of methylene chloride and acetone at the lower temperature. In addition, a considerable amount of spectral pattern due to decomposition products were seen at 28°C . The spectrum became progressively more complex as

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the sample temperature was increased. The second sample of P-BEP was heated to 50°C. under vacuum before loading the capillary tube. This sample was then heated in the mass spectrometer to 50°C., cooled to room temperature, and heated again to about 122°C. when the sample exploded in the mass spectrometer. Sample spattering was observed in the temperature range 50° to 55°C.

(C) Analysis of the mass spectrum of P-BEP shows the expected HF as one of the first products. HCN is also observed in large amounts. Mass 52 (NF₂) was not observed as one of the initial products, but increased in relative intensity at higher temperatures. A number of masses were observed that could have multiple structural assignments. These mass numbers and structures will be resolved by running a similar thermal decomposition in the high resolution mass spectrometer.

2. Slow Thermal Decomposition (U)

a. Monel Reactor (U)

(U) Decomposition of P-BEP in the presence of the product gases was run at 150°C. for 24 hours in a monel reactor. Mass spectral analysis of the final product gases, and a mass balance are given in Table VIII and Table IX, respectively. An elemental analysis of the residue and the gases indicated that a total of 18.5 mg., or 12.7%, of the available fluorine was accountable. The presence of H₂(g) suggests a reaction of the HF with the monel reactor. In addition, a large amount of solid residue was observed on the reactor walls. Because of these difficulties and possible other gas-gas, and gas-polymer reactions, this method of study was suspended.

b. Vacuum Decompositions in Glass Reactor (U)

(U) Two preliminary reactions were run in the glass reactor at 100°C. for one hour and then 150°C. for 23 hours at immersion depths of 65 mm. and 150 mm. The variation in immersion depth effectively increases the hot zone through which the product gases must pass and determines the extent of any gas phase reactions. Results from these runs were inconclusive since spattering of P-BEP was observed with the 150 mm. immersion, so that P-BEP would be reacting on the glass surface as well as in the platinum cup. Therefore, a change in the final gas phase composition between these two runs is not indicative of a gas phase reaction.

(U) Three additional reactions were run at a 150 mm. immersion for 24 hours and at temperatures of 150°, 160° and 175°C., with starting material purified by repeated solvent strippings under vacuum, followed by a warming to 40°C. for short intervals.

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Table VIII

Mass Spectrum of Product Gases from
P-BEP Decomposition at 150°C.
in Monel Reactor (C)

<u>Compound</u>	<u>Product Gas</u> <u>10⁻² moles/100 g. P-BEP</u>
N ₂ F ₄	0.019
N ₂ F ₂	0.033
HNF ₂	0.013
C ₂ N ₂	3.24
SiF ₄	2.43
N ₂ O	0.035
CO ₂	23.06
HCN	5.88
CO	14.84
H ₂ O	0.93
H ₂	1.04
N ₂	5.75
(CH ₃) ₂ SiF ₂	7.55

Table IX

Mass Balance of P-BEP Decomposition
at 150°C. in Monel Reactor (U)

<u>P-BEP</u>	<u>Wt. in mg.</u>
Original	192.2
Residue Recovered	96.5
Gas Recovered	48.9
Not Recovered *	46.8

*P-BEP spattered on inside of reactor.

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(C) Composition of the final product gases is shown in Table X. There is some, as yet unexplained, variation in the concentrations of NF_3 , HNF_2 , and N_2O with temperature. Hydrogen cyanide is the major carbon-containing component, and $\text{SiF}_4(\text{HF})$ the compound with the greatest concentration.

Table X

Mass Spectrum of Product Gases from P-BEP
Decomposition at 150 mm. Immersion,
after 24 Hours (C)

