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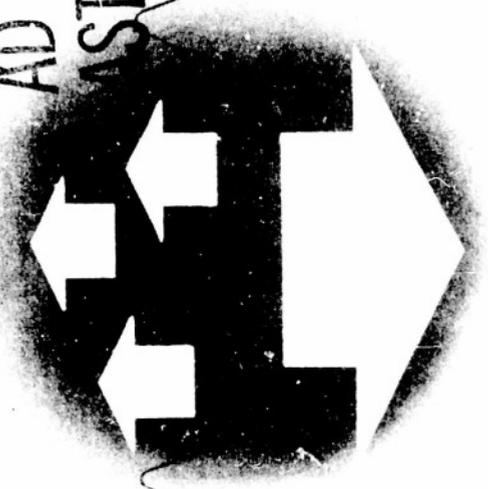
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NAVY DEPARTMENT
OFFICE OF NAVAL RESEARCH
WASHINGTON, D. C.

26 July 1954
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FEASIBILITY OF EMPLOYING ACETYLIDE SALTS AS PROPELLANT COMPONENTS



Contract N7onr-462
Task Order No. III
Project No. NR 220 023

Aerojet-General CORPORATION

A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY

A ZUSANNE CALIFORNIA



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Contract N7onr-462
Task Order III
Project NR 220 023

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CONTRACT FULFILLMENT STATEMENT

This special report is submitted in partial fulfillment of Contract N7onr-462, Task Order III, and covers a completed phase of the work performed during the period 11 November 1952 to 1 June 1954.

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I. ABSTRACT

An experimental study was conducted to determine the feasibility of preparing nonmetallic acetylide salts for use as propellant components. Five different types of reactions for the synthesis of tetramethylammonium acetylide were studied, but in no case was clear-cut evidence for the formation of the desired material found. It is concluded that additional work on this problem is unjustified in the light of present knowledge.

II. INTRODUCTION

A. In a continuing search for materials that will depress the freezing point and vapor pressure of existing propellants without simultaneously lowering the specific impulse, this study was initiated to determine the feasibility of employing nonmetallic acetylide salts as propellant components. Acetylene, because of its positive heat of formation resulting from the carbon-carbon triple bond, has a prominent position as a rocket propellant. However, the handling and shock sensitivity characteristics of acetylene are poor. Attempts to improve these characteristics by mixing acetylene with other substances such as ammonia have resulted in solutions with impractically high vapor pressures. Acetylide salts, on the other hand, are nonvolatile, and ionic types such as sodium acetylide are soluble in solvents such as ammonia. Although compounds containing metallic elements would be undesirable because of the formation of solid exhaust products, the replacement of the metallic ion with an oxidizable, nonmetallic cation such as guanidinium or tetramethylammonium ion would eliminate this objection. Thus, the production of a nonmetallic analog of the alkali metal acetylides would provide a propellant component that would contribute to the depression of freezing point by virtue of its ionization, and be both stable and relatively high in energy.

B. Initially, the preparation of guanidine acetylide was attempted by reaction of sodium acetylide with guanidine sulfate in liquid ammonia. Stoichiometric quantities of the two dry reagents were mixed in a three-necked flask fitted with a mercury-sealed stirrer and a dry ice reflux condenser, the system first being flushed with dry nitrogen. As liquid ammonia was pumped onto the solids from a Dewar flask, gas was evolved; when this gas was passed through ammoniacal silver nitrate solution, a precipitate of silver acetylide formed. This formation of free acetylene indicated that the acetylide ion had a stronger affinity for a proton than the guanidinium ion, and hence a stronger base than guanidine would have to be employed. Accordingly, attention was directed to the preparation of a quaternary ammonium acetylide, tetramethylammonium acetylide, from which abstraction of a proton could not occur.

C. The methods studied for the preparation of tetramethylammonium acetylide were:

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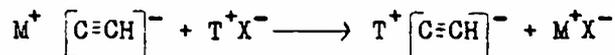
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1. Metathetical reactions of tetramethylammonium salts with sodium acetylide in liquid ammonia and in organic solvents.
2. Reaction of trimethylammonium methyld with acetylene.
3. Reaction of tetramethylammonium free radical with acetylene in liquid ammonia.
4. Reaction of tetramethylammonium triphenylmethide with acetylene.
5. Decarboxylation of tetramethylammonium propiolate.

