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WASHINGTON, D. C.

27 March 1952

Report No. 590

(Quarterly)

Copy No. 24

RESEARCH IN
NITROPOLYMERS AND
THEIR APPLICATION TO
SOLID SMOKELESS
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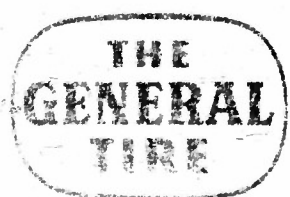
Contract N7 onr-462

Task Order I

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27 March 1952

Report No. 590
(Quarterly)

RESEARCH IN NITRO POLYMERS AND THEIR APPLICATION TO SOLID SMOKELESS PROPELLANTS

Contract N7onr-462

Task Order I

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Azusa, California

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CONTRACT FULFILLMENT

This quarterly report is submitted in partial fulfillment of Contract N7omr-462, Task Order I.

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I. SUMMARY

A. This quarterly summary covers research work conducted in partial fulfillment of Contract N7onr-462, Task Order I, during the period 16 November 1951 to 15 February 1952.¹

B. The more important results and conclusions of the work reported are presented below.

1. A program has been initiated to study the chain-transfer characteristics of vinyl monomers containing nitro groups and aliphatic nitro groups generally. Preliminary results indicate that the trinitromethyl group has very strong chain-transfer tendencies.

2. The kinetics of polymerization for pentaerythritol acrylate trinitrate have been studied dilatometrically at 30, 40, and 50°C. The rate constants at these temperatures have been determined and the activation energy of the reaction has been calculated.

3. It has been found that boron trifluoride etherate is a catalyst for polyurethane formation. However, increasing catalyst concentration causes decreasing molecular weight, in a nonlinear manner. The mechanism of the reaction appears to be complex and has not yet been clarified.

4. Continued attempts to substitute cellulose and polyvinyl alcohol by means of trinitrobutyric acid or trinitropropyl isocyanate have not been successful. Accordingly, this work will be discontinued.

5. Further attempts to prepare high polymers of glycidyl 4,4,4-trinitrobutyrate have not been successful. New work on the polymerization of nitro epoxides will be concentrated on compounds of lower molecular weight.

6. Three new nitro polyurethanes have been prepared and successfully postnitrated. These polyurethanes are prepared from

a. 3,3,5,7,7-pentanitro-1,9-nonane diisocyanate and 2,2-dinitro-1,3-propanediol

b. 3,3-dinitro-1,5-pentane diisocyanate and 4,4,6,8,8-pentanitro-1,11-undecanediol

c. 3,3-dinitro-1,5-pentane diisocyanate and 4,4,6,6,8,8-hexanitro-1,11-undecanediol.

¹Previous work on this contract was covered in Aerojet Reports No. 330, 345, 371, 386, 386A, 404, 416, 417, 417A, 424, 457, 461, 468, 482, 494, 499, 515, 540, and 563.

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7. It was found that thermal stabilities of nitro polymers may be greatly improved by a thorough bicarbonate washing.

8. The solubility parameter of 2,2-dinitro-1,3-propanediol has been determined from its solubility in acetone, methanol, and ethanol.

9. The specific-impulse table for condensation polymers, first presented in Aerojet Report No. 540, has been revised and greatly expanded.

10. Creep measurements have been made on molded sheets of polyurethane I-A and polyurea III-4; the creep curves are presented.

11. Burning-rate studies in the Crawford bomb have been conducted on polyurethane I-A. At 1000 lb and 60°F the burning rate was found to be 0.144 in./sec.

12. A rapid method has been found for the preparation of esters of nitro alcohols, by conducting the reaction in concentrated sulfuric acid. However, the yields are generally lower than those obtained by the standard procedure.

13. Work has been conducted on the purification of 2,2-dinitro-butyl acrylate so as to obtain a monomer with reproducible characteristics. The purified material now gives good high-molecular-weight polymer which is soluble in solvents such as acetone.

14. The synthesis of α -(2,2-dinitropropyl) acrylic acid has been completed. If esters of this acid can be polymerized, many new monomers will be available as potential propellant ingredients.

15. A relatively safe method has been developed for the distillation of 4,4,4-trinitrobutyryl chloride from a "carrier solvent" in a glass falling-film still.

16. The following new compounds have been prepared for use as intermediates or plasticizers:

- a. bis(5,5,5-trinitro-2-keto-1-pentyl) carbonate
- b. bis-chloroformate of 4,4,6,8,8-pentanitro-1,11-undecanediol
- c. 1,2-bis(4,4,4-trinitrobutyroxy) ethane
- d. 1,2,3-tris(4,4,4-trinitrobutyroxy) propane
- e. 1,2-bis(4,4,4-trinitrobutyroxy) propane
- f. 1,5-bis(4,4,4-trinitrobutyroxy)-3-oxa-pentane

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- g. 1,2-diacryloxypropane
- h. 1,5-diacryloxy-3-oxapentane
- i. 3-trinitromethyl cyclohexanone

17. Data sheets (SPIA) have been completed for four nitro compounds previously prepared on the program.

II. TECHNICAL PROGRESS: NITRO POLYMERS

A. VINYL POLYMERS

1. Chain-Transfer Study of Nitro Compounds

a. Introduction

(1) The primary objective of the nitro polymer program is to produce an "ideal" monopropellant containing aliphatic nitro groups. The two approaches being pursued at present for the preparation of nitro polymers are (1) condensation of appropriate functional nitro monomers and (2) the vinyl-type polymerization of unsaturated nitro compounds. Of the latter type only three monomers have been available in sufficient quantity for study. It became apparent that these monomers differed from other vinyl monomers, such as styrene and methyl methacrylate, in the following respects: (1) the polymerization rates were slower than those observed for compounds which do not contain nitro groups; and (2) the molecular weights of the polymers were very low. This fact was substantiated by the low molecular weights (determined osmotically), low intrinsic viscosities, and extreme brittleness of the polymers. Inasmuch as polymers of very low molecular weight usually possess undesirable physical properties, it was important to determine the cause of these characteristics. This information must be available, so that either the properties of these polymers may be improved, or specifications given for the preparation of new nitro monomers.

(2) Although explanations may be advanced for the behavior described above, no experimental data have been available to substantiate them. However, by comparison with monomers which do not contain nitro groups, it seemed that the nitro group was actively participating in the polymerization. Nitro aromatic compounds are well known as polymerization inhibitors. Also, the low molecular weights obtained could be explained by assuming that the nitro group was involved in chain transfer of the polymeric radical to the monomer. In order to obtain a better understanding of the polymerization of olefinic nitro monomers, a program was initiated to study the chain-terminating effects of the nitro group.

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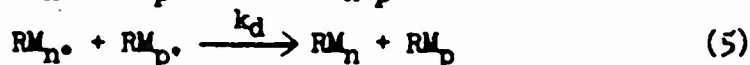
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b. Discussion

(1) So that the problems involved may be more clearly understood, it is appropriate first to discuss briefly the fundamental theories of bulk and solution polymerization. Studies by a number of workers on radical chain-polymerization of vinyl monomers have shown that the facts are consistent with the following mechanism:²



where

cat. = catalyst

R. = catalyst radical

M = monomer

RM₁. - - - RM_n. = chain radical

(2) The kinetic consequences of these equations show that the rate of conversion of monomer to polymer is given by the following expression:

$$\frac{-d[M]}{dt} = k_2 [C^*] [M] = k_2 \left(\frac{k_1}{k_3} \right)^{1/2} [\text{cat}]^{1/2} M \quad (6)$$

where

[C*] = conc. of all free radicals

$$k_3 = k_c + k_d$$

²Mark and Tobolsky, Physical Chemistry of High Polymeric Systems (Interscience Publishers, Inc., N.Y., 1950).

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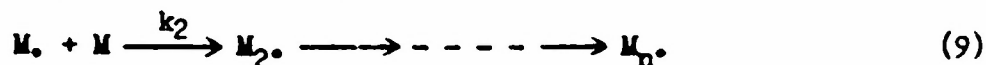
II Technical Progress, A (cont.)

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(3) The kinetic chain length, V , is given by:

$$V = \frac{\text{velocity of growth}}{\text{velocity of termination}} = \frac{k_2 [C^*] [M]}{k_3 [C^*]^2} = \frac{k_2 [M]}{k_3 [C^*]} = \frac{k_2 [M]}{(k_1/k_3)^{1/2} [cat]^{1/2}} \quad (7)$$

(4) In order to obtain a complete understanding of vinyl polymerization it is necessary to introduce the concept of chain transfer to monomer and to polymer.



Chain transfer to monomer or to catalyst affects the number average degree of polymerization, $\bar{P}_n$. Chain transfer to polymer does not affect $\bar{P}_n$, but introduces branching. In cases of mono-radical initiation and no chain transfer to catalyst the following relations can be derived:

$$\frac{1}{\bar{P}_n} = \frac{k_{TM}}{k_2} + \frac{(k_c + k_d)^{1/2} (k_1)^{1/2} [cat]^{1/2}}{2k_2 [M]} \left(\frac{k_c + 2k_d}{k_c + k_d} \right) \quad (10)$$

$$\frac{1}{\bar{P}_n} = \frac{k_{TM}}{k_2} + \frac{(k_2 + 2k_d) \left(\frac{-d[M]}{dt} \right)}{(2k_2)^2 [M]^2} \quad (11)$$

Plots of $\frac{1}{\bar{P}_n}$ vs $[cat]^{1/2}$ or $\frac{1}{\bar{P}_n}$ vs $\frac{-d[M]}{dt}$ give the values of $\frac{k_{TM}}{k_2}$ at the intercept.

The relative values of k_c and k_d can be determined from the relation

$$\frac{k_c}{2(k_c + k_d)} = \frac{\left\{ k_1 [cat] / \left(\frac{-d[M]}{dt} \right) \right\} + k_{TM}/k_2 - \frac{1}{\bar{P}_n}}{k_1 [cat] / \left(\frac{-d[M]}{dt} \right)} \quad (12)$$

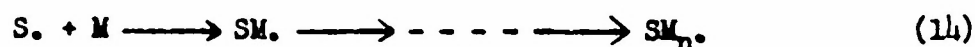
provided that $k_1 [cat]$, the rate of spontaneous decomposition of catalyst, can be determined by independent measurements.

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(5) In order to determine the effect of the nitro group on the polymerization of vinyl monomers which do not contain nitro groups, it has been decided to investigate the chain-transfer abilities of certain polynitro compounds, such as trinitroethyl propionate, 1,1,1-trinitroethane, and 2,2-dinitropropane. The monomers selected are styrene, methyl methacrylate, and vinyl acetate. Chain transfer of this type can take place by the following equations:



where

SX = chain-transfer agent

S $\cdot$ = chain-transfer radical

Under these conditions the expression for $\bar{P}_n$ becomes:

$\bar{P}_n$ = velocity of propagation/velocity of termination + velocity of transfer to monomer + velocity of transfer to SX

$$= \frac{k_2 [C^*] [M]}{k_3 [C^*]^2 + k_T [C^*] [S] + k_{TM} [C^*] [M]} \quad (15)$$

$$= \frac{k_2 [M]}{k_3 [C^*] + k_T [S] + k_{TM} [M]} \quad (16)$$

$$\frac{1}{\bar{P}_n} = \frac{(k_1 k_3)^{1/2} [\text{cat}]^{1/2}}{k_2 [M]} + \frac{k_{TM}}{k_2} + \frac{k_T [S]}{k_2 [M]} \quad (17)$$

Plots of $\frac{1}{\bar{P}_n}$ vs $[S]/[M]$ should therefore give straight lines whose intercept is $(k_1 k_3)^{1/2} [\text{cat}]^{1/2} / k_2 + k_{TM} / k_2$ and whose slope is k_T / k_2 .

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II Technical Progress, A (cont.)

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(6) Styrene, methyl methacrylate, and vinyl acetate were selected because they are monomers containing both electron-donating and electron-attracting groups. In addition, the literature contains valuable information from which $\bar{P}_n$ can be calculated. Trinitroethyl propionate and trinitroethane were selected because of their structural similarities to trinitroethyl acrylate and methacrylate. It was also decided to study the effect of dinitropropane on the polymerization of the above-mentioned monomers.

(7) Equation (17) can be applied to obtain valuable information on the polymerization of ordinary vinyl monomers in the presence of polynitro additives. A plot of $\frac{1}{\bar{P}_n}$ vs $[S]/[M]$ should be a straight line

whose slope is k_{TS}/k_2 , the ratio of the rate constant of chain transfer to nitro compound and rate constant of chain propagation.

(8) In order to study the chain transfer of trinitroethyl methacrylate it is proposed to study the polymerization of this monomer in a solvent of similar structure, containing no nitro groups. An ester such as ethyl propionate would be suitable. If this nitro monomer follows the kinetics of other vinyl monomers the rate given by Equation (6) would be expected to be valid. This equation predicts that the rate is proportional to the square root of the catalyst concentration and to the monomer concentration. However, since chain transfer to catalyst usually is small enough to be neglected, and since the solvent is inert, the average degree of polymerization $\bar{P}_n$ should be independent of solvent concentration. This means that the first and third terms in Equation (17) may be neglected; the equation then reduces to $1/\bar{P}_n = k_{TM}/k_2$. Indeed, the degree of polymerization in an inert solvent should be the same as that obtained in bulk (using the same catalyst concentration, temperature, etc.).

(9) The experimental work necessary to confirm the above predictions would consist of polymerizing trinitroethyl methacrylate in several solvent/monomer ratios between 0.001 and 2.0, using the same catalyst concentration (relative to monomer). At each $[S]/[M]$ ratio a yield vs time curve would be plotted and the intrinsic viscosity of each sample would be determined. For certain solvent/monomer ratios the catalyst concentration would then be varied and the polymerization rate would be determined.

(10) By plotting the rate vs square root of the catalyst concentration a linear relationship should be obtained. Also, a plot of the rate vs monomer concentration should be linear.

(11) The data obtained from the experiments outlined above should serve to define the function of the nitro group during polymerization.

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II Technical Progress, A (cont.)

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c. Chain Transfer of Trinitroethyl Propionate

(1) Polymerization of Styrene - Discussion

(a) Because of its structural similarity to trinitroethyl acrylate, it was decided to investigate first the effect of trinitroethyl propionate on the polymerization of styrene. In order to do so it was necessary to carry out some preliminary polymerizations to define approximately the effect of the trinitroethyl propionate molecule on styrene. The polymerization of styrene was carried out at 45°C for 40 hr, using methyl *n*-amyl ketone peroxide as catalyst. The concentration of catalyst was kept constant at 2 mol percent and the amount of trinitroethyl propionate was varied from 0 to 20 mol percent. The data obtained are listed in Table I.

(b) It can be seen from these data that practically complete inhibition occurs at trinitroethyl propionate concentrations of 1 mol percent or more. The nature of the inhibition is questionable, since the addition of trinitroethyl propionate to styrene gave an immediate yellow color. This may have resulted from the formation of some type of molecular complex.

(c) In sample No. 1 (20 mol percent trinitroethyl propionate used) a crystalline compound different from the original starting materials was obtained. Elemental analysis indicates that this substance has the empirical formula $C_{5.5}H_{5.5}N_{.5}O_{1.3}$. Further efforts will be made to identify this substance, since it may indicate the nature of the reactions involved.

(d) The intrinsic viscosities of the polymers obtained are also listed. Examination of these values shows that the viscosity increases as the concentration of the trinitroethyl propionate decreases. Inasmuch as the percentages of conversion also increases, these values give only qualitative evidence for chain transfer by trinitroethyl propionate.

(e) A quantitative determination of the chain-transfer ability of trinitroethyl propionate in styrene (i.e., the determination of k_T/k_2 ,³ the ratio of rate constants for chain transfer and chain propagation) is now in progress. Although the results are still incomplete, it appears that complete inhibition takes place at 45°C when 1 mol percent of the ester is used, the polymerization being catalyzed by 0.1 mol percent methyl *n*-amyl ketone peroxide. Using the same amount of catalyst, the polymerization is very slow when 0.1 mol percent of trinitroethyl propionate is used; the conversion is about 3% after one week at 45°C. In view of these results a comparative study of the polymerization of styrene at three concentrations of methyl *n*-amyl ketone peroxide, 0.1, 0.25, and 0.50 mol percent, was carried out. The values for the rate of polymerization, R_p , at the corresponding catalyst concentrations, are 0.0596, 0.101, and 0.124 mol liter⁻¹hr⁻¹ for conversions which are between 25 and 30% complete. Although the determination of the viscosities is not complete, from a consideration of time involved it appears more feasible to use concentrations of catalyst greater than 0.1 mol percent.

³See Equation (17).

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TABLE I
POLYMERIZATION OF STYRENE IN PRESENCE OF TRINITROETHYL PROPIONATE,
USING 2 MOL PERCENT METHYL n-AMYL KETONE PEROXIDE

Sample No.	Styrene		Trinitroethyl Propionate		mol percent	Amount Converted	Intr. Visc. $[\eta]$
	gm	mols $\times 10^{-2}$	gm	mols $\times 10^{-2}$			
1	4.00	3.84	2.270	0.96	20	0	—
2	4.50	4.32	1.138	0.48	10	0	—
3	4.65	4.47	0.782	0.33	7	0	—
4	4.76	4.56	0.568	0.24	5	0	—
5	4.85	4.66	0.379	0.16	3	0	—
6	4.91	4.71	0.213	0.09	2	trace	—
7	4.95	4.75	0.119	0.05	1	trace	—
8	5.00	4.80	0.0568	0.025	0.5	0.054	0.052
9	5.00	4.80	0.0213	0.010	0.2	1.63	0.121
10	5.00	4.80	0.0119	0.005	0.1	2.66	0.132
11	5.00	4.80	0.0060	0.0025	0.05	2.95	0.144
12	5.00	4.80	0	0	0	3.10	0.144

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(2) Polymerization of Styrene - Experimental

(a) The styrene used in the polymerization was distilled under nitrogen through a 3-ft glass-helices-packed column just before use; the bp was 63°C at 50 mm. The polymerizations were carried out in the following manner: The appropriate quantities of trinitroethyl propionate, styrene, and methyl *n*-amyl ketone peroxide were placed, in order, in thoroughly clean test tubes (16 x 150 mm). The total number of mols of constituents was kept at 0.048. The concentration of methyl *n*-amyl ketone peroxide was kept constant at 2 mol percent, based on styrene. The concentration of trinitroethyl propionate varied from 0 to 20 mol percent. The test tubes were cooled in dry ice, flushed with nitrogen, sealed, and then placed in the 45°C bath. After 40 hr the samples were dissolved in an equivalent volume of acetone and the mixtures poured into 50 ml of methanol containing a small amount of *n*-butyl catechol. The precipitated polymers were collected, dried in the vacuum desiccator using an oil pump for 48 hr, then weighed. The dried polymers were next dissolved in about 25 times their weight of benzene and precipitated into five to six volumes of methanol. The samples were then thoroughly dried.

(b) Viscosity measurements were taken by dissolving 0.200 gm of reprecipitated polymer in 50.00 ml of anhydrous benzene; the mixture was permitted to stand for 48 hr and the time of flow was determined in a modified Ostwald viscometer. The viscosity was calculated from the relationship

$$[\eta] = \frac{2.30 \log \frac{t}{t_0}}{c}$$

where t = time of flow for polymer solution, t_0 = time of flow for solvent, and c = concentration in grams of polymer per 100 ml of solution.

(c) The experiments to determine the value of k_1/k_2 were carried out in a modified manner. The appropriate quantities of styrene, trinitroethyl propionate, and methyl *n*-amyl ketone peroxide (enough for six runs) were weighed and mixed, and 10.00-ml aliquots were taken. The density of the mixture was determined in order to calculate the total volume of solution present. The test tubes containing the samples were then treated in the usual manner.

(d) A mixture of 2.270 gm (0.0096 mol) of trinitroethyl propionate, 4.000 gm (0.0384 mol) of styrene, and 0.226 gm (0.000768 mol) of methyl *n*-amyl ketone peroxide, when subjected to the polymerization conditions described above, resulted in no polystyrene but gave a small amount of crystalline product. This unknown colorless substance, when crystallized several times from methylene chloride and *n*-hexane, melted at 98 to 99°C.

Analysis Found: %C, 66.89; %H, 5.49; %N, 6.79

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(3) Polymerization of Methyl Methacrylate - Discussion

To determine values of k_T/k_2 for methyl methacrylate and various nitro compounds, a relationship between intrinsic viscosity and the degree of polymerization $\bar{P}_n$ is needed. Tobolsky has determined such a relationship:⁴ $[\eta] = 2.52 \times 10^{-3} \bar{P}_n^{0.80}$. Two polymerizations of methyl methacrylate using benzoyl peroxide as a catalyst were carried out according to the method of Tobolsky to see whether comparable results could be obtained. The polymerizations were carried out for 29 and 30 min, using 0.160 mol/liter of benzoyl peroxide at 60°C. The corresponding conversions were 13.2 and 15.5%, respectively. Tobolsky reported 15% conversion and an intrinsic viscosity of 0.874. The viscosity of the crude polymer was found to be 0.61. When the polymer was reprecipitated once from chloroform and methanol the viscosity was essentially the same.

(4) Polymerization of Methyl Methacrylate - Experimental

Methyl methacrylate (Du Pont) was distilled under nitrogen at 30 mm pressure. A 0.9683-gm quantity of benzoyl peroxide (0.160 mol/liter) was weighed into a 25-ml volumetric flask and methyl methacrylate was added to make 25 ml of solution. Two 10-ml aliquots were taken and placed in test tubes; the tubes were flushed with nitrogen, sealed, and placed in the 60°C bath. The first sample was polymerized for 29 min and the second for 30 min. The polymers were precipitated in methanol containing t-butyl catechol, collected, and dried in a vacuum desiccator for 24 hr. The yields were 1.249 gm (13.2%) and 1.476 (15.5%), respectively. The viscosities were determined in the usual manner.

d. Chain Transfer of Trinitroethyl Methacrylate

(1) As an introduction to the determination of the chain-transfer characteristics of trinitroethyl methacrylate, bulk polymerization of this material is being studied, using methyl n-amyl ketone peroxide (MAKP) as initiator.

(2) If the polymerization is terminated while the percentage of conversion is low, the concentration of the monomer will remain essentially constant and the rate becomes zero order with respect to monomer. Thus, $\frac{-dM}{dT} = k_2 [C^*]$ rather than being defined by Equation (6).

(3) The rate of polymerization vs catalyst concentration is being studied. A plot of the rate vs the square root of catalyst concentration should be linear, provided that the catalyst itself does not exhibit chain transfer. Since no information is available on the initiator MAKP, the rate vs catalyst concentration is being investigated. The data available are insufficient to warrant conclusions.

⁴Paper in press.

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(4) Experimental

(a) A mixture of 0.3097 gm of MAKP and 30.9984 gm of trinitroethyl methacrylate was divided, in known portions, among six 16- x 150-mm test tubes which had been specially cleaned. The air above the monomer mixture was displaced with nitrogen and the tubes were placed in a $50.0 \pm 0.15^\circ\text{C}$ stirred oil bath. At intervals a tube was withdrawn and the polymer was immediately precipitated by pouring the mixture into 100 ml of *n*-hexane. The polymer was filtered and washed with an additional 100 ml of hexane. The relative and intrinsic viscosities were determined on samples of sufficient weight. The results are summarized in Table II.

TABLE II
BULK POLYMERIZATION OF TRINITROETHYL METHACRYLATE WITH
1% MAKP AT 50°C

Weight of Monomer Mixture <u>gm</u>	Weight of Polymer Formed <u>gm</u>	Time <u>hr</u>	% Polymerized	Rate Constant <i>k</i> <u>mol/liter/sec</u>	η_r^a	$[\eta]^c$
5.5537	0.0939	1.5	1.691	1.68×10^{-5}	—	—
5.4530	0.1347	2.5	2.470	1.47×10^{-5}	1.059 ^b	0.058
5.0104	0.1734	3.5	3.461	1.47×10^{-5}	1.059 ^b	0.058
5.0016	0.2345	5.0	4.689	1.39×10^{-5}	1.126	0.060
5.0785	0.5057	10.0	9.958	1.49×10^{-5}	1.122	0.058
5.0559	0.5567	11.0	11.01	1.49×10^{-5}	1.118	0.056

^aConcentration of 2 gm of polymer in 100 ml of acetone

^bConcentration of 1 gm of polymer in 100 ml of acetone

^cCalculated by the Baker equation $[\eta] = \frac{8}{c} \left(\eta_r^{0.125} - 1 \right)$, where
c = concentration.

(b) Another rate determination was carried out in the same manner, using a mixture containing 0.0773 gm MAKP and 30.9979 gm of trinitroethyl methacrylate. These results are given in Table III.

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TABLE III

BULK POLYMERIZATION OF TRINITROETHYL METHACRYLATE WITH
0.25% MAKP AT 50°C

Weight of Monomer Mixture <u>gm</u>	Weight of Polymer Formed <u>gm</u>	Time <u>hr</u>	% Polymerized	Rate Constant k <u>mol/liter/sec</u>	η_r	$[\eta]^e$
5.3182	0.0876	2.0	1.647	1.24×10^{-5}	—	—
5.4265	0.1696	4.0	3.125	1.17×10^{-5}	1.058 ^a	0.056
5.0632	0.2071	5.5	4.090	1.12×10^{-5}	1.089 ^b	0.057
5.0258	0.2916	8.0	5.802	1.09×10^{-5}	1.122 ^c	0.058
5.0273	0.3417	9.83	6.797	1.04×10^{-5}	1.127 ^c	0.060
5.0689	0.8634	21.5	17.03	1.19×10^{-5}	1.257 ^d	0.058

^aConcentration of 1.00 gm of polymer/100 ml of acetone

^bConcentration of 1.50 gm of polymer/100 ml of acetone

^cConcentration of 2.00 gm of polymer/100 ml of acetone

^dConcentration of 4.00 gm of polymer/100 ml of acetone

^eCalculated by the Baker equation.

(c) It is observed that there is no detectable change in the intrinsic viscosity, although fourfold change of catalyst concentration occurred. It is also to be noted that the rate at 0.25% catalyst concentration is not half the rate at 1% initiator concentration, as would be expected.

2. Pentaerythritol Trinitrate Acrylate

a. Determination of Polymerization Rate

(1) The polymerization rate of pentaerythritol trinitrate acrylate (petrin acrylate) in acetone solution has been determined

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at 30, 40, and 50°C. The over-all activation energy has been calculated from the rate constants. The dilatometric method described in an earlier report⁵ was used to determine these values. The rate constants were calculated for a zero-order reaction, expressed as percent per hour, although the polymerization appeared to be of complex order. The rate constant, k , was found to be 2.2%/hr at 30°C, 5.3%/hr at 40°C, and 10.07%/hr at 50°C. The activation energy was found to be approximately 14 kcal/mol. The data are given in Tables IV, V, and VI, and plotted in Figures 1, 2, 3, and 4. Density data are presented in Figure 5.

(2) The dilatometers were prepared by blowing 1.5- to 2-ml bulbs on 1-mm capillary tubing. After calibration, the dilatometers were filled with a solution of 5.049 gm of acetone containing 5.000 gm of petrin acrylate and 0.0501 gm of methyl *n*-amyl ketone peroxide. The filled dilatometers were placed in the appropriate baths and the rate of polymerization was followed by checking the fall in the level of the meniscus, until sufficient data were collected to plot a rate curve. The solutions were cured at 50°C for seven days, then removed; the polymer was precipitated by pouring into methanol. The polymer from the 30°C bath had a relative viscosity of 1.49 in acetone at a concentration of 2 gm/100 ml.

b. Solution Polymerization

(1) It was observed from the kinetic study that the 50 wt% solutions of polymer had not gelled. It had been reported in preliminary experiments that the polymer was acetone-insoluble. Another set of experiments was then carried out to confirm these observations. A 50% solution, using 1 or 0.25% methyl *n*-amyl ketone peroxide catalyst, gave soluble polymers. At 75% monomer concentration, using the same quantities of catalyst, gels were formed which appear to be completely acetone-insoluble. However, they imbibed solvent and swelled considerably.

(2) The soluble polymer prepared using 1% catalyst had a relative viscosity of 1.73. With 0.25% catalyst the relative viscosity was of 1.67. Although these data are not consistent, the monomer appears promising and future work is indicated.

3. Vinyl Trinitrobutyrate

It was reported that a possible co-polymer of vinyl trinitrobutyrate (VTB) and acrylonitrile had been obtained. Additional experiments, in attempts to obtain a co-polymer with higher molar ratios of VTB, have failed. Inasmuch as all of the past work with this monomer has been unsuccessful, no future work is anticipated.

⁵Aerojet Report No. 499 (16 March 1951).