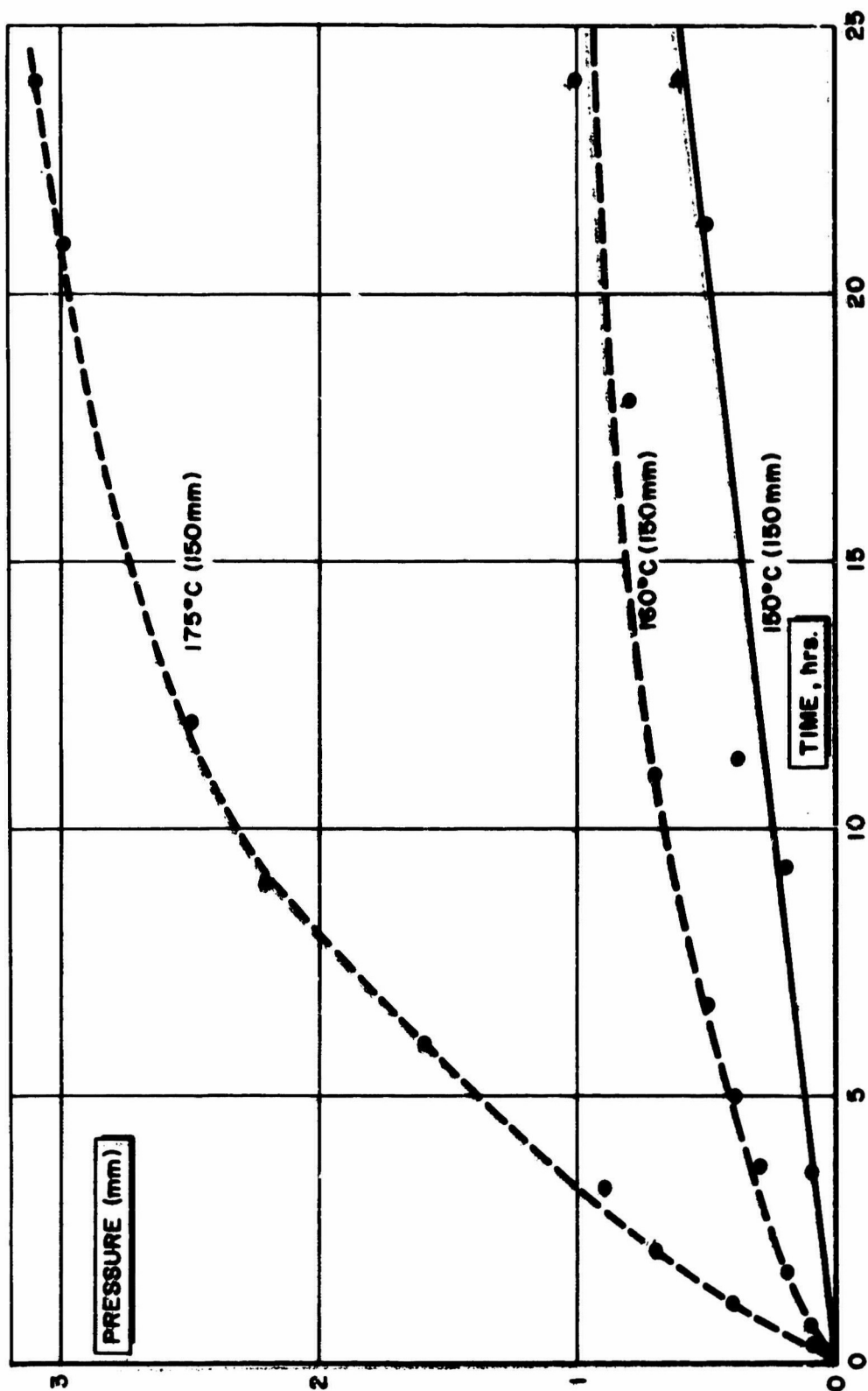
Compound	Concentration, 10 ⁻³ Moles gas/100 g. P-BEP			
	Temperature, °C.			
	150 ^a	150	160	175
NF_3	2.49	2.07	1.65	2.64
N_2F_4	4.85	3.46	8.90	19.62
N_2F_2	1.13	1.30	1.76	2.55
HNF_2	1.33	2.87	4.11	3.17
SiF_4	160.00	140.	186	264.
CO_2	6.70	6.05	13.24	33.44
N_2O	1.31	1.94	1.60	4.88
HCN	20.01	20.26	42.04	68.20
N_2	12.4	--	8.79	32.08
H_2O	5.89	--	11.18	9.59
NO	0.40	--	--	--

^aThis sample heated to 100°C. for 1 hour then to 150°C. for 23 hours.

(U) Elemental analysis of the solid residue and the product gases together with the mass balance, Table XI and XII, show that about 1 to 4% of the available carbon is in the gas phase, and that weight loss due to spattering onto the reactor walls amounts to 14 to 24% of the initial weight.

(U) Uncondensable gas pressure was assumed to result from nitrogen gas and is illustrated in Figure 1.

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(U) Fig. 1 - Uncondensable Gas Pressure from Vacuum Decomposition of P-BEP in Glass Reactor

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(C) The decomposition as suggested by the data is apparently initiated at the pendant $-\text{CH}_2\text{NF}_2$ group by HF elimination and then formation of HCN from $-\text{C}-\text{CN}$ bond cleavage. There is no indication of any chain scission; however, because of the intractable nature of the residue cross linking has most likely occurred.