III. PREPARATION OF TETRAMETHYLAMMONIUM ACETYLIDE

A. METATHETICAL REACTIONS

Metathetical reactions of the type studied are represented by the equation:



where

M = a metal, e.g., sodium

T = tetramethylammonium ion

X = a suitable anion, e.g., halide or nitrate

1. Experiments in Liquid Ammonia

a. Under conditions similar to those described above for the attempted preparation of guanidine acetylide, tetramethylammonium chloride and sodium acetylide were agitated in liquid ammonia for 2 hr, and the resulting mixture was extracted with ammonia in a Soxhlet extractor. No acetylene-containing gas was generated, and no clear-cut separation was obtained. An extraction with dioxane likewise did not result in the desired separation.

b. It became obvious at this point that quantitative information on the solubilities of tetramethylammonium salts in liquid ammonia would be necessary if the proper salts were to be chosen for the metathetical reaction. Reagent-grade tetramethylammonium chloride was dried at 100°C for 12 hr, and then analyzed for chloride ion by titration with silver nitrate. Results indicated a purity of 99.1%. Tetramethylammonium nitrate was prepared by titration of a solution of tetramethylammonium chloride with silver nitrate to the dichlorofluorescein end point. After filtration, the solution was evaporated to dryness, and then purified by recrystallization twice from a mixed solvent of ethanol and water. A nitrogen determination indicated that the purity was 99.1%.

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III Preparation of Tetramethylammonium Acetylide,
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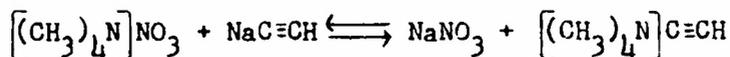
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c. The apparatus for the determination of the solubilities consisted of an unsilvered Dewar flask fitted with a stopper containing a mercury-sealed stirrer, a thermometer, a fitting for a drying tube, and a stainless steel rod upon which a calibrated volumetric cup was fastened. The liquid, containing an excess of the salt to be tested, was stirred for a sufficient time to produce a saturated solution. The solution was then permitted to settle, and the volumetric cup was submerged in the liquid. It was then raised above the solution, where it was permitted to remain until all the ammonia had evaporated. After being dried in an oven, the outside was wiped thoroughly, and the tube was weighed to determine the amount of salt originally present in the solution contained in the volumetric cup. The results were as follows:

Solubilities in Liquid Ammonia at -30°C

Salt	g/100 ml Sol'n
$[(CH_3)_4N]Cl$	0.81
$[(CH_3)_4N]NO_3$	0.40
$[(CH_3)_4N]Br$	0.05
$NaC\equiv CH$	5.12
$[(CH_3)_4N]I$	0.08

d. The extreme solubility of sodium nitrate in liquid ammonia (Reference 1)* suggested its use in the preparation of tetramethylammonium acetylide. In this method, sodium nitrate would be extracted from a mixture of sodium acetylide and tetramethylammonium nitrate, using liquid ammonia in a Soxhlet extractor. In the reaction



the removal of the sodium nitrate would force the reaction to the right, while the less soluble tetramethylammonium acetylide would concentrate in the thimble. The extraction was carried on for a period of 8 hr using a mixture of sodium acetylide and tetramethylammonium nitrate in a mole ratio of 17:1. The large excess of sodium acetylide was used in order to ensure the presence of sufficient reagent throughout the extraction; its solubility is approximately 30 times greater than that of tetramethylammonium nitrate. Intermittent tests of the thimble residue served to determine when all the nitrate

* A list of references is given on page 13.

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ion had been removed. When diphenylamine in concentrated sulfuric acid gave a negative test for nitrate ion, the thimble residue was analyzed for nitrogen by the Kjeldahl method; a portion of the residue was also treated with water and then titrated with standard acid for total alkalinity. The absence of nitrate ion permitted a separate calculation of the distribution of sodium acetylide and tetramethylammonium acetylide, based first on the acid-base titration, then on the nitrogen determination. The results were as follows:

<u>Acid-Base Analysis</u>		<u>Kjeldahl Nitrogen Analysis</u>
$\text{NaC}\equiv\text{CH}$	96%	94%
$(\text{CH}_3)_4\text{NC}\equiv\text{CH}$	4%	6%

This experiment was repeated with similar results, indicating the possible presence of tetramethylammonium acetylide. The loss of unreacted tetramethylammonium nitrate and tetramethylammonium acetylide by direct solution during extraction could not be determined. Probably the solubility of tetramethylammonium acetylide is high enough so that the time required for complete removal of nitrate ion also allowed removal of a considerable portion of the desired acetylide salt. Extraction of other salts was tried in a similar manner in an effort to produce a residue richer in tetramethylammonium acetylide.

e. Extraction of a mixture of tetramethylammonium iodide and sodium acetylide (10:1 molar ratio $\text{NaC}\equiv\text{CH}/(\text{CH}_3)_4\text{NI}$) produced a residue that contained 78% tetramethylammonium iodide and 22% sodium acetylide; none of the desired product was found. A weight loss of 70.3% from the original mixture was observed in 2-1/4 hr, 84.3% of which was sodium acetylide and 15.7% tetramethylammonium iodide. Soxhlet extraction of a mixture of tetramethylammonium chloride and sodium acetylide resulted in weight loss of 70% from the original mixture (2:1 molar ratio $\text{NaC}\equiv\text{CH}/(\text{CH}_3)_4\text{NCl}$) in 1/2 hr and included 50% of the tetramethylammonium ion originally present. These weight losses constitute a serious disadvantage to the use of the liquid ammonia extractive method for the synthesis of tetramethylammonium acetylide.