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TABLE IV

POLYMERIZATION OF PETRIN ACRYLATE AT 30°C

($\Delta V_T = 4.78 \times 10^{-2}$ ml)

<u>Δt, hr</u>	<u>Δh, cm</u>	<u>ΔV, ml</u>	<u>% Polymerized</u>
0	0	0	0
0.5	0	0	0
1.0	0	0	0
2.0	0	0	0
4.5	0	0	0
5.0	0.01	7.61×10^{-5}	0.159
6.0	0.08	6.09×10^{-4}	1.28
7.0	0.08	6.09×10^{-4}	1.28
8.0	0.09	6.84×10^{-4}	1.43
9.0	0.10	7.61×10^{-4}	1.59
10.75	0.19	1.45×10^{-3}	3.03
12.0	0.20	1.52×10^{-3}	3.19
17.0	0.22	1.67×10^{-3}	3.50
19.0	0.35	2.66×10^{-3}	5.57
21.0	0.55	4.18×10^{-3}	8.75
22.0	0.66	5.03×10^{-3}	10.5
23.0	0.79	6.01×10^{-3}	12.6
24.0	0.93	7.07×10^{-3}	14.8
25.0	1.08	8.22×10^{-3}	17.2
26.0	1.19	9.06×10^{-3}	19.0
27.5	1.39	1.06×10^{-2}	22.2
29.5	1.69	1.29×10^{-2}	26.9
31.5	1.84	1.40×10^{-2}	29.3
33.25	2.09	1.59×10^{-2}	33.3
35.25	2.27	1.73×10^{-2}	36.2
37.0	2.40	1.83×10^{-2}	38.2
39.0	2.57	1.96×10^{-2}	40.9
41.5	2.78	2.12×10^{-2}	44.2
43.0	2.85	2.17×10^{-2}	45.4
47.0	3.09	2.35×10^{-2}	49.2
50.0	3.29	2.51×10^{-2}	52.5

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TABLE V

POLYMERIZATION OF PETRIN ACRYLATE AT 40°C

($\Delta V_T = 3.91 \times 10^{-2}$ ml)

<u>Δt, hr</u>	<u>Δh, cm</u>	<u>ΔV, ml</u>	<u>% Polymerized</u>
0	0	0	0
0.5	0	0	0
1.0	0.02	1.45×10^{-4}	0.371
1.5	0.05	3.63×10^{-4}	0.927
2.0	0.07	5.08×10^{-4}	1.30
4.0	0.15	1.05×10^{-3}	2.78
5.0	0.19	1.38×10^{-3}	3.52
6.0	0.40	2.90×10^{-3}	7.42
7.0	0.65	4.71×10^{-3}	12.1
7.75	0.87	6.31×10^{-3}	16.2
8.75	1.08	7.84×10^{-3}	20.1
10.5	1.59	1.15×10^{-2}	29.5
11.75	1.67	1.21×10^{-2}	31.0
13.25	2.06	1.50×10^{-2}	38.2
14.75	2.28	1.66×10^{-2}	42.3
16.0	2.52	1.83×10^{-2}	46.7
17.0	2.61	1.89×10^{-2}	48.4
19.0	2.86	2.06×10^{-2}	52.5
22.0	3.19	2.31×10^{-2}	59.1
24.0	3.39	2.46×10^{-2}	62.9
25.0	3.49	2.53×10^{-2}	64.7
26.0	3.57	2.59×10^{-2}	66.2
41.25	4.57	3.32×10^{-2}	85.0
43.0	4.67	3.39×10^{-2}	86.7
46.0	4.77	3.46×10^{-2}	88.5
50.0	4.93	3.58×10^{-2}	91.5

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TABLE VI

POLYMERIZATION OF PETRIN ACRYLATE AT 50°C

($\Delta V_T = 3.76 \times 10^{-2}$ ml)

<u>Δt, hr</u>	<u>Δh, cm</u>	<u>ΔV, ml</u>	<u>$\bar{x}$ Polymerized</u>
0	0	0	0
0.5	0.03	2.36×10^{-4}	0.628
1.0	0.05	3.94×10^{-4}	1.05
1.5	0.05	3.94×10^{-4}	1.05
1.75	0.10	7.87×10^{-4}	2.09
3.5	0.97	7.63×10^{-3}	20.3
4.0	1.18	9.29×10^{-3}	24.7
4.5	1.38	1.09×10^{-2}	28.9
5.0	1.61	1.27×10^{-2}	33.7
5.5	1.79	1.41×10^{-2}	37.5
6.0	1.98	1.56×10^{-2}	41.5
6.5	2.13	1.68×10^{-2}	44.6
7.25	2.28	1.80×10^{-2}	47.7
8.25	2.46	1.94×10^{-2}	51.7
10.0	2.76	2.17×10^{-2}	57.7
11.33	2.88	2.27×10^{-2}	60.4
12.67	3.06	2.41×10^{-2}	64.1
14.33	3.09	2.43×10^{-2}	64.6
15.5	3.23	2.54×10^{-2}	67.9
16.5	3.33	2.62×10^{-2}	69.7
18.5	3.51	2.76×10^{-2}	73.4
21.5	3.71	2.92×10^{-2}	77.6
22.0	3.72	2.93×10^{-2}	78.0
24.0	3.83	3.02×10^{-2}	80.2
25.0	3.85	3.03×10^{-2}	80.6
25.5	3.88	3.06×10^{-2}	81.2
41.0	3.97	3.13×10^{-2}	83.1
43.0	3.97	3.13×10^{-2}	83.1
46.0	3.85	3.03×10^{-2}	80.6
49.0	3.82	3.01×10^{-2}	80.0

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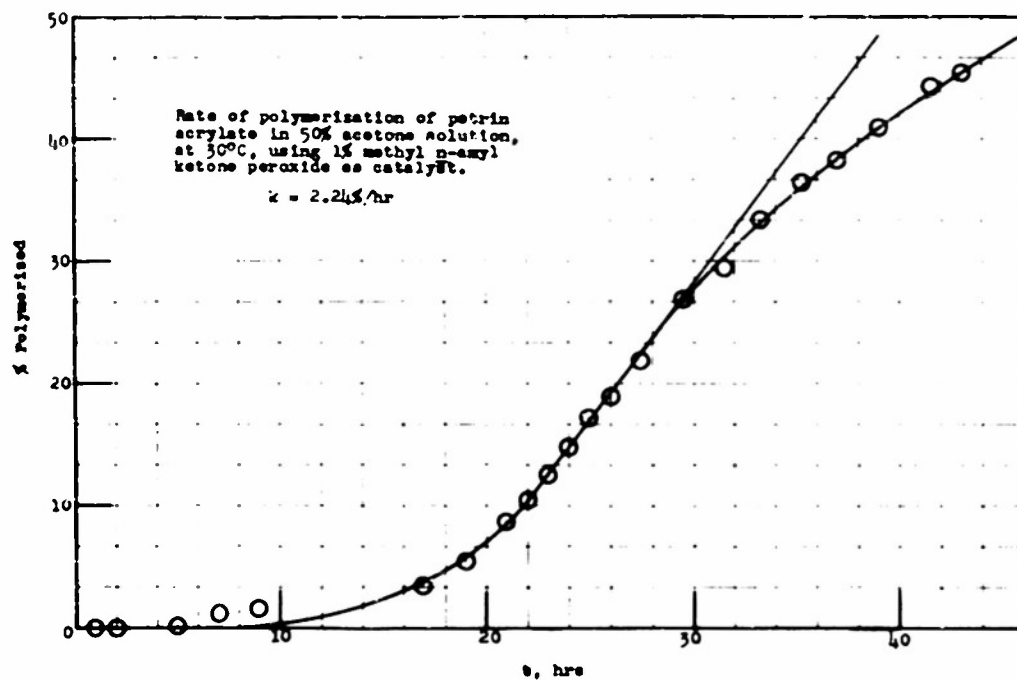


Figure 1

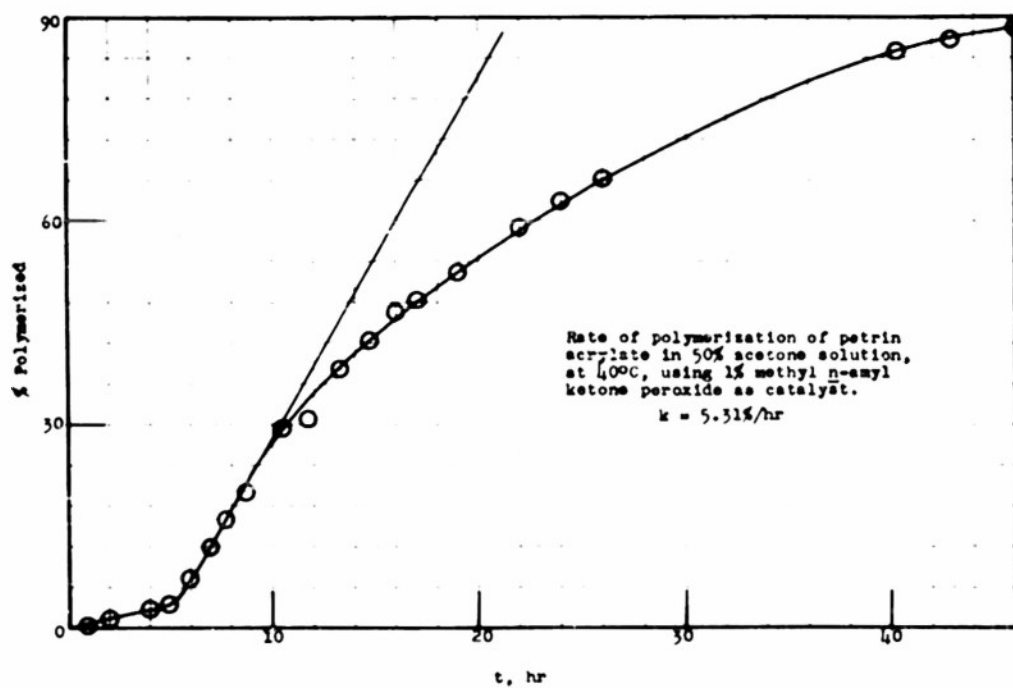


Figure 2

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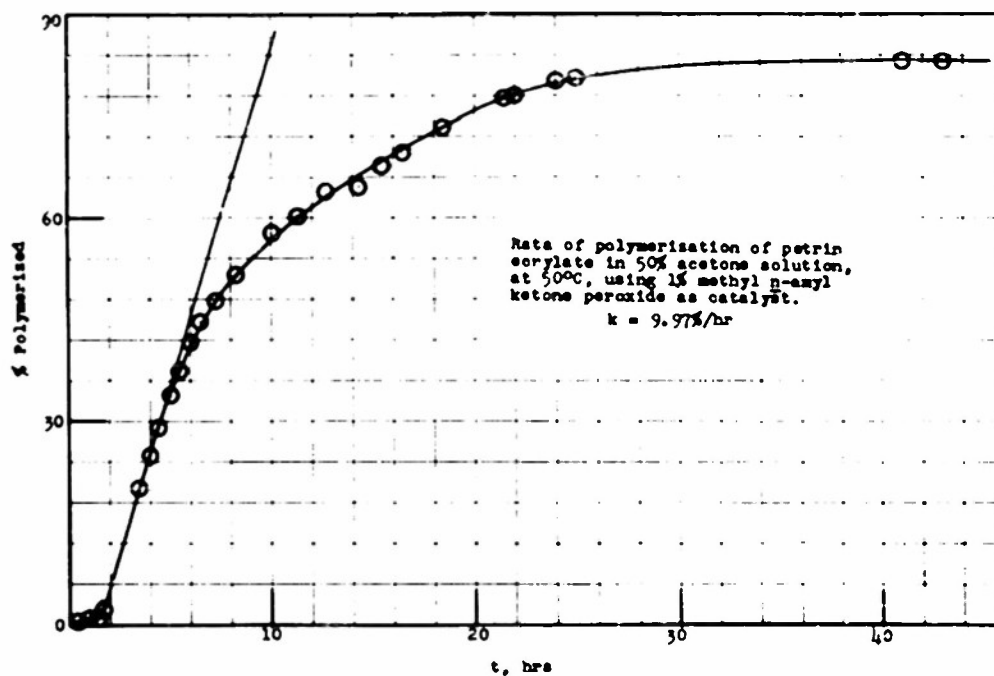


Figure 3

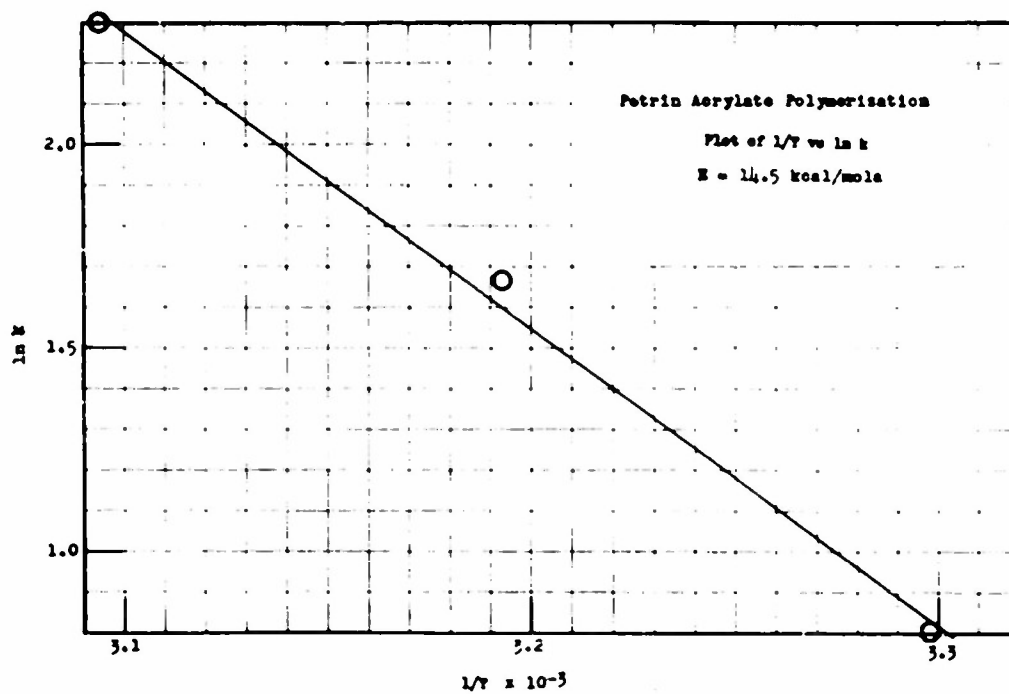


Figure 4

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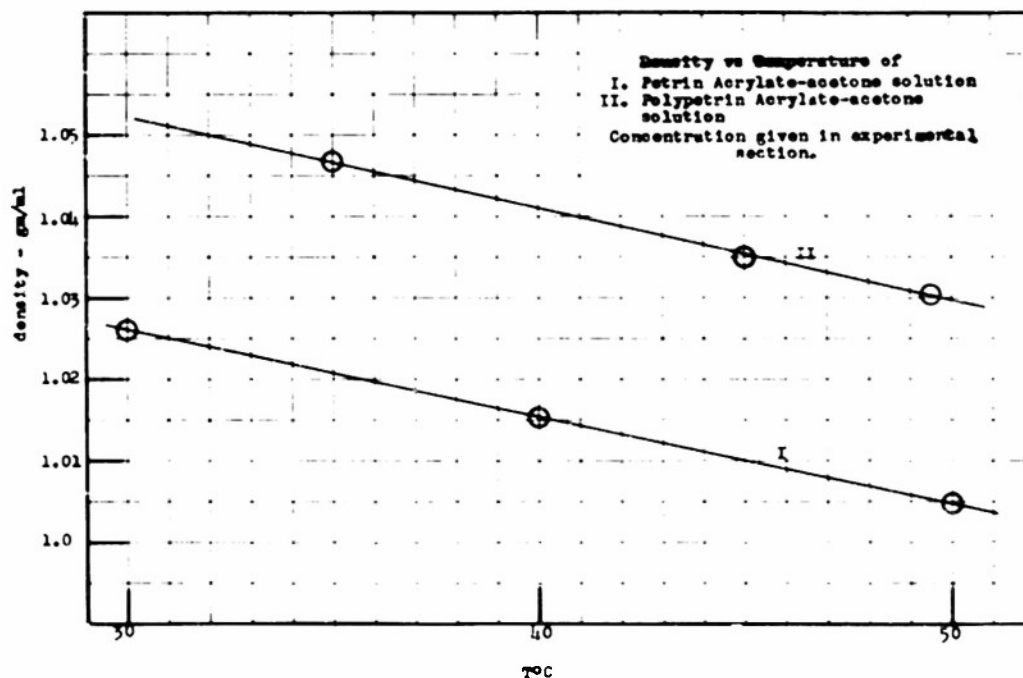


Figure 5

4. Trinitroethyl Methacrylate

a. A sample of polytrinitroethyl methacrylate which was to be used in the determination of data for the SPIA data sheet was prepared several months ago. Because of the rather poor analysis of this sample (JPK-4), before and after steam distillation, and the poor agreement with the predicted heat of combustion, the sample was not used in the evaluation tests.

b. Another sample (JPK-30) of polymer was prepared to replace the previous batch. However, again it was observed that the elemental analysis was in poor agreement with the theoretical. The carbon and hydrogen values were high; added confirmation of the disagreement was obtained from the heat of combustion data, which was higher than that predicted for the postulated structure.

c. Experimental

A 0.3125-gm (0.25%) quantity of methyl n-amyl ketone peroxide was added to 125.0 gm of trinitroethyl methacrylate. The mixture was melted and thoroughly mixed, then evenly divided among 13 test tubes (16 x 150 mm) which had been cleaned in chromic acid, washed with distilled water, washed with acetone, and finally dried at 75°C. Nitrogen was used to displace

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the air above the monomer and the tubes were sealed. Polymerization proceeded for 172 hr at 40°C, followed by 87 hr at 50°C. The polymer (115 gm) was dissolved in an equal weight of acetone and precipitated in 4 liters of hexane. The supernatant liquid was decanted and the polymer was slurried with 2 liters of hexane. After the material was filtered and dried by pumping in vacuo for two days, a sample was submitted for analysis. The softening range was 160 to 170°C, and the impact stability was 30 cm/2 kg; the relative viscosity at a concentration of 2 gm/100 ml acetone solution was 1.19, and the mp of the monomer 28.30°C.

Anal. calc'd for $C_6H_7N_3O_8$: %C, 28.93; %H, 2.83; %N, 16.87

Monomer: %C, 29.51; %H, 2.90; %N, 17.10

Polymer: %C, 33.67; %H, 3.72; %N, 13.41

Heat of combustion of polymer: 3171, 3065 cal/gm

Predicted: 2817 cal/gm

B. ADDITION AND CONDENSATION POLYMERS

1. Introduction

a. In general, monomers containing nitro groups react less rapidly than those without nitro groups. As the number of nitro groups per monomer is increased, the tendency to decompose usually increases with an increase in temperature. A material that would catalyze the polymerization reaction would make the rate of polymerization of highly nitrated monomers practical at lower temperatures, thus decreasing decomposition. Of the materials tested, boron trifluoride etherate showed the largest catalytic effect on the rate of nitro polyurethane formation. During this report period, boron trifluoride catalysis has been further studied and used as a practical method of increasing the rate of nitro polyurethane formation.

b. Work was continued on the preparation of new polyurethanes and larger quantities of those previously prepared.

c. Further attempts to esterify polyvinyl alcohol and α -cellulose with nitro acid chlorides and anhydrides have failed. The reaction of polyvinyl alcohol with 3,3,3-trinitropropyl isocyanate was also unsuccessful. This work will not be continued.

d. Alkaline catalysis of the polymerization of glycidyl 4,4,4-trinitrobutyrate was not effective. In several cases there was indication of degradation of the trinitromethyl end group. Hydrogen chloride, boron trifluoride, and an alkane sulfonic acid were also ineffective. This work will be continued using glycidyl butyrate as a model.

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2. Polyurethanes

a. Kinetic Studies

- (1) Boron Trifluoride Catalysis of Polyurethane I-J, from 3,3-Dinitro-1,5-pentane Diisocyanate and 2-Nitro-2-methyl-1,3-propanediol

(a) Work reported previously⁶ indicated that boron trifluoride etherate was an excellent catalyst for the reaction of nitro diisocyanates with nitro diols in dioxan solution. This catalytic effect was studied in more detail using the monomers 3,3-dinitro-1,5-pentane diisocyanate and 2-nitro-2-methyl-1,3-propanediol in dioxan solution. This particular polymer, I-J, was chosen for the experiments because the rate of $[-NCO]$ disappearance could be readily measured by the standard analytical procedure.

(b) All of the experiments were performed on a single mixture of the monomers in anhydrous dioxan. Equivalent amounts of the reactive groups $[-OH]$ and $[-NCO]$ were used. In three separate experiments, increasing amounts of boron trifluoride etherate were added to the standard mixture and all were maintained at 30°C in the same constant-temperature bath, together with the control containing no catalyst. Samples were periodically removed and analyzed for $[-NCO]$. Figure 6 is a plot of isocyanate concentration vs time for the uncatalyzed reaction and two of the catalyzed reactions. The third catalyzed reaction, in which an equivalent quantity of boron trifluoride etherate was used, was too rapid to measure and the heat evolved raised the temperature above that of the bath.

(c) The uncatalyzed reaction was found to be second order and the value of the rate constant at 30°C was $K_{30^\circ} = 6.6 \times 10^{-4}$ liters equivalent⁻¹ hr⁻¹. At 50°C the rate constant was $K_{50^\circ} = 2.3 \times 10^{-3}$ liters equivalent⁻¹ hr⁻¹. The catalyzed reactions were more complex and, when plotted as second-order reactions, straight lines were not obtained. The initial rate of $[-NCO]$ disappearance increased as the amount of boron trifluoride etherate was increased. Another control experiment showed that isocyanate is not consumed by boron trifluoride etherate in dioxan at 30°C.

(d) Curve 2 of Figure 6 shows the rate of isocyanate disappearance in the presence of 0.0193 equivalent of catalyst per equivalent of $[-NCO]$ or $[OH]$. The initially rapid rate decreased to the rate of the uncatalyzed reaction after about half of the total isocyanate had been consumed. Addition of more catalyst at this point increased the rate of isocyanate consumption. This indicates that the catalyst is slowly consumed, probably by forming a complex with the polyurethane that is formed.

⁶ Aerojet Report No. 563 (31 December 1951), p. 12.

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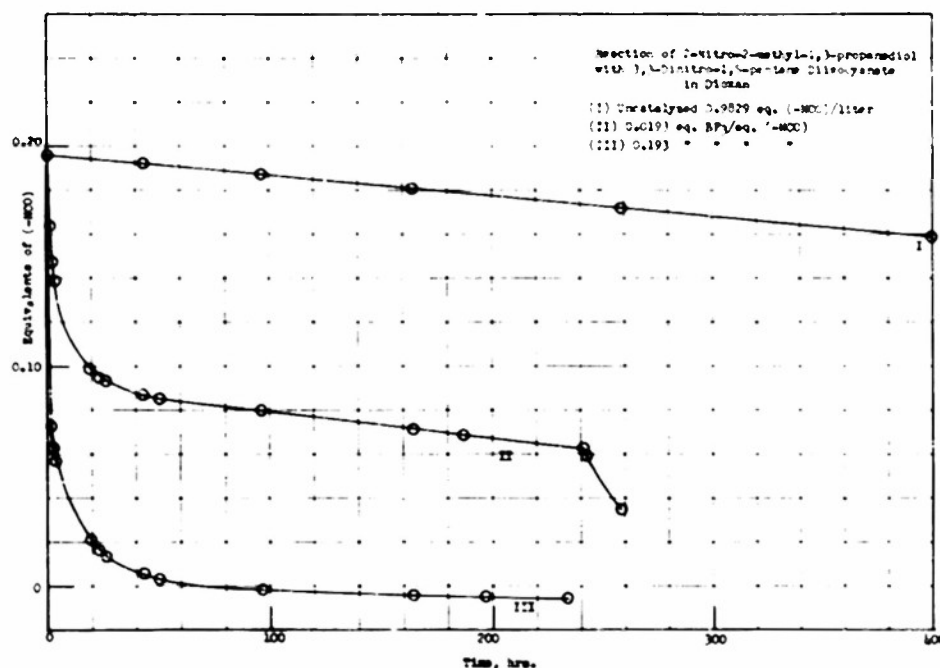


Figure 6

(e) Further evidence of boron trifluoride consumption by the reaction products was observed in the second catalyzed reaction, shown in curve 3 of Figure 6. Inasmuch as the analytical procedure used for determining $[-NCO]$ does not serve to differentiate between $[-NCO]$ and boron trifluoride, the amount of boron trifluoride added to the reaction must be subtracted from the total amount of di-*n*-butylamine consumed to obtain the $[-NCO]$ concentration. Proceeding in this manner resulted in negative values for $[-NCO]$ in later stages of the polymerization, indicating that the amount of free boron trifluoride still present was less than the amount originally added.

(f) The relative viscosities of acetone solutions of the polymers prepared in the three catalyzed reactions were about the same. However, later experiments have shown that the relative viscosity is related to the number of equivalents of boron trifluoride used per equivalent of monomer. The polymer obtained from the reaction in which an equivalent quantity of catalyst was used was submitted for elementary analysis. Good agreement with theoretical values was obtained. If the boron trifluoride does form a complex with the polyurethane, it must be removed during the washing process.

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(g) Experimental (JRF-111)

The 3,3-dinitro-1,5-pentane diisocyanate was analyzed for $[-NCO]$ as follows: Approximately 1 gm of the crystalline diisocyanate was weighed accurately into a glass-stoppered, 125-ml Erlenmeyer flask. Twenty-five ml of a 1N solution of di-n-butylamine in anhydrous dioxan was added. After standing 5 to 10 min at room temperature the mixture was transferred to a 400-ml beaker; acetone was used to wash out the flask. Twenty-five ml of water was added and the excess amine was back-titrated with 0.5N HCl to a pH of 5.0. A blank determination was run simultaneously. The observed values were 96.30 and 96.34% purity, assuming that all the $[-NCO]$ was present as 3,3-dinitro-1,5-pentane diisocyanate.

(h) Commercially available 2-nitro-2-methyl-1,3-propanediol was recrystallized from benzene. The observed melting point was 149°C. Dioxan was refluxed 8 hr over sodium metal, decanted, then distilled from fresh sodium discarding a forerun. Boron trifluoride etherate was prepared by saturating anhydrous ether with boron trifluoride, then distilling the product, discarding a forerun.

(i) A standard dioxan solution containing 1.3106 eq./liter of each of the monomers was prepared. Ten ml of boron trifluoride etherate was diluted to 100 ml with dioxan. One ml of this solution contained 0.758 meq. of catalyst. The final mixtures were made as follows:

JRF-111-A	JRF-111-B	JRF-111-C	JRF-111-D
150 ml monomer sol'n.	150 ml monomer sol'n.	150 ml monomer sol'n.	50 ml monomer sol'n.
5 ml BF_3 sol'n.	No BF_3 sol'n.	50 ml BF_3 sol'n.	8.6 ml $BF_3O(C_2H_5)_2$
45 ml dioxan	50 ml dioxan		
Equivalent to:			
0.9829 eq./liter monomers	0.9829 eq./liter monomers	0.9829 eq./liter monomers	1.118 eq./liter
0.01895 eq./liter BF_3		0.1895 eq./liter BF_3	1.112 eq./liter BF_3

Total equivalents of $[-NCO]$ vs time for these reactions are listed in Table VII. The analyses were made by removing 10-ml samples of the reaction mixture, adding excess normal di-n-butylamine solution, then back-titrating with 0.5N acid.

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TABLE VII

REACTION OF 2-NITRO-2-METHYL-1,3-PROPANEDIOL WITH
3,3-DINITRO-1,5-PENTANE DIISOCYANATE IN DIOXAN

Elapsed Time hr	JRF-111-A* Equivalents [-NCO]	JRF-111-B [†] Equivalents [-NCO]	JRF-111-C [‡] Equivalents [-NCO]
0	0.1966	0.1966	0.1966
0.33	0.1787	—	0.0880
1.00	0.1642	0.1950	0.0730
2.00	0.1482	—	0.0635
3.00	0.1397	—	0.0575
19.0	0.0997	0.1950	0.0215
23.0	0.0957	—	0.0170
26.0	0.0942	—	0.0140
43.0	0.0877	0.1920	0.0065
50.0	0.0857	0.1918	0.0040
96.0	0.0807	0.1875	-0.0010
164.0	0.0727	0.1810	-0.0035
187.0	0.0692	—	-0.0040
234.0	—	—	-0.0045
241.5	0.0630 ($\eta_r = 1.09$) added 0.0039 eq. BF ₃	—	Precipitated polymer
242.5	0.0600	—	($\eta_r = 1.31$)
258.5	0.0355	0.1720	
400.0	—	0.1590	
500.0	added 0.0075 eq. BF ₃	—	
668.0	Precipitated polymer	—	
716.0	($\eta_r = 1.25$)	0.1365	

*0.9829 eq./liter monomers; 0.01895 eq./liter BF₃.

[†]0.9829 eq./liter monomers; no BF₃.

[‡]0.9829 eq./liter monomers; 0.1895 eq./liter BF₃.

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(j) JRF-111-D

The reaction mixture became warm immediately, and after the initial reaction was over, the temperature was maintained at 60°C for 48 hr. The polymer was precipitated into water, washed, then vacuum steam-distilled and dried. The relative viscosity of a solution in acetone containing 2.00 gm/100 ml was $\eta_r = 1.28$ at 25°C.

Anal. calc'd for $C_{11}H_{17}N_5O_{10}$: %C, 34.83; %H, 4.52; %N, 18.47

Found: %C, 34.79; %H, 4.68; %N, 18.44

(k) The kinetic data observed in the uncatalyzed reactions are listed in Table VIII. The rate constants were evaluated from the slope of the plot of $\overline{DP}$ vs time.

(2) A Study of the Effect of Boron Trifluoride Concentration on Molecular Weight of Polyurethane I-A, from 3,3-Dinitro-1,5-pentane Diisocyanate and 2,2-Dinitro-1,3-propanediol

(a) Previous studies have shown that the function of boron trifluoride in polyurethane formation is complex. To clarify this problem, in part, an experiment was undertaken to determine the effect, if any, of boron trifluoride concentration and of portion-wise addition of boron trifluoride on molecular weight.

(b) As an approach to this problem, a dioxan solution of equivalent amounts of monomers was divided into five aliquots; to each was added a different amount of boron trifluoride etherate. The polymerizations were followed by measurements of the viscosities of the reaction solutions; and at the point where no further increase in viscosity was observed, each polymer was precipitated from solution, washed, and dried. As a qualitative measure of molecular weight, relative viscosities of the precipitated polymers were determined under standard conditions. These data are presented in Table IX. The effect of boron trifluoride concentration on relative viscosity is shown in Figure 7.

(c) Conclusions

These data show immediately the profound effect of boron trifluoride concentration on molecular weight, in a manner somewhat suggestive of vinyl-type catalysis. Smaller amounts of boron trifluoride favor higher relative viscosities, and in the limiting case, the polymer obtained using no boron trifluoride was insoluble in acetone and dimethylformamide. Portion-wise addition of boron trifluoride is clearly shown to effect no increase in molecular weight. The rate of reaction, as shown by reaction times to constant viscosity, is seen to be an increasing function of

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TABLE VIII

UNCATALYZED POLYMERIZATIONS 2-NITRO-2-METHYL-1,3-PROPANEDIOL
AND 3,3-DINITRO-1,5-PENTANE DIISOCYANATE IN DIOXAN SOLUTION

Dioxan Solution at 30°C

Original concentration: 0.9829 equivalent liter⁻¹ [-NCO]
0.9829 equivalent liter⁻¹ [-OH]

<u>Time</u> <u>hr</u>	<u>Observed</u> <u>Degree of Polymerization</u>
43	1.015
96	1.040
164	1.078
259	1.133
400	1.227
716	1.430

$$K_{30^{\circ}\text{C}} = \frac{6.5 \times 10^{-4}}{0.9829} = 6.6 \times 10^{-4} \text{ liter eq.}^{-1} \text{ hr}^{-1}$$

Dioxan Solution at 50°C

Original concentration: 2.37 equivalent liter⁻¹ [-NCO]
2.37 equivalent liter⁻¹ [-OH]

<u>Time</u> <u>hr</u>	<u>Observed</u> <u>Degree of Polymerization</u>
22.0	1.110
43.0	1.220
68.0	1.365

$$K_{50^{\circ}\text{C}} = \frac{5.46 \times 10^{-3}}{2.37} = 2.3 \times 10^{-3} \text{ liter eq.}^{-1} \text{ hr}^{-1}$$

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TABLE IX

RELATIVE VISCOSITIES AND REACTION TIMES OF
POLYURETHANE I-A PREPARATIONS

No.	Equiv.% $\text{BF}_3 \cdot \text{Et}_2\text{O}$	Reaction Time to Const. Viscosity, hr	Relative Viscosity
JKE-12 ^a	0	800 (to a gel)	Insoluble
JKE-24	1	140	1.51
JKE-29	5	50	1.46
JKE-28	5 + 5 at hr 48 ^b	50	1.45
JKE-30	10	10	1.40
JKE-25	10 + 10 at hr 48 ^b	10	1.40
JKE-26	50	5	1.23
JKE-27	100	2	1.19

^aPolymer from different initial reaction mixture.

^bAdded after viscosity of reaction solution had reached a constant value. No increase in viscosity was observed after addition.

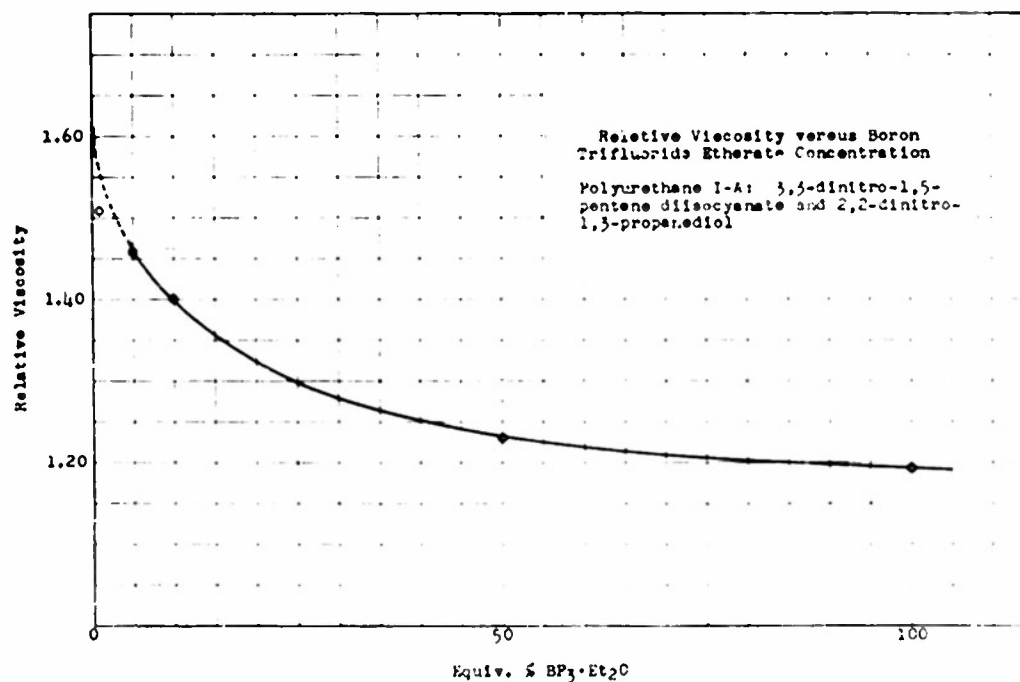


Figure 7

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the boron trifluoride concentration. This is in agreement with results of the kinetic study of polyurethane I-J. To avoid the exceedingly long reaction times obtained when only catalytic amounts of boron trifluoride are present, a compromise must undoubtedly be made, sacrificing something in degree of polymerization for a more feasible rate. Rheological studies will probably best indicate the correct choice.

