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ACETYLENIC COMPOUNDS FOR ROCKET FUELS

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1 June 1955 – 30 November 1955

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Acetylenic Compounds

for

Rocket Fuels

Department of the Navy:
Office of Naval Research
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Contract No. Nonr-285(04)

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SUMMARY

During the six-month period covered by this report syntheses of acetylenic compounds that contain the high energy cyclopropyl and nitrile groups were investigated.

A successful synthesis of cyclopropyl acetylene was accomplished. The compound was hypergolic with red fuming nitric acid (RFNA), and was quite stable at 71°C.

Cyclopropyl cyanide was synthesized and tested. It is quite stable at 71°C, but it is not hypergolic with red fuming nitric acid (RFNA).

Cyclopropylvinylacetylene was prepared from methyl cyclopropyl ketone and sodium acetylide. Cyclopropylvinylacetylene is hypergolic with red fuming nitric acid, but it exhibits a tendency to polymerize when kept at 71°C. This tendency was not decreased by the addition of 0.3% quinone as inhibitor.

A new synthesis of cyanoacetylene was developed. It involves the preparation of propargyl aldoxime from propargyl aldehyde, a readily available product, and the dehydration of the aldoxime to cyanoacetylene by means of acetic anhydride. This compound was quite stable when heated at 71°C for five days and did not polymerize to any appreciable degree. The product was quite sensitive to thermal shock, and immediately burst into flame when dropped onto a hot plate at 800°F. It is hoped that a synthesis of this type can be developed for the preparation of 2-butyne-1,4-dinitrile.

The theoretical performances as rocket fuels of cyclopropylacetylene, cyclopropyl cyanide and 2-butyne-1,4-dinitrile have been calculated, and these data are listed in the body of this report.

The investigation of the process variables in the reactions involved in the synthesis of methyldivinylacetylene has been continued. The final development of a vapor phase dehydration unit has been delayed because of a solid coke-like deposit which after a few hours completely blocks the flow of material through the vaporizer. An attempt to eliminate this problem will be made in the immediate future.

INTRODUCTION

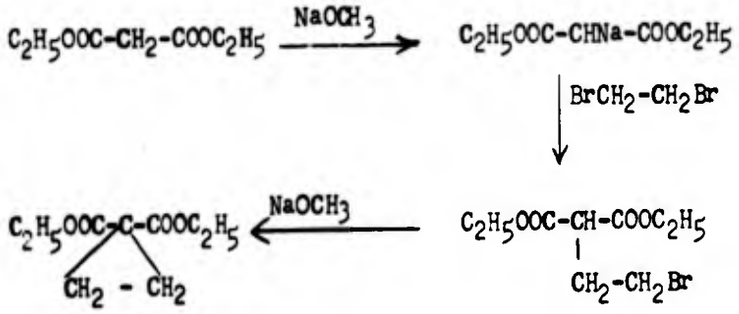
Since strained rings have a considerable amount of "built-in energy" and are relatively stable, it was felt that a combination of this structure with the acetylenics would produce compounds of potential interest as rocket fuels. Several derivatives of cyclopropane have been synthesized and their physical and chemical properties determined.

Since 2-butyne-1,4-dinitrile has a higher specific impulse with red fuming nitric acid than acetylene, work has been directed at the development of a relatively simple and economical synthesis of this and related compounds. Cyanoacetylene has been synthesized, and it is hoped that this synthesis can be extended to the preparation of 2-butyne-1,4-dinitrile.

SYNTHESIS WORK

1,1-Dicarbethoxycyclopropane

This compound was prepared by the method of Lucas and Pressman, Organic Chemistry, p. 450 (1949) involving the following reaction:

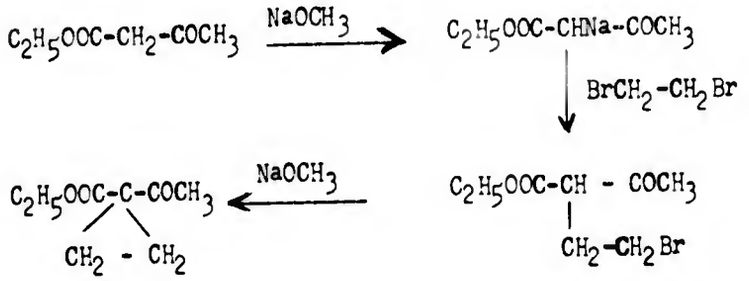


In order to minimize side reactions, the sodium malonic ester was added to an excess of ethylene bromide. After the reaction was complete, additional sodium ethoxide was added to accomplish the ring closure. A 65% yield of liquid b.p. 103-112°C/20 mm, n_D^{20} 1.3298, d_4^{20} 1.056 was obtained.

It was believed that this method could be extended to acetoacetic ester to furnish a route to the synthesis of methyl cyclopropyl ketone.