f. The possibility of direct precipitation of tetramethylammonium acetylide from a saturated solution of the chloride by the addition of sufficient sodium acetylide solution was also investigated. An experiment carried out at -30°C produced a light, flocculent precipitate. After a preliminary observation, the experiment was repeated on a larger scale to furnish sufficient quantity of precipitate for analysis. A 5.2-g quantity of tetramethylammonium chloride was dissolved in 650 ml of anhydrous ammonia to produce a saturated solution at -30°C. A solution of 2.4 g of sodium acetylide in 75 ml of ammonia was added and the light, fluffy precipitate was obtained in small amount. In attempting to increase the quantity of precipitate by evaporation of the solvent, it was found impossible to prevent the

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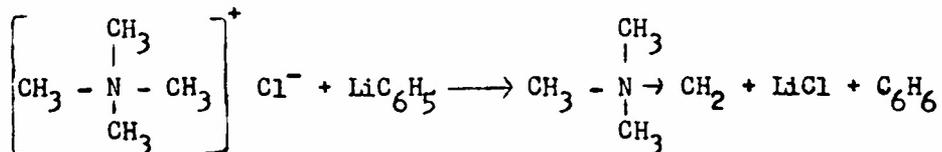
precipitation of the salts on the sides of the Dewar flask in their original proportions. The procedure for addition of components was therefore modified in the following manner: Acetylene was bubbled into a clear, agitated solution of 2.06 g tetramethylammonium chloride in approximately 300 ml of ammonia. Simultaneously, under an atmosphere of nitrogen, 0.50 g of metallic sodium was added in small bits at a rate such that the solution was never colored to a great extent by the dissolving sodium. After addition of the sodium, the solution was refluxed at -33°C for 1-1/2 hr. A gelatinous precipitate which had formed during the reaction was removed by filtration, and the last traces of ammonia were removed under reduced pressure. The extremely small amount of product permitted only cursory examination, consisting of a chloride analysis and an acid-base titration. On the basis of these two analyses, it appears that some tetramethylammonium acetylide may have been present. It was hoped that better solubility relationships would exist at 25°C and that the reaction could be carried out in a pressure vessel, but the solubility of tetramethylammonium chloride at 25°C was found to be 0.452 g/100 ml of solution, which is only half the solubility at -33°C . As a result of these experiments in liquid ammonia, it was concluded that this solvent would not be suitable for the metathetical reaction.

2. Experiments in Organic Solvents

Investigation of the metathetical reaction was extended to the following organic solvents representing aliphatic, halogenated aliphatic, ether, nitrogen- and oxygen-containing heterocyclic and aromatic types. The solvents used were heptane, carbon tetrachloride, diethylether, pyridine, dimethylformamide, tetrahydrofuran, and benzene. Dimethylformamide was found to be reactive with sodium acetylide. Saturated solutions of tetramethylammonium chloride and sodium acetylide were prepared in each of the other anhydrous solvents and mixed in an atmosphere of dry nitrogen in a dry box. No evidence of reaction was apparent after 96 hr. Because the possibility of preparing alkylammonium acetylides by the metathetical reaction appeared remote, attention was directed to other synthetic approaches.

B. REACTION OF TRIMETHYLAMMONIUM METHYLID WITH ACETYLENE

1. It has been shown (Reference 2) that the reaction of tetramethylammonium chloride with phenyl lithium proceeds as follows:

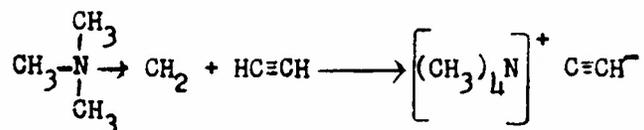


The compound produced, trimethylammonium methylid, has a great affinity for a proton, and the possibility that it would react with acetylene to produce tetramethylammonium acetylide

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III Preparation of Tetramethylammonium Acetylde,
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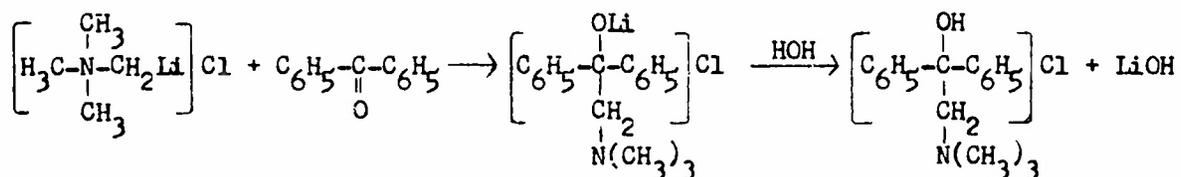
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was investigated.

