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CHEMISTRY OF CATENATED NITROGEN COMPOUNDS

Final Report

(11 April 1971 to 11 April 1972)

April 1972

By

L. R. Grant

Exploratory Chemistry

Prepared Under Contract N0019-71-C-0374

Rocketdyne
North American Rockwell, Inc.
Canoga Park, California

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FOREWORD

This technical document is the final report describing the work performed under Contract N00019-71-C-0374. Dr. H. Rosenwasser served as project monitor. The report covers the period from 11 April 1971 through 11 April 1972.

The Responsible Scientist and Principal Investigator for the program was Dr. Louis R. Grant. The work was supervised by Dr. Donald Pilipovich, Manager of the Exploratory Chemistry Group of the Advanced Programs Department at Rocketdyne. Dr. E. A. Lawton was Program Manager for this effort.

ABSTRACT

Studies were conducted on the preparation and characterization of triazanium salts. A method was devised for synthesis of 2,2-dimethyltriazanium sulfate. The sulfate was converted to its perchlorate and nitrate by metathetical reactions. The isomer 1,1-dimethyltriazanium bisulfate was also prepared, but its conversion to the perchlorate was not successful. Triazanium bisulfate and methylsulfonate were prepared and characterized by ir spectroscopy. A hydrated triazanium perchlorate was apparently prepared, but attempts to obtain the anhydrous salt gave only decomposition products.

INTRODUCTION

Compounds that have a high percentage of nitrogen have found applications in those areas requiring "high-energy" chemicals. A high nitrogen content usually indicates the presence of N-N bonds and, less often, amine or related functional groups. Representatives of such materials that possess high nitrogen content are the hydrazines, aminoguanidines, aminotetrazoles, and their salts. These materials have been the subject of numerous investigations.

In recent years, reports have appeared concerning the preparation of simple dialkyl-substituted triazanium salts, $NH_2NR_2^+ NH_2 X^-$. It was the objective of this research effort to investigate the chemistry of these salts, to prepare new triazanium derivatives (preferably unsubstituted ones), and to characterize those materials formed so that their potential uses might be properly assessed.

SUMMARY AND CONCLUSIONS

Investigations were conducted on the preparation and chemistry of triazanium salts. Synthesis of new triazanium salts was based on amination of hydrazines by such reagents as chloramine, hydroxylamine-O-sulfonic acid and their N-methyl derivatives.

Several factors appeared to influence the reaction of these reagents with the hydrazines since the hydroxylamine-O-sulfonic acids and chloramines can potentially serve as either aminating or oxidizing agents for hydrazines. From prior work on triazanium salts, it was known that amination of unsymmetrical substituted hydrazines occurred by attack of the azinium ion (NH_2^+) on the most basic nitrogen. The fact that this is the preferred reaction site proved to be detrimental to synthesis of several new methyl-substituted triazanium salts. Thus, the reaction of both methyl- and 1,1-dimethylhydrazine with methyl-substituted aminating agents did not give the expected methyl triazanium salt; oxidation of the hydrazine occurred instead. The failure to obtain the desired reaction is attributed to the steric hindrance of methyl groups present on adjacent tertiary and quaternary nitrogen atoms.

In contrast to these oxidation reactions, it was found possible to aminate both $(CH_3)_2NNH_2$ and N_2H_4 with NH_2OSO_3H to form 2,2-dimethyltriazanium sulfate and triazanium bisulfate, respectively. The 2,2-dimethyltriazanium sulfate proved to be thermally stable and water soluble, and served as an intermediate for preparation of the corresponding perchlorate and nitrate salts. Identification of the thermally unstable triazanium bisulfate was determined by infrared spectroscopy. Its instability in aqueous solutions and insolubility in the other solvents tested, precluded its use in metathetical reactions.

1,1-Dimethyltriazanium bisulfate was prepared by the reaction of N_2H_4 and $(CH_3)_2NOSO_3H$. This compound was more thermally stable than the unsubstituted analog, but its reaction with barium perchlorate did not give a perchlorate derivative.