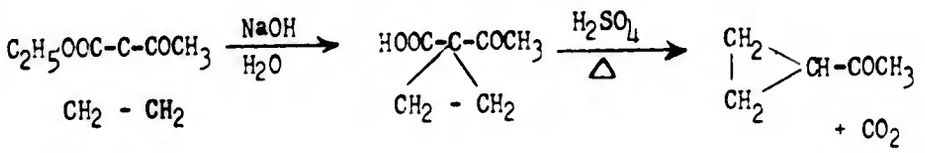
1-Carbethoxy-1-acetyl cyclopropane

The method of the previous reaction was extended to the acetoacetic ester condensation:

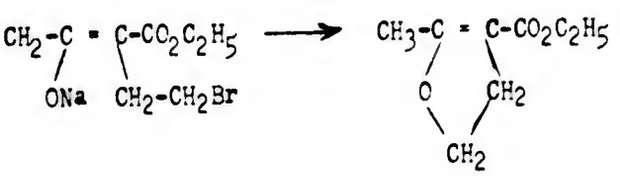


A 25% yield of liquid, b.p. 49-51°C/2 mm, d_4^{20} 1.073, n_D^{20} 1.4415 was obtained. Infra-red spectra for this material did not clearly indicate the presence of a cyclopropyl ring. Because of the limited infra-red data available on this type of compound, this result was not considered conclusive.

This material could lead to methyl cyclopropyl ketone on decarboxylation:



However, Perkin, JCS, 1347 (1929) indicated that the acetoacetic ester condensation leads to a substantial side reaction involving the enol form of the ester:

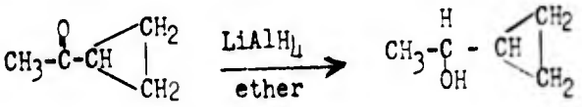


Therefore the method is inconvenient for the preparation of methyl cyclopropyl ketone. It was learned at this time that a substantial

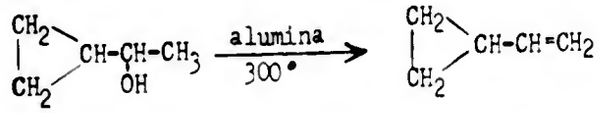
sample of the ketone would be furnished by USI, consequently attempts at synthesis were discontinued.

Cyclopropylacetylene

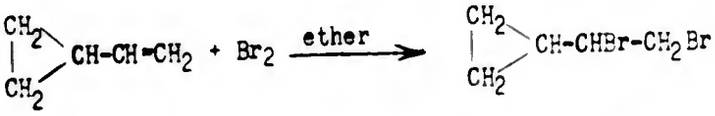
Methyl cyclopropyl carbinol was prepared from cyclopropyl methyl ketone by reduction with $LiAlH_4$ in ethyl ether.

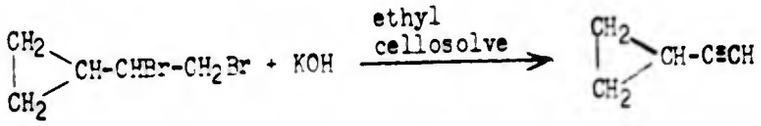


Dehydration of the alcohol by means of sulfuric acid was unsatisfactory because extensive ring cleavage occurred, but reasonable yields of vinylcyclopropane were obtained by vapor phase dehydrations over alumina.



Cyclopropylacetylene was obtained by dehydrohalogenation of the dibromide that was obtained from vinylcyclopropane.





Cyclopropylacetylene boils at 52-55°C, and the density is $d_4^{20} = 0.773$. This compound was found to be hypergolic with red fuming nitric acid, but it was not hypergolic with white fuming nitric acid. Other characteristics of the compound are being investigated.

Cyclopropyl Cyanide

Cyclopropyl cyanide was prepared using 1,3-dibromopropane as a starting reagent; an excess of the dibromide was allowed to react with KCN in methanol, and γ-bromobutyronitrile was formed.

$$Br\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Br + KCN \xrightarrow{CH_3OH} Br\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}C{\equiv}N$$

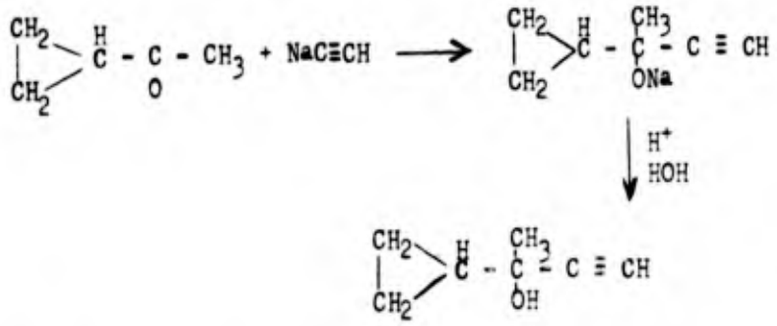
Under the influence of strong base, γ-bromobutyronitrile undergoes ring closure, and cyclopropyl cyanide is formed.

$$Br\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}C{\equiv}N \xrightarrow{NaNH_2} \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \!\!>\!\! CH\text{-}C{\equiv}N$$

This reaction was carried out in liquid ammonia solvent, but no cyclopropyl cyanide was obtained. When diethyl ether was substituted for liquid ammonia, the colorless liquid, cyclopropyl cyanide, was obtained. Cyclopropyl cyanide boils at 133-134°C, and the density is $d_4^{20} = .910$. The compound was not hypergolic with either red fuming nitric acid or white fuming nitric acid.

2-Cyclopropylbutyn-3-ol-2

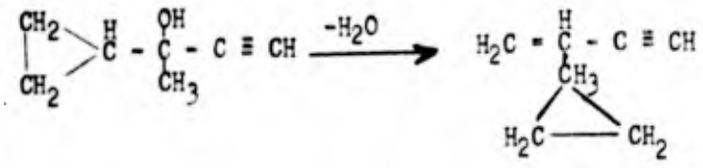
This compound was prepared by the condensation of methyl cyclopropyl ketone with sodium acetylide in liquid ammonia and hydrolysis of the sodium salt of the alcohol that resulted.