2. Phenyl lithium was prepared by the reaction of small pieces of lithium metal with bromobenzene in ether solution. The phenyl lithium solution was then shaken with tetramethylammonium chloride in a closed system. The reaction mixture was allowed to settle overnight, and after decanting the supernatant liquid the solid was washed four times with ether and dried in vacuum. Tetrahydrofuran (a solvent for the methylid) was added to the solid white residue and, after filtration, dry acetylene was bubbled into the clear solution. A cloudy solution resulted, but no precipitate could be separated.

3. Because the purity of the methylid may have been low, another attempt to prepare it in a purer condition was made. A three-necked, round-bottom flask was fitted with a reflux condenser, a mercury-sealed stirrer, a dropping funnel, and a stopcock for draining at the bottom of the flask. Sixteen grams of lithium were heated in mineral oil under an atmosphere of dry nitrogen to a temperature of 250°C. When the reaction mixture was cooled rapidly with vigorous stirring, small balls of lithium were produced. The oil was drawn off through the stopcock and the lithium repeatedly washed with anhydrous ether until oil-free. Anhydrous ether (700 cc) was then added and the flask warmed carefully until the ether began to reflux, at which time bromobenzene was added slowly. After addition of 157 g of bromobenzene, a receiver was attached to the bottom of the reaction flask to form a closed system and the wine-red solution containing the phenyl lithium was drawn off. After transfer to the dry box and decantation of the clear-red liquid, a 142-ml portion was allowed to react with 5.4 g of tetramethylammonium chloride for 5 days at ambient temperature. To definitely establish the existence of the methylid, benzophenone in absolute ether was added in an attempt to prepare a derivative of the methylid (Reference 2).



Addition of benzophenone was accompanied by a vigorous reaction and precipitated a large quantity of white solid which, after hydrolysis with water and digestion with 6N HCl and recrystallization from n-amyl alcohol, melted at 140-145°C. This melting point is in accord with Reference 2, but the solubility data are

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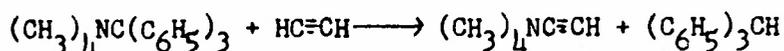
not in agreement. Since the expenditure of an undue amount of time in the elucidation of the methylid reaction was not warranted, this approach to the preparation of tetramethylammonium acetylide was discontinued.

C. ATTEMPT TO REACT TETRAMETHYLAMMONIUM FREE RADICAL AND ACETYLENE

The possibility of producing tetramethylammonium acetylide from tetramethylammonium free radical and acetylene was considered. Only one analogous reaction, the reaction of tetraethylammonium free radical with acetylene in liquid ammonia at -33°C (Reference 3), has been found in the literature. Though discoloration was noted, the product obtained did not appear to be the acetylide salt. An attempt was made to prepare the tetramethylammonium free radical by treating a solution of lithium in liquid ammonia with a solution of tetramethylammonium chloride in liquid ammonia at -33°C (Reference 4). Decoloration of the lithium solution was observed. After filtration, the addition of acetylene produced a cloudy solution, but no solid could be collected.

D. REACTION OF TETRAMETHYLAMMONIUM TRIPHENYLMETHIDE WITH ACETYLENE

1. This procedure for the preparation of tetramethylammonium acetylide was conceived as a result of a study of the synthesis of tetramethylammonium triphenylmethide (Reference 5) and the relative acidities of triphenylmethane and acetylene (Reference 6). The greater acidity of acetylene suggested that the acetylide ion might replace the triphenylmethide ion if acetylene was bubbled into a solution of tetramethylammonium triphenylmethide:



In order to prepare tetramethylammonium triphenylmethide, triphenyl chloromethane (recrystallized from petroleum ether) was permitted to react with 2% sodium amalgam in dry ether solution to form sodium triphenylmethide. Reaction of this ether-soluble compound with tetramethylammonium chloride caused a decoloration of the sodium triphenylmethide solution and the deposition of a dark precipitate on the surface of the unreacted tetramethylammonium chloride. After repeated washing of the precipitate with ether, dry pyridine was added, producing a dark-red solution which was filtered under nitrogen. After bubbling acetylene into this pyridine solution, it was concentrated by evaporation under vacuum at 40°C . A large excess of ether was added in an attempt to precipitate any tetramethylammonium acetylide. After standing overnight at 0°C , a small amount of white solid formed which was unreactive with water and did not melt at 300°C .