(d) Experimental

The monomers were recrystallized and analyzed immediately prior to the experiment; the purity of both samples was 98.8%; 2.426 equivalents of the diol were combined with 2.426 equivalents of the diisocyanate in dioxan, and the solution was diluted to 750 ml. Aliquots (150 ml) were then pipetted into five reaction vessels. Boron trifluoride etherate (normality = 7.58 meq./ml) was pipetted into each vessel in an amount equivalent to 1, 5, 10, 50, and 100%, respectively, of the monomer present. The reaction solutions were placed in a 60°C constant-temperature bath, and stirred intermittently. Immediately before the second addition of boron trifluoride etherate to runs JKE-25 and JKE-28, a small portion of each was removed as a control. When no further increase in viscosity of a sample was observed, the solution was removed from the bath, and filtered. The polymer was precipitated in water in a Waring Blendor, vacuum steam-distilled at 25 to 30°C, and dried in vacuo. The relative viscosities of the dry polymers were determined in acetone at a concentration of 2.000 gm/100 ml at 25°C.

b. Solution Polymerizations

(1) Discussion

The new polyurethanes prepared during this period are listed in Table X. These polymerizations were started before the influence of boron trifluoride concentration on molecular weight was known. Accordingly, relatively large amounts of boron trifluoride were used.

(2) Preparation of Polyurethane XI-A, from 3,3,5,7,7-Pentanitro-1,9-nonane Diisocyanate and 2,2-Dinitro-1,3-propanediol

(a) JRF-112

Equivalent amounts of the monomers (52.6 gm total weight) were dissolved in 77 gm anhydrous dioxan. Five ml of boron trifluoride etherate was added. This amount is equivalent to 0.43 eq. BF_3 per equivalent of $[-\text{NCQ}]$. The mixture was placed in a special flask in which the viscosity of the solution could be measured during the reaction. Viscosity of the solution vs time in hours is listed in Table XI. The temperature was maintained at 40°C.

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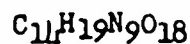
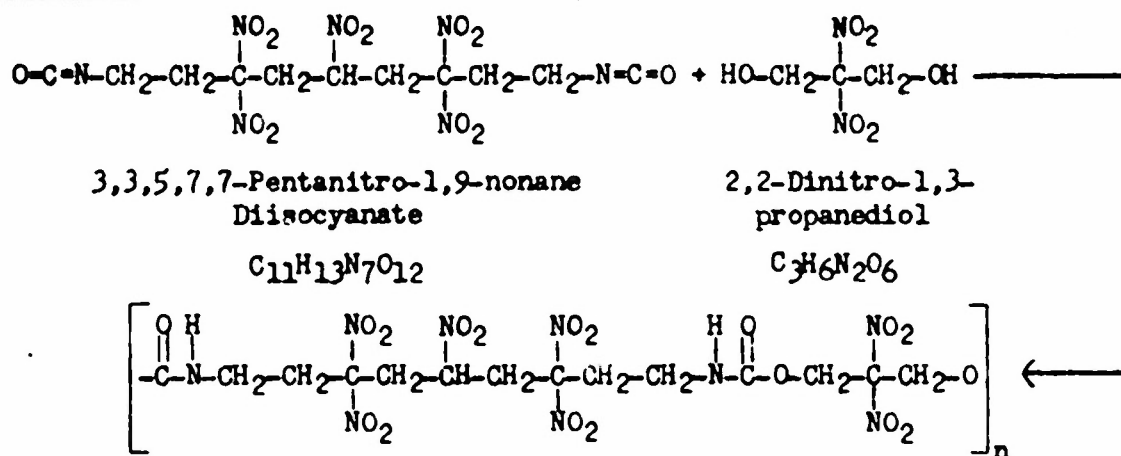
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TABLE X

SCHEDULE OF POLYMERS STUDIED: POLYURETHANES

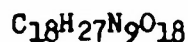
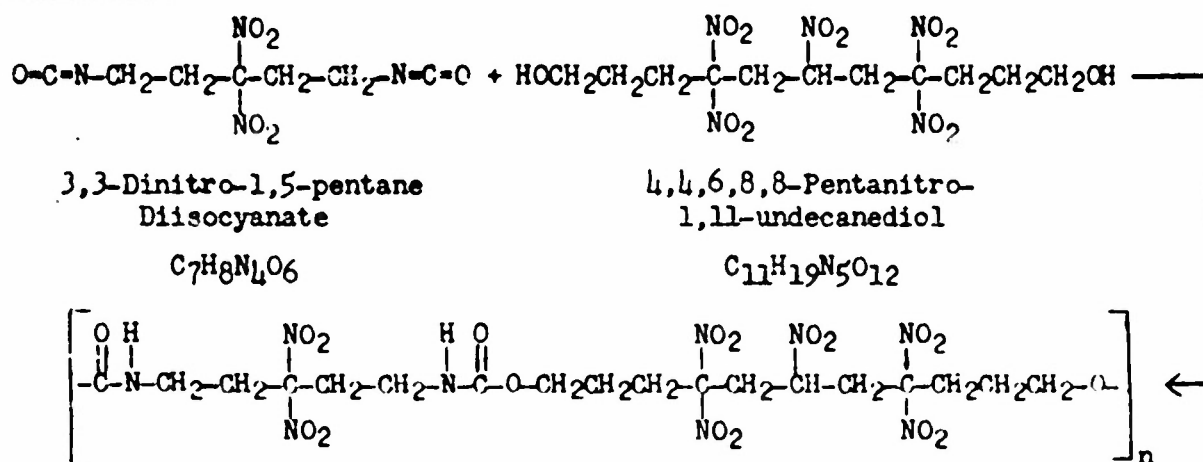
Polymer XI-A



Theoretical $I_{sp} = 203 \text{ lbf sec lbm}^{-1}$

After Nitration $I_{sp} = 231 \text{ lbf sec lbm}^{-1}$

Polymer I-K



Theoretical $I_{sp} = 175 \text{ lbf sec lbm}^{-1}$

After Nitration $I_{sp} = 209 \text{ lbf sec lbm}^{-1}$

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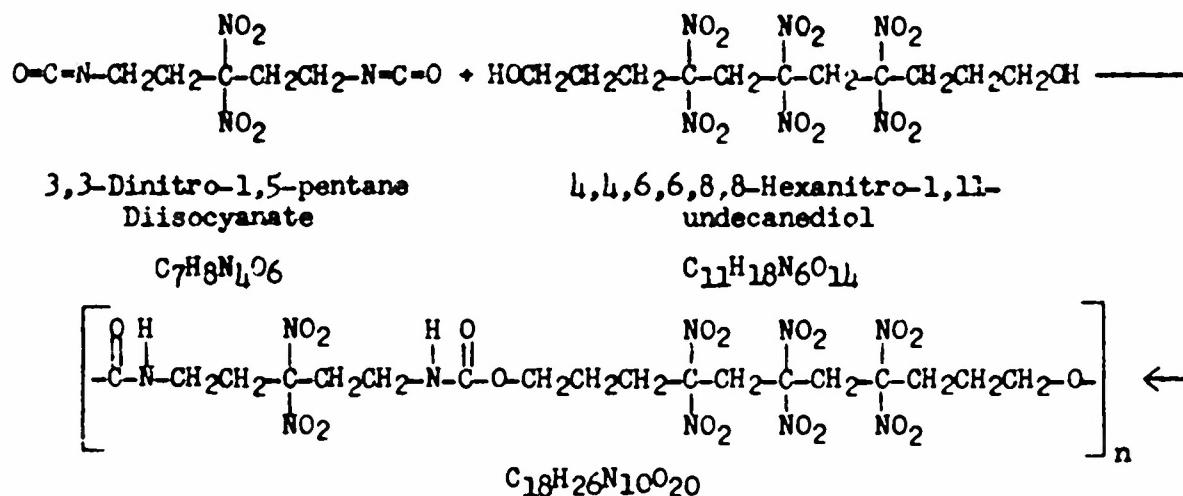
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TABLE X (cont.)

SCHEDULE OF POLYMERS STUDIED: POLYURETHANES

Polymer I-L



Theoretical $I_{sp} = 191 \text{ lbf sec lbm}^{-1}$
 After Nitration $I_{sp} = 219 \text{ lbf sec lbm}^{-1}$

TABLE XI

VISCOSITY OF POLYURETHANE XI-A - JRF-112 AT 40°C

Time hr	Viscosity centipoise	Remarks
0	5	
16	10	
21	14	
25	17	
40	24	
45	26	
48	28	
64	32	
72	36	
88	36	
Added 6.6 ml $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2 = 0.57 \text{ eq. BF}_3/\text{eq. (NCO)}$		
88	27	
96	27	
160	27	Removed from bath

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(b) The polymer was precipitated into water, washed, vacuum steam-distilled, and dried. A yield of 49.5 gm (94% of theoretical) was obtained. The product softened in the range 85 to 90°C and had an impact stability of 80 cm/2 kg as compared with RDX at 29 cm/2 kg. The relative viscosity of a solution of 2.00 gm in 100 ml acetone was 1.11 at 25°C.

Anal. calc'd for $C_{11}H_{19}N_9O_{18}$: %C, 27.96; %H, 3.18; %N, 20.97

Found: %C, 27.95; %H, 3.25; %N, 21.02

Heat of combustion calculated: 2847 cal/gm

Found: 2887 cal/gm

Heat stability tests: 65.5°C - 10 min

134.5°C - 7 min; exploded
after 29 min

- (3) Preparation of Polyurethane XI-AN: Nitration of Polyurethane XI-A, 3,3,5,7,7-Pentanitro-1,9-nonane Diisocyanate and 2,2-Dinitro-1,3-propanediol

(a) JRF-115

Fifty-three ml of 100% nitric acid at 0°C was added to 5.355 gm of polyurethane XI-A (JRF-112). After standing 30 min at 0°C, the clear solution was poured into 1 liter of ice water and the precipitated polymer was filtered, washed, and dried. The nitrated product weighed 5.742 gm (93% of theoretical). It softened in the range 55 to 60°C and had an impact stability of 26 cm/2 kg relative to RDX at 29 cm/2 kg. The relative viscosity of a solution of 2.000 gm in 100 ml of acetone was 1.10.

Anal. calc'd for $C_{14}H_{17}N_{11}O_{22}$: %C, 24.32; %H, 2.48; %N, 22.29

Found: %C, 24.39; %H, 2.39; %N, 22.02

Heat of combustion calculated: 2420 cal/gm

Found: 2424 cal/gm

- (4) Preparation of Polyurethane I-K: 3,3-Dinitro-1,5-pentane Diisocyanate and 4,4,6,8-Pentanitro-1,11-undecanediol

(a) JRF-113

Equivalent amounts of the monomers (37.4 gm total weight) were dissolved in 47 gm of anhydrous dioxan. Three ml of boron trifluoride etherate was added. This amount is equivalent to

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0.40 eq. BF_3 /eq. of $[-\text{NCO}]$. The mixture evolved heat and rapidly became more viscous. After the initial reaction was over the temperature was maintained at 40°C . Viscosity of the solution vs time in hours is listed in Table XII.

TABLE XII

VISCOSITY OF POLYURETHANE I-K (JRF-113) AT 40°C

<u>Time</u> <u>hr</u>	<u>Viscosity</u> <u>centipoise</u>	<u>Remarks</u>
0	10	
1	61	
2	270	
3	Too viscous to measure; added 100 ml dioxan	
18	22	
42	22	Added 4.6 ml $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ - 0.60 eq. BF_3 /eq. (NCO)
50	16	
138	16	Removed from bath

(b) The polymer was precipitated into water, washed, vacuum steam-distilled, and dried. A yield of 36.5 gm (97% of theoretical) was obtained. The product softened in the range 35 to 40°C and had an impact stability >100 cm/2 kg, relative to RDX at 29 cm/2 kg. The relative viscosity of a solution of 2.00 gm in 100 ml of acetone was 1.48 at 25°C .

Anal. calc'd for $\text{C}_{18}\text{H}_{27}\text{N}_9\text{O}_{18}$: %C, 32.88; %H, 4.14; %N, 19.18

Found: %C, 33.06; %H, 4.43; %N, 18.88

Heat of combustion calculated: 3555 cal/gm

Found: 3563 cal/gm

Heat stability tests: 65.5°C 10 min

134.5°C 11 min; exploded after
22 min

(5) Preparation of Polyurethane I-KN: Nitration of Polyurethane I-K, 3,3-Dinitro-1,5-pentane Diisocyanate and 4,4,6,8,8-Pentanitro-1,11-undecanediol

(c) JRF-116

Fifty-two ml of 100% nitric acid at 0°C was added to 5.251 gm of polyurethane I-K (JRF-113). After standing 30 min at 0°C ,

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the clear solution was poured into 1 liter of ice water and the precipitated polymer was filtered, washed, and dried. The nitrated product weighed 5.784 gm (97% of theoretical). The product softened in the range 30 to 35°C and had an impact stability of 40 cm/2 kg, relative to RDX at 29 cm/2 kg. The relative viscosity of a solution of 2.000 gm in 100 ml of acetone was 1.37.

Anal. calc'd for $C_{18}H_{25}N_{11}O_{22}$: %C, 28.92; %H, 3.37; %N, 20.62

Found: %C, 29.37; %H, 3.41; %N, 20.92

Heat of combustion calculated: 3075 cal/gm

Found: 3015 cal/gm

- (6) Preparation of Polyurethane I-L: 3,3-Dinitro-1,5-pentane Diisocyanate and 4,4,6,6,8,8-Hexanitro-1,11-undecanediol

(a) JRF-114

Equivalent amounts of the monomers (45 gm total weight) were dissolved in 66 gm of dioxan. Five ml of boron trifluoride etherate was added. This amount is equivalent to 0.59 eq. BF_3 /eq. of (NCO). The mixture evolved heat and rapidly became more viscous. After the initial reaction was over the temperature was maintained at 40°C. Viscosity of the solution vs time in hours is listed in Table XIII.

TABLE XIII

VISCOSITY OF POLYURETHANE I-L (JRF-114) AT 40°C

<u>Time</u> <u>hr</u>	<u>Viscosity</u> <u>centipoise</u>	<u>Remarks</u>
0	10	
1	50	
2	167	Efflux time 10.2 sec
17	—	Efflux time 40.5 sec; above calibration of viscosity pipette.
24	—	Efflux time 40.5 sec; added 3.5 ml $BF_3O(C_2H_5)_2$ = 0.41 eq. BF_3 /eq. (NCO)
25	—	Efflux time 33.8 sec
89	—	Efflux time 33.6 sec
137	—	Efflux time 33.6 sec; removed from bath

(b) The polymer was precipitated into water, washed, vacuum steam-distilled, and dried. A yield of 43.0 gm (95.5% of theoretical) was obtained. The product softened in the range 35 to 40°C and

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had an impact stability of 100 cm/2 kg, relative to RDX at 29 cm/2 kg. The relative viscosity of a solution of 2.00 gm in 100 ml acetone was 1.36 at 25°C.

Anal. calc'd for $C_{18}H_{26}N_{10}O_{20}$: %C, 30.78; %H, 3.73; %N, 19.94

Found: %C, 33.06; %H, 4.87; %N, 20.12

Heat of combustion calculated: 3280 cal/gm

Found: 3372 cal/gm

The analytical values are poor but better values were obtained after nitration.

Heat stability: 65.5°C 8 min

134.5°C 8 min; exploded

- (7) Preparation of Polyurethane I-LN: Nitration of Polyurethane I-L, 3,3-Dinitro-1,5-pentane Diisocyanate and 4,4,6,6,8,8-Hexanitro-1,11-undecanediol

(a) JRF-117

Fifty-two ml of 100% nitric acid at 0°C was added to 5.170 gm of polyurethane I-L (JRF-114). After standing 30 min at 0°C, the clear solution was poured into 1 liter of ice water and the precipitated polymer was filtered, washed, and dried. The nitrated product weighed 5.646 gm (97% of theoretical). It softened in the range 30 to 35°C and had an impact stability of 35 cm/2 kg, relative to RDX at 29 cm/2 kg. The relative viscosity of a solution of 2.000 gm in 100 ml of acetone was 1.28.

Anal. calc'd for $C_{18}H_{24}N_{12}O_{24}$: %C, 27.28; %H, 3.05; %N, 21.21

Found: %C, 27.85; %H, 3.12; %N, 20.79

Heat of combustion calculated: 2858 cal/gm

Found: 2823 cal/gm

- (8) Preparation of Polyurethane I-H: 3,3-Dinitro-1,5-pentane Diisocyanate and 5,5,5-Trinitro-1,2-pentanediol

(a) Since no analytical method is available, equivalence of functional groups must be determined by a trial-and-error method. In order to determine whether diol which had not been previously purified via the isopropylidene derivative might be used for polymerizations, four small-scale polymerizations of this type have been carried out. In this set of experiments the assumed purity of the diol was varied from 94 to 100%, all other variables being held constant. The relative viscosities of the polymers so obtained varied from 1.09 to 1.14.

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(b) A portion of this diol was purified through the isopropylidene derivative. Crystallization of this derivative was difficult to initiate, and the yield was very low. The derivative was subsequently hydrolyzed, the diol recovered, and another run (JKE-31) using the purified diol was made. The relative viscosity of this polymer was found to be 1.17.

(c) Conclusions

The isopropylidene purification of the diol has effected no appreciable increase in relative viscosity of polyurethane I-H. However, in view of the amount of boron trifluoride present (30 to 40 equiv.%), and the results of the polyurethane I-A—boron trifluoride concentration experiment,⁷ it may well be that the effect of equivalence on molecular weight has been masked by the effect of the high concentration of boron trifluoride. Further study is scheduled.

(d) Experimental (JKE-14, -18, -19, -20)

The monomers (20 gm total weight) were combined in 25 ml of dioxan at room temperature, and 1 ml of boron trifluoride etherate was added. A temperature of 50°C was maintained, and the viscosities of the reaction solutions were measured periodically. At constant viscosity, the reaction solutions were removed from the bath and filtered; the polymer was precipitated in water, vacuum steam-distilled at 20 to 25°C, and dried in vacuo over phosphorus pentoxide. The relative viscosities were determined in acetone solution, at a concentration of 2.000 gm/100 ml at 25°C.

(9) Preparation of Polyurethane I-AN, from Nitration of Polyurethane I-A, 3,3-Dinitro-1,5-pentane Diisocyanate and 2,2-Dinitro-1,3-propanediol

(a) Purified anhydrous nitric acid was used to nitrate the polymer JKE-12 which was insoluble in acetone and DMF.⁸ The polymer was only slightly soluble in the acid at 0°C, and only after the temperature had been raised to and maintained at 40°C for 40 min did the polymer dissolve completely.

(b) The data on the postnitrated polymer are as follows:

Polymer	Identification	Yield of Postnitrated Polymer, %	Rel. Viscosity	Heat of Combustion cal/gm (Pred. = 2320)
Polyurethane I-AN	JKE-23	94.4	1.44	2355
Polyurethane I-AN	Control*	98.0	1.40	2307

*Control was from polyurethane I-A (RCF-41) nitrated with 100% nitric acid for 30 min at 0°C. Viscosity of the polymer before nitration was 1.69.

⁷Section II, B, 2, a, (2), above.

⁸Ibid.

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(c) Conclusions

In view of the heat of combustion, which agrees well with the predicted value, it appears that the polymer has been completely nitrated; further, the agreement of the predicted and experimental heats of combustion of the postnitrated polyurethane I-A is much better than the agreement between the heats of combustion (predicted and experimental) of the unnitrated (JKE-12), demonstrating again the effect of nitric acid in removing impurities in polymers.

(d) In all previous post-polymerization nitrations, the nitric acid was purified by distillation from a sulfuric acid-nitric acid mixture at reduced pressure. The elimination of the purification step would be very desirable. However, commercially available anhydrous nitric acid contains small amounts of impurities that may affect adversely the nitration and the heat stability of the postnitrated polyurethane.

(e) To determine the utility of this commercially available nitric acid in postnitration, a sample of polyurethane I-A was nitrated according to optimum conditions determined for this polymer, 30 min at 0°C.

<u>Polymer</u>	<u>Identification</u>	<u>Yield of Postnitrated Polymer, %</u>	<u>Rel. Viscosity</u>	<u>Heat of Combustion cal/gm (Pred. = 2320)</u>
Polyurethane I-AN	JKE-21	98.2	1.44	2270, 2276
Polyurethane I-AN	Control*	98.0	1.40	2307

*Control was nitrated with distilled 100% nitric acid.

(f) Larger quantities were prepared for heat stability tests. The postnitrated polymers were washed repeatedly with distilled water to remove the nitric acid, then tested using Picatinny Arsenal test procedure No. 1401 (KI-starch paper test at 65.5°C) and the method described in OSRD 3401, p. 8 (methyl violet paper at 134.5°C).

<u>Polymer</u>	<u>Identification</u>	<u>Thermal Stability</u>		<u>Remarks</u>
		<u>KI-Starch at 65.5°C</u>	<u>Methyl Violet at 134.5°C</u>	
Polyurethane I-AN JRF-121	Nitrated with commercial acid	5 min	no failure	Slow decomposition after 13 min at 134.5°C
Polyurethane I-AN JRF-120	Nitrated with purified acid	5 min	no failure	Slow decomposition after 13 min at 134.5°C

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(g) An earlier preparation of polyurethane I-AN, described in the SPIA data sheet, failed after 14 min at 65.5°C. It was suspected that insufficient washing of the postnitrated polymer was the cause of this discrepancy. Both JRF-120 and JRF-121 were washed with dilute sodium bicarbonate solution in the Waring Blender, filtered, water-washed, and dried.

<u>Thermal Stability</u>			
<u>Polymer</u>	<u>Identification</u>	KI-Starch at 65.5°C	<u>Remarks</u>
Polyurethane I-AN (JRF-121-A)	Nitrated with commercial acid & washed with NaHCO ₃	3 min	Both samples swelled after 20 hr at 65.5°C
		150 min	
Polyurethane I-AN (JRF-120-A)	Nitrated with purified acid & washed with NaHCO ₃	>48 hr	One sample swelled after 20 hr at 65.5°C
		>48 hr	

(h) Conclusions

A thorough washing of the postnitrated polymer is essential. Commercial anhydrous nitric acid should be purified in order to obtain maximum heat stability of the postnitrated polymer.

(i) Experimental (JRF-120)

Two hundred and fifty ml of distilled anhydrous nitric acid was added to 25 gm of polyurethane I-A (JRF-38). After standing 30 min at 0°C, the clear solution was poured into 1500 ml of ice and water. The precipitated polymer was filtered, water-washed, and dried. Using Picatinny Arsenal test procedure No. 1401, KI-starch paper became colored after 5 min at 65.5°C. Using the method described in OSRD 3401, p. 8, methyl violet paper did not change color but the sample swelled and started to decompose after 13 min.

(j) JRF-121

The procedure was identical with that described above. Baker and Adamson commercial anhydrous nitric acid was used. The heat stability test results were identical with those of JRF-120.

(10) Attempted Preparation of Polyvinyl 3,3,3-Trinitropropyl Carbamate

(a) Discussion

Attempts to prepare polyvinyl 3,3,3-trinitropropyl carbamate from polyvinyl alcohol and 3,3,3-trinitropropyl

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isocyanate were described in the previous quarterly report. These attempts included the use of dioxan and dimethylsulfolane as solvents and boron trifluoride etherate as catalyst. In all cases starting material was recovered. Another attempt was made to prepare the desired carbamate, this time using polyvinyl alcohol which was specially pretreated by swelling in water and acetone. A product was obtained which was insoluble in water, but elemental analysis showed that only a small portion of the hydroxyls had reacted to form carbamate linkages. This work will be discontinued.

(b) Experimental

1 Polyvinyl alcohol (2.5 gm of low-viscosity Elvanol 70-05) was dissolved in 25 ml of water by first preparing a slurry in a small amount of water, adding more water, and heating on a steam bath. The clear solution was added to 150 ml of acetone, with stirring. The swollen polyvinyl alcohol which precipitated was collected, pressed dry, and placed in a flask attached to a Dean-Stark water trap. Benzene was added and the mixture was heated until no more water was collected. The anhydrous polyvinyl alcohol was filtered and pressed dry of benzene.

2 Swollen polyvinyl alcohol (0.3 gm) was covered with 2.0 gm of 3,3,3-trinitropropyl isocyanate and five drops of boron trifluoride etherate was added. The mixture was stirred and heated at 50°C for 18 hr, after which 2.0 ml of dimethylsulfolane was added. After stirring for a total of 96 hr, the clear, viscous mixture which resulted was poured into water. The semi-solid mass which separated was collected by centrifuging, and was then triturated several times in methanol, water, and acetone. Elemental analysis of a dried sample showed 1.13% nitrogen.

3. Polyesters

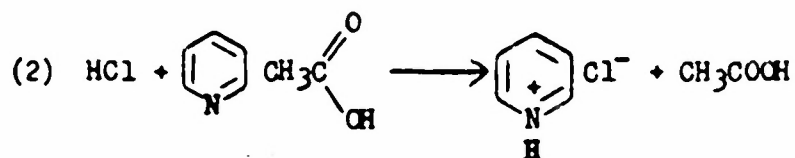
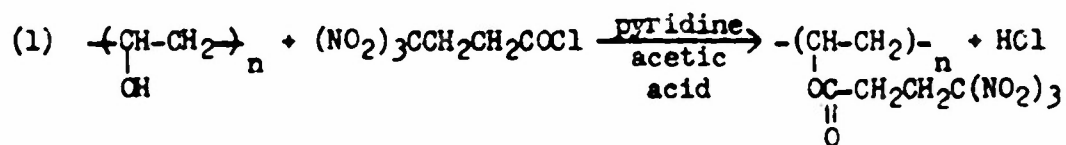
a. Attempted Esterification of Polyvinyl Alcohol - Discussion

(1) Further attempts were made to prepare polyvinyl 4,4,4-trinitrobutyrate by the direct esterification of polyvinyl alcohol. The action of 4,4,4-trinitrobutyryl chloride on polyvinyl alcohol was studied and found to give a black amorphous solid which was insoluble in water, acetone, methylene chloride, and dioxan. Quantities of hydrogen chloride gas were evolved. It appears likely that the acid catalyzed the dehydration of the polyvinyl alcohol to the corresponding conjugated olefinic polymer, thus accounting for the black color. In order to avoid this undesirable side reaction, pyridine was employed in a series of reactions, even though basic reagents are known to catalyze the decomposition of the trinitromethyl group. To avoid the effect of pyridine on the trinitromethyl group a mixture of acetic acid and pyridine was used, and it was hoped that the following reactions would take place.

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After three attempts, a substance was isolated which showed 3.57% nitrogen. However, observations during the progress of the reaction indicated some decomposition of the reactants (continuous gassing).

(2) An attempt was made to react polyvinyl alcohol with 4,4,4-trinitrobutyric anhydride and 4,4,4-trinitrobutyric acid at 90°C, at which temperature the mixture formed a melt. Boron trifluoride etherate was used as the catalyst. Polyvinyl alcohol was recovered unchanged. The same reaction at 60°C, using swollen polyvinyl alcohol and zinc chloride as a catalyst, gave a product which contained 1.02% nitrogen.

(3) The reaction between polyvinyl alcohol and 4,4,4-trinitrobutyric anhydride was tried in mixed alkane sulfonic acid (obtained from the Standard Oil Co. of Indiana, equivalent weight 110). At 0°C, polyvinyl alcohol was recovered in a highly swollen state. The same reaction, when carried out at room temperature, gave a black product which was insoluble in acetone, methanol, and water.

b. Attempted Esterification of α -Cellulose - Discussion

(1) Attempts were continued to completely esterify α -cellulose 4,4,4-trinitrobutyrate (4.17% nitrogen) with 4,4,4-trinitrobutyric anhydride and various catalysts. Since sulfuric acid appeared to be the best catalyst (8.14% nitrogen) an additional experiment was carried out in which the temperature was raised to 85°C, as compared with the temperature of 50 to 60°C used previously. The product (8.35% nitrogen) obtained, however, was not much better than the substance obtained at the lower temperature. The reaction between partially esterified α -cellulose obtained from wood pulp (SW-40-A, Brown Co.) and 4,4,4-trinitrobutyric anhydride, using sulfuric acid as a catalyst, gave a product which contained 6.45% nitrogen.

(2) The use of boron trifluoride etherate as a solvent was also warranted, since previous work showed that increasing the amount of boron trifluoride etherate increased the percent of esterification. This was tried, but only a dark brown product was isolated. It was not investigated further.

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(3) When mixed alkane sulfonic acid was used as a catalyst, a product which contained 6.07% nitrogen was obtained.

4. Polyoxyethylenes

a. Attempted Polymerization of Glycidyl 4,4,4-Trinitrobutyrate

(1) Discussion

(a) The literature⁹ indicates that alkaline catalysts lead to polyoxyethylenes of higher molecular weight than do acidic catalysts. Lohmann also cites triethyl phosphine as an effective catalyst for higher-molecular-weight polyoxyethylenes. Four alkaline agents, triethyl amine, triamyl amine, benzyl trimethyl ammonium butoxide, and powdered soft glass, have been used as catalysts for the polymerization of glycidyl 4,4,4-trinitrobutyrate. These have yielded products that are principally starting material, the relative viscosity of a 2% solution in acetone being only slightly higher than the value of 1.04 for the monomer. The dark red-brown color of the reaction product from the three amines used indicated degradation of the trinitromethyl group. Neither triphenyl nor triethyl phosphine were effective catalysts. The latter compound was sufficiently alkaline to degrade the trinitromethyl group, as indicated by the dark red-brown color developed.

(b) The acidic agents, an alkane sulfonic acid (equivalent weight, 110), boron trifluoride in carbon tetrachloride, and hydrogen chloride in carbon tetrachloride, were also ineffective as catalysts for the polymerization of glycidyl 4,4,4-trinitrobutyrate.

(2) Experimental

The experimental work is summarized in Tables

XIV and XV.

⁹H. Lohmann, in H. Staudinger, Die hochmolekularen Verbindungen (T. Springer, Berlin, 1932), p. 287; H. R. Fife and F. H. Roberts, British Patents No. 584367, 601604, 610505.

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TABLE XIV

POLYMERIZATIONS OF GLYCIDYL 4,4,4-TRINITROBUTYRATE,
CATALYZED BY ACIDIC AGENTS

<u>Run No.</u>	<u>Mol% Catalyst Based on GTNB</u>	<u>Temp., °C</u>	<u>Time hr</u>	<u>Rel. Vis., % in Acetone</u>
WB-1Ac	1 of alkane sulfonic acid	40 to 50	3	1.045
	Same batch	Room temp.	13 days	1.045
WB-2Ac	1 of hydrogen chloride	77*	12	1.045
WB-16B	1 of boron trifluoride	Room temp. 77*	16 5	1.04
WB-17B	1 of boron trifluoride	77*	18	1.04

*Reflux in carbon tetrachloride.