An 85% yield of a clear, colorless liquid was obtained; $n_D^{18} = 1.4570$, $d_4^{25} = 0.926$, b.p. 51-53° at 14 to 16 mm.

Cyclopropylvinylacetylene

Cyclopropylvinylacetylene was prepared by the dehydration of 2-cyclopropylbutyn-3-ol-2



Attempts to dehydrate the alcohol with an aqueous 3% toluenesulfonic acid solution or a 35% aqueous sulfuric acid solution were unsuccessful. When toluenesulfonic acid was used, dehydration was incomplete, and a considerable amount of rearrangement took place. Extensive polymerization occurred when the sulfuric acid solution was used. A 25% yield of a pale yellow liquid,

d_4^{20} = 0.824, n_D^{17} = 1.4683, b.p. 56-59°C at 140 mm, was obtained by passing a solution of 100 cc of the alcohol in 300 cc of xylene through an alumina column that was maintained at 250-280°C. An analysis of the infra-red spectrum of this compound indicated the presence of the cyclopropyl group, the -C≡C-H group and the vinyl group.

Cyclopropylvinylacetylene was found to be hypergolic with red fuming nitric acid (RFNA).

Propargyl aldoxime

Propargyl aldoxime was prepared by allowing a solution of hydroxylamine hydrochloride and K_2CO_3 to react with an aqueous solution of propargyl aldehyde.

$$H\text{-}C{\equiv}C\text{-}\overset{H}{\underset{|}{C}}{=}O + H_2NOH \longrightarrow H\text{-}C{\equiv}C\text{-}\overset{H}{\underset{|}{C}}{=}N\text{-}OH + H_2O$$

The oxime was extracted from the aqueous solution with several portions of ether, and the ether was removed under vacuum. The oxime was not further purified.

Cyanoacetylene

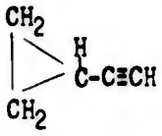
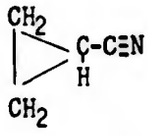
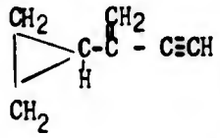
The crude propargyl aldoxime was dehydrated to cyanoacetylene with acetic anhydride.

$$H\text{-}C{\equiv}C\text{-}\overset{H}{\underset{|}{C}}{=}N\text{-}OH \xrightarrow{Ac_2O} H\text{-}C{\equiv}C\text{-}C{\equiv}N$$

A 28% yield of water-white cyanoacetylene was obtained, $d_4^{20} = 0.804$, $n_D^{21} = 1.3820$. On exposure to light and air, the water-white product quickly darkened. The product was not hypergolic with red fuming nitric acid (RFNA).

Table I

Physical Properties of Some Derivatives of Acetylene and Cyclopropane

Compound	Structure	Density g/cc	M.P.	B.P.	Refractive Index (M_D)
Cyclopropyl-acetylene		0.773 at 20°C	-105°C	52-55°C	1.4294 at 21°C
Cyclopropyl Cyanide		0.910 at 20°C	-18°C	133-4°C	1.4210 at 21°C
Cyclopropyl-vinylacetylene		0.824 at 20°C	-110°C	103-104°C	1.4683 at 17°C
Cyanoacetylene	H-C≡C-C≡N	0.804 at 20°C	5°C	42.5°C	1.3820 at 21°C

THERMAL STABILITY TESTS

Polymerization Tests

In order to evaluate the tendencies to polymerize of cyclopropylacetylene, cyanoacetylene, cyclopropylvinylacetylene and cyclopropyl cyanide, pure samples and samples that contained 0.3% by weight of quinone were sealed in heavy-walled Carius tubes and were thermostated at 71.0 ± 0.2°C for five days. The quinone was added to measure its value as a polymerization inhibitor. After five days the Carius tubes were opened, and the amounts of polymer present were determined by the methanol precipitation test. This method depends on the fact that the starting materials are soluble in methanol, but the polymers are insoluble.

In the tests one mole samples were placed in graduated centrifuge tubes, and each sample was then diluted with methanol so that the total volume in each tube was 6.5 moles. After standing for ten minutes to insure the complete precipitation of the polymers, the mixtures were centrifuged until the volume of the precipitate was constant, and the volumes of the solids were recorded. The results tabulated in Table II are in % by volume.

Table II.

Polymerization Tendencies of Some Cyclopropyl and Acetylenic Derivatives

Sample	Inhibitor	Polymer by Volume
Cyclopropylacetylene	none	1%
Cyclopropylacetylene	0.3% quinone	0.5%
Vinylcyclopropylacetylene	none	50%
Vinylcyclopropylacetylene	0.3% quinone	50%
Cyclopropyl cyanide	none	less than 0.5%
Cyclopropyl cyanide	0.3% quinone	less than 0.5%
Cyanoacetylene	none	1%
Cyanoacetylene	0.3% quinone	0.5%

Study of Stability to Thermal Shock

Cyclopropylacetylene, cyclopropylvinylacetylene, cyclopropyl cyanide and cyanoacetylene were tested for their resistance to thermal shock. The test apparatus consisted simply of a 2000 watt hot plate set on high; the temperature of the surface was approximately 800°F. The material to be tested was dropped on to the hot plate with a medicine dropper. The results of these tests are listed in Table III.