2. In another attempt to carry out the triphenylmethide reaction, extreme precautions were taken at all times to avoid contamination of the reaction mixtures with water, oxygen, or carbon dioxide, because each of

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these materials is known to be highly reactive toward, for example, the triphenylmethide anion. The various operations involved, such as that of filtration, were conducted precisely in the manner described by Schlenk (Reference 5). All materials were specially purified, and all gases were scrupulously freed of moisture, oxygen, and carbon dioxide. Cylinder nitrogen was purified by respective passage through soda lime, pyrogallol, Drierite, sulfuric acid, phosphorus pentoxide, and benzophenone sodium in ether. The latter reagent served as an indicator since water, oxygen, or carbon dioxide react with this metal ketyl and discharge the blue color of the solution. The acetylene used was passed respectively through water (to remove most of the acetone present), pyrogallol, sulfuric acid, and soda lime. The solvents (diethylether and pyridine) required for the reactions were distilled in a stream of nitrogen which had been purified as indicated above. The distillation receivers were three-necked flasks fitted with drying tubes of soda lime and siphon tubes. These flasks had been dried for several hours at 130°C. Diethylether was distilled from sodium after drying for two days over sodium, and after the distillation, fresh sodium was introduced into the receiver. Pyridine was dried over barium oxide for two days, and then distilled from fresh barium oxide. The sodium amalgam required was freshly prepared, and stored in tightly capped bottles. Triphenylchloromethane (Matheson, Coleman, and Bell, mp 103°C) was purified by recrystallization from benzene-light petroleum ether to which about ten volume percent of acetyl chloride had been added, followed by titration of the solid under light petroleum ether containing 20 volume percent of acetyl chloride. The purified material was dried in an Abderhalden drier at 85°C for two days and melted at 111 to 112°C (lit. 112°C). Tetramethylammonium chloride (Eastman Kodak Co.) was dried in a vacuum oven at 110°C for two days, and was found to be about 99.6% pure from a chloride ion analysis.

3. The triphenylchloromethane (6.8 g) was allowed to react with 2% sodium amalgam (58 g) in ether (150 ml) for form sodium triphenylmethide. The solution was filtered under nitrogen in the manner described by Schlenk (Reference 5), and the clear, deep-red solution was treated with tetramethylammonium chloride (13 g) until the chloride became coated with a red precipitate of tetramethylammonium triphenylmethide, with the simultaneous decoloration of the solution to light yellow. The precipitate was washed repeatedly with 30-ml portions of ether until the ether washings were no longer yellow, and it was then extracted with 100 ml of pyridine which had been cooled to -30°C. The resulting dark-red solution was filtered under nitrogen, and acetylene bubbled into the cold filtrate. Decoloration to light yellow occurred and a very small amount of a white precipitate formed as the acetylene was absorbed.

4. The solid, after filtration and drying, did not melt at 300°C. It was found to be insoluble in water, acetic acid, benzene, ether, and dimethylformamide. However, it was soluble in concentrated hydrochloric acid, but without the liberation of gas. The latter observation indicates that the isolated solid could not have been tetramethylammonium acetylde. The pyridine filtrate was evaporated to dryness in vacuo, and the residual white solid was

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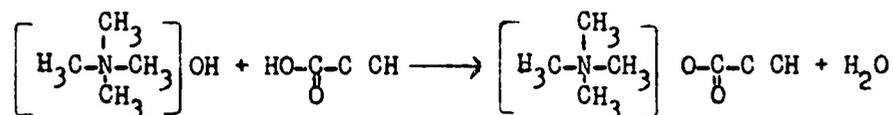
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extracted with ether. Only partial solution occurred, and the insoluble portion was found to have the same properties as the high-melting material described above. The evaporation of the ether solution yielded a white solid, insoluble in water, mp 90 to 91°C. This is presumed to be triphenylmethane, lit. mp 94°C. Less than one gram of total solid material was isolated in these experiments, and it is evident that the extraction of tetramethylammonium triphenylmethide with pyridine is inefficient. Moreover, no indications of the formation of tetramethylammonium acetylide by this action of acetylene on tetramethylammonium triphenylmethide were obtained from the analytical procedures described above, even though extreme preparative precautions were taken.