TABLE XV

POLYMERIZATIONS OF GLYCIDYL 4,4,4-TRINITROBUTYRATE,
CATALYZED BY ALKALINE AGENTS

<u>Run No.</u>	<u>Mol% Catalyst Based on GTNB</u>	<u>Temp. °C</u>	<u>Time hr</u>	<u>Appearance</u>	<u>Rel. Vis., % in Acetone</u>
WB-1P	1 of triphenyl phosphine	40 to 50	3	non-viscous, pale-yellow oil	1.03
WB-2P	1 of triethyl phosphine	40 to 45	24	mod. viscous, light-brown oil	1.045
WB-3P	5 of triethyl phosphine	40 to 45	18	mod. viscous, red-brown oil	1.045
WB-1A1	1 of triethyl amine	40 to 50	3	red-brown oil	1.04
WB-2A1	1 of triamyl amine	40 to 50 Room temp.	7 90	red-brown oil	1.045
WB-3A1	1 of benzyl tri- methyl ammonium butoxide	40 to 41 Room temp.	2-1/2 90	red-brown oil	1.045
WB-4A1	5% by weight of soft glass (270 to 325 mesh)	40 to 45 Room temp.	3 13 days	pale-yellow oil	1.045

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III. TECHNICAL PROGRESS: PHYSICAL STUDIES

A. SOLUBILITY PARAMETERS OF 2,2-DINITRO-1,3-PROPANEDIOL

The solubilities of 2,2-dinitro-1,3-propanediol were determined in acetone, in methanol, and in ethanol, and from these values the entropy of fusion at the melting point, ΔS_m^F , and the solubility parameter, δ_2 , of the 2,2-dinitro-1,3-propanediol were calculated.¹⁰ The results are presented in the table below. It will be noted that the entropy of fusion for this compound is unusually low.

<u>Solvent</u>	<u>Solubility</u> <u>gm/100 ml</u>	<u>Volume Fraction</u> <u>Solute, ϕ_2</u>	ΔS_m^F <u>cm³·gm-mol⁻¹</u>	δ_2 <u>(cal·cm⁻³)^{1/2}</u>
Acetone	180	0.542	3.36	10.9
Methanol	246	0.615		
Acetone	180	0.542	3.30	10.9
Ethanol	176	0.534		
Methanol	246	0.615	3.43	10.9
Ethanol	176	0.534		
			Mean 3.37	10.9

B. SPECIFIC-IMPULSE CALCULATIONS

1. During the past quarter the specific-impulse table presented in Aerojet Report No. 540, Appendix A, has been revised and greatly enlarged. These data are presented in Table XVI. The diols react with diacid chlorides, diisocyanates and formaldehyde to form polyesters, polyurethanes, and acetals, respectively. The diamines react with diacid chlorides and diisocyanates to form polyamides and polyureas, respectively. In certain special cases diols in which the hydroxyl groups are alpha to a gem dinitromethyl group may condense with diamines to produce polyamines. Values prefixed by the notation PN were calculated assuming that all hydrogen atoms bound to nitrogen in the polymer have been replaced with nitro groups, by means of a postnitration process. The prefix $\frac{PN}{2}$ denotes calculations based on the assumption that one-half of these labile hydrogens have been replaced by nitro groups; experience has shown that this "half-nitration" takes place stoichiometrically with the polyureas.¹¹

2. In addition to the above-mentioned table, calculations of specific impulse have been made for seven nitro monomers which are currently under consideration. These values are listed in Table XVII.

¹⁰Using the method described in Aerojet Report No. 538, pp. 15-19.

¹¹Aerojet Report No. 540, pp. 13-14.

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SPECIFIC-HEAT CALCULATIONS, NITRO POLYMERS

	Acid Chlorides						Diisocyanates			Aldehyde	Monomers	
	C_2H_4	$\text{C}_2\text{H}_4\text{Cl}_2$	$\text{C}_2\text{H}_3\text{Cl}_3$	$\text{C}_2\text{H}_2\text{Cl}_4$	$\text{C}_2\text{H}_2\text{Cl}_3\text{Br}$	$\text{C}_2\text{H}_2\text{Cl}_2\text{Br}_2$	$\text{C}_2\text{H}_4\text{N}_2$	$\text{C}_2\text{H}_4\text{N}_2\text{O}$	$\text{C}_2\text{H}_4\text{N}_2\text{O}_2$		$\text{C}_2\text{H}_4\text{N}_2$	$\text{C}_2\text{H}_4\text{N}_2\text{O}$
$\text{C}_2\text{H}_4\text{Cl}_2$	215	206			178	199	168	175	195			
$\text{C}_2\text{H}_3\text{Cl}_3$	206	193				191		165	188			
$\text{C}_2\text{H}_2\text{Cl}_4$	237	228	185	207	221	165	180	203	216		193	196
$\text{C}_2\text{H}_2\text{Cl}_3\text{Br}$	211	203	130	181	200	122	132	179	196		193	196
$\text{C}_2\text{H}_2\text{Cl}_2\text{Br}_2$	205	235	228	198	207	221	180	205	217		193	196
$\text{C}_2\text{H}_4\text{N}_2$	225	261	235	207	218	228	203	216	225	238	195	195
$\text{C}_2\text{H}_4\text{N}_2\text{O}$	220	212	165		206		165	189	206			
$\text{C}_2\text{H}_4\text{N}_2\text{O}_2$	180	170		150	173		58	166	171			
$\text{C}_2\text{H}_3\text{N}_3$	213	230	238	199	215	226	199	212	222	231		
$\text{C}_2\text{H}_2\text{N}_4$	212	206					167	188	199			
$\text{C}_2\text{H}_2\text{N}_3\text{O}$	170	161					96	160	166			
$\text{C}_2\text{H}_2\text{N}_3\text{O}_2$	209	234	226	197	211	221	193	207	217	220		
$\text{C}_2\text{H}_2\text{N}_3\text{O}_3$	219	212		197	209	166	176	196	206			
$\text{C}_2\text{H}_2\text{N}_3\text{O}_4$	223	218		206	216	180	188	202	211			
$\text{C}_2\text{H}_2\text{N}_3\text{O}_5$	181	215	210	178	195	206	175	183	206			
$\text{C}_2\text{H}_2\text{N}_3\text{O}_6$	208	226	220	195	206	215	191	206	213			
$\text{C}_2\text{H}_4\text{N}_2\text{O}_7$							177	197	198	191		
$\text{C}_2\text{H}_4\text{N}_2\text{O}_8$							103	172	191			
$\text{C}_2\text{H}_4\text{N}_2\text{O}_9$							122	156	185	200		

• PE - American patent notation

• PE - American half patent notation in the case of urea structures

LITERATURE

Male

$\text{C}_2\text{H}_4\text{Cl}_2$	ethylene glycol
$\text{C}_2\text{H}_3\text{Cl}_3$	trichloroethylene glycol
$\text{C}_2\text{H}_2\text{Cl}_4$	2,3-dichloro-1,3-propanediol
$\text{C}_2\text{H}_2\text{Cl}_3\text{Br}$	2-chloro-2-bromo-1,3-propanediol
$\text{C}_2\text{H}_2\text{Cl}_2\text{Br}_2$	5,5-dichloro-2,3-pentanediol
$\text{C}_2\text{H}_4\text{N}_2$	2,7,9,11-tetraamino-2,3-pentanediol
$\text{C}_2\text{H}_4\text{N}_2\text{O}$	3,3-dichloro-1,5-pentanediol
$\text{C}_2\text{H}_4\text{N}_2\text{O}_2$	2-(2-chloro-2-trimethyl-1,1,1,3,3,3-hexafluoroethyl)-1,3-butanediol
$\text{C}_2\text{H}_4\text{N}_2\text{O}_3$	5,5-dichloro-2,3-pentanediol
$\text{C}_2\text{H}_4\text{N}_2\text{O}_4$	2-(2-chloro-2-trimethyl-1,1,1,3,3,3-hexafluoroethyl)-1,3-pentanediol
$\text{C}_2\text{H}_4\text{N}_2\text{O}_5$	5,7,9-trichloro-2,3,5-triamino-1,3,11-tridecanediol
$\text{C}_2\text{H}_4\text{N}_2\text{O}_6$	5,7,9,11-tetraamino-2,3,5-triamino-1,3,11-tridecanediol
$\text{C}_2\text{H}_4\text{N}_2\text{O}_7$	4,6,8,10-tetraamino-2,3,11-undecanediol
$\text{C}_2\text{H}_4\text{N}_2\text{O}_8$	4,6,8,10,12-pentaamino-2,3,11-undecanediol

Diisocyanates

$\text{C}_2\text{H}_4\text{N}_2$	ethylene diamine
$\text{C}_2\text{H}_4\text{N}_2\text{O}$	ethanolamine
$\text{C}_2\text{H}_4\text{N}_2\text{O}_2$	3,3-dichloro-1,5-pentanediol

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Acid Chlorides

$\text{C}_2\text{H}_4\text{Cl}_2$	phosgene
$\text{C}_2\text{H}_3\text{Cl}_3$	2-chloro-2-trimethyl-1,1,1,3,3,3-hexafluoroethyl chloride
$\text{C}_2\text{H}_2\text{Cl}_4$	2-chloro-2-trimethyl-1,1,1,3,3,3-hexafluoroethyl chloride
$\text{C}_2\text{H}_2\text{Cl}_3\text{Br}$	4,6-dichloro-2,7-octanediol chloride
$\text{C}_2\text{H}_2\text{Cl}_2\text{Br}_2$	4,6,8,10-tetraamino-2,3,11-undecanediol chloride
$\text{C}_2\text{H}_2\text{Cl}_3\text{Br}_2$	4,6,8,10,12-pentaamino-2,3,11-undecanediol chloride

Diisocyanates

$\text{C}_2\text{H}_4\text{N}_2$	ethylene diisocyanate
$\text{C}_2\text{H}_4\text{N}_2\text{O}$	3,3-dichloro-1,5-pentanediol diisocyanate
$\text{C}_2\text{H}_4\text{N}_2\text{O}_2$	3,3,5,7,7-pentachloro-2,3,11-undecanediol diisocyanate
$\text{C}_2\text{H}_4\text{N}_2\text{O}_3$	3,3,5,5,7,7-hexamino-2,3,11-undecanediol diisocyanate

Aldehyde

$\text{C}_2\text{H}_4\text{O}$	formaldehyde
--------------------------------	--------------

TABLE XVII
SPECIFIC-IMPULSE CALCULATIONS, NITRO MONOMERS

	Specific Impulse (lbf sec lbm ⁻¹)	Heat of Combustion (cal gm ⁻¹)	Molecular Weight	Percentage Composition		
				C	H	N
C ₅ H ₉ N ₃ O ₇	224	3102	223	26.9	4.0	18.8
C ₈ H ₁₁ N ₃ O ₈	187	3708	277	34.7	4.0	15.2
C ₈ H ₁₂ N ₄ O ₇	181	3969	276	34.8	4.3	20.3
C ₈ H ₁₁ N ₅ O ₉	220	3367	321	29.9	3.4	21.8
C ₅ H ₇ N ₃ O ₇	239	3189	221	27.1	3.2	19.0
C ₅ H ₇ N ₃ O ₆ (trans)	239	3406	205	29.3	3.4	20.5
C ₅ H ₇ N ₃ O ₆ (cis)	242	3438	205	29.3	3.4	20.5
C ₅ H ₉ N ₃ O ₈	239	2703	239	25.1	3.8	53.6
C ₇ H ₁₁ N ₅ O ₁₁	226	2752	341	24.6	3.2	20.5

LEGEND

C ₅ H ₉ N ₃ O ₇	5,5,5-trinitro-2-pentanol	$\text{C}(\text{NO}_2)_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$
C ₈ H ₁₁ N ₃ O ₈	(5,5,5-trinitro-2-pentyl) acrylate	$\text{C}(\text{NO}_2)_3(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{OCCH}=\text{CH}_2$
C ₈ H ₁₂ N ₄ O ₇	N-(5,5,5-trinitro-2-pentyl) acrylamide	$\text{C}(\text{NO}_2)_3(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{NHCCH}=\text{CH}_2$
C ₈ H ₁₁ N ₅ O ₉	N-nitro-N-(5,5,5-trinitro-2-pentyl) acrylamide	$\text{C}(\text{NO}_2)_3(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{N}(\text{NO}_2)\text{CCH}=\text{CH}_2$
C ₅ H ₇ N ₃ O ₇	poly-1-(2',2',2'-trinitroethyl)-1,2-propyleneglycol	$\text{C}(\text{NO}_2)_3\text{CH}_2\text{CH}(\text{CH}_2\text{CH}(\text{NO}_2)_2)_2$
C ₅ H ₇ N ₃ O ₆ (trans)	5,5,5-trinitro-2-pentene	$\text{C}(\text{NO}_2)_3\text{CH}_2\text{CH}=\text{CHCH}_3$
C ₅ H ₇ N ₃ O ₆ (cis)	5,5,5-trinitro-2,3-pentenediol	$\text{C}(\text{NO}_2)_3\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_3$
C ₅ H ₉ N ₃ O ₈	2,2,6,6,6-pentanitro-4-(hydroxymethyl) hexane	$\text{CH}_3\text{C}(\text{NO}_2)_2\text{CH}_2\text{CH}(\text{CH}_2\text{C}(\text{NO}_2)_3)\text{CH}_2\text{OH}$

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IV. TECHNICAL PROGRESS: RHEOLOGY OF NITRO POLYMERS

A. INTRODUCTION

1. The following material is an excerpt from work conducted under Contract NOa(s) 52-359.

2. The rheological properties of various experimental nitro polymers synthesized at Aerojet are to be determined for use in (a) the selection of materials for further investigation, (b) the selection of suitable propellant-grain manufacturing processes, and (c) the characterization of the mechanical properties of nitro polymers at the various temperatures to which propellant grains are exposed in application. The rheological data are to be fitted by a suitable equation of state.

B. FABRICATION OF SPECIMENS

1. Attempts to extrude the polyurethane, I-A, of 3,3-dinitro-1,5-pentanediiisocyanate and 2,2-dinitro-1,3-propanediol through a 3/32-in. die have been unsuccessful. The maximum pressure, 19,000 psi, of the extrusion press did not cause extrusion below 200°F, but at 220°F a greatly enlarged strand of porous material with a specific gravity of only 0.64 was produced. The specific gravity of a pellet molded with the Carver press was 1.57. Apparently the polymer decomposed to some extent at the high extrusion temperature. A 3/16-in. die will be made to permit extrusion at lower temperatures.

2. Sheets of nitro polymers listed in Table XVIII were pressed on the Carver platen press, but the sheets were brittle and could not be cut to size. Strip specimens of polyurethane I-A were pressed under the Carver press

TABLE XVIII

COMPRESSION MOLDING OF SHEET SPECIMENS OF NITRO POLYMERS

Identification	I-A	II-A	III-A
Composition	Polyurethane of 3,3-dinitro-1,5-pentane-diisocyanate and 2,2-dinitro-1,3-propanediol	Polyester of 4,4-dinitro-1,7-heptanedioyl chloride and 2,2-dinitro-1,3-propanediol	Polyurea of 3,3-dinitro-1,5-pentane-diisocyanate and 3,3-dinitro-1,5-pentanediamine
Molding Temp., °F	160 to 180	Various	220 to 240
Molding Press., psi	1800	Various	1400
Results	Brittle, could not be cut on a hot plate at 160°F	Crazed upon cooling	Brittle, could not be cut

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IV Technical Progress, B (cont.)

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inside a 1/2-in. x 1-7/8-in. x 0.020-in. confining shim. These were used in subsequent creep tests. However, a molding die for pressing strip specimens to final dimensions without cutting has been designed, and will be constructed to permit preparation of specimens with more closely controlled dimensions.

C. CREEP MEASUREMENTS

1. The creep of polyurethane I-A at 160°F has been measured under an initial stress of 275 psi for a period of 100 sec, which corresponds to a logarithmic strain of 42.6%. The final stress was estimated to be 0.9 of the initial stress. The test was interrupted by a mechanical interference within the rheometer. A log-log plot of compliance, which is the reciprocal of the apparent modulus, vs time is shown in Figure 8. After the test, the specimen was observed to be markedly nonuniform in cross-sectional area.

2. Creep tests on polyurea III-A have been run at temperatures from 138 to 176°F and at stresses from 420 to 1610 psi for periods as long as 19 hr. From these data plots of log compliance vs log time were made; these plots are shown in Figure 9. The overlapping of curves for different temperatures indicates the need for additional studies of the reproducibility of the measurements at a single temperature.

3. An investigation of the error in compliance resulting from errors in the determination of elongation was made. The following values were calculated for errors of 1 and 3 mm in the determination of elongation, assuming an initial length of 25.4 mm.

Specimen Length mm	Compliance Error, %	
	1 mm	3 mm
26	194	583
28	37.5	113
30	20.00	60

Hence, if the specimen slips or if there is slack or unnecessary stretching, the compliance may be greatly in error. Because of the magnitude of this effect, the specimen clamp holders have been fixed rigidly to their supports by means of screws, in an effort to obtain reproducible data. Although the initial length of the specimen will not be known accurately, it will always be the same for each run.

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IV Technical Progress, C (cont.)

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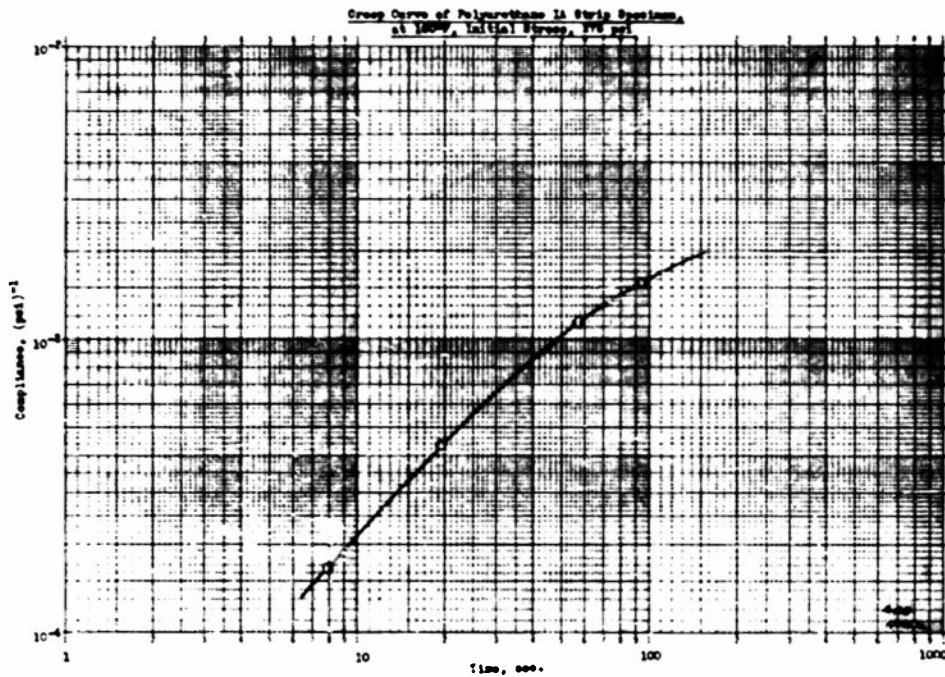
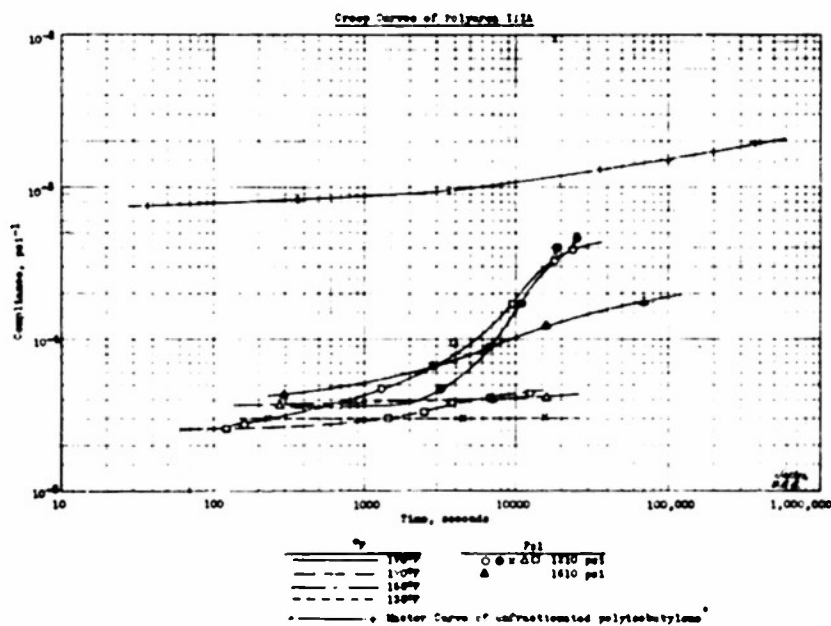


Figure 8



• E. Hurt and A. V. Tobolsky, "Phys. Chem. of High Polymeric Systems", 333

Figure 9

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D. BUBBLE FORMATION IN POLYUREA III-A AT ELEVATED TEMPERATURES

At elevated temperatures during creep tests the occurrence of small bubbles in polyurea III-A has been observed. It was necessary to determine whether these bubbles were the result of decomposition or moisture in the polymer. A sample pressed on the Carver press was placed in an evacuated tube connected to a manometer. The whole system was then heated to 78.6°C, and the pressure was recorded periodically. After 900 min the pressure of the evolved gases leveled off. When the temperature was raised to 83.0°C, the pressure increased and then leveled off again. Use of the ultimate pressure obtained and of the perfect-gas-law expression yielded an average molecular weight of 19. In addition, at room temperature the pressure of the gaseous products corresponded to the vapor pressure of water at that temperature. Because the pressure did not increase continuously, as might be expected in decomposition, the evidence suggests that water is sorbed in the polymer.

V. TECHNICAL PROGRESS: BALLISTIC STUDIES

A. INTRODUCTION

1. The following discussion is an excerpt from work conducted under Contract NOa(s) 52-359.

2. The present report introduces a new phase in the nitro polymer program. The purpose of this phase will be to determine the various ballistic properties of formulated nitro polymers so as to evaluate their utility as potential solid propellants. Some initial studies on the Crawford-bomb burning rate of polyurethane I-A are described in this report.

B. CRAWFORD BOMB BURNING RATES OF POLYURETHANE I-A

1. Small samples, which were cut from a molded disk of polyurethane I-A (from 3,3-dinitro-1,5-pentane diisocyanate and 2,2-dinitro-1,3-propanediol) were burned at 60°F in a Crawford bomb. The burning rates obtained were:

<u>Pressure</u> <u>psia</u>	<u>Burning Rate at 60°F</u> <u>(0.5-in. interval)</u> <u>in. sec⁻¹</u>
515	0.0815
1015	0.114
2015	0.215

The results are plotted in Figure 10.

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Chamber Pressure vs Burning Rate

II-JE-3 Propellant

Rate for 1/8" interval

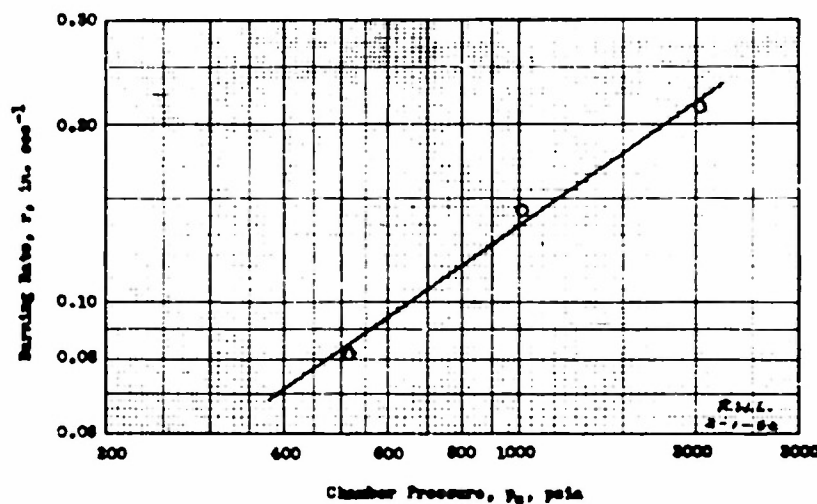


Figure 10

2. The pressure exponent n , in the burning rate equation

$$r = cp^n$$

where r is the linear burning rate in in. sec⁻¹, p is the pressure in psia, and n and c are constants, is approximately 0.7 over the pressure range from 515 to 2015 psia. The burning rate of this propellant at a given pressure is therefore about half that of the Aeroplex propellant AN-525J.

3. The autoignition temperature of the propellant was 445°F, as compared with 490 to 510°F for an Aeroplex AN-525 propellant. The autoignition temperature is the temperature at which a small sample inserted in a copper block will ignite when the block is heated at a fixed rate of 17 to 20°F min⁻¹.

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VI. TECHNICAL PROGRESS: ORGANIC SYNTHESIS

A. PREPARATION OF NITRO OLEFINS

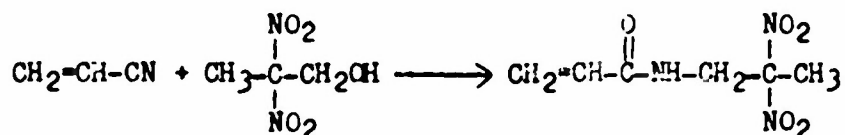
1. Introduction

Polymerizable nitro olefins continue to be of great interest for the preparation of propellant materials. Those of particular interest are the acrylates and methacrylates of polynitro alcohols. The present report deals with the establishment of improved procedures for the preparation of 2,2-dinitrobutyl and 2,2-dinitropropyl acrylate. In addition, a description of work leading to the preparation of substituted acrylic acids containing nitro groups is presented. Dehydration studies on 5,5,5-trinitro-2-pentanol, in order to prepare a trinitropentene, are also described.

2. The Preparation of Esters of Polynitro Alcohols

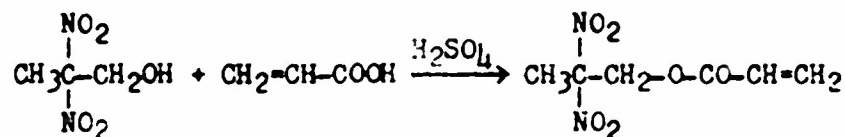
a. Discussion

(1) Plaut and Ritter¹² reported the reaction of secondary and tertiary alcohols with unsaturated nitriles such as acrylonitrile, to yield unsaturated amides. The following equation indicates how this reaction could be used to prepare nitroacrylamides:



Using the procedure reported, a mixture of 2,2-dinitro-1-propanol and acrylonitrile in sulfuric acid yielded no water-insoluble material. When a solution of 2,2-dinitro-1-propanol and acrylonitrile in acetic acid was treated with sulfuric acid and poured onto ice, an oil was obtained which was identified as 2,2-dinitro-1-propyl acetate instead of the expected amide.

(2) In order to make use of this reaction for the preparation of acrylates, a solution of 2,2-dinitro-1-propanol in an excess of acrylic acid was treated with sulfuric acid. The reaction, which proceeded according to the equation



¹²J. Am. Chem. Soc., 73, 4076 (1951).

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gave a 56% yield of crude ester which on distillation yielded an oil with the proper refractive index.

(3) 2,2-Dinitro-1-butanol in excess acrylic acid was treated with sulfuric acid at room temperature in a manner similar to that used in the preparation of the corresponding propyl derivative. This gave the crude acrylate in a yield of 34%.

(4) In view of the small yields, this method of preparation of the dinitroacrylates does not seem to possess an advantage over the old method. This is especially true since this new method probably does not obviate the problem of purification of the acrylate ester itself.

b. Experimental

(1) 2,2-Dinitropropyl acrylate: An Erlenmeyer flask was charged with 15-ml acrylic acid (containing 0.1% trinitrobenzene) and 6 gm (0.04 mol) of 2,2-dinitro-1-propanol. The addition of 7 gm sulfuric acid to this solution caused darkening and some heat evolution. After standing overnight the mixture was poured onto ice and water. The heavy oil was taken up with 25 ml methylene chloride. The methylene chloride solution was washed twice with water, dried for a short time over anhydrous sodium sulfate, and evaporated to dryness. The residue was 4.5 gm (56%) of an oil. Some of this material was distilled from a bulb tube at 0.5 μ pressure and in an air bath at 70 to 80°C. A faintly yellow distillate resulted ($n_D^{25} = 1.4590$). The reported value for 2,2-dinitro-1-propyl acrylate is $n_D^{25} = 1.4600$.

(2) 2,2-Dinitrobutyl acrylate: A flask was charged with 6.4 gm (0.04 mol) of 2,2-dinitro-1-butanol and 10 ml (0.15 mol) of acrylic acid (containing 0.1% trinitrobenzene). To this solution was added 5 ml sulfuric acid. This caused darkening and heat evolution. A small sample added to water produced only a trace of oil. After standing at room temperature for two days, the mixture was poured onto ice and water. This gave a heavy brown oil. The mixture was extracted first with 50 ml, then with 25 ml cyclohexane. Not all the brown oil dissolved. The cyclohexane solution was washed well with water and after addition of a small quantity of trinitrobenzene, dried over sodium sulfate. On evaporation, there was left 3 gm (34%) of an oil, $n_D^{25} = 1.4585$. The reported value for 2,2-dinitro-1-butyl acrylate is $n_D^{25} = 1.4575-83$.

3. The Purification of Dinitrobutyl Acrylate

a. Discussion

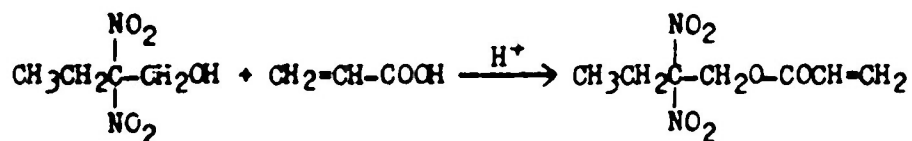
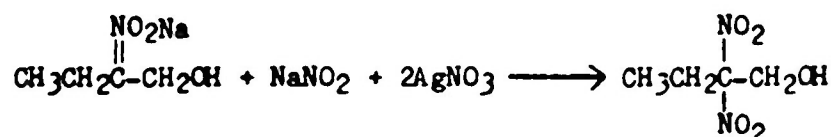
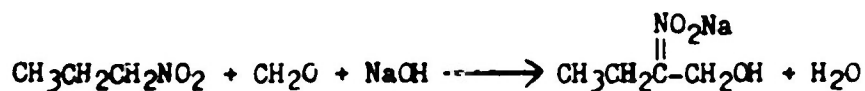
(1) Dinitrobutyl acrylate has been found to be an important basic fuel for solid propellants in the nitro polymer and Aeroplex

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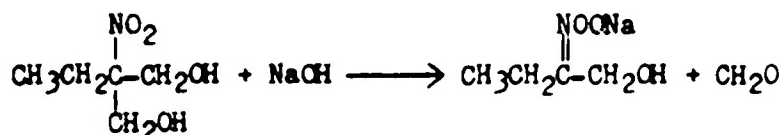
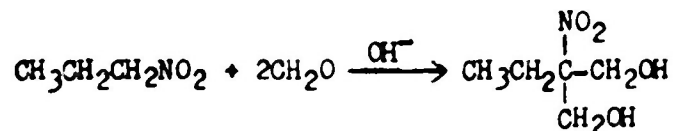
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programs. In addition, dinitrobutyl acrylate is used in its polymeric form for the coating of RDX. The compound was originally prepared according to the following equations:



This synthesis seems, at first sight, to be straightforward. However, although the physical constants and analysis corresponded with the predicted, several batches of this compound exhibited different physical properties on polymerization.