Table III.

Thermal Shock Tests Using
2000 Watt Hot Plate.

Compound	Remarks
Cyclopropylacetylene	Evaporated without ignition.
Cyclopropylvinylacetylene	Evaporated without ignition.
Cyclopropyl cyanide	Evaporated without ignition.
Cyanoacetylene	Immediately burst into flame.

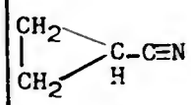
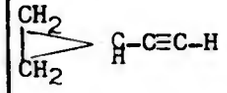
CALCULATION OF THE THEORETICAL PERFORMANCES AS ROCKET FUELS OF SOME DERIVATIVES OF CYCLOPROPANE AND ACETYLENE

The specific impulses of the cyclopropyl and acetylenic derivatives as the fuels in bipropellant mixtures have been calculated. The oxidants used were RFNA (14% NO_2), WFNA (100% HNO_3), and liquid oxygen (LOX). These data are summarized in Table IV. Included in Table IV for purposes of comparison are similar data for methyl vinyl acetylene, methyl divinyl acetylene, and unsymmetrical dimethyl hydrazine.

The method of computation of these data is discussed in the Appendix of this report.

Table IV

Specific Impulses for Cyclopropyl and Acetylenic Compounds as Bipropellants

Compound	Structure	Maximum I_{sp} (sec)			Stoichiometric Isp	
		With dry RFNA (14% NO_2)	With WFNA (100% HNO_3)	With Liquid Oxygen (LOX)	With WFNA (100% HNO_3)	With Liquid Oxygen (LOX)
2-Methyl-1-buten-3-yne (Methyl Vinyl Acetylene)	$H_2C{=}C(CH_3)-C{\equiv}CH$	228.6	227.2	-	223.3	-
2-Methyl-1,5-hexadiene-3-yne (Methyl Divinyl Acetylene)	$H_2C{=}C(CH_3)-C{\equiv}C-C(H){=}C-H_2$	226.4	225.0	-	221.0	-
Unsymmetrical dimethyl hydrazine	$(CH_3)_2N-NH_2$	235.2	233.8	-	232.0	-
Cyclopropyl cyanide		226.5	225.1	261.3	221.3	254.8
Cyclopropyl acetylene		232.2	230.8	271.3	226.8	264.6
2-Butyne-1,4-dinitrile	$N{\equiv}C-C{\equiv}C-C{\equiv}N$	244.4	243.0	263.6	236.7	247.8