E. DECARBOXYLATION OF TETRAMETHYLAMMONIUM PROPIOATE

1. The decarboxylation of copper propionate to produce copper acetylide (Reference 7) suggested that tetramethylammonium acetylide might be prepared by decarboxylation of tetramethylammonium propionate. The synthesis of tetramethylammonium propionate, a compound as yet unreported in the literature, was carried out as follows:



Tetramethylammonium hydroxide was prepared by reaction of tetramethylammonium bromide with an excess of silver oxide in water solution. After shaking for 3 hr at room temperature, the solution was filtered, and a portion was acidified with acetic acid and tested with silver nitrate. The absence of cloudiness indicated that the aqueous tetramethylammonium hydroxide was free from bromide ion. Propionic acid (Farchan Chemical Corporation) was titrated with a water solution of tetramethylammonium hydroxide, using a pH meter to determine the end point. After evaporation to dryness under vacuum (12 mm) at a temperature of 33 to 35°C, the salt was recrystallized twice from n-amyl alcohol and a small portion was dried in an Abderhalden drier for 3 hr at 40°C. The melting point in a sealed capillary tube was 129°C. Analysis of a sample yielded the following:

	% C	% H	%N
Calculated for C ₇ H ₁₃ O ₂ N	58.70	9.15	9.78
Found	55.78	9.19	9.28

The calculated carbon/nitrogen ratio is 7; the found ratio is 7.01.

2. The major portion of the salt was dried in a vacuum desiccator over phosphoric anhydride for 6 days. The melting point was 134 to 135°C and

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remained unchanged after 5 days of additional drying. The extremely hygroscopic salt was dried further before analysis and was found to contain 57.28% carbon, 8.72% hydrogen, and 9.62% nitrogen, thus yielding a carbon-to-nitrogen ratio of 6.95.

3. Further characterization of the compound showed that it was soluble in ethyl alcohol, slightly soluble in n-butanol, and insoluble in ether, pyridine, carbon tetrachloride, and tetralin. The presence of acetylenic function is demonstrated by the formation of a precipitate when ammoniacal silver nitrate is added to an aqueous solution of the compound. Vigorous reaction and decoloration was observed when bromine in carbon tetrachloride was added to the solid salt. The presence of the tetramethylammonium ion was confirmed by the preparation of the picrate, mp 312°C (lit. 312 to 313°C).

4. The infrared spectrum of propiolic acid (Figure 1) in cyclohexane shows absorption at 4.8 microns for the triple bond and at 5.9 microns for the carboxyl group. An infrared spectrum (Figure 2) of the tetramethylammonium propiolate in n-butanol with a solvent compensating cell shows absorption at 4.9 and 6.3 microns. The shift of the carboxyl group to a longer wavelength when comparing an acid and its salt is described by Gilman (Reference 8).

5. In attempts to decarboxylate the propiolate, the compound was heated to its melting point (135°C) in an evacuated system and in the presence of nitrogen at one atmosphere. In both cases, a gas was evolved which mass spectrometer analysis showed to be acetylene. In the case of the evacuated system, as acetylene was evolved at the melting point, the liquid rapidly turned dark brown. After gas evolution was complete, the liquid resolidified at the same temperature, becoming progressively darker with time. Under nitrogen, a colorless liquid was produced at the melting point. After evolving the gas, the liquid resolidified to a light, almost white solid. One portion of this solid was heated further and at 210 to 225°C , began to darken slowly. At 260 to 265°C , the solid suddenly evolved a large quantity of gas and a fluffy carbonaceous residue resulted. Treatment of a second portion of the light, almost white solid described above with 6N HCl caused the vigorous evolution of a gas which was identified as CO_2 .

6. Decarboxylation of tetramethylammonium propiolate was attempted in pyridine (bp 115°C) under an atmosphere of nitrogen. No apparent change could be observed at 50°C after 15 minutes, nor at 70°C after 15 to 20 minutes. When the temperature was raised to 100°C , gas was evolved from the solid at an appreciable rate. After approximately 20 minutes, a sample of the gas was collected and identified as acetylene by mass spectrometer analysis.

7. The propiolate was mixed with copper chromite, a catalyst frequently used for decarboxylation, and heated to 135°C under nitrogen. The sample liquefied and the gas evolution in this case proved to be a mixture of

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III Preparation of Tetramethylammonium Acetylde,
E (cont.)

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acetylene and carbon dioxide, in a ratio of approximately 9:1. Subsequent treatment of this residue with 6N HCl, after evacuation of the reaction vessel, produced a gas composed of approximately 67% carbon dioxide and 33% acetylene. Under the conditions of these different attempts at decarboxylation, it is evident that the favored mechanism for decomposition of the propiolate is the production of acetylene rather than carbon dioxide.

