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ACETYLENIC COMPOUNDS FOR ROCKET FUELS

PREPARED FOR
OFFICE OF NAVAL RESEARCH
AND
BUREAU OF AERONAUTICS, DEPT. OF THE NAVY
CONTRACT NO. NONR-285(04)
PROJECT NO. NR 092-159

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Bi-Monthly Progress Report No. 16
for the period
1 February 1955 - 31 March 1955

Acetylenic Compounds for Rocket Fuels

Prepared for

The Department of the Navy:
Office of Naval Research
and
Bureau of Aeronautics

Contract No. Nonr-285(04)
Project No. NR 092-159

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Project Director

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15 April 1955

Chief of Naval Research
Department of the Navy
Washington, 25, D. C.

Subject: Contract Nonr-285(04)
Bi-Monthly Progress
Report

Gentlemen:

We are submitting for your inspection and approval the sixteenth (16) Bi-Monthly Progress Report, performed under the subject contract, for the period 1 February 1955 - 31 March 1955.

Very truly yours,

John Happel

John Happel
Project Director

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TABLE OF CONTENTS

LIST OF TABLES

SUMMARY

Studies were continued on the preparation of divinyl diacetylene, to be used as an additive to JP-4. Several twelve liter scale runs were made. The technique of reuse of the catalyst mixture was investigated and it was found that while the first and second recycle gave good results, repeated use caused the catalyst mixture to deteriorate. An increase in concentration of vinyl acetylene from 50% to 67% in toluene, was found to give greater conversion to divinyl diacetylene. A six lb. sample of 50% divinyl diacetylene in toluene has been sent out to Reaction Motors for test evaluation. As an inhibitor, 0.2% of p-quinone was added.

Triallyl hydrazine and dipropargyl hydrazine, both of potential interest to the JP-4 additive program, were prepared from the corresponding halides and hydrazine. Hypergolicity tests ~~(Table I)~~ showed that dipropargyl hydrazine is less hypergolic than triallyl hydrazine but about the same order as dimethyl hydrazine.

The pilot plant to produce methyl divinyl acetylene has continued in operation. During the two months covered by this report, 105 lbs. of methyl divinyl acetylene have been produced and distributed to interested groups for test evaluation. In general, yields of 48-55% were obtained. The effects of variations in time, temperature and feed rates are explained and summarized in Table II.

Since it is believed that a major factor in keeping the conversion less than theoretical is the sulfuric acid dehydration process, construction of a vapor phase catalytic dehydration unit has been started.

SYNTHESIS WORK

Divinyl diacetylene

Experimentation on the preparation of divinyl diacetylene to be used as an additive to JP-4, has been continued. The primary objective was to develop a larger scale preparation to supply the quantities needed for rocket motor testing at RMI.

The basic reaction is the same as detailed in previous reports, that is the oxidative coupling of vinyl acetylene in cuprous ammonium chloride solution:

$$CH_2{=}CH{-}C{\equiv}CH + CuCl \xrightarrow[H_2O]{NH_4Cl} CH_2{=}CH{-}C{\equiv}C{-}Cu + HCl$$

$$CH_2{=}CH{-}C{\equiv}C{-}Cu + HCl + O_2 \longrightarrow CH_2{=}CH{-}C{\equiv}C{-}C{\equiv}C{-}CH{=}CH_2$$

The reactions were carried out on a 12 liter scale. Since previously it had been found that reuse of the catalyst mixture from previous batches increased the recovery of organic material from 80-85% to 90%, the used catalyst mixture from a previous 12 liter run was employed in four subsequent runs. The catalyst mixture had originally been prepared from 6 moles of cuprous chloride, 34 moles of ammonium chloride and 6 liters of water. After each run the catalyst mixture was recovered and stored in the freezer at -20°C.

In the past a 50% solution of vinyl acetylene in toluene had been used in these reactions. The presence of toluene

prevented shock detonation of the product, divinyl diacetylene. However at this dilution, the vinyl acetylene was not completely converted to divinyl diacetylene. Therefore the vinyl acetylene concentration was increased to 67% in toluene.

These modifications gave significant changes in the course of the reaction. Whereas previous runs of this size did not give complete reaction in an oxygen bubbling time of 4.5 hours, 2 hours were now sufficient time for complete reaction when the catalyst is reused for the first time. The reaction involving a second recycle of the catalyst mixture was complete in 2.5 hours. In both of these cases a steady temperature rise occurred during the reaction up to a maximum of over 30°C.