(2) The following factors must be considered if dinitrobutyl acrylate is to be purified, since the purification cannot be accomplished by distillation or by crystallization. The chemistry of the preparation of 2,2-dinitrobutanol is more involved than can be expressed by the simple equation above. The conversion of 1-nitropropane to sodium 2-nitrobutanol using formaldehyde and sodium hydroxide actually does not proceed according to the over-all equation listed above, but according to the following two equations:



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The first reaction is very rapid. The second reaction, in which the formation of the ~~aci~~-sodium salt liberates formaldehyde, is slow. The liberated formaldehyde is in turn consumed again in the first reaction with the remaining nitropropane; thus the process starts again, and this cycle continues until all the nitropropane is consumed. However, in these reactions some of the side products, i.e., unreacted 1-nitropropane in form of its sodium salt and 2-ethyl-2-nitro-1,3-propanediol, will always be carried down in the main product. The whole system is water-soluble and may consequently be used for the oxidative nitration.

(3) Because most of the solution used is sodium mononitrobutanol it is safe to say that the main product after the oxidative nitration will be 2,2-dinitrobutanol. The side products of the first step in the reaction must also be considered in the oxidative nitration. The 2-ethyl-2-nitro-1,3-propanediol does not take part in the oxidative nitration, but the sodium salt of 1-nitropropane will be converted into the 1,1-dinitropropane. In addition, because of the pH change during the oxidative nitration some of the sodium salt of 2-nitrobutanol will be reconverted to 2-nitrobutanol.

(4) In the esterification all the alcohols present are converted into the acrylates in a straightforward reaction and only minor impurities can be expected as side products during the time-consuming esterification at reflux temperature. Therefore, in the final reaction mixture, it is necessary to consider the presence of the following products:

Main product: 2,2-dinitrobutyl acrylate

Side products: 2-nitrobutyl acrylate

2-ethyl-2-nitro-1,3-propanediol
diacrylate

1,1-dinitropropane

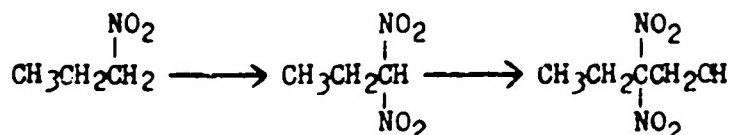
1,1-Dinitropropane is separated during the workup procedure. However, the other esters will give a mixture which is not readily purified. These impurities function as crosslinking agents and are responsible for the peculiar behavior of the 2,2-dinitrobutyl acrylate in the polymerization. Instead of soluble rubber-like products, acetone-insoluble crosslinked polymers were obtained.

(5) In conclusion, the process requires a method of preparing 2,2-dinitrobutanol in pure form before the esterification. Low-temperature crystallization has been tried and was found unsatisfactory because of the lack of suitable solvents. Another method would involve a change of the present preparation, in that 1-nitropropane would be converted according to the method of Shechter and Kaplan into 1,1-dinitropropane, which can easily be purified by distillation. Finally, the Henry reaction would lead to the desired 2,2-dinitrobutanol, free of side products, according to the following equation:

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(6) The final step in the preparation is the esterification of 2,2-dinitrobutanol and acrylic acid. This is a slow reaction and is completed after a long reflux time in benzene by separating the water azeotropically. Small amounts of NO₂ fumes were evolved, indicating some decomposition. Although only very minor impurities are expected in this reaction, these must be separated in order to prepare pure dinitrobutyl acrylate. These impurities occur even when pure 2,2-dinitrobutanol is used initially. They are greenish-yellow in color and are distilled with the first 25% of product. These fractions do not differ greatly in refractive index from a polymerizable, analytical sample of 2,2-dinitrobutyl acrylate, but they do not polymerize at all. However, the heat of combustion indicates impurities of lower carbon content. Apparently these impurities prevent the polymerization. The remaining 75% of the product does polymerize and gives rubbery, acetone-soluble polymers.

(7) Some impurities were eliminated by washing the benzene solution of the ester with 5% aqueous sodium carbonate, 0.1N sodium hydroxide, and 10% aqueous sodium bisulfite. Although a large quantity of colored material was removed, those fractions which did not polymerize previously continued to resist polymerization after these additional washings. The heat of combustion of cuts I, III, and V gave the following values before and after washing with sodium carbonate and sodium bisulfite.

<u>Cut</u>	<u>Before Washing</u> cal/gm	<u>After Washing</u> cal/gm	<u>Theory</u> cal/gm
I	3969	4047	4100
III	3994	4053	4100
V	4029	4030	4100

The improvement is apparent but still not quite satisfactory. Work on this purification will be continued.

b. Experimental

(1) 1,1-Dinitropropane

A three-necked flask provided with a stirrer, dropping funnel, and thermometer was charged with 220 (5.5 mols) of sodium

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hydroxide and 600 ml of water. At a temperature below 20°C, 445 gm (5.0 mols) of 1-nitropropane was introduced dropwise and stirred for 1 hr. The solution of 380 gm (5.5 mols) of technical sodium nitrite was then added and stirred for an additional 15 min. In the meantime 1100 gm of silver metal was dissolved in 1000 ml of 70% nitric acid, diluted with 2000 ml of water, and neutralized with 50% sodium hydroxide solution to a pH of 4.2. The solution of the acisodium salt of the 1-nitropropane-sodium nitrite complex was poured into the silver nitrate solution at 0°C. The white precipitate turned black and finally greenish gray. After stirring for 45 min, 400 gm of 50% sodium hydroxide solution was added dropwise, keeping the temperature at 10 to 15°C. After the addition was completed the pH was 11.8. The silver precipitate was then collected on a filter and washed twice with 500-ml portions of water. The clear yellow filtrate was acidified with a mixture of 250 ml conc. sulfuric acid and 1000 ml water at a temperature below 20°C. The pH was 2 after all the sulfuric acid had been added. The oily 1,1-dinitropropane was separated in a separatory funnel to yield 487 gm of material, $n_D^{25} = 1.4350$. Purification by distillation gave 459 gm of colorless product, $n_D^{25} = 1.4323$.

(2) 2,2-Dinitrobutanol

A three-necked flask provided with a stirrer, thermometer, and dropping funnel was charged with 134 gm (1 mol) of 1,1-dinitropropane and 536 ml water. A solution of 44 gm (1.1 mols) of sodium hydroxide and 90 ml water was added dropwise at 25°C within 15 min. After additional stirring for 5 min, 86 gm (1.05 mols) of 37% aqueous formaldehyde solution was added and stirred for 1 hr. A solution of 49 gm conc. sulfuric acid in 450 ml water was then added dropwise over a period of 2 hr at 20 to 25°C. After additional stirring for 1 hr, the mixture was extracted twice with 150-ml portions of methylene chloride. The methylene chloride solutions were dried over sodium sulfate and concentrated in vacuum. The residue gave 133 gm of 2,2-dinitrobutanol, mp -3 to -5°C, $n_D^{25} = 1.4581$.

(3) 2,2-Dinitrobutyl Acrylate

(a) A 12-liter flask provided with a Dean-Stark water trap was charged with 1230 gm (7.5 mols) of crystallized 2,2-dinitrobutanol, 649 gm (9 mols) acrylic acid and 6000 ml benzene. Fifty gm of copper turnings was added as a polymerization inhibitor. The refluxing mixture was charged at 12-hr intervals with a total of 31 ml conc. sulfuric acid and in a period of 186 hr a total of 138 ml water (7.1 mols) was collected by azeotropic distillation. The mixture was then washed three times with 1000-ml portions of 10% sodium bicarbonate, and twice with 1000 ml water. After drying over sodium sulfate the remaining oil was distilled:

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Cut	Color	Vacuum microns	Head Temp. °C	Pot Temp. °C	Yield gm	n_D^{25}
I	green	55	84 to 86.5	93	54	1.4568
II	yellow	55	86.5 to 87.5	93 to 95	224	1.4578
III	yellow	50	87.5 to 86	95 to 97	318	1.4583
IV	slightly colored	20	74.5 to 75	93 to 95	298	1.4581
V	colorless	18	75 to 76	105 to 110	208	1.4581
VI	colorless	18	74 to 75	110	22	1.4582

Cuts I and II did not polymerize in bulk after 48 hr at 45°C using 1% MAKP; cuts III to VI gave rubbery, acetone-soluble polymers.

(b) Each of these cuts was dissolved in 1000 ml benzene and extracted four times with 5% aqueous sodium carbonate, twice with 0.1N sodium hydroxide, and once with aqueous sodium bisulfite solution. Each fraction was distilled after the benzene was removed.

Cut	Color	Vacuum mm	Head Temp. °C	Pot Temp. °C	Yield gm	n_D^{25}
I	colorless	1.5	91 to 94	95 to 96	34	1.4576
II	slightly yellow	2	95	101 to 102	169	1.4583
III	slightly yellow	1	92 to 93	95 to 96	268	1.4582
IV	slightly yellow	1.5	92.5 to 94	98 to 96	212	1.4582
V & VI	colorless	1.5	93	98 to 100	179	1.4584

The attempts to polymerize cuts I and II were still unsuccessful; cuts III, IV, and V gave rubbery, acetone-soluble polymer, using 1% MAKP at 45°C for 48 hr. The alkali-soluble fractions were acidified and extracted with methylene chloride. The yields were as follows:

Cut	Yield	n_D^{25}
I	4.1 gm	$n_D^{25} = 1.4362$
II	18.7 gm	$n_D^{25} = 1.4399$
III	12.2 gm	$n_D^{25} = 1.4370$
IV & V	less than 1 gm	

Distillation of the combined extracts gave 14.2 gm of 1,1-dinitropropane, $n_D^{25} = 1.4325$, bp 41 to 43°C at 2 mm. The residue appeared to be 2,2-dinitrobutanol (14.5 gm, $n_D^{25} = 1.4562$).

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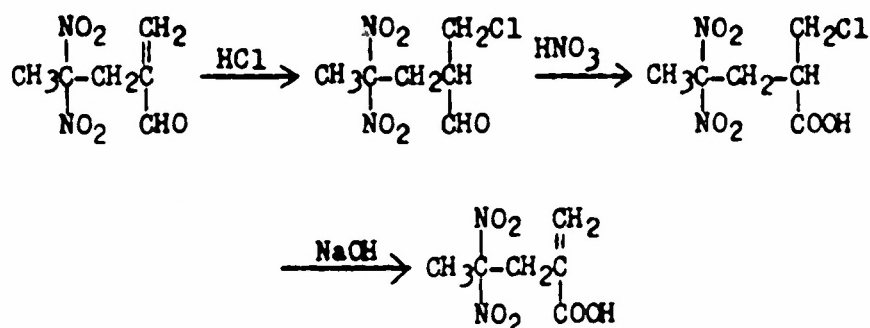
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4. The Preparation of α -(2,2-Dinitropropyl) Acrylic Acid

a. Discussion

(1) The conversion of α -(2,2-dinitropropyl) acrolein into the methyl α -(2,2-dinitropropyl) acrylate was discussed in an earlier report.¹³ The method reported is applicable to all alcohols which withstand treatment with base. However, for the preparation of alkali-sensitive esters, such as those containing the trinitroethyl group, another method must be developed. One possible method might be the esterification of the free α -(2,2-dinitropropyl) acrylic acid with the desired alcohol.

(2) The preparation of α -(2,2-dinitropropyl) acrylic acid was conducted according to the following equation:



The first and second steps have been described previously.¹⁴ On treatment of the β -chloro- α -(2,2-dinitropropyl) acrylic acid with 2 mols of sodium hydroxide in aqueous solution the double bond was introduced by the removal of hydrogen chloride. This reaction is apparently accompanied by a competing side-reaction, because on acidification of the reaction solution, NO_2 is evolved. This indicates that some degradation occurs as a result of the treatment. The new acid was obtained in fair yield and has a melting point of 116°C.

(3) Other reactions of the α -(2,2-dinitropropyl) acrolein have been attempted without success. The conversion of α -substituted

¹³ Aerojet Report No. 563 (31 December 1951), pp. 56-60.

¹⁴ Ibid.

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acroleins into the corresponding nitriles by treating the oximes of the aldehyde with acetic anhydride has been reported.¹⁵ The method failed in the attempt to prepare the oxime of α -(2,2-dinitropropyl) acrolein. The classical method of converting aldehydes into acid is the treatment of aldehydes with wet silver oxide. In the case of α -(2,2-dinitropropyl) acrolein only a minor amount was transformed into acidic material.

b. Experimental

In an Erlenmeyer flask 2 gm of β -chloro- α -(2,2-dinitropropyl) acrylic acid was dissolved in a solution of 0.9 gm sodium hydroxide and 25 ml water. A small temperature rise was noticed. After 4 hr at room temperature the brown solution was acidified with 5 ml of 30% sulfuric acid. Red fumes of NO_2 were evolved and an oil was formed, which crystallized upon scratching. The crystals were collected and dried to yield 0.4 gm. The acid was dissolved in carbon tetrachloride and the solution was concentrated. On addition of hexane the crystals formed were collected and recrystallized several times from *n*-hexane. The melting point was 114 to 116°C.

Anal. calc'd for $\text{C}_6\text{H}_8\text{N}_2\text{O}_6$: %C, 35.30; %H, 3.95; %N, 13.73

Found: %C, 35.67; %H, 4.18; %N, 13.92

5. The Preparation of Methyl α -(2,2-Dinitropropyl) Acrylate

a. Discussion

(1) The preparation of methyl α -(2,2-dinitropropyl) acrylate has been described previously.¹⁶ In the preparation of a greater amount of this compound it was observed that instead of reformation of the double bond by treatment of the ester of 3-chloro-2-(2',2'-dinitropropyl) propionic acid with sodium methoxide, a methoxyl group was substituted for the chlorine. The new compound is the methyl 3-methoxy-2-(2',2'-dinitropropyl) propionate.

(2) In order to avoid introduction of the methoxyl group the dehydrohalogenation was carried out using pyridine in methanol solution. The methyl α -(2,2-dinitropropyl) acrylate was obtained in the same yield without side products.

b. Experimental

(1) Methyl 3-Methoxy-2-(2',2'-dinitropropyl) Propionate

(a) A round-bottomed flask was charged with 100 gm 3-chloro-2-(2',2'-dinitropropyl) propionic acid, 100 ml methanol, and 50 ml conc. sulfuric acid. The mixture was refluxed for 2 hr on a steam bath.

¹⁵ B. C. Marvel, W. R. Miller, and L. C. Chou, J. Am. Chem. Soc. 72, 5408 (1951); D. T. Mowry and R. R. Morner, J. Am. Chem. Soc. 69, 1331 (1947).

¹⁶ Aerojet Report No. 562, p. 56.

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The solution was then diluted with 1000 ml methylene chloride and extracted with 500 ml water. The aqueous phase was extracted once more with 250 ml methylene chloride. The combined methylene chloride extracts were washed twice with 500 ml water, once with 500 ml of 2% aqueous sodium bicarbonate, and once with 500 ml water. The methylene chloride solution was dried over sodium sulfate and filtered, and the solvent was evaporated. The residue was the methyl 3-chloro-2-(2',2'-dinitropropyl) propionate.

(b) This residue was dissolved in 200 ml methanol and a solution of 14 gm sodium metal in 300 ml methanol was added. After refluxing for 3 hr the mixture was diluted with 1000 ml methylene chloride and extracted with 500 ml water. The aqueous phase was extracted once more with 250 ml methylene chloride. The combined methylene chloride solution was washed with water, 5% hydrochloric acid, and water. The solution was dried over sodium sulfate and evaporated. The methyl 3-methoxy-2-(2',2'-dinitropropyl) propionate distilled at 1 micron at 96 to 98°C. The yield was 38 gm, $n_D^{25} = 1.4552$.

Anal. calc'd: %OCH₃, 24.81

Found: %OCH₃, 23.25

(2) Methyl α-(2,2-Dinitropropyl) Acrylate

The ester, as obtained above, was dissolved in 150 ml methanol and 150 ml pyridine. The mixture turned brown at reflux temperature and was held on a steam bath under reflux for 5 hr, during which time the methanol was removed by distillation. The brown pyridine solution was permitted to stand overnight. Then 1000 ml methylene chloride was added and the solution was washed with 500 ml water, 5% hydrochloric acid, and again with water. The pyridine-free methylene chloride solution was dried over sodium sulfate and concentrated. The residue distilled at 3 microns at 78°C to yield 38 gm, $n_D^{25} = 1.4675$.

Anal. calc'd for C₇H₁₀N₂O₆: %C, 38.53; %H, 4.62; %N, 12.84

Found: %C, 38.70; %H, 4.82; %N, 12.37

6. Preparation of 5,5,5-Trinitro-1 or -2-pentene

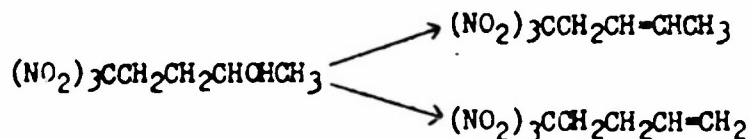
a. Discussion

During an investigation of another reaction it was found that treatment of 5,5,5-trinitro-2-pentanol with an approximately equivalent volume of sulfuric acid yielded a homogeneous solution which, when heated, reacted exothermically and separated to yield a colorless organic phase. This oil was separated and distilled; the analysis corresponded well with that of the 5,5,5-trinitro-2-pentene. It should be noted that the dehydration of this trinitropentanol can give either the 1- or 2-pentene, although the 2-pentene is probably formed preferentially.

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A study is currently in progress to elucidate the structure of the trinitropentene, inasmuch as it has become an important intermediate for further chemical synthesis.

b. Experimental

A 100-ml, three-necked, round-bottomed flask fitted with a mechanical stirrer and internal thermometer was charged with 25 gm of molten 5,5,5-trinitro-2-pentanol. With gentle stirring, 30 ml conc. sulfuric acid was added all at once. The temperature rose to 55°C (when only a small amount of sulfuric acid was added, decomposition with brown fumes took place). An acetone-dry-ice bath was available for quick cooling. The stirrer was so adjusted that it gave mild stirring with no turbulence; i.e., when two layers were present it stirred but did not mix them. With mild stirring, the mixture was cautiously heated with a Bunsen burner to 81°C, whereupon the temperature began to rise spontaneously. When it reached 100°C, the mixture was cooled to 95°C and a large colorless phase was noted. When the temperature reached 100°C it was again cooled, without stirring, to 35°C. The top phase and the sulfuric acid layer were extracted separately with hexane. The combined hexane extracts from two such runs were washed well with water, dried over Drierite, and distilled. Most of the hexane was removed through a 30-in. helices-packed column. The residual hexane was removed in vacuo. The remaining light-colored oil weighed 17 gm and had a characteristic camphor-like odor. It was distilled at 1 micron, yielding 15 gm (33%) of colorless liquid, bp 32°C, $n_D^{25} = 1.4613$. The refractive index of the material distilled from three separate preparations has never varied more than .0001. A sample from another preparation was distilled twice, $n_D^{25} = 1.4613$, $d_4^{25} = 1.3144$, and submitted for analysis.

Anal. calc'd for $\text{C}_5\text{H}_7\text{N}_3\text{O}_6$: %C, 29.27; %H, 3.44; %N, 20.48

Found: %C, 29.60; %H, 3.44; %N, 19.67, 19.74

B. PREPARATION OF NITRO ALCOHOLS

1. Introduction

Hitherto the only methods available for the synthesis of nitro alcohols have been by means of the Henry and the Hunsdiecker reactions. The development of the sodium borohydride reduction of nitro carbonyl compounds such as ketones, aldehydes, and acid chlorides to nitro alcohols has aided considerably in the preparation of these very necessary reagents. The present report deals with the preparation of 4,4,4-trinitro-1-butanol. This alcohol, when converted to the acrylate ester, should lead to a polymer having an estimated specific impulse of 200 lbf sec/lbm.

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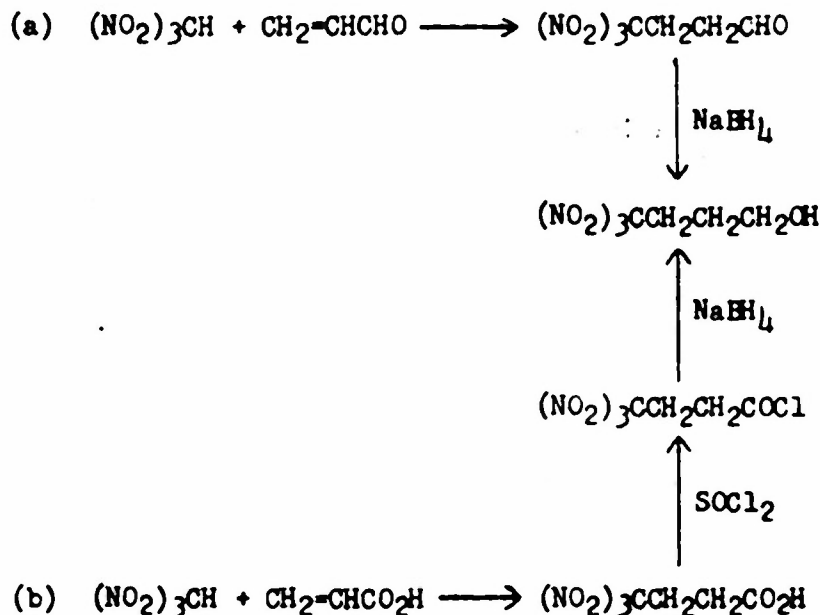
VI Technical Progress, B (cont.)

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2. Preparation of 4,4,4-Trinitro-1-butanol

a. Discussion

(1) There are two probable synthetic routes to 4,4,4-trinitro-1-butanol:



(2) This alcohol was first characterized from the product of reactions that proceed via route (b).¹⁷ Shechter¹⁸ has reported the isolation of a crude material containing the alcohol prepared via route (a). Route (a) appeared to be the most direct approach and has been further investigated. Shechter reported the addition of nitroform to acrolein in ether solution. Since the Michael condensation with nitroform is known to proceed better in aqueous media, a solution of acrolein in water was added to a solution of nitroform in water at 0°C. This yielded a heavy oil which was dissolved in methanol and immediately treated with sodium borohydride. There resulted a 50% yield of a crude material whose refractive index did not change on distillation. This oil was not the expected trinitrobutanol, as evidenced by the fact that it did not react with p-nitrobenzoyl chloride, and it had an impact stability of 5 cm/2 kg, whereas the known 4,4,4-trinitro-1-butanol reacts readily with p-nitrobenzoyl chloride and is much more stable toward impact.

¹⁷Aerogel Report No. 540, p. 34.

¹⁸Private communication.

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(a) By the use of the less equivocal route (b) a relatively large quantity of 4,4,4-trinitro-n-butyryl chloride has been reduced with sodium borohydride. A reduction in dioxan under the usual conditions resulted in a low yield of crude material. This was probably a result of the difficulty of isolating the alcohol from an aqueous dioxan solution. In a second run diethyl ether was used as a solvent. This was run at reflux. No yellow color developed, indicating that no decomposition had occurred. However, the use of ether presented a problem, in that on addition of the reaction mixture to water under normal hydrolysis conditions, it burst into flame. This was avoided by dilution of the mixture with methylene chloride before hydrolysis. A 65% yield of crude alcohol was isolated.

(b) This crude alcohol was mixed with tricresyl phosphate as a carrier and the mixture was distilled at 0.5 to 1 micron in a falling-film still. All fractions obtained contained tricresyl phosphate, as indicated by solubility tests. Evidently the boiling points of trinitrobutanol and tricresyl phosphate are too close for a separation to be effected. Both the crude and pure trinitrobutanol are thermally stable up to 280°C, i.e., merely boil away when dropped into a hot Woods metal bath. The next batch of crude alcohol was distilled in a falling-film still without a carrier. This distillation afforded little or no purification. All attempts to crystallize this alcohol have failed. Attempts to prepare crystalline derivatives have been only partially successful. A p-nitrobenzoate and a p-toluenesulfonate have been prepared, but in poor yields.

b. Experimental

(1) Addition of Nitroform to Acrolein, Followed by Treatment with Sodium Borohydride

(a) A 200-ml, 3-necked flask fitted with thermometer, stirrer, and dropping funnel, was charged with a solution of 9.5 gm nitroform (0.063 mol) in 35 ml water containing 3 drops of 10% sodium hydroxide solution. At -1 to +2°C, a solution of 4.2 ml (3.5 gm, 0.063 mol) of acrolein in 30 ml water was added dropwise over about a half hour. A heavy yellow oil began to separate almost immediately. After all the acrolein solution was added, the mixture was stirred at $\pm 10^\circ\text{C}$ for a half hour longer. The oil was separated, dissolved in 75 ml methanol, and transferred to a 400-ml beaker mounted in an ice bath and fitted with a stirrer, pH electrodes, thermometer, and two dropping funnels. Then, with the temperature maintained at 18 to 23°C and the pH at 3 to 4, a solution of 2.3 gm (0.05 mol) sodium borohydride in 18 ml water containing a few drops of 10% sodium hydroxide solution was added dropwise. The yellow solution was diluted with 300 ml water and extracted with five 50-ml portions of methylene chloride. The methylene chloride solution was washed three times with water, dried for a short time over anhydrous sodium sulfate, and evaporated to dryness at 35°C in vacuo. The residue was 6 gm (50%) of an oil, $n_D^{25} = 1.4742$.

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(b) This material was distilled in a bulb tube at 0.5 μ and 80 to 90°C, to yield 3 gm of a faintly yellow oil (n_D^{25} = 1.4742; I.S. = 5 cm/2 kg), which would not react with p-nitrobenzoyl chloride.

Anal. calc'd for $C_4H_7N_3O_7$: %C, 22.97; %H, 3.37; %N, 20.09

Found: %C, 23.72; %H, 3.16; %N, 20.64

(2) Reduction of Trinitrobutyryl Chloride with Sodium Borohydride

(a) A one-liter, round-bottomed flask was charged with 85 gm (2.24 mols) sodium borohydride (finely divided, 84% by analysis). The flask was evacuated at 1 mm for 3 hr. Two 100-ml portions of absolute ether were added and the flask was evaporated to dryness again, in order to remove all traces of ammonia. The solid was transferred to a 1-liter, three-necked, round-bottomed flask fitted with a mechanical stirrer and a distillation head, and containing some glass marbles. Ether was added and 500 ml was distilled, 250 ml remaining on the sodium borohydride.

(b) A solution of 122 gm crude 4,4,4-trinitrobutyryl chloride¹⁹ in 200 ml ether was added dropwise to the sodium borohydride over about a half hour; this caused the ether to reflux. The mixture was refluxed and stirred for 24 hr. The mixture was cream-colored throughout the reaction. Methylene chloride (300 ml) was added and the reaction mixture was hydrolyzed by dropping slowly into a well-stirred mixture of 250 ml conc. hydrochloric acid and excess ice. The mixture was extracted with methylene chloride, then with ether. The combined extracts were then washed, first with saturated sodium chloride solution, then three times with 50:50 sat. sodium chloride—1N sodium bicarbonate, then with acidulated sat. sodium chloride and finally with sat. sodium chloride solution, then dried over Drierite. Evaporation to dryness left 63 gm of a dark oil.

(c) An attempt to distill the oil in an ordinary Claisen-type apparatus was stopped when at 0.5 μ , because it proved necessary to heat the oil bath to 125°C at 0.5 μ before the material barely started to distill. It was distilled by dropping through a falling-film still at 0.5 μ at a temperature of 75 to 90°C, and came over as a yellow to yellow-orange oil, n_D^{25} = 1.4732 to 1.4778.

(d) Preparation of p-toluenesulfonate: 1 gm of the above crude alcohol was dissolved in 2 ml dioxan and 1.5 ml pyridine. At 10 to 15°C, 1 gm of p-toluenesulfonyl chloride was added. After 45 min, the mixture was poured into water; the oil was washed with water and taken up with 8 ml methanol. The solution soon deposited crystals which were removed by filtration. The yield was 0.4 gm, mp 74 to 75°C. A sample was recrystallized for analysis from benzene-cyclohexane, then from methanol, and yielded colorless needles, mp 75 to 76°C.

¹⁹Prepared by refluxing 110 gm 4,4,4-trinitrobutyric acid (0.493 mol) with 250 ml thionyl chloride for 24 hr followed by removal of the excess thionyl chloride in vacuo.

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Anal. calc'd for $C_{11}H_{13}N_3O_9S$: %N, 11.57; %S, 8.82

Found: %N, 11.80; %S, 8.82

3. Preparation of 5,5,5-Trinitro-2-pentanol

a. Discussion

(1) For some purposes the 5,5,5-trinitro-2-pentanone derived directly from the reaction of potassium nitroform, sulfuric acid, and methyl vinyl ketone is not pure enough. A purification procedure for this ketone is described below.

(2) A larger-scale reduction of the ketone with sodium borohydride was run in the same manner as previously reported,²⁰ except that recrystallized ketone was used and the sodium bisulfite washings were omitted. The resulting product crystallized. This crystalline material, which melts at 45 to 50°C, could not be recrystallized.

(3) One of the principal reasons for the preparation of this alcohol is that it may lead to the olefin, 5,5,5-trinitro-2-pentene. This might be accomplished by acidic dehydration of the alcohol (see above) or conversion of the alcohol to a bromide or a p-toluene sulfonate, followed by dehydrohalogenation or removal of p-toluenesulfonic acid. Since it was expected that the 5,5,5-trinitro-2-bromopentane might be a liquid, the p-toluenesulfonate of this alcohol, which might be as useful as the bromide, was first prepared. By treatment of the alcohol with p-tosyl chloride in the presence of pyridine at room temperature, 5,5,5-trinitro-2-pentyl p-toluenesulfonate has been prepared in appreciable yield. The trinitropentano compounds, such as the 5,5,5-trinitro-2-pentanone, 5,5,5-trinitro-2-keto-1-pentanol, and 5,5,5-trinitro-2-pentanol, are all reasonably stable to pyridine. This fact will simplify the preparation of other derivatives in this series.

b. Experimental

(1) Purification of 5,5,5-Trinitro-2-pentanone

One hundred gm of crude ketone, derived from the reaction mixture previously described,²¹ was dissolved in 100 ml benzene with slight warming. The cloudy yellow solution was shaken with 30 gm anhydrous sodium sulfate and filtered. The solid was washed with 50 ml of 50:50 benzene-hexane. Addition of 500 ml n-hexane, 100 ml at a time, caused the separation of the ketone in colorless plates. The product was separated after cooling in an ice bath and was dried in vacuo. The yield was 78 gm (78%), mp 41.5 to 42.0°C.

²⁰ Aerojet Report No. 563, p. 70.

²¹ Ibid.

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(2) Preparation of 5,5,5-Trinitro-2-pentyl p-Toluenesulfonate

In a test tube, 1.1 gm (0.005 mol) of once-distilled 5,5,5-trinitro-2-pentanol, and 1.1 gm (.006 mol) p-toluenesulfonyl chloride were mixed with 1.5 ml (0.15 mol) anhydrous pyridine. This caused some heat evolution and darkening. The mixture was kept at room temperature for 2 hr, at which time it was quite dark and very thick with crystals. On dilution with water, a heavy brown oil was produced. This oil was washed with acidified water and set to a semi-solid. Rubbing with a few ml methanol, cooling, and filtering, yielded 1.2 gm (64%) of crystalline material, mp 67 to 68°C. A sample was purified for analysis by two recrystallizations from methanol, followed by two recrystallizations from benzene-hexane. The sample was obtained as large colorless prisms, mp 69 to 70°C.