IV. DISCUSSION

A. During this study of the feasibility of synthesizing nonmetallic acetylde salts, consideration was given to five different methods. The metathetical reaction in liquid ammonia appeared to be the most direct approach, and it was given initial consideration. The Soxhlet extraction of a mixture of tetramethylammonium nitrate, chloride, or iodide, and sodium acetylde by liquid ammonia constituted one procedure; and the direct precipitation of tetramethylammonium acetylde by interaction of a tetramethylammonium chloride - liquid ammonia solution with a sodium acetylde - liquid ammonia solution constituted another procedure. This metathetical approach was based largely on the concept that one of the products would be considerably less soluble in the selected solvent than either of the reactants. Because of the insolubility of tetramethylammonium compounds in liquid ammonia, the concentrations of the saturated solutions were necessarily low. If tetramethylammonium acetylde had been formed in the metathetical reaction, it would have to be markedly more insoluble than the reactant tetramethylammonium compound in order to favor the formation of a well-defined precipitate. From the experimental results, liquid ammonia did not appear to be a sufficiently differentiating solvent for the conduct of this reaction. Moreover, no evidence of reaction was apparent when the metathetical reaction was conducted in different organic solvents. These results imply that the solubility of tetramethylammonium acetylde, if formed, is not sufficiently different from the reactant tetramethylammonium compound to warrant further investigation of the metathetical reaction.

B. The formation of tetramethylammonium acetylde from trimethylammonium methylid and acetylene appeared feasible, primarily because the methylid is a strong proton acceptor. Moreover, phenylacetylene, an acid of approximately the same strength as acetylene (Reference 9), is a stronger acid than fluorene (Reference 6). The existence of 9-fluorenyl tetramethylammonium thus offered further basis for the methylid reaction (Reference 10). In the experiments conducted in this program, interfering substances may have arisen from the preparation of phenyl lithium, which is not isolated in the pure state, but is used in the medium in which it is prepared. The clarification of this aspect of the problem, plus the difficulties in definitely establishing the purity of the tetramethylammonium methylid, mitigated against the further pursuit of this procedure for making tetramethylammonium acetylde.

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IV Discussion (cont.)

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C. The procedure involving the reaction of tetramethylammonium triphenylmethide with acetylene was based on the principle that acetylene is a stronger acid, e.g., a stronger proton donor, than triphenylmethane (Reference 6). Although the triphenylmethide was prepared successfully and it was evident that a reaction occurred when acetylene was added, no tetramethylammonium acetylide was isolated. Extreme precautions were taken, but the possibility always exists that a trace of contaminant such as oxygen, water, or carbon dioxide may have entered the reaction system. In any event, the procedural difficulties would make this process very impractical and expensive.

D. The decarboxylation of acetylenic acids and salts described in the literature served as a strong basis for the investigation of this approach to the preparation of the tetramethylammonium acetylide. Decarboxylation is, however, very system- and compound-dependent. Thus, in the decarboxylation of acetylene dicarboxylic acid - monopotassium salt, the decomposition at 60°C yields carbon dioxide. The presence of acetylene is not detected at 60° for 180 minutes but is observed after 100 minutes and 30 minutes at 80 and 98.5°C, respectively (Reference 11). In the case of copper propiolate, decarboxylation proceeds readily with only mild heating (Reference 7). The three methods of decarboxylation, viz., heating of the dried tetramethylammonium propiolate alone, and with copper chromite, and by heating of the propiolate suspended in pyridine, produced acetylene as the major constituent, and it appears that this is the favored mechanism for decomposition of the propiolate. While these experiments do not preclude the decarboxylation reaction, it is apparent that considerable work would be required to determine the exact conditions.

E. Although each of the methods for the preparation of tetramethylammonium acetylide embodies a different principle, none of the desired compound was isolated. Investigation of any one method may yet produce the desired acetylide salt, but such investigations would require extensive effort which appears to be unjustified in the light of present information.

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REFERENCES

1. L. F. Audrieth and J. Kleinberg, Non-Aqueous Solvents, John Wiley & Sons, N. Y. (1952).
2. G. Wittig and M. H. Wetterling, Ann., 557, 193-201 (1947).
3. H. H. Schlubach, Ber., 53B, 1689-93 (1920).
4. F. C. Whitmore, Organic Chemistry, D. Van Nostrand Co., Inc., (1937).
5. W. Schlenk, Ber., 49, 607 (1916).
6. J. B. Conant and G. W. Wheland, J. Am. Chem. Soc., 56, 1212 (1932).
7. F. Straus, et al., Ber., 63B, 1086-92 (1930).
8. H. Gilman and F. A. Miller, Organic Chemistry, Vol 3, p. 140, John Wiley & Sons, N.Y. (1953).
9. W. C. Fernelius and F. W. Bergstrom, Chem. Rev., 20, 431-81 (1937).
10. G. Wittig, M. Heintzeler, and M. H. Wetterburg, Ann., 557, 201-205 (1947).
11. M. S. Dudkin, Zhur. Obshchei Khim., 20, 1729-34 (1950).