Table XI

Elemental Analysis of Solid and Gaseous Products of P-BEP Decomposition, 150 mm. Immersion for 24 Hours (C)

Element	Weight, mg.							
	Temperature, °C.							
	150 ^a		150		160		175 ^b	
	Solid	Gas	Solid	Gas	Solid	Gas	Solid	Gas
C	20.03	0.36	20.13	0.26	17.43	0.93	--	1.01
H	1.44	0.04	1.32	0.03	1.13	0.03	--	0.07
N	11.14	0.76	11.41	0.45	9.53	0.31	--	2.22
F	16.01	11.07	16.35	9.49	10.54	12.26	--	18.09
O	12.26	0.31	10.89	0.19	9.16	0.51	--	1.07

^aThis sample heated to 100°C. for 1 hour then to 150°C. for 23 hours.

^bNot enough solid residue recovered for analysis.

Table XII

Mass Balance of P-BEP Decomposition
150 mm. Immersion for 24 Hours (U)

P-BEP	Weight, mg.			
	Temperature, °C.			
	150 ^a	150	160	175
Original	84.8	84.6	80.9	82.5
Solid residue Recovered	60.9	60.1	47.8	41.6
Gas Recovered	12.5	10.4	14.0	22.5
Not Recovered	11.4	14.1	19.1	12.3

^aThis sample heated to 100°C. for 1 hour then to 150°C. for 23 hours.

^bWeight of residue in platinum cup.

^cApparent weight of residue on sides of reactor due to spattering.

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SECTION IV

EXPERIMENTAL (U)

A. PREPARATION OF MATERIALS (U)

1. Poly(2,3-epoxypropene) (C)

(C) Poly(2,3-epoxypropene) was received from Shell Development Company as a solid containing 0.25% hydroquinone as inhibitor. The material is purified as needed in the following manner. The sample is dissolved in methylene chloride; hexane is then added until a precipitate is just observable. This is filtered, leaving a colorless liquid. Additional hexane is added to precipitate the colorless propene polymer.

2. Poly[1,2-bis(difluoramino)-2,3-epoxypropane] (C)

(C) The P-BEP was received from Shell Development Company as a 35% solution in methylene chloride. The original solvent is stripped off under vacuum. Distilled methylene chloride is re-added to the viscous polymer, stirred and stripped off again. This procedure is repeated twice before each sample is used to insure the removal of extraneous volatile material. Before the final stripping of solvent, the solution is usually placed in a platinum cup, which is then put in the reactor. The sample is kept under vacuum for several days and intermittently warmed to 40°C. to facilitate removal of the solvent.

B. STRUCTURAL ANALYSIS (U)

1. Poly(2,3-epoxypropene), PEP (C)

a. Determination of Hydroxyl Functionality (U)

Method 1 - The sample was dissolved in pyridine, phthalic anhydride added, and the mixture refluxed for four hours on a steam bath, after which the excess phthalic anhydride was titrated.

Method 2 - The sample was dissolved in pyridine, acetic anhydride added, and the mixture heated to 70°C. overnight, after which the excess acetic anhydride was titrated.

b. Determination of Unsaturation (U)

Method 1 - The sample was dissolved in THF and Br₂ added. The reaction was followed coulometrically.

Method 2 - The sample was dissolved in dichlorobenzene, excess ICl was added to the solution and allowed to stand overnight, after which the excess iodine was titrated.

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Method 3 - Quantitative hydrogenation of the propene polymer was performed using palladium on carbon as the catalyst.

2. Poly[bis 1,2-(difluoromino)-2,3-epoxypropene], P-BEP (C)

a. NMR Spectroscopy (U)

(U) Nuclear magnetic resonance spectroscopy of P-BEP was taken of the "as received" and of purified samples in CHCl_3 and in CH_2Cl_2 .

b. Hydroxyl Functionality (U)

(U) Approximately 100 mg. of P-BEP was placed in a 50 cc. glass reactor and purified by multiple solvent strippings. The solvent (1.0 cc. CH_2Cl_2) was added again and an excess of tri-fluoroacetic anhydride added. The mixture was stirred at room temperature for one hour. The resulting solution was considerably darker. The solvent and unreacted TFA were stripped, additional solvent was added, and stripped off three times to insure the removal of all the excess TFA anhydride. NMR of the TFA ester of P-BEP was taken in methylene chloride solvent.

C. THERMAL DECOMPOSITION (U)

1. Mass Thermal Analysis (U)

(U) A 1 to 2 mg. sample of P-BEP was pressed into a small glass capillary 5 mm. long, which was then placed on top of a metallic probe in spectrometer. The final assembly was placed within 2 mm. of the ionizing beam of the Bendix time-of-flight mass spectrometer.