The third recycling run did not give the expected temperature rise and the reaction did not go to completion after a 5 hour oxygen bubbling period. The fourth recycle run gave greater conversion but the reaction did not go to completion.

It was found that a combination of reused catalyst and substantially complete conversion of vinyl acetylene to divinyl diacetylene was accompanied by emulsification which made separation of the organic phase difficult. The fourth recycle run gave large quantities of emulsion and the catalyst mixture began to deposit a yellow solid.

The variations encountered in this series of runs are difficult to interpret. Obviously the catalyst deteriorated after repeated use.

Another run was tried using a fresh catalyst mixture, 67% vinyl acetylene in toluene and a 5.5 hour oxygen bubbling time. This gave almost complete reaction with no appreciable solid formation or emulsification.

Thus it has become apparent that until the exact cause of the variations in catalyst efficiency is better understood, the reaction is best run with a fresh or once reused catalyst. No set time can be predicted for the oxygen bubbling period. The addition should be continued until the organic layer has a refractive index of 1.54-1.55, at which point the reaction is complete.

One of the batches of divinyl diacetylene was worked up by distillation to determine how closely the amount of divinyl diacetylene, estimated on the basis of index of refraction, compared with the actual amount obtained. It was assumed that all of the toluene which was originally present in the reaction remained and the remaining organic materials were a mixture of divinyl diacetylene and vinyl acetylene.

Calculations for this batch indicated 115 g of divinyl diacetylene was present. Actually 92.5 g was isolated. The difference between observed and calculated may be due to non-additivity of refractive indices, presence of polymer or distillation losses.

Triallylhydrazine and Dipropargyl Hydrazine

A study has been initiated on the synthesis and properties of hydrazine derivatives with particular emphasis on propargyl hydrazine derivatives. A preliminary investigation was made on the known reactions between allyl chloride and hydrazine to form mono-, di-, and triallyl hydrazine. This was undertaken to determine the type of reaction procedures and isolation techniques which would be necessary in the synthesis of propargyl hydrazines from propargyl chloride and hydrazine.

Allyl hydrazines

$$CH_2{=}CH{-}CH_2{-}Cl + NH_2{-}NH_2 \longrightarrow$$

$$CH_2{=}CH{-}CH_2{-}NH{-}NH_2 + (CH_2{=}CH{-}CH_2)_2\ N{-}NH_2$$

$$+ (CH_2{=}CH_2{-}CH_2)_2{-}N{-}NH{-}CH_2{-}CH{=}CH_2 + NH_2{-}CH_3Cl$$

Propargyl hydrazines

$$HC{\equiv}C{-}CH_2Cl + NH_2{-}NH_2 \longrightarrow$$

$$HC{\equiv}C{-}CH_2{-}NH{-}NH_2 + (HC{\equiv}C{-}CH_2)_2\ N{-}NH_2$$

$$+ (HC{\equiv}C{-}CH_2)_2\ N{-}NH{-}CH_2{-}C{\equiv}CH + NH_2{-}NH_3Cl$$

In these reactions mono, di, and trisubstituted derivatives would be expected to form simultaneously. However variation of the molar ratios of reagents should favor formation of one derivative. The known procedure for preparing mono-, and diallyl hydrazine requires a number of fractional crystallizations to separate the allylhydrazine

hydrochlorides from the byproduct hydrazine hydrochloride. This preparation was abandoned in favor of the method reported for triallyl hydrazine.

In this procedure 2.6 moles of allyl chloride was added to a solution of 3.12 moles of hydrazine (95% +) in absolute ethanol at a rate sufficient to maintain a moderate reflux. Occasional shaking prevented the formation of two layers. After the initial vigorous reaction had subsided the mixture was warmed on the steam bath for two hours. Cooling produced a white solid, hydrazine hydrochloride, which was filtered from the solution. The free base, triallyl hydrazine, was liberated from its hydrochloride by addition of 40% sodium hydroxide. The organic phase was then separated and distilled under reduced pressure. Two fractions of triallyl hydrazine were taken, b.p. $_{11.5}$ 59°-64°C and b.p. $_{11}$ 64°-65°C. These had the same refractive index N_D^{20} 1.4619. The yield was 43%.