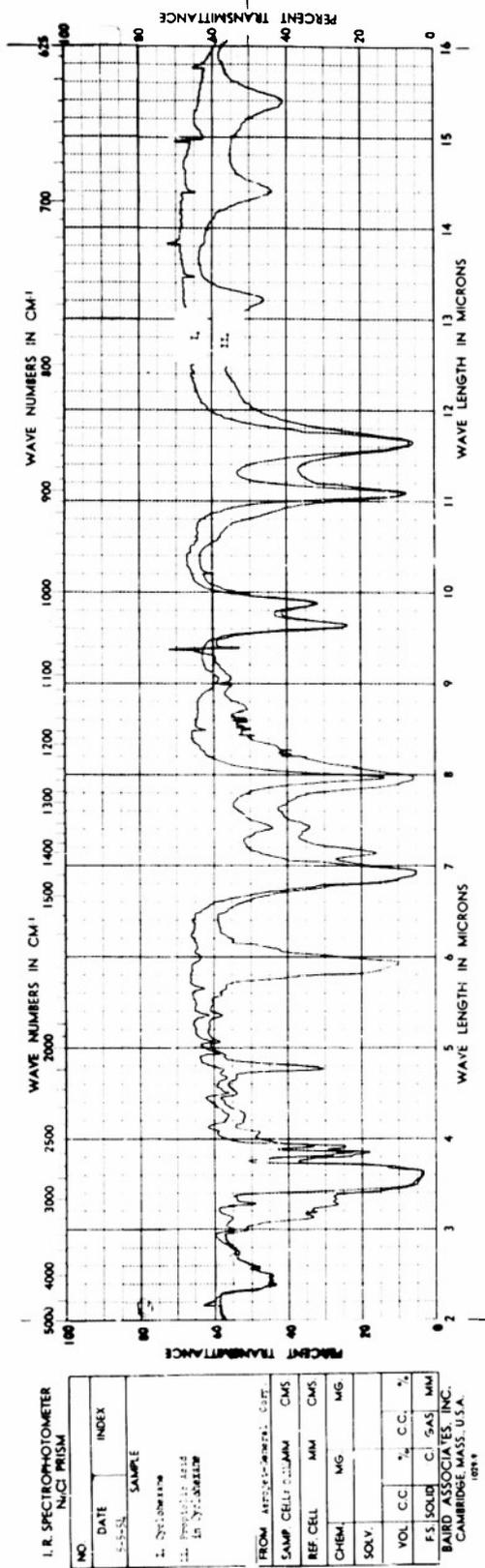


Fig. 1 Infrared Spectrum of Propiolic Acid

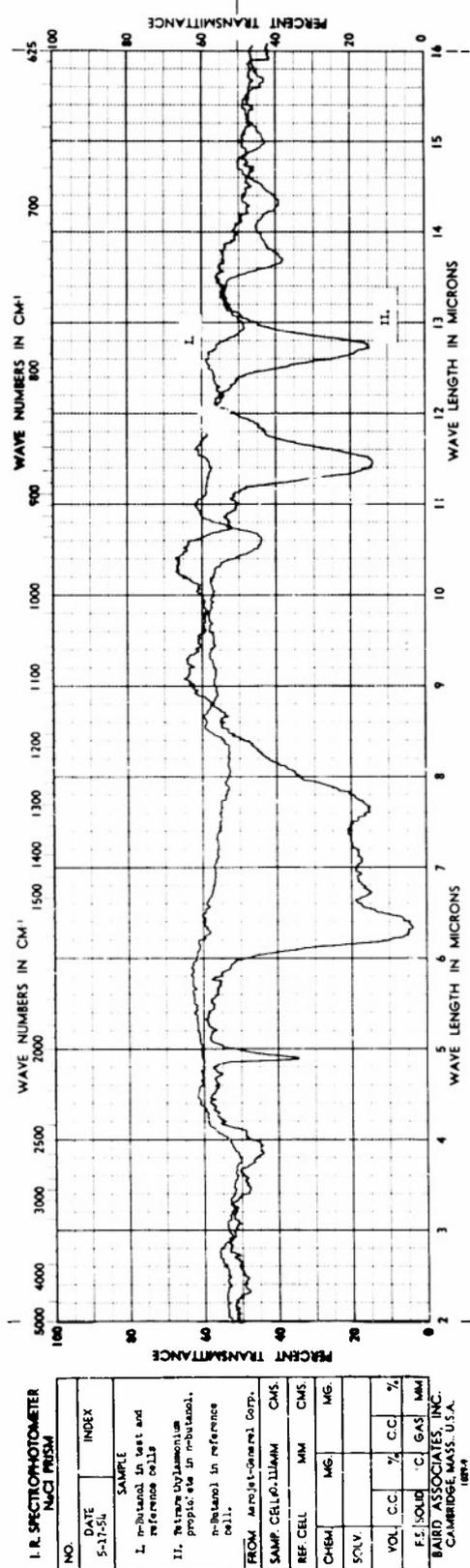


Fig. 2 Infrared Spectrum of Tetramethylammonium Propiolate

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