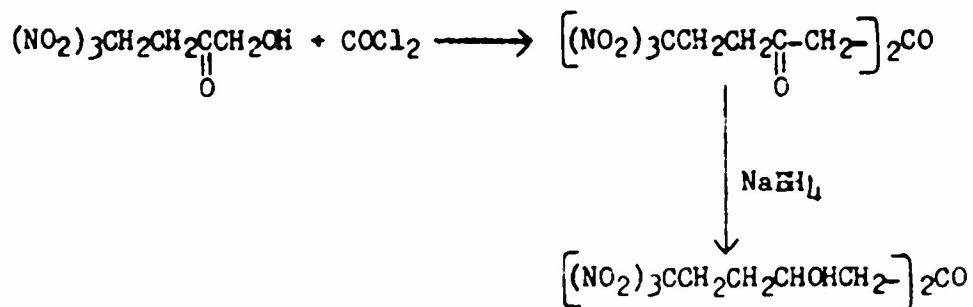
Anal. calc'd for $C_{12}H_{15}N_3O_9S$: %C, 38.20; %H, 4.01; %S, 8.50

Found: %C, 38.82; %H, 4.23; %S, 8.85

4. Attempted Preparation of bis(5,5,5-Trinitro-2-hydroxy-1-pentyl) Carbonate

a. Discussion

(1) Since 5,5,5-trinitro-1,2-pentanediol is an uncrystallizable oil difficult to purify and analyze, the following series of reactions, to yield a related compound with similar specific impulse and which might possibly be crystalline, was proposed.



(2) When an excess of 5,5,5-trinitro-2-keto-1-pentanol in chloroform was treated with phosgene at room temperature and again at reflux temperatures, only starting material was recovered. However, in the presence of pyridine at or below room temperature, the same reactants yielded a high-melting (181°C) solid which had the elemental analysis expected for the bis(5,5,5-trinitro-2-keto-1-pentyl) carbonate. Attempts to reduce this ketone with sodium borohydride are now in progress.

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b. Experimental

A 500-ml three-necked flask fitted with a mechanical stirrer, thermometer, dropping funnel and drying tube, was charged with 39 gm (0.16 mol) 5,5,5-trinitro-2-keto-1-pentanol and 100 ml methylene chloride. The mixture was cooled in an ice bath and a solution containing 8 gm (0.08 mol) phosgene in 30 ml methylene chloride was added. The keto alcohol did not dissolve. At 0 to 10°C, a solution of 12.8 ml (0.16 mol) pyridine in 40 ml methylene chloride was added dropwise over about 15 min. The keto alcohol dissolved rapidly and a clear yellow solution was produced. The ice bath was removed and stirring was continued. After a short time crystals began to appear and the solution darkened. Two hours later the color was deep purple. The mixture was filtered by suction, the filtrate being discarded. The solid was washed with methanol and air-dried; the yield was 17 gm (42.5%), mp 172 to 175°C. A sample which was twice recrystallized from di-n-propyl ether-acetone yielded colorless prisms, mp 180 to 181°C, and was submitted for analysis.

Anal. calc'd for $C_{11}H_{12}N_6O_{17}$: %C, 26.41; %H, 2.42; %N, 16.30

Found: %C, 27.08; %H, 2.48; %N, 16.76

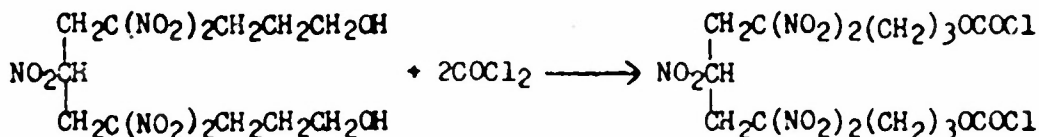
c. PREPARATION OF NITROCARBOXYLIC ACIDS

1. Introduction

Nitrodicarboxylic acids are valuable starting materials for the preparation of diisocyanates and in the form of the acid chlorides they are used for the preparation of polyesters. This report deals with the preparation of the bis-chloroformate of a polynitro alcohol, which can be used for the preparation of polyesters. Furthermore, it presents a means for handling the distillation of 4,4,4-trinitrobutyryl chloride in a relatively safe manner.

2. Preparation of the bis-Chloroformate of 4,4,6,8,8-Pentanitro-1,11-undecanediol

Treatment of 4,4,6,8,8-pentanitro-1,11-undecanediol with a large excess of phosgene in diethyl cellosolve yielded a crystalline bis-chloroformate. This derivative will also be made from the 4,4,6,6,8,8-hexanitro-1,11-undecanediol when it becomes available.



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3. Experimental

A 200-ml three-necked flask fitted with a stirrer, thermometer, and gas inlet tube was cooled in an ice-salt bath and about 50 gm liquid phosgene was condensed into the flask. At 0 to 5°C, a solution of 10 gm (0.024 mol) of pentanitro-undecanediol in 50 ml diethyl cellosolve was added dropwise. At first a milky suspension formed, then a homogeneous solution resulted. The mixture was stirred a half hour longer at 0 to 5°C and was then allowed to warm to 15°C. About a half hour later a white precipitate formed which did not dissolve on addition of 30 ml methylene chloride. The mixture was left overnight at room temperature. The following morning the mixture was evaporated to dryness at reduced pressure, leaving a residue of 12 gm. A sample was recrystallized from methylene chloride-carbon tetrachloride; the mp was 84 to 86°C.

Anal. calc'd. for $C_{13}H_{17}N_5O_{11}Cl_2$: %C, 29.01; %H, 3.19; %N, 13.01;
%Cl, 13.17
Found: %C, 29.54; %H, 3.12; %N, 13.07;
%Cl, 13.24

4. 4,4,4-Trinitrobutyryl Chloride

a. Discussion

Although the preparation of 4,4,4-trinitrobutyryl chloride has already been described,²² current demands have necessitated a method of preparing larger quantities of this substance. Impact-stability tests showed that the compound detonated at 20 cm/2 kg and thermal stability tests showed instantaneous decomposition at 190°C, and detonation at 240°C when the compound was dropped on a Wood's metal bath. In view of reports from Rohm and Haas of the occurrence of a first-degree explosion during the distillation of 4,4,4-trinitrobutyryl chloride by the usual high-vacuum method, the "falling film" technique was employed. This experiment illustrates the usefulness of the "falling film" molecular still.²³

b. Experimental

A 500-ml round-bottomed flask containing 220 ml of purified thionyl chloride was charged portionwise with 110 gm (0.493 mol) of 4,4,4-trinitrobutyric acid, the mixture being swirled after each addition of acid. A calcium chloride drying tube was attached to the condenser and the solution was refluxed for 22 hr. The excess thionyl chloride was then removed

²² Aerojet Report No. 540, p. 52.

²³ M. H. Gold, Anal. Chem. 21, 636 (1949).

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under reduced pressure, a water aspirator being used for the first 15 min and then an oil pump. About 170 ml of the unreacted thionyl chloride was recovered in a dry-ice trap. The residual 4,4,4-trinitrobutyryl chloride was then subjected to oil pump pressure for 4 hr, in order to remove traces of thionyl chloride. Then 80 ml of tricresyl phosphate was added to the impure acid chloride as a carrier solvent and the product was distilled in the "falling film" molecular still. The following table gives conditions which were found to be satisfactory for the distillation of 4,4,4-trinitrobutyryl chloride.

<u>Pass</u>	<u>Time</u> <u>hr</u>	<u>Pressure</u> <u>mm</u>	<u>Temp.</u> <u>°C</u>	<u>Yield</u> <u>gm</u>	<u>n_D²⁵</u>
1	0.5	water aspir.	75	2	—
2	2.3	2	95 to 105	60	1.4838
3	1.7	2	110 to 120	39	1.4856
4	2.0	2	120 to 123	18.2	1.4998

Temperatures higher than 120°C are not recommended, since the refractive indices show that some tricresyl phosphate ($n_D^{25} = 1.5541$) is also collected at high temperatures.

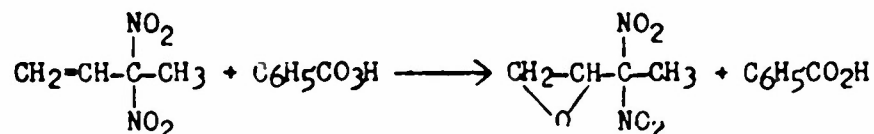
D. PREPARATION OF NITRO EPOXIDES

1. Introduction

Epoxides, when permitted to polymerize, produce a polyethylene oxide chain. If such an epoxide containing sufficient nitro groups in a side chain could be induced to yield a high polymer, a new type of polymeric structure would be available for propellant evaluation. The present report deals with methods for the preparation of new nitro epoxides.

2. Attempted Preparation of 1,2-Epoxy-3,3-dinitrobutane

a. One of the simplest epoxides potentially capable of producing a polymer of high specific impulse would be 1,2-epoxy-3,3-dinitrobutane, with an estimated specific impulse of 212 lbf sec/lbm for the polymer. Inasmuch as a sample of 3,3-dinitro-1-butene was available from a preparation at Ohio State University, the following synthesis was attempted:



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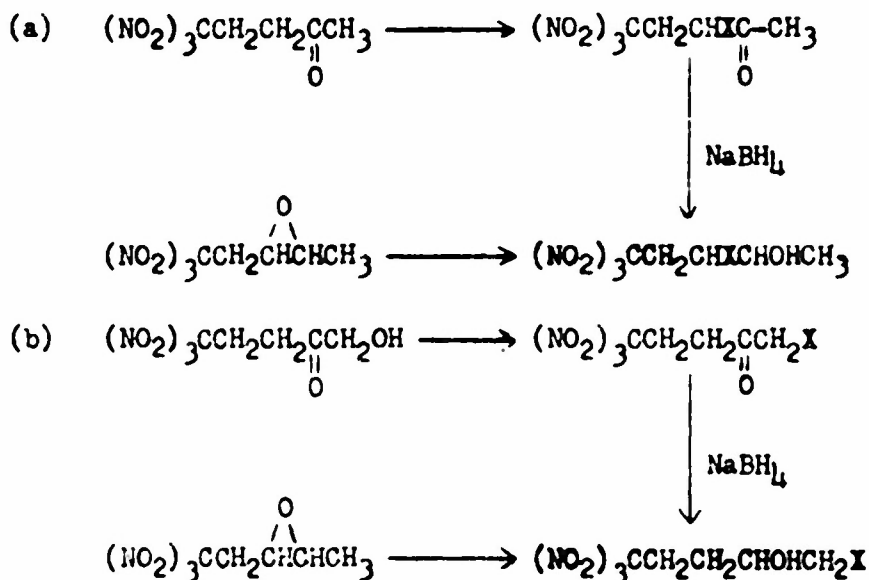
b. The reaction was conducted in chloroform solution with an excess of perbenzoic acid over the dinitrobutene. The rate of utilization of perbenzoic acid was measured at intervals by means of iodometric titration, and it was found that the disappearance of peroxide was extremely slow both at room temperature and at elevated temperatures. In one experiment such a reaction was allowed to stand for 20 days. Although 75% of the required perbenzoic acid had been used up, the rate of disappearance of perbenzoic acid was more rapid in the chloroform solution control sample which contained no olefin. After the reaction mixture had been extracted to remove benzoic acid and perbenzoic acid, the chloroform solution was distilled. Half the original 3,3-dinitrobutene was recovered. This was followed by a small quantity of additional distillate, representing approximately 25% of a higher boiling material. This material has not yet been characterized.

c. The apparent lack of reactivity of the dinitrobutene with perbenzoic acid was rather surprising. Accordingly, it was tested to determine the reactivity toward bromine and hypohalous acid. In neither case was there any noticeable addition.

3. The Attempted Preparation of 2,3-Epoxy-5,5,5-trinitropentane

a. Discussion

(1) Another synthesis for a nitro epoxide is currently under investigation, according to the following equations:



Several attempts via route (a) to chlorinate 5,5,5-trinitro-2-pentanone with chlorine in the presence of water and calcium carbonate, and with sulfuryl

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chloride in chloroform have failed to yield 5,5,5-trinitro-3-chloro-2-pentanone. Bromination with bromine in ether or chloroform did succeed, and gave a high-boiling oil which had the proper elemental analysis and reacted with thiourea to yield the expected substituted thiazole, probably 2-amino-4-methyl-5-(2,2',2'-trinitroethyl) thiazole. Bromination with N-bromosuccinimide or with bromine in the presence of water and calcium carbonate was unsuccessful.

(2) Treatment of 5,5,5-trinitro-2-keto-1-pentanol with thionyl chloride in chloroform, via route (b), did not yield the expected chloro compound. No sulfur dioxide was evolved. (Evidently only a sulfite was formed.) Since it was found that the starting material is reasonably stable to pyridine this reaction will be tried again in the presence of pyridine. Treatment of the keto alcohol with p-toluenesulfonyl chloride in pyridine produced 5,5,5-trinitro-2-keto-1-pentyl p-toluenesulfonate in poor yield.

b. Experimental

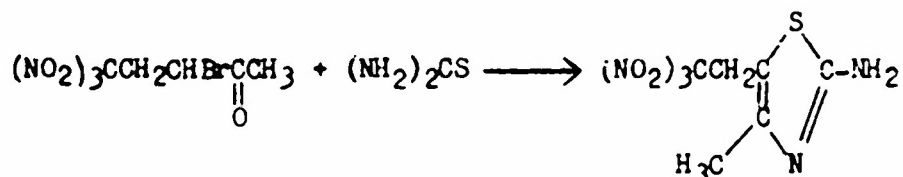
(1) Bromination of 5,5,5-Trinitro-2-pentanone

(a) A 200-ml three-necked flask fitted with a stirrer and dropping funnel was charged with a solution of 4.4 gm (0.02 mol) of 5,5,5-trinitro-2-pentanone in 30 ml chloroform and a few drops of 48% hydrobromic acid. A solution of 32 gm (0.02 mol) bromine in 20 ml chloroform was added dropwise. The first portion of the bromine was absorbed slowly, the remainder more rapidly. After all the bromine had been added and absorbed the mixture was washed well with water, dried over anhydrous sodium sulfate, and evaporated to dryness. The residue was 5.0 gm of a light-colored oil, $n_D^{25} = 1.5075$. A sample was distilled twice from a bulb tube at 0.5μ and an 80 to 90°C air bath. A middle cut was taken each time. For the second middle cut n_D^{25} was 1.5045; the sample was submitted for analysis.

Anal. calc'd. for $\text{C}_5\text{H}_6\text{N}_3\text{O}_7\text{Br}$: %C, 20.01; %H, 2.02; %N, 14.00; %Br, 26.63

Found: %C, 19.86; %H, 1.83; %N, 13.42; %Br, 28.01

(b) Reaction with Thiourea



The above bromoketone (0.3 gm) and thiourea (0.1 gm) were mixed in a test tube with 2 ml methanol. The reaction was exothermic and the mixture

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darkened. After 2 hr of standing with occasional shaking, all the thiourea had dissolved and the color was dark brown. The solution was diluted with 3 to 5 ml water and a dark oil was separated and discarded. The filtrate, with 2 ml of 1N sodium bicarbonate solution, gave 0.1 gm of a brown solid. This was isolated by filtration and purified by two recrystallizations each from benzene and chloroform, yielding orange crystals. This material does not have a sharp melting point; it darkens suddenly at 105°C, and decomposes slowly up to 180°C.

Anal. calc'd for $C_6H_7N_5O_6S$: %N, 25.27; %S, 11.57

Found: %N, 24.95; %S, 11.16

(2) Preparation of 5,5,5-Trinitro-2-keto-1-pentyl p-Toluenesulfonate

A 200-ml three-necked flask fitted with a stirrer, dropping funnel, and thermometer, was charged with 40 ml anhydrous pyridine. At -5 to 0°C, 4.8 gm (0.02 mol) of 5,5,5-trinitro-2-keto-1-pentanol was added. A clear, light-tan solution resulted. At -5 to 0°C, 3.8 gm (0.02 mol) p-toluenesulfonyl chloride was added portionwise. After 1.5 hr, the color was deep brown. The reaction mixture was poured onto ice and the heavy brown oil was washed with dilute hydrochloric acid. The oil was taken up in 10 ml of methanol and the solution deposited a solid, 1.2 gm, mp 100 to 102°C. A sample was purified for analysis by three recrystallizations from methanol and yielded colorless crystals, mp 104.5 to 105°C.

Anal. calc'd for $C_{12}H_{13}N_3O_{10}S$: %C, 36.83; %H, 3.35; %S, 8.19

Found: %C, 37.19; %H, 3.64; %S, 8.36

E. PREPARATION OF PLASTICIZERS

1. Introduction

The nitro polymers prepared on this program are, for the most part, hard, brittle materials. These properties prohibit their use on the roller mill and the extrusion press except at high temperatures and pressures, and these conditions cause extensive degradation of nitro polymers. It is apparent that a plasticizer will be necessary to permit the fabrication of nitro polymers with the usual plastics-processing equipment. The ideal additive must possess the properties of low volatility, low melting point, and mutual solubility with the polymer, as well as the ability to plasticize the polymer. In addition, a high specific impulse is desirable, to maintain the specific impulse of the final propellant at a high level. Also, as would be expected, high thermal and impact stabilities are a primary requirement. The present report deals with the preparation of such compounds, in an attempt to meet the above requirements.

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2. Preparation of Esters of Trinitrobutyric Acid

a. Discussion

The preparation of esters of trinitrobutyric acid was initiated earlier.²⁴ This work has been continued with the preparation of 1,2,3-tris(4,4,4-trinitrobutyroy) propane, 1,2-bis(4,4,4-trinitrobutyroy) propane, and 1,5-bis(4,4,4-trinitrobutyroy)-3-oxa-pentane. The available data on these compounds are presented in Table XIX.

TABLE XIX

ESTERS OF 4,4,4-TRINITROBUTYRIC ACID

<u>Compound</u>	<u>Melting Point, °C (obs.)</u>	<u>Impact Stability cm/2 kg</u>
1,2-bis(4,4,4-Trinitro- butyroy) ethane	94 to 95 93.9 (corr.)	>100
1,2,3-tris(4,4,4-Trinitro- butyroy) propane	90 to 92	25 to 30
1,2-bis(4,4,4-Trinitro- butyroy) propane	63.5 to 64.5	>100
1,5-bis(4,4,4-Trinitro- butyroy)-3-oxa-pentane	34.5 to 35.5	>100

<u>Compound</u>	<u>Analysis</u>						<u>Heat of Combustion cal/gm</u>	
	<u>Calc'd</u>			<u>Found</u>			<u>Calc'd</u>	<u>Found</u>
	<u>%C</u>	<u>%H</u>	<u>%N</u>	<u>%C</u>	<u>%H</u>	<u>%N</u>		
1,2-bis(4,4,4-Trinitro- butyroy) ethane	25.43	2.56	17.80	25.32	2.88	18.09	2420	2382
1,2,3-tris(4,4,4-Trinitro- butyroy) propane	25.47	2.42	17.83	26.07	2.42	17.88	2387	2404
1,2-bis(4,4,4-Trinitro- butyroy) propane	27.17	2.90	17.29	27.47	2.90	17.06	2672	2610
1,5-bis(4,4,4-Trinitro- butyroy)-3-oxa-pentane	27.91	3.12	16.28	28.30	3.14	16.05	2756	2717

²⁴Aerojet Report No. 563, p. 83.

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b. Experimental

(1) Preparation of 1,2,3-tris(4,4,4-Trinitrobutyroxyl) Propane

A solution of 223 gm (1 mol) of trinitrobutyric acid and 30.7 gm (1/3 mol) of glycerol in 650 ml benzene was dried at reflux temperature, using a Dean-Stark trap for the removal of water. The solution was then cooled somewhat to allow the addition of 5 ml sulfuric acid, and heating was continued. The theoretical amount of water was removed after 23 to 25 hr of reflux. The solution was decanted from the tar-like material formed during the esterification. An additional 200 to 250 ml benzene was added, and the solution was washed four times with saturated sodium chloride solution. Following two washes with dilute sodium carbonate, the organic layer was washed four times with water. The solvent was then distilled at reduced pressure. The residue of crude 1,2,3-tris(4,4,4-trinitrobutyroxyl) propane was dissolved in 350 ml hot absolute ethanol. As the solution cooled to room temperature, a portion of the product separated from solution as a dark-colored viscous oil. The supernatant liquid (sol'n I) was decanted from this oil, and the latter was redissolved in 400 ml hot absolute ethanol (sol'n II). It was necessary to decant sol'n. II twice from the highly colored oil which separated (and was discarded). The light-colored solid which eventually separated from sol'ns. I and II weighed 77.3 gm, corresponding to 32.7% of the theoretical. Pure 1,2,3-tris(4,4,4-trinitrobutyroxyl) propane (49.2 gm, 20.9%) was obtained, following successive recrystallizations from 580, 520, and 350 ml absolute ethanol.

(2) Preparation of 1,2-bis(4,4,4-Trinitrobutyroxyl) Propane

(a) Direct Esterification of Trinitrobutyric Acid and Propylene Glycol

A solution of 145 gm (0.65 mol) of trinitrobutyric acid and 24.7 gm (.325 mol) propylene glycol in 500 ml benzene was dried during an initial reflux period, using a Dean-Stark trap. Sulfuric acid (5 ml) was added, and reflux was continued for 6-2/3 hr, during which time the theoretical amount of water was removed. The benzene solution was filtered to remove some charred material and washed five times with saturated salt solution, twice with dilute sodium carbonate solution, and five times with water. The solvent was distilled under reduced pressure. The 92-gm residue was recrystallized successively from 250, 150, and 135 ml portions of absolute ethanol. During the third recrystallization, an appreciable quantity of the product was lost because of accidental breakage of the flask containing the mixture of product and ethanol. Seven additional recrystallizations were required for complete removal of the color from the recovered product. The 36-gm yield of 1,2-bis(4,4,4-trinitrobutyroxyl) propane corresponds to only 22.8% of the theoretical.

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(b) Addition of Nitroform to 1,2-Diacryloxypropane

A solution of 18.4 gm (0.1 mol) of 1,2-diacryloxypropane in 40 ml absolute ethanol was added dropwise with stirring at 25°C during a 15-min period to a solution of 33.2 gm (0.22 mol) nitroform in 100 ml ethanol. The resulting solution was stirred at 25°C for 30 min; the temperature was then raised to 40°C and stirring was continued for 2.5 hr. The solution was allowed to stand at room temperature overnight, and the solvent and excess nitroform were distilled at reduced pressure. The 50.3-gm residue was recrystallized twice from 65-ml portions of absolute ethanol and a third time from 50 ml of ethanol. The 22.1-gm yield of 1,2-bis(4,4,4-trinitrobutyroxyl)propane, mp 63.5 to 64.5°C, corresponds to 45.5% of the theoretical.

(3) Preparation of 1,5-bis(4,4,4-Trinitrobutyroxyl)-3-oxapentane

A solution of 214 gm (0.96 mol) of 4,4,4-trinitrobutyric acid and 42.4 gm (0.4 mol) diethylene glycol in 700 ml benzene was dried at reflux temperature, using a Dean-Stark trap. Sulfuric acid (5 ml) was added, and heating was continued at the reflux temperature of the solvent. The theoretical amount of water was removed in a period of 6 hr. The solution was filtered to remove some charred material in suspension, and the filtrate was washed successively with three 300-ml portions of saturated sodium chloride solution, two 300-ml portions of dilute sodium carbonate solution, and three 300-ml portions of saturated salt solution. The solvent was distilled at reduced pressure, and the 192-gm residue was dissolved in 500 ml hot absolute ethanol. A small amount of suspended sodium chloride was removed by filtration. A portion of the product separated from the filtrate as a tan-colored, viscous oil. The supernatant solution (sol'n. I) was decanted, and the residual oil was redissolved in 200 ml of hot absolute ethanol (sol'n. II). The white crystalline product which separated from sol'n. I was recrystallized a second time from 300 ml ethanol, yielding pure 1,5-bis(4,4,4-trinitrobutyroxyl)-3-oxapentane. The tan-colored product from sol'n. II was recrystallized from 200 ml ethanol and 120 ml ethanol. The use of the decreased volume of solvent during the third recrystallization caused an initial small portion of the product to separate as an oil, and the color was carried from the solution with this oil, which was discarded. The material which crystallized from the colorless supernatant solution following decantation was pure product. The combined yield of 111.3 gm 1,5-bis(4,4,4-trinitrobutyroxyl)-3-oxapentane corresponds to 53.9% of the theoretical.

3. Preparation of 5,5,5-Trinitro-2-ketopentyl Acetate

a. Discussion

Esters in general have been used as plasticizers for polymers. In addition to the esters of trinitrobutyric acid, it is also

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possible to prepare potential plasticizers from various esters of highly nitrated alcohols, such as the 5,5,5-trinitro-2-ketopentanol. The 5,5,5-trinitro-2-ketopentyl acetate has been previously prepared in these laboratories.²⁵ Because of the low melting point, apparent stability, moderately high specific impulse, and chemical structure of this compound, it was considered advisable to prepare larger quantities of the material for testing as a plasticizer for nitro polymers. The compound was prepared by the reaction of 5,5,5-trinitro-2-ketopentanol and acetyl chloride, using the latter reagent in quantities 20 and 100% in excess of the theoretical. These experiments gave 5,5,5-trinitro-2-ketopentyl acetate in 43.4 and 48.5% yields, respectively.

b. Experimental

A solution of 113.6 gm (0.5 mol) of 5,5,5-trinitro-2-ketopentanol in 440 ml dry chloroform was warmed to gentle reflux temperature, and 47.1 gm (0.6 mol) acetyl chloride was added dropwise to the solution. The addition was regulated to maintain the reaction solution at reflux temperature. Heating was continued for 3 hr, following the 1/2-hr period of acetyl chloride addition. The dark-red solution was washed once with water, twice with dilute sodium bicarbonate solution, and twice with water. The solvent was distilled under reduced pressure, and the residue (109.5 gm) was recrystallized from 500 ml isopropyl ether. Following two additional recrystallizations from isopropyl ether, the 5,5,5-trinitro-2-ketopentyl acetate was obtained in 43.4% yield (60.8 gm). The product melted at 52.5 to 53.5°C and had impact stability >100 cm/2 kg.

Anal. calc'd. for $C_7H_9O_9N_3$: %C, 30.12; %H, 3.25; %N, 15.05

Found: %C, 30.66; %H, 3.07; %N, 15.35

F. INTERMEDIATES

1. Preparation of Acrylic Esters of Polyhydric Alcohols

a. Discussion

With the successful preparation of 1,2-bis(4,4,4-trinitrobutyroxyl) ethane by the addition of nitroform to 1,2-diacryloxyethane,²⁶ it was planned to use this method for the preparation of other trinitrobutyrates. The distillation of 1,2-diacryloxyethane was accompanied by considerable polymerization, and when the preparation of higher-boiling acrylates was attempted the polymerization was even more extensive. An attempt to distill crude 1,2,3-triacryloxypropane, obtained by the direct esterification of acrylic acid and glycerol, was unsuccessful. The yields of 1,2-diacryloxypropane and 1,5-diacryloxy-3-oxapentane, prepared from propylene glycol and diethylene glycol, respectively, were low because of the polymerization which occurred during distillation.

²⁵ Aerojet Report No. 515, p. 6.

²⁶ Aerojet Report No. 563, p. 83.

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b. Experimental

(1) Preparation of 1,2-Diacryloxypropane

A mixture of 317 gm (4.4 mols) acrylic acid, 102 gm (1.34 mols) propylene glycol, 2 gm hydroquinone, copper turnings, and 900 ml benzene was dried during an initial reflux period, using a Dean-Stark trap. Sulfuric acid (5 ml) was added, and heating was continued at reflux temperature for a period of 28 hr. The solution was decanted, filtered, and washed five times with saturated sodium chloride solution. The solution was washed twice with dilute sodium carbonate solution and twice with saturated salt solution. Additional hydroquinone was added to the benzene solution together with copper turnings, and the solvent was distilled at diminished pressure. The following data were taken during the distillation of the residue.

Cut I: bp, 51 to 53°C/0.5 mm; 16.3 gm; n_D^{25} , 1.4462
Cut II: bp, 51 to 106°C/0.5 mm; 12.9 gm; n_D^{25} , 1.4491
Cut III: bp, 106 to 111°C/0.5 mm; 29.1 gm; n_D^{25} , 1.4570
Residue: ~170 gm (polymer)

(2) Preparation of 1,5-Diacryloxy-3-oxa-pentane

A solution of 156.5 gm (2.2 mols) acrylic acid and 106.1 gm (1 mol) diethylene glycol in 500 ml benzene (with 2 gm hydroquinone and 30 gm copper turnings for polymerization inhibition) was dried by means of a Dean-Stark trap during an initial reflux period of 30 to 45 min. Sulfuric acid (5 ml) was added, and refluxing was continued for 9.5 hr. The theoretical amount of water was removed during this period. The mixture was filtered and the filtrate was given four 250-ml water washes, a single 250-ml wash with sodium carbonate solution, and four additional water washes. Hydroquinone (2 gm) was added to the benzene solution, and the solvent was distilled under reduced pressure. The 178-gm residue was divided into two portions, which were distilled separately. The following data were taken during the distillation of a 96.5-gm sample of the residue.

Pre-cut: bp, <77°C/0.5 mm; 2.5 gm (discarded)
Product Cut: bp, 81 to 83°C/0.5 mm; 64.4 gm; n_D^{25} , 1.4574
Residue: 29.2 gm (polymer)

The combined yield from the two distillations corresponded to approximately 53% of the theoretical.

2. The Preparation of 3-Trinitromethyl-cyclohexanone

a. Discussion

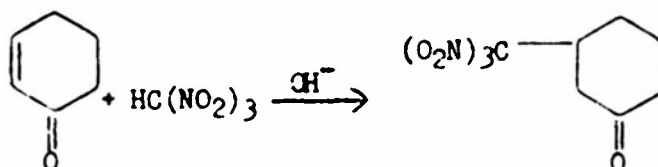
(1) . A great increase in the oxygen balance of compounds can be achieved whenever it is possible to introduce the trinitromethyl group into a molecule.. A great deal of work has already been done and is now in progress on the addition of nitroform to unsaturated systems. Certain rules have been observed so that today predictions can be made as to whether or not nitroform will add to an unsaturated system. However, only in few cases is the introduction of the trinitromethyl group possible²⁷ when it is desired to prepare suitable monomers for the preparation of condensation polymers. Such compounds seldom possess the necessary functional groups in the molecule, to make them useful for polymerization.

(2) An alternate procedure for the preparation of the monomers is to introduce the trinitromethyl group first and later the functional groups of the desired compound. Such a procedure is exemplified by the preparation of acids by oxidative ring-opening of cyclic ketones. Thus, cyclohexanone is converted into adipic acid on a large scale. Similarly, a trinitromethyl adipic acid would be made available if it were possible to prepare a cyclohexanone with a trinitromethyl group in the correct position.

(3) The addition of nitroform to cyclic compounds has occurred only in the reaction with dihydropyran.²⁸ The Michael reaction with conjugated systems such as 2-cyclohexene-1-one or 1-cyclohexene-1-carboxylic acid or its derivatives offers the simplest method for the preparation of cyclic compounds containing the trinitromethyl grouping



The present report deals with the addition of nitroform to 2-cyclohexene-1-one in order to prepare 3-trinitrocyclohexanone according to the equation:



²⁷ Purdue Quarterly Report No. 1, p. 6; Schenck and von der Forst BIOS/Gr 2 HEC No. 5475; Purdue Quarterly Report No. 2, p. 10-16.

²⁸ Aerojet Report No. 404, p. 53; No. 468, p. 17.

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The reaction was carried out in aqueous solution and a crystalline compound was isolated, mp 61 to 61.5°C.

Anal. calc'd for $C_7H_9N_3O_7$: %C, 34.01; %H, 3.67; %N, 17.00

Found: %C, 34.45; %H, 3.63; %N, 17.16

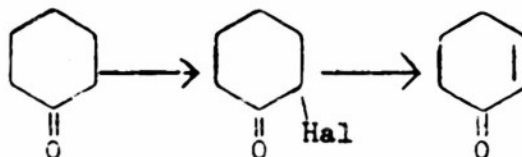
b. Experimental

A three-necked flask provided with a stirrer, dropping funnel and thermometer was charged with 3 gm nitroform in 35 ml water and 0.3 ml of a 20% aqueous solution of sodium hydroxide. The solution of 2.2 gm 2-cyclohexene-1-one in 5 ml methanol was added slowly at a temperature of 10 to 20°C. A milky suspension was formed and stirring was continued for 2 hr at room temperature. Then 50 ml methylene chloride was added and the solution was washed twice with saturated sodium chloride solution, once with 5% sodium bicarbonate solution and once with saturated sodium chloride solution again. The almost colorless solution was dried over sodium sulfate and evaporated. The yield was 3.1 gm of a yellowish viscous oil which was crystallized from ether at -70°C and recrystallized from isopropyl ether. The melting point was 61 to 61.5°C.