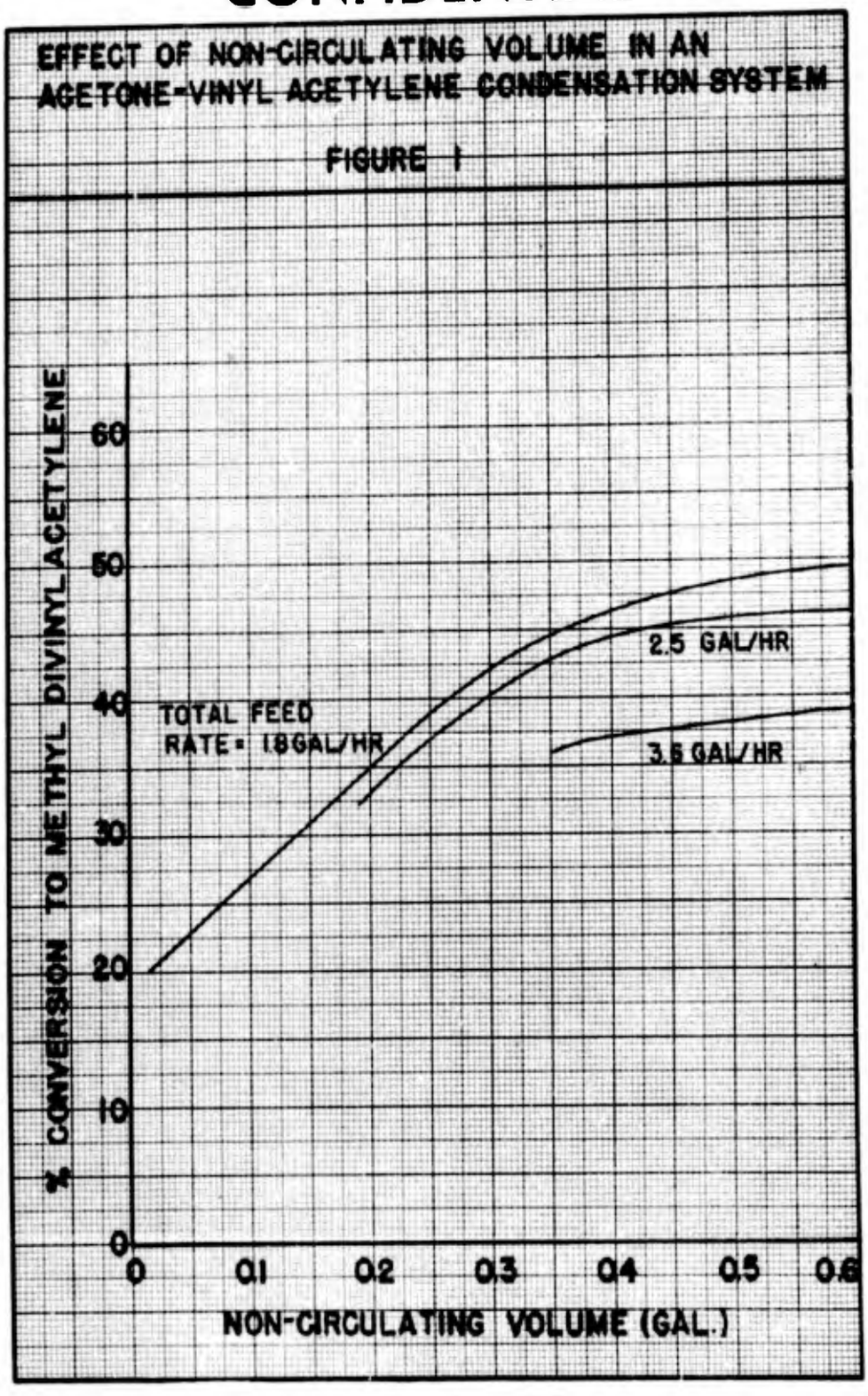
PILOT PLANT WORK

The pilot plant work that was conducted during the six month period covered by this report was devoted to a further investigation of the process variables in the reactions involved in the synthesis of methyl divinyl acetylene.

The process equipment that was used to carry out the synthesis steps was described fully in a previous Technical Report (1). Essentially the process consists of continuously condensing acetone and vinyl acetylene in a caustic potash media, dehydrating the resulting acetylenic alcohol to the methyl divinyl acetylene, and then purifying the product by fractionation. The dehydration is usually carried out allowing the organic material to come in contact with hot (80-90°C) 40% sulfuric acid. Recently development work has been carried out on a vapor phase dehydration unit. This is described later in the report.

Further data were obtained on the effect of changing the relative volumes of the circulating and non-circulating portions of the condensation reaction apparatus. Figure 1 is a plot showing the percent conversion of vinyl acetylene to methyl divinyl acetylene as a function of the volume of the non-circulating section. This volume was varied by changing the length of the vertical holdup column. The volume of the circulating system was constant at 0.17 gallons.

(1) Acetylenic Compounds for Rocket Fuels
NYU Technical Report No. 7, Dec. 15, 1954 (Confidential)


EFFECT OF NON-CIRCULATING VOLUME IN AN
ACETONE-VINYL ACETYLENE CONDENSATION SYSTEM
FIGURE 1
% CONVERSION TO METHYL DIVINYLACETYLENE
60
50
40
30
20
10
0
TOTAL FEED
RATE = 1.8 GAL/HR
2.5 GAL/HR
3.6 GAL/HR
0
0.1
0.2
0.3
0.4
0.5
0.6
NON-CIRCULATING VOLUME (GAL.)

In the runs used to obtain this plot, the reactants consisted of a solution composed of 31 parts by weight of vinyl acetylene, 38 parts by weight of acetone, and 31 parts by weight of xylene. This corresponds to a 10% molar excess of acetone over the vinyl acetylene. The potassium hydroxide slurry consisted of one part KOH to two parts xylene. The potassium hydroxide was used in a 20 to 30% excess over the vinyl acetylene. The dehydrations were carried out with hot 40% sulfuric acid.

Each curve was obtained by varying the length of the vertical holdup column while the feed rates were kept constant.

As expected, the lower feed rates (longer reaction time for a given reactor volume) resulted in higher conversions for any given non-circulating volume. Increasing the non-circulating volume, while keeping the feed rates constant, affects two variables: the total reaction time is increased and the ratio of circulating volume to total volume of reactor space is decreased. The effect of the recirculation ratio can be isolated by choosing a value of holdup time (equal to the total reaction time) and multiplying it by each of the feed rates. The product yields the total volume, which when divided into the circulating volume of 0.17 gallons gives the ratio of circulating to non-circulating reactor volumes. A plot may then be obtained of the percent conversion of vinyl acetylene to methyl divinyl acetylene as a function of the recirculating volume ratio. Thus for a total reaction time of 0.25 hours a curve is obtained that shows a maximum conversion at about 30% recirculation.

The development work that has been carried out on the vapor phase

dehydration unit that was described in our previous report (2), has encountered difficulty in the vaporization of the organic feed material. This material is essentially a 20% solution of the acetylenic alcohol, 2-methyl-5-hexene-3-yne-2-ol, in xylene. Upon vaporization, a solid coke-like material is deposited in the vaporizer, which after a period of a few hours completely blocks the flow of additional material through the vaporizer. The source of this blockage may be either polymer material that is originally in the feed or it may be polymer formed from the acetylenic alcohol due to the high temperatures used for vaporization. The normal boiling point of the acetylenic alcohol is 160°C. This acetylenic alcohol is known to polymerize very easily.

A possible solution to this problem of vaporizer blockage might be the addition of a high boiling solvent to the feed material. If the solvent's boiling point is higher than the vaporizer temperature, then it should remain liquid and continuously flush out the polymer from the vaporizer. This approach to the problem will be tried in the immediate future.

(2) Acetylenic Compounds for Rocket Fuels,
NYU Technical Report No. 8, (1 Dec. 1954-31 May 1955).