2. Thermal Decomposition in Monel Reactor (U)

(U) The experimental apparatus was described in an earlier report (8). The procedure, briefly, is to place a solution of P-BEP into a platinum cup, strip the solvent, weigh the cup and the polymer, and then place it in the monel reactor. The reactor is fitted with a pressure transducer and a fast response thermocouple. The reactor is then attached to the vacuum line and evacuated. The pyrolysis may be initiated in vacuo, or the bomb may be pressured with any selected gas prior to the thermal initiation. The temperature and pressure are continually monitored, while the reaction in the presence of the product gases proceeds to completion.

3. Vacuum Pyrolysis in Glass Reactor (U)

(U) Loading of the platinum cup was described earlier. The cup is placed in the glass reactor, which is essentially a 8" long tube that can be attached to a small vacuum manifold. A "U" trap is also attached; the complete system is evacuated

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mechanically then isolated from the pump. The pyrolysis is initiated by raising a hot oil bath around the reactor tube to the desired depth. A partial vacuum is maintained over the decomposing material by cryogenically pumping the product gases into the "U" trap.

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SECTION V

CONCLUSIONS AND FUTURE WORK (U)

(U) Structural characterization of P-BEP and its unsaturated precursor PEP indicates that they deviate from the proposed structures.

(C) The presence of carbonyl as determined by infrared spectroscopy could have an effect on the hydroxyl functionality of the final product, especially if the carbonyl structure is also present in the starting polyepichlorohydrin (PECH) polymer. The carbonyl could result from a pinacol type reaction of the glycerol with the acid catalyst.

(U) Trifluoroacetic anhydride has been used as a means of quantitatively determining the hydroxyl functionality of P-BEP. A standard TFA ester will be prepared by reacting 3-chloro-1,2-propanediol with TFA anhydride to determine the absolute value of primary and secondary hydroxyl concentration.

(C) Although the unsaturation value as determined by catalytic hydrogenation is in agreement with that report by Shell, the value is still lower than would be expected based upon the assigned ideal structure and molecular weight. This low value for unsaturation is confirmed by the lower than expected nitrogen and fluorine content of P-BEP. This is based upon the assigned ideal structure and the experimentally determined molecular weight of P-BEP.

(C) The residual unsaturation in P-BEP initially proposed to account for the low N-F content was not confirmed by infrared spectroscopy. However, the lower than expected values for unsaturation and N-F content may be rationalized if a competing reaction is postulated in the synthesis of P-BEP and in particular the dehydrochlorination step. Specifically, the methoxide reacts

with $-\text{CH}_2\text{Cl}$, forming the structure $-\text{CH}_2-\overset{\text{CH}_2\text{OCH}_3}{\underset{\text{H}}{\text{C}}}-\text{O}-$. Subsequent addition

of N_2F_4 to PEP polymer results in the addition of NF_2 to the carbon-carbon double bond and in the abstraction of tertiary hydrogen. Thus, the third NF_2 structure observed by ^{19}F nmr analysis is accounted for, as well as the low N-F content and the low unsaturation value.

(U) Structural characterization of P-BEP and PEP will be continued as future samples are received.

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(C) The slow thermal decomposition of P-BEP is similar to many other compounds containing the $-\text{CH}_2\text{NF}_2$ group. The mechanism is probably initiated by HF elimination, and, since HCN is a product, the reaction is most likely initiated at the pendant $-\text{CH}_2\text{NF}_2$ groups.

(U) All thermal decompositions have been carried out for 24 hours before the final products were analyzed. For the future isothermal pyrolysis, reactions will be run at shorter time intervals to determine the relative changes in composition of the gases and the residue, from which kinetic parameters of the decomposition may be obtained.

(U) The spattering of P-BEP as reported will be investigated more fully in the future, specifically to determine the chemical and physical change in the polymer and in the gases immediately after the spattering. For example, the polymer remaining after spattering will be analyzed by gel permeation chromatography to determine the effect on the molecular weight and any new molecular weight fractions. These fractions will then be characterized.

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SECTION VI

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Studies on the structural characterization of P-BEP and its unsaturated precursor PEP indicated that the structures of these compounds deviate from the previously proposed. This is based upon fluorine-19 and hydrogen-1 nmr analysis of the "as received" samples. Thermal studies in a static reactor indicate that P-BEP spatters during pyrolysis. Quantitative analysis of the product gases from the 160°C. pyrolysis indicates that hydrogen fluoride is one of the most abundant products. Mass spectrometric study of the pyrolytic decomposition has shown that spattering with gas evolution occurs at 50°C. to 55°C. Hydrogen fluoride is also the largest fragment observed at this low temperature.		

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