3. The Preparation of 2-Cyclohexene-1-one

a. Discussion

(1) The 2-cyclohexene-1-one was prepared by Kötzt et al.²⁹ by several methods, starting from cyclohexanone by halogenation and introducing the double bond by elimination of hydrogen halide.



All methods reported give a very poor yield and were found unsuitable for the preparation of a sizable amount of the desired product.

(2) Another possibility is the introduction of the double bond by removal of water from 2-cyclohexanol-1-one as reported by Kötzt and Grethe³⁰ according to the equation:

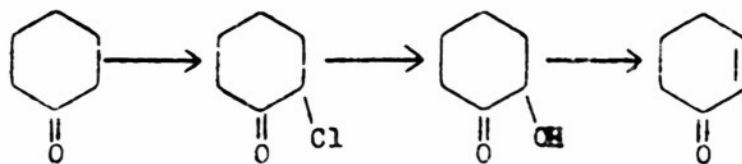
²⁹ J. prakt. Chem. [2] 80, 489 (1909); Ann. 358, 196 (1909); 400, 80 (1913).

³⁰ J. prakt. Chem. [2] 80, 489 (1909).

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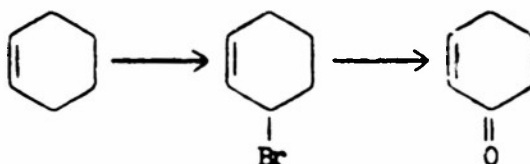
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The chlorination yields 2-chloro-cyclohexanone in about 50% of theoretical and the hydrolysis proceeds in about 10% of the theoretical amount. The isolation of 2-cyclohexanol-1-one was improved, as reported in Paragraph b, below.

(3) Inasmuch as the reported methods were found unsatisfactory for the preparation of the desired 2-cyclohexene-1-one, the present synthesis started from cyclohexene, with the introduction of bromine by a Ziegler bromination with N-bromosuccinimide.³¹ Direct oxidation of the 3-bromo-1-cyclohexene with chromic acid in dilute sulfuric acid gave the desired 2-cyclohexene-1-one. The reaction proceeds according to the following equation:



The yield was about 30% of theoretical.

(4) A better result was obtained when the bromine was replaced by the acetate group. This was carried out by reacting the 3-bromo-1-cyclohexene with potassium acetate in acetic acid. The oxidation of the acetate or of the hydrolysis product to 2-cyclohexene-1-ol gave the 2-cyclohexene-1-one in about 50% yield.

b. Experimental

(1) 2-Cyclohexanol-1-one

A round-bottomed flask provided with a stirrer and thermometer and reflux condenser was charged with 300 gm chlorocyclohexanone, 900 gm potassium carbonate, and 900 gm water. The mixture was refluxed with rapid stirring for 3 hr. The mixture, consisting of two layers, was then steam-distilled and 1000 ml of distillate was taken. One thousand gm of potassium

³¹Ann. 551, 80 (1942).

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carbonate was added to the distillate and the mixture was cooled in ice water. The white crystals obtained were collected and dissolved in ethyl acetate while still damp. The water was separated in a separatory funnel and cooled to -40 to -50°C. On the addition of ether 72 gm of white crystals was obtained. the mp was 95°C (literature 92 to 93°C).

(2) 2-Cyclohexene-1-one

The bromination of cyclohexene was carried out according to Ziegler et al.³² A three-necked flask provided with a stirrer, dropping burette, and thermometer was charged with 75 ml water and 14 gm conc. sulfuric acid. The solution was cooled to 0 to +5°C and 6.5 gm of 3-bromo-1-cyclohexene was added. A solution of 3 gm chromic acid in 25 ml water was slowly added to this mixture within 60 min, with rapid stirring. The temperature was maintained at 0 to 5°C. After 2 hr continued stirring the mixture was slowly warmed to room temperature and allowed to stand overnight. The reaction mixture was steam-distilled and 250 ml of distillate was taken. The distillate was extracted three times with ether and the ether solution was dried over sodium sulfate. The ether was then evaporated and the residue distilled at 65 to 80°C air-bath temperature at 20 mm. The yield was 2.2 gm of 2-cyclohexene-1-one.

(3) 3-Acetoxy-1-cyclohexene

A mixture of 55 gm anhydrous potassium acetate and 210 ml glacial acetic acid was heated to 60 to 65°C in a three-necked flask provided with thermometer, stirrer, dropping funnel, and reflux condenser. Then 88 gm of 3-bromo-1-cyclohexene was introduced dropwise and potassium bromide in increasing amounts was precipitated during the course of the reaction. The mixture was stirred for 2 hr at 70 to 75°C. After cooling to room temperature 61.3 gm potassium bromide was separated on a filter. The filtrate was diluted with 500 ml methylene chloride and washed with 250 ml of 15% aqueous sodium chloride solution. After another extraction of the aqueous layer with 200 ml methylene chloride the combined extracts were washed twice with saturated sodium chloride solution, once with 5% sodium bicarbonate solution, and once again with saturated sodium chloride solution. The solution was dried over sodium sulfate and concentrated. The residue distilled at 14 mm at 74 to 77°C to yield 60.4 gm of 3-acetoxy-1-cyclohexene.

4. Trinitroethyl Propionate

a. Discussion

Because of its structural similarity to trinitroethyl acrylate, it was decided to investigate the ability of trinitroethyl propionate

³²Ann. 551, 80 (1942).

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to act as a chain-transfer agent in the polymerization of styrene, methyl methacrylate, etc.³³ This compound was prepared according to the method of Marans and Zelinski,³⁴ with some minor modifications.

b. Experimental

A solution of 10 gm of trinitroethanol and 10 ml of ether was added to 50 ml of propionyl chloride (prepared from propionic acid and thionyl chloride, bp 78 to 79°C). The resulting mixture was heated on the steam bath until most of the ether was removed and then refluxed vigorously for 4 hr, until no more hydrogen chloride gas was evolved. The excess propionyl chloride was removed under reduced pressure and the residue was poured slowly, with stirring, into cold water. The oil which separated was taken up in hexane; the hexane solution of the ester was washed several times with water (until the water extracts were colorless), dried over anhydrous magnesium sulfate for several hours, then concentrated and cooled in dry ice. The colorless needles which separated were collected and recrystallized several times from hexane. The yield of product melting at 23 to 24°C, $n_D^{25} = 1.4449$, was 11 gm, 86% of theoretical.

5. Preparation of Polymerization Catalysts

a. Discussion

It has been recently suggested that polymerization catalysts currently used on the nitro polymer and Aeroplex programs be replaced by symmetrical compounds of the azo- type as a possible means of obtaining increased molecular weights. This suggestion is based on work by Tobolsky³⁵ which has shown that the symmetrical azo compounds are unique, as compared with the peroxide and hydroperoxide catalysts, in that the rate of decomposition of the former at a given temperature is independent of the solvent. Tobolsky also showed that in the polymerization of styrene and methyl methacrylate there was no chain-terminating reaction involving the catalyst or its decomposition products when azo- type catalysts were used, in sharp contrast with the results obtained when cumene hydroperoxide or t-butyl hydroperoxide was used. Azo bis-isobutyronitrile³⁶ and methyl azo bis-isobutyrate³⁷ have been prepared for use as catalysts in the polymerization of nitro monomers.

³³ Cf. Section II, A, 1, c, on vinyl polymers.

³⁴ J. Am. Chem. Soc. 72, 5329 (1951).

³⁵ In press.

³⁶ Thiele and Hauser, Ann. 290, 30 (1896).

³⁷ Ibid., p. 35.

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b. Experimental

(1) Preparation of N,N'-bis(2-Cyano-2-propyl) Hydrazine

A solution of 195 gm (1.5 mols) of hydrazine sulfate in 1125 ml water was warmed to 40 to 45°C; a solution of 147 gm (3 mols) sodium cyanide in 525 ml water and 175 gm (3 mols) of acetone was added in 20 to 25 min while the temperature was maintained at 40 to 50°C. Following this addition, the reaction mixture was held at 40 to 45°C for 3 hr with continued stirring, and then stored at 0°C overnight. The white, crystalline product was separated on a Buchner funnel, and the filtrate was further reacted, as above, with a solution of 49 gm (1 mol) of sodium cyanide in 175 ml water and 58 gm (1 mol) acetone. The additional product was combined with the first crop on the Buchner funnel and washed well with ice water. The material was thoroughly dried over potassium hydroxide pellets in a vacuum desiccator. The yield of N,N'-bis(2-cyano-2-propyl) hydrazine varied from 225 gm (90% yield, based on hydrazine sulfate) to 325 gm, depending largely on how well the inorganic salts were removed during the washing.

(2) Preparation of Azo bis-Isobutyronitrile

A mixture of 250 gm (1.5 mols) of impure N,N'-bis(2-cyano-2-propyl) hydrazine and 250 ml methanol was chilled to -5 to 0°C, and 500 ml of 37% hydrochloric acid was added rapidly with cooling and vigorous stirring at 0 to 10°C. Water (1000 ml) was added and the mixture was chilled to -5 to 0°C. A solution of 51 ml (1 mol) bromine in 750 ml methanol was added in three portions with vigorous stirring while the temperature was maintained below 10°C. This quantity of bromine is usually sufficient, as the N,N'-bis(2-cyano-2-propyl) hydrazine is not pure. The mixture was diluted with 1000 ml ice water and the product was collected on a Buchner funnel, washed free of bromine with ice water, then dried over potassium hydroxide pellets in a vacuum desiccator. The over-all conversion of hydrazine sulfate to azo bis-isobutyronitrile through the N,N'-bis(2-cyano-2-propyl) hydrazine was effected in about 66% yield.

(3) Preparation of Methyl Azo bis-Isobutyrate

Dry hydrogen chloride was added rapidly to a suspension of 100 gm (0.61 mol) of azo bis-isobutyronitrile in 750 ml methanol at 20 to 25°C. Solution of the azo bis-isobutyronitrile was completed in approximately 1 hr. The addition of hydrogen chloride was continued at a slower rate at 5 to 10°C for a period of 5.5 hr. The final mixture was stored at 0°C overnight and the precipitate was removed by filtration and washed with cold, absolute ether. The precipitate of imido-hydrochloride was immediately converted to methyl azo bis-isobutyrate on dissolving in 500 ml water. The layer of oily product was separated, freed of a small amount of ether, and recrystallized from 100 ml hexane. The yield of 104.5 gm of methyl azo bis-isobutyrate (mp 25 to 26°C) corresponds to 36.4% of the theoretical.

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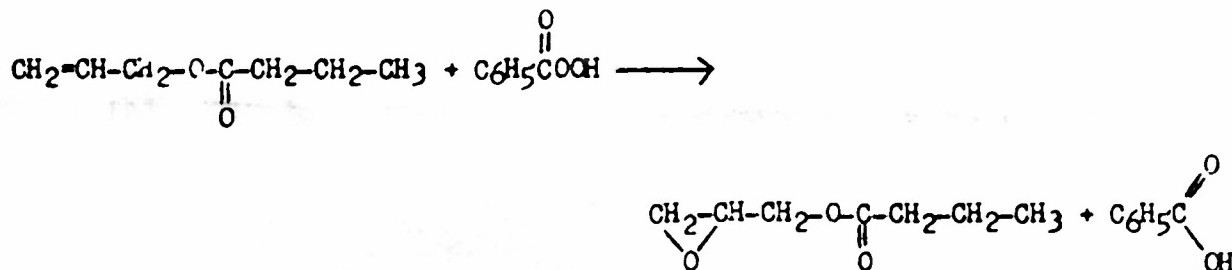
6. Preparation of Glycidyl Butyrate

a. Discussion

(1) Work to date has shown that glycidyl 4,4,4-trinitrobutyrate does not polymerize readily to high-molecular-weight products. The literature on ethylene oxide and propylene oxide polymerization³⁸ indicates that (1) acidic catalysts do not yield products of as high molecular weight as do alkaline catalysts; (2) 1,2-propylene oxide does not polymerize as readily to higher-molecular-weight polymers as does ethylene oxide.

(2) To determine whether the limited results obtained to date are due to the rather large butyroxymethyl side chain of the glycidyl 4,4,4-trinitrobutyrate molecule or to specific effects of the terminal trinitromethyl group, it has been suggested that a model compound, glycidyl butyrate, be prepared for polymerization studies which will include the use of alkaline catalysts.

(3) The desired compound was prepared by the following reaction:



b. Experimental

(1) Allyl Butyrate

Approximately 132 gm (1.5 mols) n-butyric acid, 131 gm (2.25 mols) allyl alcohol, 200 ml benzene, 5 gm of p-toluene sulfonic acid monohydrate, and 0.5 gm of 1,3,5-trinitrobenzene were refluxed until water could no longer be removed by azeotropic distillation. The initial reaction temperature of 79°C rose to 81 to 82°C. The mixture was then refluxed for an additional half hour (total reflux time, 2-1/4 hr). The aqueous azeotrope layer weighed 33 gm (theory requires 27 gm of water). The acid

³⁸Carbide and Carbon Chem. Corp., British patents 584,367 and 610,505; H. R. Fife and F. H. Roberts (to Carbide and Carbon Chem. Corp.), British patent 601,604.

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VI Technical Progress, F (cont.)

Report No. 590

catalyst was then neutralized with 5 gm of sodium bicarbonate and the benzene and excess allyl alcohol was distilled off through a two-foot, packed, total-condensation-head column. From 55°C/34 mm to 59°C/31 mm a small intermediate fraction was collected. Almost all of the main product came over at 59 to 60°C/31 mm, yielding 176 gm (92% of theoretical); the n_D^{25} was 1.4130. After redistillation at atmospheric pressure the middle fraction, bp 140 to 141°C, had an n_D^{25} of 1.4131 and d^{25} of 0.896. The determined M_R^{25} was 35.21, as compared with the calculated value of 35.69.

(2) Glycidyl Butyrate

For the conversion to the epoxide, 51 gm (0.4 mol) allyl butyrate was dissolved in 50 ml chloroform, chilled to 0°C, and reacted with 1100 ml of 0.48M perbenzoic acid (1/3 excess) in chloroform. The utilization of the perbenzoic acid was more rapid than by allyl 4,4,4-trinitrobutyrate. To ensure complete conversion to the epoxide, an additional 40% of the perbenzoic acid solution was added when the disappearance of active oxygen ceased. The benzoic and perbenzoic acid were removed in the usual manner. The residual oil obtained after evaporation of the chloroform weighed 56 gm (97%). Fractionation of this oil at 7.5 mm yielded 12 gm, bp 78 to 79°C, $n_D^{25} = 1.4282$, $d^{25} = 1.034$. The first 1.4 gm that distilled over had an n_D^{25} of 1.4281; in subsequent fractions the n_D^{25} was 1.4274 and 1.4272. The equivalent weights on saponification were 143.5 and 143.4 (theoretical 144.18).

Anal. calc'd for $C_7H_{12}O_3$: %C, 58.31; %H, 8.39; M_R^{25} , 36.1

Found: %C, 58.35; %H, 8.32; M_R^{25} , 35.89

VII. SAFETY PRACTICE

A. INTRODUCTION

It has become the practice on this contract to maintain a section on safety procedures in order to report fires, fume-offs and explosions as well as the methods adopted for their prevention. During the past quarter one fume-off was encountered which may be expected in other cases where the silver nitrate-sodium nitrite oxidative nitration is used.

B. FUME-OFF IN THE PREPARATION OF 1,1-DINITROETHANE

During the preparation of 1,1-dinitroethane from nitroethane by the silver nitrate-sodium nitrite oxidation the silver is reduced to silver metal. On a 45-mol scale the quantity of reduced silver metal is appreciable.

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VII Safety Practice, B (cont.)

Report No. 59C

This silver must be separated from the reaction mixture before it can be worked up. The silver in this instance was collected on a large Buchner funnel and washed with water. However, a good deal of the oily dinitroethane was apparently still adsorbed on the surface of the finely divided silver. As air was drawn through the silver mass the dinitroethane started to react, evolving large volumes of nitric oxides. This decomposition could not be stopped by further water washings and it was necessary to dump the contents of the funnel into a large crock of water in order to stop further and more violent decomposition. In order to prevent such occurrences the procedure of isolation for the dinitroethane has been changed. The reaction mixture is now made basic so as to convert all the dinitroethane to the soluble sodium salt. Then, on filtration, the silver is readily purified by water washing. Acidification of the filtrate permits the separation of the dinitroethane in good yield with a minimum of danger.

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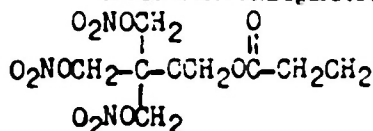
Data Questionnaire on
COMPOUNDS FOR USE AS INGREDIENTS OF PROPELLANTS AND OTHER EXPLOSIVES

Listed below are the characteristics which are believed to be of importance in the study of a compound which may possibly be used as a constituent of solid propellants or other explosives. It is not expected that all this information will be available for every compound. For example, with a compound showing poor stability, it is probably not advisable to investigate that compound farther. After placing such information as is available for a compound which you have prepared or tested on one of these forms, send it to SOLID PROPELLANT INFORMATION AGENCY, APL/JHU, 8621 Georgia Ave., Silver Spring, Maryland. As additional information on the same or new compounds accrues, forward it on a similar form at a later date. The information submitted on these forms will be rewritten and published by SPIA in loose-leaf manual form. These forms may also be used as work or data sheets for your experimental studies. Extra copies are available upon request from SPIA. Suggestions for improvement of these forms are invited. If insufficient space has been provided for any item, attach separate sheets.

COMPOUND:

Name Pentaerythritol Acrylate TrinitrateEmpirical formula C₈H₁₁N₃O₁₁

Structure: (configuration)



Information submitted by:

Activity Aerojet Engineering Corporation*Person C. Vanneman, R. ParretteDate 25 January 1952

Preparation reaction(s): $(\text{O}_2\text{NOCH}_2)_3\text{CCH}_2\text{OH} + \text{CH}_2=\text{CHCOCl} \longrightarrow$
 $(\text{O}_2\text{NOCH}_2)_3\text{CCH}_2\text{OCCCH}=\text{CH}_2$

1. Quantitative analysis: (% by weight)

	Carbon	Hydrogen	Oxygen	Nitrogen	Impurity, determined
Calculated from formula	29.55	3.41	54.12	12.92	from melting-point
By determination	28.99	3.22		12.66	curve, 1.0 mol%

2. Burning properties: (compared to nitrocellulose, under nitrogen at atmospheric pressure:)

(Faster? slower? residue? etc.)

3. Stability and Sensitivity: Plot any graphs on separate sheet

Discuss methods used when they vary from references. Give temperature used. (Use separate sheet if necessary.)

Name of test	Recommended method
a. Impact Sensitivity	OSRD 3185
b. Thermal Stability	OSRD 3401 p.8 <u>134.5°C, methyl violet paper</u>
c. Vacuum Stability	OSRD 3401 p.10
d. Temperature of Explosion	OSRD 3401 p.8
e. Temperature of Ignition	OSRD 3401 p.8
f. Thermal Stability, 65.5°C	Picatinny Arsenal Report No. 1401. 1.3-gm sample, KI-starch paper.
g. <u>Impact Stability</u>	Bureau of Mines Bull. No. 346, 2 kg wt., 50% shots

RESULTS OF ABOVE TESTS

Reference compound _____
(designation-TNT, Tetryl, H.C., etc.)

New Compound test results

a.		
b.	Nitrocellulose; 30 min, no color	Colored, 3 hr; no change in appearance, 5 hr
c.		
d.		
e.		
f.	Nitrocellulose; 10 min, no color	No color or change in appearance, 5 hr
g.		
h.	RDX 28 cm, PETN 17 cm	100 cm, no shots

4. Heat of formation: $(\Delta H) + \frac{-155}{(\text{Indicate sign})}$ Kg. calories at 25°C., 1 atm. pressure

*Compound was first prepared by Allegany Ballistics Laboratory.

- | | By Experiment | By Calculation | Method
Description or reference. Separate sheet if necessary. |
|---|--------------------|-------------------------|--|
| 5. Energy of explosion (Q)
(at 250°C. H ₂ O liquid) | | cal/gm | |
| 6. Heat of combustion (H _c)
(at 250°C. H ₂ O liquid) | 2850 | cal/gm | 2994 |
| 7. Specific impulse (I _{sp}) calc: | | lb-sec/lb | |
| 8. Physical form of compound (viscous liquid, crystalline type, etc.) | | | |
| 9. Simple microscope analysis data: Small, white, rod-shaped or needle-shaped crystals (crystal studies) | | | |
| 10. Density (Macro method) | gm/cm ³ | (Micro or other method) | 1.58 gm/cm ³ |
| (Explain on separate sheet any unique methods you use.) | | | |
| 11. Index of refraction: (n _D ^{25°C.}) | | 12. Color | White |
| | | 13. Odor | None |
| 14. pH at 25°C. 6.3 (Method reference OSRD 3401 p.4, or OSRD 5968. Indicate method used, i.e., solvent and concentrations used. pH indicator name or Beckman pH meter.) Water, saturated solution, Beckman meter. | | | |

15. Hygroscopicity:

New Compound

Reference Compound

Visible change on exposure to ambient air.

% wt increase by* (a) or (b)

(Strike out method (a) or (b) if not used.)

*Method:

(If other than below methods are used, explain on separate sheet.)

(a) The sample (approx. 5-10 g. of whole grain small powder or 1 grain of large powder) is placed in a glass weighing bottle. The weighing bottle (cover removed) is placed in a vacuum drying oven for 5 hrs. @ 55°C. Remove weighing bottle from oven, cover with glass stopper, cool in a desiccator and weigh accurately. This is taken as original dry weight of sample. Then place weighing bottle (cover removed) in a humidior (a 10-in. desiccator is a satisfactory vessel) containing 1 liter of 18.6 ± .5% H₂SO₄. (This gives relative humidity 90 ± .25%). Place in an oven maintained at 30 ± 2°C. On the fourth day remove weighing bottle from the humidior, cover with glass stopper, cool in a desiccator and weigh. Then return to humidior for 24 hours, cool and reweigh. Continue daily weighings until constant weight indicates sample has reached equilibrium with 90% R.H. The % weight increase is then reported as hygroscopicity of the sample.

(b) An alternate method is in OSRD 3401 p.3.

16. Volatility: Report as rate of loss in wt % per unit area (for liquid samples measure the surface area; for solids, the sample should be screened between 100-120 mesh U.S. Standard certified sieve) per 4 hrs., after constant rate of loss is obtained during three consecutive 4-hr. periods at (a) 25°C in a vessel through which a stream of dry air is forced, (b) in an oven at 65.5°C or (c) under other test method or conditions.

(Description or reference to other test or conditions used. Use separate sheet if necessary.)

Volatility results on:

New Compound

Reference Compound

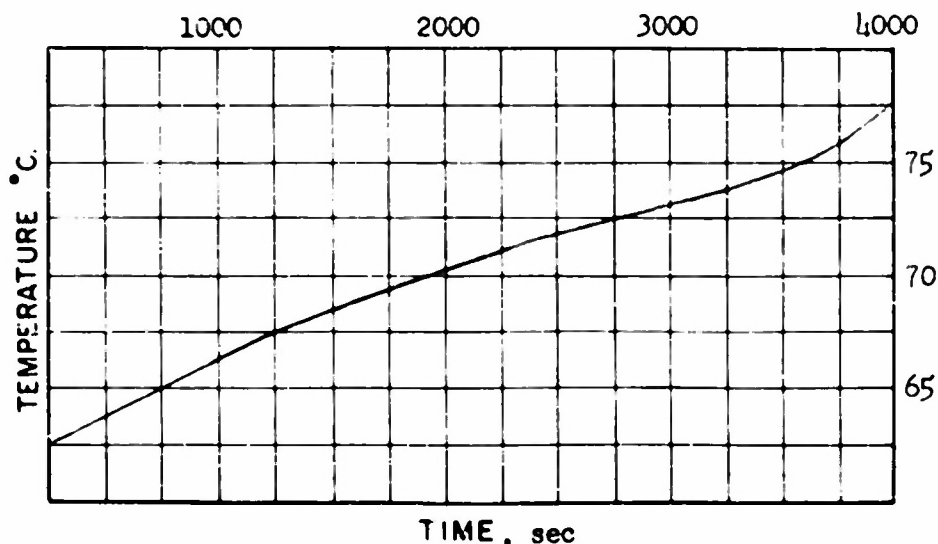
(designation)

a. _____
b. _____
c. _____

a. _____
b. _____
c. _____

17. Boiling point, or decomposition temperature: _____ °C.
(underline which temperature is reported)
18. Heat of Vaporization: _____ g-cal./gm _____ BTU/lb.
19. Heat of Fusion: _____ g-cal./gm _____ BTU/lb.
20. Melting point: 73.7 °C.

21. Freezing point vs. Time Curve: (Please mark the coordinates with scale values that apply to the compound under study.)



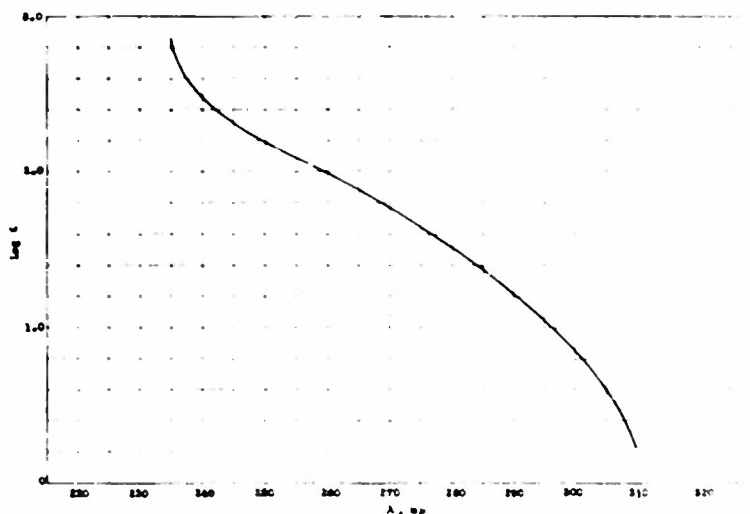
22. Solubility of new compound:

0.01 g/100 ml H₂O at 25°C. _____ g/100 ml H₂O at _____ °C.
 132 g/100 ml Acetone at 25 °C.
 (name material used as solvent)
 4.11 g/100 ml Toluene at 25 °C.
 (name material used as solvent)

23. Viscosity of the new compound and its solutions:

	NEW COMPOUND	SOLVENT		VISCOSITY at TEMP.		METHOD USED
	wt. % in solution	NAME	wt. % in solution	Centipoises	°C.	
a.	100		NONE		25	
b.	100		NONE			
c.	95	N.C. (13.15% N.)	5		25	
d.						
e.						
f.						

Ultraviolet Absorption Spectrum of
 Polyacrylonitrile Acrylate Triacrylate in Ether



Under compatibility we are considering the ability of two compounds to be in intimate contact (Note CSRD 5758 p. 21-22) over a long period of time without adverse effects on either the chemical or physical properties of either material. These tests will probably be of varied extent. They might be some of the followings: (a) Standard stability tests. (b) Simple observations of exudation or separation at ambient or accelerated temperature. (c) Prepare thin sheets (.025" thick, 1" square) of the plasticized material. Separate the sheets with strips of cigarette paper or carbon paper and compress the stack in a "C" clamp. After several days note the oily collection on the paper. Please give reference to or describe procedure used. Item 28 is to indicate results when the compound is in contact with some material other than ethyl cellulose, nitrocellulose or rubber. Test performed by dissolving sample and standard substance in a common solvent, drying rapidly on a glass plate, and examining the resulting film for clarity and homogeneity.

25. Compatibility with ethyl cellulose: _____

26. Compatibility with nitrocellulose:	Ratio,	wt sample	
		wt NC	
		20/80	Compatible
		50/50	Compatible
		80/20	Compatible
27. Compatibility with rubber:	Ratio,	wt sample	
		wt rubber	
		20/80	Incompatible
		50/50	Incompatible
		80/20	Incompatible
28. Compatibility with _____:			

29. Polymerizing properties of the new compound:

- (a) By itself gives acetone-insoluble polymer. In 50% acetone solution-soluble
 (b) In mixtures (with additives) polymer is obtained.
 (c) Inhibiting action on polymerization of:
 Thiokol _____
 Methacrylate _____
 Other compounds _____

30. Availability

- a. Amount now available? _____ Research quantities.
 b. When was available material first prepared? _____
 c. Amount prepared at that time? _____
 d. Is large production feasible? _____
 e. Plant capacity in existence, lbs/day? _____
 f. Outline steps for a quantity production method _____

31. Additional information: (toxicity, hazards, deterioration, oxygen balance, detonation rate, explosive power, ease of hydrolysis by water, etc. List references, reports, data books, etc. that refer to the compound.) _____

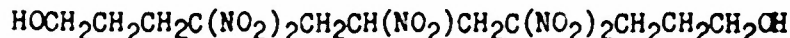
Data Questionnaire on

COMPOUNDS FOR USE AS INGREDIENTS OF PROPELLANTS AND OTHER EXPLOSIVES

Listed below are the characteristics which are believed to be of importance in the study of a compound which may possibly be used as a constituent of solid propellants or other explosives. It is not expected that all this information will be available for every compound. For example, with a compound showing poor stability, it is probably not advisable to investigate that compound farther. After placing such information as is available for a compound which you have prepared or tested on one of these forms, send it to SOLID PROPELLANT INFORMATION AGENCY, APL/JHU, 8621 Georgia Ave., Silver Spring, Maryland. As additional information on the same or new compounds accrues, forward it on a similar form at a later date. The information submitted on these forms will be rewritten and published by SPIA in loose-leaf manual form. These forms may also be used as work or data sheets for your experimental studies. Extra copies are available upon request from SPIA. Suggestions for improvement of these forms are invited. If insufficient space has been provided for any item, attach separate sheets.

COMPOUND:

Name 4,4,6,8,8-Pentanitro-1,11-undecanediol Information submitted by:
 Empirical formula C₁₁H₁₉N₅O₁₂ Activity Aerojet Engineering Corporation
 Structure:(configuration) Person G. Linden, R. Parrette
 Date 25 January 1952



Preparation reaction(s): Reduction of 4,4,6,8,8-pentanitro-undecanedioyl chloride with NaBH₄

1. Quantitative analysis:(% by weight)

	Carbon	Hydrogen	Oxygen	Nitrogen		
Calculated from formula	31.96	4.63	46.46	16.95		
By determination	32.46	4.60		16.90		

2. Burning properties:(compared to nitrocellulose, under nitrogen at atmospheric pressure:)

(faster? slower? residue? etc.)

3. Stability and Sensitivity: Plot any graphs on separate sheet

Discuss methods used when they vary from references. Give temperature used. (Use separate sheet if necessary.)

Name of test	Recommended method	
a. Impact Sensitivity	OSRD 3185	
b. Thermal Stability	OSRD 3401 p.8	<u>134.5°C, methyl violet paper</u>
c. Vacuum Stability	OSRD 3401 p.10	
d. Temperature of Explosion	OSRD 3401 p.6	
e. Temperature of Ignition	OSRD 3401 p.6	
f. Thermal Stability, 65.5°C	Picatinny Arsenal	<u>Report No. 1401, 1.3 gm sample, KI-starch paper.</u>
g.		
h. Impact Stability	Bureau of Mines Bull. No. 346	<u>2-kg wt. 50% shots</u>

RESULTS OF ABOVE TESTS

Reference compound
(designation-TNT, Tetryl, N.C., etc.)