APPENDIX - EXPERIMENTAL DETAILS

The Synthesis of Cyclopropyl Cyanide

This compound can be prepared by using 1,3-dibromopropane as a starting reagent; when an excess of the dibromide is allowed to react with KCN in methanol, γ -bromobutyronitrile is formed.

$$Br\text{-}CH_2\text{-}CH_2\text{-}CH_2Br + KCN \xrightarrow{CH_3OH} BrCH_2\text{-}CH_2CH_2CN$$

Under the influence of strong base, γ -bromobutyronitrile undergoes ring closure, and cyclopropyl cyanide is formed.

$$BrCH_2\text{-}CH_2\text{-}CH_2\text{-}C\equiv N \xrightarrow{NaNH_2} \begin{matrix} CH_2 & - & CH\text{-}C\equiv N \\ & \diagdown & \diagup \\ & CH_2 & \end{matrix}$$

A reaction was run in liquid ammonia using a 30% excess of sodium amide. After an hour, ether was added, and the excess sodamide was hydrolyzed with ammonium chloride. After the ammonia had evaporated, no cyclopropyl cyanide could be isolated. This may have been a result of dehydrohalogenation which is frequently the predominant reaction when bromides are treated with sodamide in liquid ammonia.

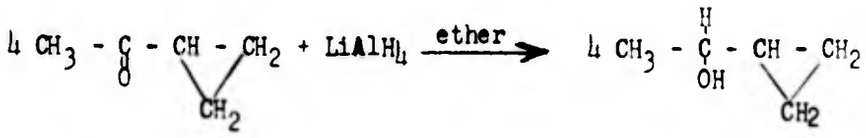
A slurry of sodium amide (18 g., 0.46 moles) in 250 cc of ether was prepared, and the γ -bromobutyronitrile (49 g., 0.3 moles) was added rapidly. Stirring was continued, and the mixture was allowed to reflux for 19.5 hours. At the end of that time the reaction mixture was hydrolyzed using ammonium chloride, and the solid was filtered off. The organic layer was separated, dried, and subjected to distillation at reduced pressures. A colorless liquid (9 g.) was obtained, b.p. 48-49°C/39 mm. An

analysis of the infra-red spectra confirmed the presence of the cyclopropyl and the nitrile groups.

The Synthesis of Cyclopropylacetylene

1.) Methylcyclopropyl carbinol

The starting material was methyl cyclopropyl ketone. This compound was reduced using lithium aluminum hydride in ether according to a procedure outlined by Slabey and Wise, J. Am. Chem. Soc. 71, 3252 (1955).



A suspension of lithium aluminum hydride (105 g., 2.8 moles) in 2.5 liters of ether was prepared. Methyl cyclopropyl ketone (613 g., 7.3 moles) was added slowly, and the mixture was kept at room temperature overnight. The reaction mixture was distilled through a 30 cm. Vigreaux column, and 458 g. of a water-white liquid were obtained. This represents a 73% yield of methyl cyclopropyl carbinol.

2.) Vinylcyclopropane

a) Sulfuric acid dehydration

Ref. Volkenberg et al., J. Am. Chem. Soc., 71, 3595 (1949)

Methyl cyclopropyl carbinol (75 g., 0.87 moles) and 16 drops of concentrated H_2SO_4 were placed in a flask that was fitted with a 6 inch Vigreaux column. The mixture was heated at a rate that allowed a very slow distillation to take place. After 19 hours of heating, about 10 grams

of an organic liquid and 2-3 grams of water had distilled. An additional 16 drops of H_2SO_4 were added to the pot, and an 8 inch packed column was substituted for the Vigreaux column. After heating was continued for 30 hours, the crude material (30 grams) was combined with that which was previously obtained and distilled through a 45 cm. packed column. Four grams of vinylcyclopropane was obtained, B.P. 41°C, n_D^{22} 1.4185, d_4^{20} 0.710. Since very little product was isolated, it was decided to try a vapor phase dehydration.

b) Vapor Phase Dehydration.

Ref. Slabey, J. Am. Chem. Soc. 74, 4930 (1952)

A 75 cm. length of pyrex tubing of 25 mm. diameter was filled with 8-14 mesh alumina, and the tube was placed in an electric furnace that measured 1.5 ft. in length. Temperatures were measured by means of a thermocouple that was placed in the middle of the packed tube. The lower end of the tube was fitted to a 25 cm. water-cooled condenser; the condenser led to a trap that was immersed in an ice-water bath and another trap that was immersed in a dry ice-acetone bath.

Methyl cyclopropyl carbinol (102 g., 1.2 moles) was mixed with 103 grams of toluene and added dropwise into the tube over a period of 1.5 hours. Most of the addition was carried out at the rate of 3 to 4 cc/min. Although a faster addition rate was desired, it could not be attained because of difficulties in controlling the temperature. For the most part the temperatures ranged between 200° and 300°C, but temperatures as high as 430°C and as low as 120°C were recorded.

Although most of the material (156 g.) was collected in the ice-

water cooled trap, about 15 g. of a lower boiling liquid were obtained in the dry-ice trap. The contents of the two traps were combined and distilled through a 35 cm. vacuum-jacketed, packed column. Three fractions were obtained:

Fraction I, 13.5 g., b.p. 24-38°C, $n_D^{21.0°} = 1.3933$,

Fraction II, 5 g., b.p. 38-40°C, $n_D^{21.3} = 1.4045$,

Fraction III, 9 g., b.p. 40-43°C, $n_D^{21.4} = 1.4187$, $d_4^{20} = 0.695$

From the results obtained by earlier workers (Volkenberg, et al, J. Am. Chem. Soc. 71, 3595 (1949), and Slabey, J. Am. Chem. Soc. 74, 4930 (1952)), it was concluded that a considerable amount of ring opening had occurred during the dehydration, and it was decided to repeat the experiment using more rigid control of the temperature and the addition.