Dipropargyl hydrazine was then prepared using a similar method. The heating period had to be shortened to one hour since at this point a color change, believed to be caused by decomposition or polymerization, appeared. Dipropargyl hydrazine(b.p. $_2$ 42°-52°C)was obtained in 13.8% yield, D_4^{20} 0.9765. A large quantity of polymer was the major product of this reaction. At first it was believed that the dipropargyl hydrazine was actually tripropargyl hydrazine since the trisubstituted derivative is formed in the analogous reaction with allyl

chloride. However, molecular weight determinations by freezing point depression gave an average value of 105, which is in good agreement with the molecular weight of dipropargyl hydrazine, 108.

Dipropargyl hydrazine forms a glassy solid at approximately -55°C which begins to crack at -85°C. It is only slightly soluble in JP-4 and its solubility in this material is only slightly increased by addition of toluene. This may be due to the fact that the dipropargyl hydrazine is present as a cyclic structure.

TEST EVALUATION

The dipropargyl hydrazine and triallyl hydrazine were test evaluated as additives to JP-4. The results are given in the following table:

Table I

Compound	Temperature Rise Test: Conc. in JP-4	Temperature Rise Test: Average Temp. rise in 10 sec.	Hypergolicity Test: Solvent	Hypergolicity Test: Rating
Dimethyl Hydrazine	5%	22°C	Benzene Hexane	10 9
Dipropargyl Hydrazine	5%	23°C	Benzene Hexane	10 insol.
Divinyl Diacetylene	5%	26°C	Benzene Hexane	10+ 10+
Methyl Divinyl Acetylene	5%	23°C	Benzene Hexane	6 8
Triallyl Hydrazine	5%	23.5°C	Benzene Hexane	11 10
Control (JP-4)	—	20°C	--	—

PILOT PLANT DEVELOPMENT WORK

During the two months covered by this report, 105 pounds of methyl divinyl acetylene were produced using the equipment described in our Report No. 175.21*. The condensation reaction between acetone and vinyl acetylene was carried out on a continuous scale. The dehydration of the 2-methyl-5-hexene-3-yne-2-ol formed in the condensation reaction was a batch type operation using 40% sulfuric acid at 80-90°C as the dehydrating agent.

The results of the runs completed during this period are summarized in Table II.

With the exception of Run IX, the conversions are constant between 48% and 55%. The higher yield of Run IX is not fully explained at the present time. Otherwise, the constant values of conversion that were obtained seem to indicate we are obtaining close to the maximum conversions that are possible with the process in its present form. In the series of runs depicted in Table II, the condensation reaction time was varied from 0.24 to 0.57 hours and the reaction temperature from 42° to 100°F without any appreciable effect on the conversions. With potassium hydroxide molar excesses of more than 10%, the conversions were not affected either. As mentioned in our previous report*, conversions

*Report No. 175.21 (Technical Report No. 7) Acetylene Compounds for Rocket Fuels, Dec. 15, 1954 (Confidential). 51 769
Report No. 175.22 (Bimonthly Report No. 15) Acetylene Compounds for Rocket Fuels. (Confidential). 54 540

were found to be low when the potassium hydroxide was used in equimolar proportions to the vinyl acetylene and acetone.

Pilot Plant Data

Table II

Run	VII	VIII	IX	X	XI	XII	XIII	XIV	XV
Length of Run hrs	11.2	10.5	11.0	10.9	10.6	10.2	10.0	6.0	10.7
Acetone Feed Rate moles/hr	.023	.027	.022	.027	.032	.033	.031	.046	.012
Vinyl Acetylene Feed Rate "	.033	.031	.020	.024	.029	.029	.028	.042	.011
Potassium Hydroxide Feed Rate "	.028	.028	.036	.041	.050	.046	.047	.080	.020
Condensation Reaction Temperature °F	70-80	70-80	70-80	70-80	70-80	90-100	43-45	70-80	75-80
Condensation Reaction time hrs	.57	.57	.54	.45	.39	.38	.37	.24	.48
Weight of Methyl Divinyl Acetylene lb.	22.3*		12.2	13.1	15.4	13.8	12.9	12.7	5.3
Overall % Conversion to MDVA based on limiting reagent	48%*		61%	59.5%	54.3%	50.5%	49.4%	54.4%	50.4%

Plans for the immediate future include determining exactly what the minimum reaction time is in the present equipment. The effect of changing the relative proportions of the circulating and non-circulating sections of the apparatus will also be investigated.

*The product from runs 7 and 8 were combined.

Since it is felt that a major factor in keeping the conversions less than theoretical is the sulfuric acid dehydration process, construction has started on a vapor phase catalytic dehydration unit for the pilot plant. Initial studies have indicated such a process is adaptable to our operation. It is expected that conversions can be increased and that material handling problems can be substantially reduced.

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