New Compound test results

a.		
b.	<u>Nitrocellulose; 30 min, no color</u>	<u>Colored, 10 min; exploded, 11 min</u>
c.		
d.		
e.		
f.	<u>Nitrocellulose; 10 min, no color</u>	<u>Colored, 22 min; no change in appearance.</u>
g.		<u>5 hr</u>
h.	<u>RDX 28 cm. PETN 17 cm</u>	<u>100 cm, no shots</u>

4. Heat of formation: $(\Delta H) + \frac{-174}{(\text{Indicate sign})}$ Kg. calories at 25°C., 1 atm. pressure

- | By Experiment | By Calculation | Method |
|---|----------------------------------|---|
| 5. Energy of explosion (Q)
(at 25°C. H ₂ O liquid) | cal/gm | Description or reference. Separate sheet if necessary. |
| 6. Heat of combustion (H _c)
(at 25°C. H ₂ O liquid) | 3567 cal/gm | 3653 Aerojet Report No. 417A |
| 7. Specific impulse (I _{sp}) calc: | lb-sec/lb | |
| 8. Physical form of compound (viscous liquid, crystalline type, etc.) | | |
| 9. Simple microscope analysis data: <u>Small, light-yellow, prismatic crystals.</u>
(crystal studies) | | |
| 10. Density (Macro method) | <u>1.58</u> gm/cm ³ . | (Micro or other method) _____ gm/cm ³ .
(Explain on separate sheet any unique methods you use.) |
| 11. Index of refraction (n _D ^{25°C.}) | _____ | 12. Color <u>Light yellow</u> 13. Odor <u>None</u> |
| 14. pH at 25°C. <u>4.7</u> (Method reference OSRD 3401 p.4, or OSRD 5968. Indicate method used, i.e. solvent and concentrations used. pH indicator paper or Beckman pH meter.) <u>Water, saturated solution, Beckman meter.</u> | | |

15. Hygroscopicity.

New Compound

Reference Compound

Visible change on exposure to ambient air.

(designation)

% wt increase by* (a) or (b)

(Strike out method (e) or (b) if not used.)

(If other than below methods are used, explain on separate sheet.)

*Method:

(e) The sample (approx. 5-10 g. of whole grain small powder or 1 grain of large powder) is placed in a glass weighing bottle. The weighing bottle (cover removed) is placed in a vacuum drying oven for 5 hrs. @ 55°C. Remove weighing bottle from oven, cover with glass stopper, cool in a desiccator and weigh accurately. This is taken as original dry weight of sample. Then place weighing bottle (cover removed) in a humidor (a 10-in. desiccator is a satisfactory vessel) containing 1 liter of 18.6 ± .5% H₂SO₄. (This gives relative humidity 90 ± .25%). Place in an oven maintained at 30 ± 2°C. On the fourth day remove weighing bottle from the humidor, cover with glass stopper, cool in a desiccator and weigh. Then return to humidor for 24 hours, cool and reweigh. Continue daily weighings until constant weight indicates sample has reached equilibrium with 90% R.H. The % weight increase is then reported as hygroscopicity of the sample.

(b) An alternate method is in OSRD 3401 p.3.

16. Volatility: Report as rate of loss in wt % per unit area (for liquid samples measure the surface area; for solids, the sample should be screened between 100-120 mesh U.S. Standard certified sieve) per 4 hrs., after constant rate of loss is obtained during three consecutive 4-hr. periods at (a) 25°C in a vessel through which a stream of dry air is forced, (b) in an oven at 65.5°C or (c) under other test method or conditions.

(Description or reference to other test or conditions used. Use separate sheet if necessary.)

Volatility results on:

New Compound

Reference Compound

(designation)

a. _____

a. _____

b. _____

b. _____

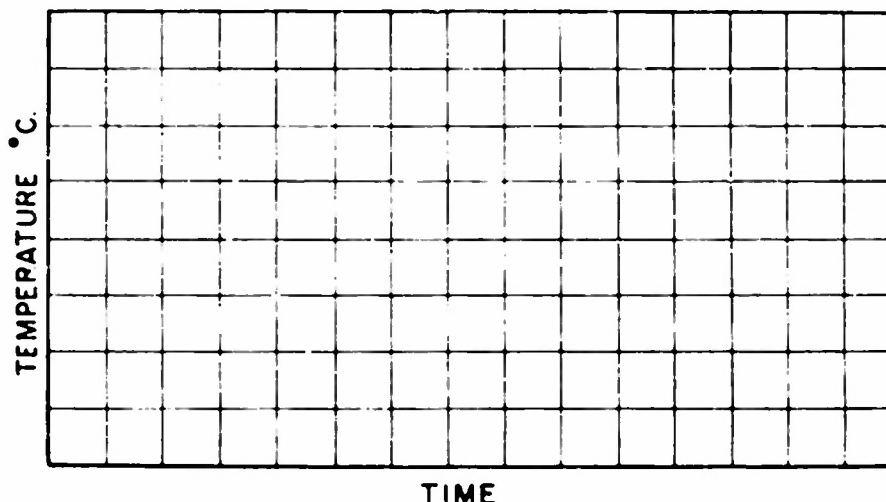
c. _____

c. _____

17. Boiling point, or decomposition temperature: _____ °C.
(underline which temperature is reported)
18. Heat of Vaporization: _____ g-cal./gm _____ BTU/lb.
19. Heat of Fusion: _____ g-cal./gm _____ BTU/lb.
20. Melting point: 109 to 110 °C.

21. Freezing point vs. Time Curve: (Please mark the coordinates with scale values that apply to the compound under study.)

Unstable at Melting Point (See 3b and 3f)



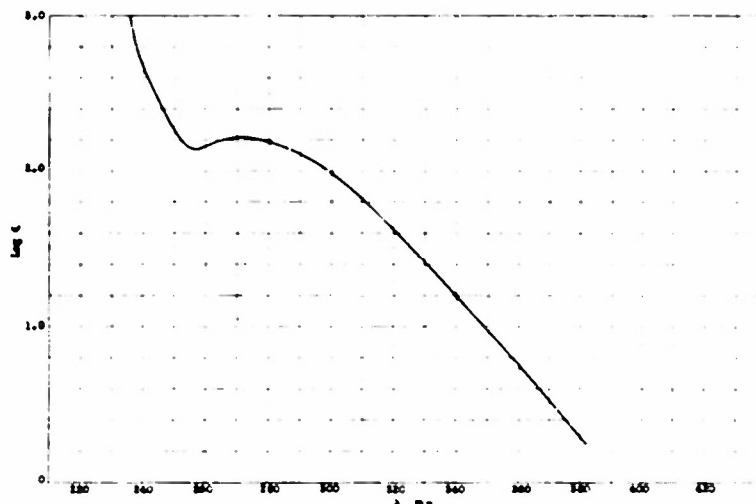
22. Solubility of new compound:

<0.01 g/100 ml H₂O at 25°C. _____ g/100 ml H₂O at _____ °C.
206 g/100 ml Acetone at 25 °C.
 (name material used as solvent)
<0.01 g/100 ml Toluene at 25 °C.
 (name material used as solvent)

23. Viscosity of the new compound and its solutions:

	NEW COMPOUND wt. % in solution	SOLVENT		VISCOSITY at Centipoises	TEMP. °C.	METHOD USED reference
		NAME	Wt. % in solution			
a.	100		NONE		25	
b.	100		NONE			
c.	95	N.C. (13.15% N.)	5		25	
d.						
e.						
f.						

Ultraviolet Absorption Spectrum of
4,4,6,6,8-pentachloro-1,11-undecadiol in Ethanol



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SPIA/M3

Under compatibility we are considering the ability of two compounds to be in intimate contact (Note OSRD 5758 p. 21-22) over a long period of time without adverse effects on either the chemical or physical properties of either material. These tests will probably be of varied extent. They might be some of the following: (a) Standard stability tests. (b) Simple observations of exudation or separation at ambient or accelerated temperature. (c) Prepare thin sheets (.025" thick, 1" square) of the plasticized material. Separate the sheets with strips of cigarette paper or carbon paper and compress the stack in a "C" clamp. After several days note the oily collection on the paper. Please give reference to or describe procedure used. Item 28 is to indicate results when the compound is in contact with some material other than ethyl cellulose, nitrocellulose or rubber. Test performed by dissolving sample and standard substance in a common solvent, drying rapidly on a glass plate, and examining the resulting film for clarity and homogeneity.

25. Compatibility with ethyl cellulose: _____

26. Compatibility with nitrocellulose:	Ratio,	wt sample	
		wt NC	
		20/80	Compatible
		50/50	Compatible
27. Compatibility with rubber:	Ratio,	wt sample	
		wt rubber	
		20/80	Compatible
		50/50	Compatible
28. Compatibility with _____:	Ratio,	80/20	Incompatible

29. Polymerizing properties of the new compound:

(a) By itself _____

(b) In mixtures (with additives) _____

(c) Inhibiting action on polymerization of:

Thiokol _____

Methacrylate _____

Other compounds _____

30. Availability

a. Amount now available? Research quantities

b. When was available material first prepared? _____

c. Amount prepared at that time? _____

d. Is large production feasible? _____

e. Plant capacity in existence, lbs/day? _____

f. Outline steps for a quantity production method _____

31. Additional information: (toxicity, hazards, deterioration, oxygen balance, detonation rate, explosive power, ease of hydrolysis by water, etc. List references, reports, data books, etc. that refer to the compound.) _____

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Data Questionnaire on

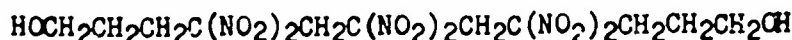
COMPOUNDS FOR USE AS INGREDIENTS OF PROPELLANTS AND OTHER EXPLOSIVES

Listed below are the characteristics which are believed to be of importance in the study of a compound which may possibly be used as a constituent of solid propellants or other explosives. It is not expected that all this information will be available for every compound. For example, with a compound showing poor stability, it is probably not advisable to investigate that compound further. After placing such information as is available for a compound which you have prepared or tested on one of these forms, send it to SOLID PROPELLANT INFORMATION AGENCY, APL/JHU, 8621 Georgia Ave., Silver Spring, Maryland. As additional information on the same or new compounds accrues, forward it on a similar form at a later date. The information submitted on these forms will be rewritten and published by SPIA in loose-leaf manual form. These forms may also be used as work or data sheets for your experimental studies. Extra copies are available upon request from SPIA. Suggestions for improvement of these forms are invited. If insufficient space has been provided for any item, attach separate sheets.

COMPOUND:

Name 4,4,6,6,8,8-Hexanitro-1,11-undecanedioyl
 Empirical formula C₁₁H₁₈N₆O₁₁
 Structure (configuration)

Information submitted by:

Activity Aerojet Engineering CorporationPerson G. Linden, R. ParretteDate 25 January 1952

Preparation reaction(s): Reduction of 4,4,6,6,8,8-hexanitro-1,11-undecanedioyl chloride with NaBH₄

1. Quantitative analysis (% by weight)

	Carbon	Hydrogen	Oxygen	Nitrogen		
Calculated from formula	28.93	3.96	48.87	18.34		
By determination	29.50	3.84	48.17	18.49		

2. Burning properties: (compared to nitrocellulose, under nitrogen at atmospheric pressure;)

(faster? slower? residue? etc.)

3. Stability and Sensitivity: Plot any graphs on separate sheet

Discuss methods used when they vary from references. Give temperature used. (Use separate sheet if necessary.)

Name of test	Recommended method
a. Impact Sensitivity	OSRD 3185
b. Thermal Stability	OSRD 3401 p.8 <u>134.5°C. methyl violet paper</u>
c. Vacuum Stability	OSRD 3401 p.10
d. Temperature of Explosion	OSRD 3401 p.6
e. Temperature of Ignition	OSRD 3401 p.6
f. Thermal Stability, 65.5°C	Picatinny Arsenal Report No. 11401; 1.3-gm sample, KI-starch paper
g. Impact Stability	Bureau of Mines Bull. No. 346; 2 kg wt., 50% shots

RESULTS OF ABOVE TESTS

Reference compound
 (designation-TNT, Teteryl, H.C., etc.)

New Compound test results

a.		
b.	Nitrocellulose; 30 min, no color	Colored, 5 min; exploded, 6 min.
c.		
d.		
e.		
f.	Nitrocellulose; 10 min, no color	Colored 16 min; no change in appearance, 5 hr
g.		
h.	RDX 28 cm, PETN 17 cm	100 cm, no shots

4. Heat of formation: (ΔH) + -173 Kg. calories at 25°C., 1 atm. pressure
 (Indicate sign)

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- | | By Experiment | By Calculation | Method
Description or reference. Separate
sheet if necessary. |
|--|---|--|---|
| 5. Energy of explosion (Q)
(at 25°C. H ₂ O liquid) | _____ | cal/gm _____ | _____ |
| 6. Heat of combustion (H _c)
(at 25°C. H ₂ O liquid) | 3205 | cal/gm 4222 | Aircraft Report No. 417A |
| 7. Specific impulse (I _{sp}) calc: | _____ | lb-sec/lb _____ | _____ |
| 8. Physical form of compound (viscous liquid, crystalline type, etc.) | _____ | | |
| 9. Simple microscope analysis data: <u>Small, light-yellow, rod-shaped or needle-shaped crystals.</u>
(crystal studies) | _____ | | |
| 10. Density (Macro method) | _____ gm/cm ³ . | (Micro or other method) _____ gm/cm ³ . | (Explain on separate sheet any unique methods you use.) |
| 11. Index of refraction: (n _D ^{25°C.}) _____ | 12. Color <u>Light yellow</u> | 13. Odor <u>None</u> | _____ |
| 14. pH at 25°C. <u>4.6</u> | (Method reference OSRD 3401 p.4, or USRD 5968. Indicate method used, i.e. solvent and concentrations used. pH indicator used or Beckman pH meter.) <u>Water, saturated solution, Beckman meter.</u> | | |

15. Hygroscopicity:

New Compound

Reference
CompoundVisible change on exposure
to ambient air. _____

(designation) _____

% wt Increase by* (a) or (b) _____

(Strike out method (a) or (b) if not used.) _____(If other than below methods are used,
explain on separate sheet.) _____

*Method:

(a) The sample (approx. 5-10 g. of whole grain small powder or 1 grain of large powder) is placed in a glass weighing bottle. The weighing bottle (cover removed) is placed in a vacuum drying oven for 5 hrs. @ 55°C. Remove weighing bottle from oven, cover with glass stopper, cool in a desiccator and weigh accurately. This is taken as original dry weight of sample. Then place weighing bottle (cover removed) in a humidifier (a 10-in. desiccator is a satisfactory vessel) containing 1 liter of 18.6 ± .5% H₂SO₄. (This gives relative humidity 90 ± .25%). Place in an oven maintained at 30 ± 2°C. On the fourth day remove weighing bottle from the humidifier, cover with glass stopper, cool in a desiccator and weigh. Then return to humidifier for 24 hours, cool and reweigh. Continue daily weighings until constant weight indicates sample has reached equilibrium with 90% R.H. The % weight increase is then reported as hygroscopicity of the sample.

(b) An alternate method is in OSRD 3401 p.3.

16. Volatility: Report as rate of loss in wt % per unit area (for liquid samples measure the surface area; for solids, the sample should be screened between 100-120 mesh U.S. Standard certified sieves) per 4 hrs., after constant rate of loss is obtained during three consecutive 4-hr. periods at (a) 25°C in a vessel through which a stream of dry air is forced, (b) in an oven at 65.5°C or (c) under other test method or conditions. _____

(Description or reference to other test or conditions used. Use separate sheet if necessary.)

Volatility results on:

New Compound

Reference Compound

(designation) _____

a. _____

a. _____

b. _____

b. _____

c. _____

c. _____

17. Boiling point, or decomposition temperature: _____ °C.
(underline which temperature is reported)

18. Heat of Vaporization: _____ g-cal./gm _____ BTU/lb.

19. Heat of Fusion: _____ g-cal./gm _____ BTU/lb.

20. Melting point 125 to 125.5°C.

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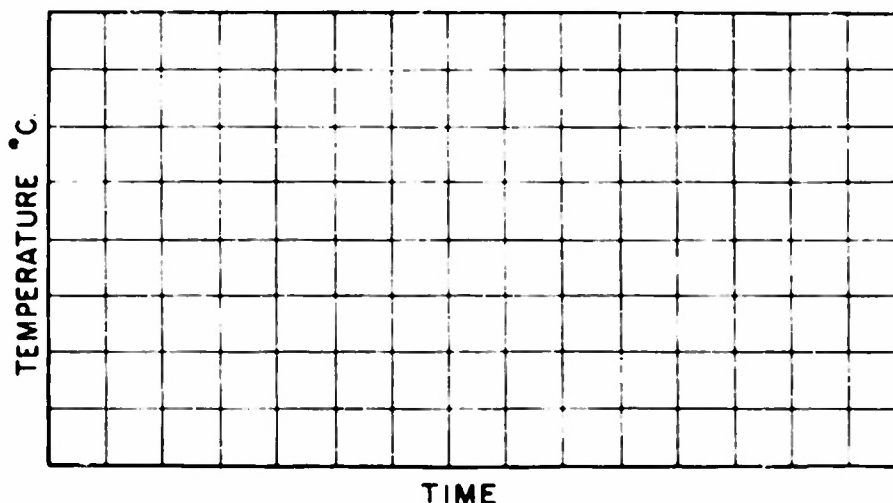
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Report No. 590

SPIA/M3

21. Freezing point vs. Time Curve: (Please mark the coordinates with scale values that apply to the compound under study.)

Unstable at Melting Point (See 3b and 3f)



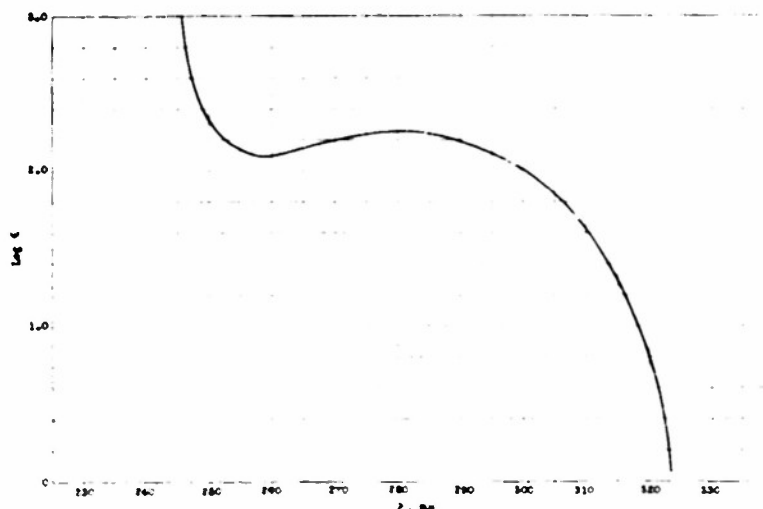
22. Solubility of new compound:

0.02 g/100 ml H₂O at 25°C. _____ g/100 ml H₂O at _____ °C.
 142 g/100 ml Acetone at 25 °C.
 (name material used as solvent)
 0.02 g/100 ml Toluene at 25 °C.
 (name material used as solvent)

23. Viscosity of the new compound and its solutions:

	NEW COMPOUND	SOLVENT		VISCOSITY at TEMP. Centipoises °C.	METHOD USED reference
	wt. % in solution	NAME	Wt. % in solution		
a.	100		NONE	25	
b.	100		NONE		
c.	95	N.C. (13.15% N.)	5	25	
d.					
e.					
f.					

Ultraviolet Absorption Spectrum of
 4,4,6,6,8,8-hexamethyl-2,11-dioxabenzodioxole in acetone



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SPLA/M3

Under compatibility we are considering the ability of two compounds to be in intimate contact (Note OSRD 5758 p. 21-22) over a long period of time without adverse effects on either the chemical or physical properties of either material. These tests will probably be of varied extent. They might be some of the following: (a) Standard stability tests. (b) Simple observations of exudation or separation at ambient or accelerated temperature. (c) Prepare thin sheets (.025" thick, 1" square) of the plasticized material. Separate the sheets with strips of cigarette paper or carbon paper and compress the stack in a "C" clamp. After several days note the oily collection on the paper. Please give reference to or describe procedure used. Item 28 is to indicate results when the compound is in contact with some material other than ethyl cellulose, nitrocellulose or rubber. Test performed by dissolving sample and standard substance in a common solvent, drying rapidly on a glass plate, and examining the resulting film for clarity and homogeneity.

25. Compatibility with ethyl cellulose: _____

26. Compatibility with nitrocellulose: Ratio,	<u>wt sample</u>	
	<u>wt NC</u>	
	20/80	Compatible
	50/50	Compatible
	80/20	Compatible

27. Compatibility with rubber: Ratio,	<u>wt sample</u>	
	<u>wt rubber</u>	
	20/80	Compatible
	50/50	Incompatible
	80/20	Incompatible

28. Compatibility with _____: _____

29. Polymerizing properties of the new compound:

(a) By itself _____

(b) In mixtures (with additives) _____

(c) Inhibiting action on polymerization of:

Thiokol _____

Methacrylate _____

Other compounds _____

30. Availability

a. Amount now available? Research quantities.

b. When was available material first prepared? _____

c. Amount prepared at that time? _____

d. Is large production feasible? _____

e. Plant capacity in existence, lbs/day? _____

f. Outline steps for a quantity production method _____

31. Additional information: (toxicity, hazards, deterioration, oxygen balance, detonation rate, explosive power, ease of hydrolysis by water, etc. List references, reports, data books, etc. that refer to the compound.) _____

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Data Questionnaire on
COMPOUNDS FOR USE AS INGREDIENTS OF PROPELLANTS AND OTHER EXPLOSIVES

Listed below are the characteristics which are believed to be of importance in the study of a compound which may possibly be used as a constituent of solid propellants or other explosives. It is not expected that all this information will be available for every compound. For example, with a compound showing poor stability, it is probably not advisable to investigate that compound farther. After placing such information as is available for a compound which you have prepared or tested on one of these forms, send it to SOLID PROPELLANT INFORMATION AGENCY, APL/JHU, 8621 Georgia Ave., Silver Spring, Maryland. As additional information on the same or new compounds accrues, forward it on a similar form at a later date. The information submitted on these forms will be rewritten and published by SPIA in loose-leaf manual form. These forms may also be used as work or data sheets for your experimental studies. Extra copies are available upon request from SPIA. Suggestions for improvement of these forms are invited. If insufficient space has been provided for any item, attach separate sheets.

COMPOUND:

Name 1,2-bis(4,4,4-Trinitrobutyroxyl) ethane Information submitted by:
 Empirical formula C₁₀H₁₂N₆O₁₆ Activity Aerjet Engineering Corporation
 Structure: (configuration) Person C. Vanneran, R. Farrette
 Date 25 January 1952

Preparation reaction(s). CH₂=CHCOOCH₂CH₂COOCH=CH₂ + CH(NO₂)₃ →
(NO₂)₃CCCH₂CH₂COOCH₂CH₂COOCHCH₂CH₂(NO₂)₃

1. Quantitative analysis: (% by weight)
- | | Carbon | Hydrogen | Oxygen | Nitrogen | Purity, determined |
|-------------------------|--------|----------|--------|----------|--------------------|
| Calculated from formula | 25.43 | 2.56 | 54.21 | 17.80 | from melting-point |
| By determination | 25.32 | 2.35 | | 18.09 | curve, 0.9 mol% |

2. Burning properties: (compared to nitrocellulose, under nitrogen at atmospheric pressure):

(faster? slower? residue? etc.)

3. Stability and Sensitivity: Plot any graphs on separate sheet

Discuss methods used when they vary from references. Give temperature used. (Use separate sheet if necessary.)

Name of test	Recommended method	
a. Impact Sensitivity	OSRD 3185	
b. Thermal Stability	OSRD 3401 p.8	134.5°C, methyl violet paper
c. Vacuum Stability	OSRD 3401 p.10	
d. Temperature of Explosion	OSRD 3401 p.8	
e. Temperature of Ignition	OSRD 3401 p.8	
f. Thermal Stability, 65.5°C	Fitching Arsenal Report No. 11501; 1.3-gm sample, KI-	
g.	starch paper	
h. Impact Stability	Bureau of Mines Bull. No. 346; 2 kg wt., 50% shots	

RESULTS OF ABOVE TESTS

Reference compound
(designation-TNT, Tetryl, N.C., etc.)

New Compound test results

a.		
b.	Nitrocellulose; 30 min, no color	Colored, 28 min; no change in appearance, 5 hr
c.		
d.		
e.		
f.	Nitrocellulose; 10 min, no color	No color or change in appearance, 5 hr
g.		
h.	RDX 28 cm, PETN 17 cm	100 cm, no shots

4. Heat of formation: (ΔH) + -208 Kg. calories at 25°C., 1 atm. pressure
 (Indicate sign)

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SFIA/M3

	By Experiment	By Calculation	Method Description or reference. Separate sheet if necessary.
5. Energy of explosion (Q) (at 250°C. H ₂ O liquid)		cal/gm	
6. Heat of combustion (H _C) (at 250°C. H ₂ O liquid)	2382	cal/gm	2420 Aerojet Report No. 417A
7. Specific impulse (I _{sp}) calc:		lb-sec/lb	
8. Physical form of compound (viscous liquid, crystalline type, etc.)			

9. Simple microscope analysis data: Small, white, prismatic crystals
(crystal studies)

10. Density (Macro method) 1.629 gm/cm³. (Micro or other method) 1.66 gm/cm³.
(Explain on separate sheet any unique methods you use.)

11. Index of refraction: (n_D^{25°C.}) _____ 12. Color White 13. Odor None.

14. pH at 25°C. 6.1 (Method reference OSRD 3401 n.4, or OSRD 5968. Indicate method used, i.e. solvent and concentrations used. pH indicator paper or Beckman pH meter.) Water, saturated solution, Beckman meter.

15. Hygroscopicity:

	New Compound	Reference Compound (designation)
Visible change on exposure to ambient air.		
% wt increase by* (a) or (b) (Strike out method (a) or (b) if not used.)		(If other than below methods are used, explain on separate sheet.)
*Method:		
(a) The sample (approx. 5-10 g. of whole grain small powder or 1 grain of large powder) is placed in a glass weighing bottle. The weighing bottle (cover removed) is placed in a vacuum drying oven for 5 hrs. @ 55°C. Remove weighing bottle from oven, cover with glass stopper, cool in a desiccator and weigh accurately. This is taken as original dry weight of sample. Then place weighing bottle (cover removed) in a humidifier (a 10-in. desiccator is a satisfactory vessel) containing 1 liter of 18.6 ± .5% H₂SO₄. (This gives relative humidity 90 ± .25%). Place in an oven maintained at 30 ± 2°C. On the fourth day remove weighing bottle from the humidifier, cover with glass stopper, cool in a desiccator and weigh. Then return to humidifier for 24 hours, cool and reweigh. Continue daily weighings until constant weight indicates sample has reached equilibrium with 90% R.H. The % weight increase is then reported as hygroscopicity of the sample.		
(b) An alternate method is in OSRD 3401 p.3.		

16. Volatility: Report as rate of loss in wt % per unit area (for liquid samples measure the surface area; for solids, the sample should be screened between 100-120 mesh U.S. Standard certified sieve) per 4 hrs., after constant rate of loss is obtained during three consecutive 4-hr. periods at (a) 25°C in a vessel through which a stream of dry air is forced, (b) in an oven at 65.5°C or (c) under other test method or conditions.

(Description or reference to other test or conditions used. Use separate sheet if necessary.)

Volatility results on:	New Compound	Reference Compound (designation)
a.		a.
b.		b.
c.		c.

17. Boiling point, or decomposition temperature: _____ °C.
(underline which temperature is reported)

18. Heat of Vaporization: _____ g-cal./gm _____ BTU/lb.

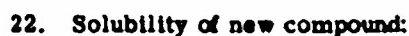
19. Heat of Fusion: _____ g-cal./gm _____ BTU/lb.

20. Melting point: 93.9 °C.

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SPLA, 43

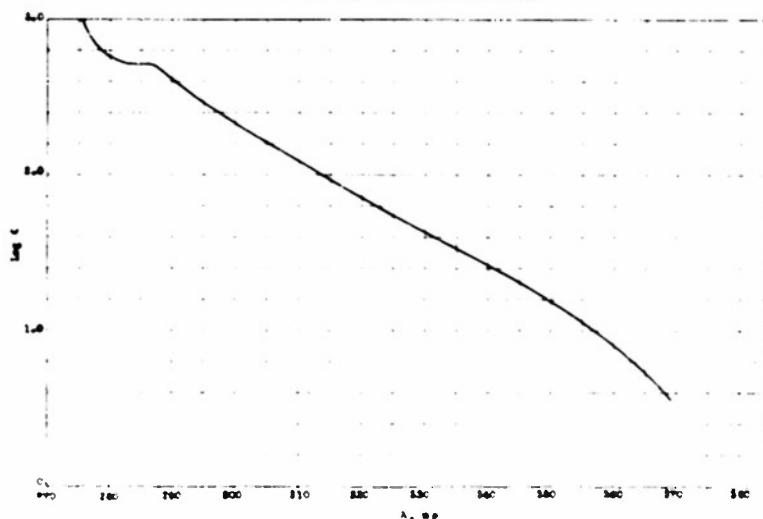
Apparatus of W. M.
Smit, Dissertation,
Amsterdam (1946)



23. Viscosity of the new compound and its solutions:

NEW COMPOUND	SOLVENT		VISCOSITY at Centipoises	TEMP. °C.	METHOD USED reference
	wt. % in solution	NAME wt. % in solution			
a. 100		None		25	
b. 100		None			
c. 95	N.C. (13.1% N.)	5		25	
d.					
e.					
f.					

Fluoride Absorption Spectra of
1,2-Bis(4,4'-F)propane(2,2') diamine



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SP1A/M3

Under compatibility we are considering the ability of two compounds to be in intimate contact (Note OSRD 5758 p. 21-22) over a long period of time without adverse effects on either the chemical or physical properties of either material. These tests will probably be of varied extent. They might be some of the following: (a) Standard stability tests. (b) Simple observations of exudation or separation at ambient or accelerated temperature. (c) Prepare thin sheets (.025" thick, 1" square) of the plasticized material. Saturate the sheets with strips of cigarette paper or carbon paper and compress the stack in a "C" clamp. After several days note the oily collection on the paper. Please give reference to or describe procedure used. Item 28 is to indicate results when the compound is in contact with some material other than ethyl cellulose, nitrocellulose or rubber. Test performed by dissolving sample and standard substance in a common solvent, drying rapidly on a glass plate, and examining the resulting film for clarity and homogeneity.

25. Compatibility with ethyl cellulose: _____

		wt sample	
		wt NC	
26. Compatibility with nitrocellulose: Ratio,		20/80	Compatible
		50/50	Compatible
		80/20	Compatible

		wt sample	
		wt rubber	
27. Compatibility with rubber: Ratio,		20/80	Compatible
		50/50	Compatible
		80/20	Incompatible

28. Compatibility with _____: _____

29. Polymerizing properties of the new compound:

- (a) By itself _____
- (b) In mixtures (with additives) _____
- (c) Inhibiting action on polymerization of:
- Thiokol _____
- Methacrylate _____
- Other compounds _____

30. Availability

- a. Amount now available? _____ Research quantities.
- b. When was available material first prepared? _____
- c. Amount prepared at that time? _____
- d. Is large production feasible? _____
- e. Plant capacity in existence, lbs/day? _____
- f. Outline steps for a quantity production method _____

31. Additional information: (toxicity, hazards, deterioration, oxygen balance, detonation rate, explosive power, ease of hydrolysis by water, etc. List references, reports, data books, etc. that refer to the compound.) _____

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N7onr-462, Task Order I

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