In the second experiment 250 g. of methyl cyclopropyl carbinol was mixed with 250 g. of toluene, and the solution was preheated to 80°C before it was added to the column. It was easier to control the temperatures of the column, and a range of 260-310°C was obtained. The rate of addition was 7-8 ml. per minute. Fractional distillation of the crude product gave the following cuts:

Fraction I, 13 g., $n_D^{21} = 1.3990$, $d_4^{20} = 0.698$, b.p. 30-39°C

Fraction II, 59.5 g., $n_D^{21.5} = 1.4132$, $d_4^{20} = 0.714$, b.p. 40-41°C

Fraction III, 21.8 g., $n_D^{21.5} = 1.4150$, $d_4^{20} = 0.715$, b.p. 41°C

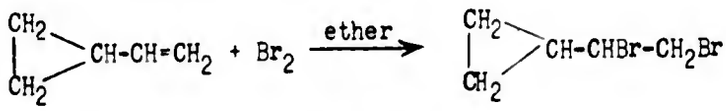
Fraction IV, 12.2 g., $n_D^{21.3} = 1.4185$, $d_4^{20} = 0.709$, b.p. 41-42°C

Fraction V, 3.5 g., $n_D^{21.2} = 1.4210$, $d_4^{20} = 0.705$, b.p. 43-45°C

The constants of fractions II and III correspond very closely to those that were reported for vinylcyclopropane. Fractions II and III represent a 40% yield of vinylcyclopropane , and additional product is undoubtedly present in fraction IV. An examination of the infra-red spectrum of the product confirmed the presence of the cyclopropyl group.

3.) 1-Cyclopropyl-1,2-dibromoethane

Equation:



Ref: Slobodin and Shokhor, J. Gen. Chem. U.S.S.R. 22, 195 (1952).

During the course of one hour, 70 g. (0.44 moles) of bromine was slowly added to a solution of 31 g. (0.45 moles) of vinylcyclopropane in 500 ml. of ether, and the temperature of the reaction mixture was kept below -15°C. The reaction mixture was fractionally distilled using a 35 cm. Vigreaux column.

Ninety grams of a water-white product were obtained, b.p. 45-57°C/1.3 mm., n_D^{21} = 1.5381, and this represented an 85% yield of the dibromide. Because of the wide boiling range, 80 g. of the product were fractionally distilled using a 35 cm. vacuum-jacketed, packed column. The following fractions were obtained:

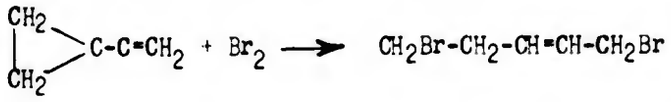
Fraction I, 7 g., b.p. 39-42°C/0.75 mm., n_D^{21} = 1.5317

Fraction II, 54 g., b.p. 36-38°C/0.6 mm., n_D^{21} = 1.5373

Fraction III, 10 g., b.p. 35.5-41°C/0.6 - 0.7 mm., n_D^{21} = 1.5374

Fraction IV, 8 g., b.p. 43.5 - 49°C/0.1 - 0.6 mm., n_D^{21} = 1.5431

An examination of the infra-red spectrum of fraction II indicated the presence of the cyclopropyl group, but it showed that an olefinic material was also present. It was suggested that the following reaction might occur:

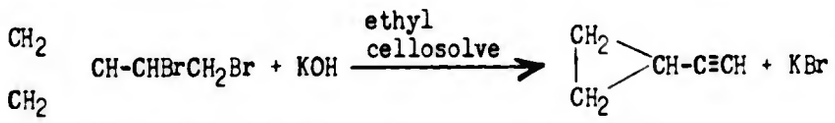


This reaction is similar to the 1,4-addition of bromine to butadiene.

Fraction II was used in the preparation of cyclopropylacetylene.

4.) Cyclopropyl Acetylene

Equation:



Ref: Slobodin and Shokhor, J. Gen. Chem. U.S.S.R. 22, 195 (1952)

Cyclopropyldibromoethane (50 g., 0.22 moles) was slowly added to a boiling solution of 50 g. (0.74 moles) of KOH in 250 ml. of ethyl cellosolve. The system was fitted with a reflux condenser that was maintained at 60°C; this enabled the product to distill off while the solvent remained behind. The distillate that was collected at 51-61°C weighed 11.5 g., an 80% yield based on the amount of dibromide used; 0.5 g. of water was also collected. Since the original dibromide contained some olefin, the actual crude yield was better than an 80% conversion. The crude product was dried over $CaCl_2$, and distilled from a 25 ml. Claisen flask; 7 grams of cyclopropylacetylene were obtained, b.p. 52-55°C; $n_D^{20.8} = 1.4294$; $d_4^{20} = 0.773$; M.R. (obs) = 22.0, M.R. (calc) = 21.7. An examination of the

product showed the presence of the cyclopropyl and acetylenic groups, and indicated that olefinic materials were absent.

The Synthesis of Propargyl Aldoxime

$$HC{\equiv}C\text{-}\overset{H}{C}{=}O + NH_2OH \longrightarrow H\text{-}C{\equiv}C\text{-}\overset{H}{C}{=}N\text{-}OH + H_2O$$

A solution of 76 g. (1.1 moles) of hydroxylamine hydrochloride in 200 ml. of water was neutralized by the addition of 76 g. (.55 moles) of K_2CO_3. The solution was cooled to below 25°C, and to it were added 47 g. of a 90% aqueous solution of propargyl aldehyde. After the addition of the aldehyde, the solution was stirred at room temperature for 1.5 hours. The oxime was extracted from the aqueous solution with one 50 ml. portion and three 25 ml. portions of ether. The ether solutions were combined and dried, and the ether was removed under reduced pressure. The red oil that was obtained was not further purified.

The Synthesis of Cyanoacetylene

$$H\text{-}C{\equiv}C\text{-}\overset{H}{C}{=}N\text{-}OH \xrightarrow{Ac_2O} H\text{-}C{\equiv}C\text{-}C{\equiv}N$$

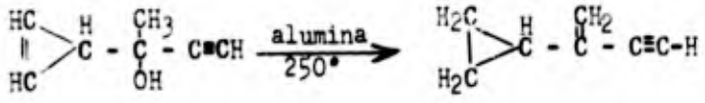
The crude propargyl aldoxime, 59 g., was slowly added to 113 ml. of acetic anhydride that was contained in a flask that was provided with a thermometer, a Vigreaux column, and a nitrogen bleed. The apparatus was agitated by manual shaking, but this agitation was very inefficient, and the oxime accumulated in the reaction mixture. The reaction was very exothermic and several times the amount of heat that was liberated was such that the distillation through the Vigreaux column was too rapid. The temperature of

the vapors held fairly constant at 80-85°C, and the vapors were condensed in a receiver that was cooled with a mixture of dry ice and acetone. The condensate was heated at 40-45°C at 200 mm pressure, and the product was collected in a trap that was cooled with dry ice and acetone. Redistillation of this product gave 11.5 grams (28% of theory) of a water-white liquid; b.p. 42-43°C, $d_4^{20} = 0.804$, $n_D^{21} = 1.3820$. The product quickly darkened on exposure to air and light.

The Synthesis of 2-Cyclopropylbutyn-3-ol-2

Over a period of 30 minutes, a solution of 142 g. (1.7 moles) of methyl cyclopropyl ketone in an equal volume of ether was added to a solution of 2 moles of sodium acetylide in liquid ammonia. After the addition, stirring was continued for eight hours. The ammonia was allowed to boil-off overnight, and the following morning 300 ml. of ether were added to the residue. The solution was then treated with 200 cc of an aqueous solution that contained 130 grams of tartaric acid while the reaction flask was cooled in an ice-water bath. The ether layer was decanted and dried, and then the ether was removed at reduced pressure. The alcohol distilled at 40-41°, at 5 mm pressure; 154 g. (83% of theory) of a clear, colorless liquid were obtained; $n_D^{18} = 1.4570$, $d_4^{25} = 0.926$.

The Synthesis of Cyclopropylvinylacetylene



A solution of 100 ml. of 2-cyclopropylbutyn-3-ol-2 in 300 ml. of xylene was passed through an alumina column that was maintained at 250-280°C.

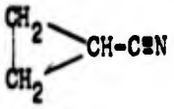
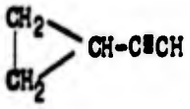
The condensate was dried and subjected to fractional distillation at 140 mm pressure. Twenty-one grams (25% of theory) of a pale yellow liquid were obtained; $n_D^{17} = 1.4683$, $d_4^{20} = 0.824$, b.p. 56-59°C at 140 mm pressure. An inspection of the infra-red spectrum of this compound indicated that this product was cyclopropylvinylacetylene.

METHOD OF COMPUTATION OF THE THEORETICAL PERFORMANCES AS ROCKET FUELS OF SOME DERIVATIVES OF CYCLOPROPANE AND ACETYLENE

All values of I_{sp} are based upon a liquid fuel and an oxidizer at 25°C and a combustion pressure of 300 psia with subsequent expansion to 14.7 psia through a nozzle. Except for the case of LOX as the oxidizer, the calculations are based upon a gas composition corresponding to a "frozen equilibrium" at the combustion chamber pressure of 300 psia. The values for LOX were calculated assuming a shifting equilibrium through the nozzle.

The computations were carried out using the short-cut method of Johnson, (Johnson, S.A., "A Short Cut Method for Calculating Performance of Fuels Containing Carbon, Hydrogen, Oxygen and Nitrogen with Nitric Acid, Liquid Oxygen or Ammonium Nitrate," Cal. Inst. Tech., Jet Propulsion Lab., Pasadena, Calif., Nov. 9, 1953).

For the new compounds cyclopropyl cyanide and cyclopropyl-acetylene, the heats of formation (as gases at 25°C) were computed by the group contribution method of Franklin. In order to determine the heat of formation of these substances as liquids, it was assumed that the latent heat for each of these substances was 10 kcal/g.mole. The values obtained were:

Compound	$(\Delta H_f)_{liq.(25°C)}$
	43.7 kcal/g.mole
	68.7 kcal/g.mole

From previous calculations the heat of formation of liquid 2-butyne-1,4-dinitrile was taken as

$$(\Delta H_f)_{liq.(25°C)} = 138.9 \text{ kcal/g.mole}$$

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