The thermal instability and decomposition of aqueous solutions of triazanium bisulfates was attributed to the acidity of the bisulfate ion. A preparative method was therefore devised for the synthesis of hydroxylamine-O-methylsulfonate. This material served as an aminating agent for hydrazine to give triazanium methylsulfonate. A metathetical reaction of this salt with barium perchlorate yielded a material which was indicated to be triazanium perchlorate monohydrate. However, a pure sample of this material was not obtained, and attempts to dehydrate the presumed monohydrate only gave unidentified decomposition products.

All reactions between N-methyl- and N,N-dimethylchloramine with hydrazine, monomethyl- and 1,1-dimethylhydrazine were unsuccessful. The only reaction observed was due to oxidation of the hydrazine.

DISCUSSION

BACKGROUND

The first successful preparation of an alkytriazanium derivative was reported as a brief note by Gosl (Ref. 1). Gosl, by the reaction of hydroxylamine-O-sulfonic acid and 1,1-dimethylhydrazine in methanol, apparently synthesized 2,2-dimethyltriazanium sulfate. In this report, however, no experimental conditions nor analytical data supporting its preparation were described. Utvary and Sisler, by reaction of chloramine and hydrazines, amines or 2-dialkylamino-1,3,2-dioxoaphospholanes, have reported in a series of more detailed papers the synthesis of a number of 2,2-dialkyltriazanium chlorides (Ref. 2 through 7). These authors have unequivocally shown that the azinium ion (NH_2^+) reacts at the more basic nitrogen atom of unsymmetrically substituted hydrazines, the one containing the alkyl groups.

A literature survey revealed the synthesis of only one monoalkyl-substituted triazanium derivative (Ref. 8). With monomethylhydrazine, 2-acyloxaziridines react to form the triazanium derivative $NH_2N(H)CH_3NHC(O)NH_2$. This compound is reported to decompose readily at ambient temperature to ammonia, formaldehyde and semicarbazide.

Amination of N_2H_4 by NH_2Cl and NH_2OSO_3H has also been reported. The reaction of N_2H_4 and NH_2Cl at low temperatures (-50 C) probably gives, as the first step, triazanium chloride. However, this product was not isolated since only N_2, NH_4Cl, and N_2H_5Cl were observed after warming the reaction mixture to room temperature. Similarly, a thermally unstable product was isolated from the reaction of N_2H_4 and NH_2OSO_3H in methanol (Ref. 9). However, the stability of this product was sufficiently high to allow its characterization as the triazanium bisulfate.

Thus, with the exception of 2,2-dialkyl-substituted triazanium salts, none of the triazanium salts reported to date has demonstrated any marked thermal stability. One of the principal objectives of this effort was to determine if stable triazanium salts other than the 2,2-dialkyl-substituted isomers could be synthesized.

AMINATION OF HYDRAZINES

Compounds investigated as aminating agents for hydrazines during the course of this program were: hydroxylamine-O-sulfonic acid, chloramine, N-methylchloramine, N,N-dimethylchloramine, N-methylhydroxylamine-O-sulfonic acid, N,N-dimethylhydroxylamine-O-sulfonic acid, and hydroxylamine-O-methylsulfonate. Discussion of the chemistry of these compounds and their reactions with hydrazine, and some of its methyl derivatives, is given in the following sections of this report.

PREPARATION OF 2,2-DIMETHYLTRIAZANIUM SULFATE

As previously mentioned, synthesis of the title compound was first reported by Gosl from the reaction of hydroxylamine-O-sulfonic acid and 1,1-dimethylhydrazine (Ref. 1). Experimental details for this reaction were lacking, and the failure to obtain additional information from Gosl (deceased) prompted an independent investigation of the preparation of $[(CH_3)_2N(NH_2)_2]_2SO_4$.

Reaction of methanolic solutions of $(CH_3)_2NNH_2$ and NH_2OSO_3H in a 2:1 mmole ratio, respectively, at 0 C resulted in precipitation of a colorless, stable solid in a yield of 60 to 65 percent. Elemental analyses, ir spectroscopic examination, and iodometric titration of the product served to identify it as the desired material. Fifty- to 60-gram preparations of 2,2-dimethyltriazanium sulfate were run without difficulty.

2,2-DIMETHYLTRIAZANIUM PERCHLORATE AND NITRATE

The sulfate was soluble and recrystallizable from its neutral aqueous solutions. Acidic and basic solutions of the compound rapidly decomposed. The sulfate was converted to its nitrate and perchlorate by methathetical reactions with aqueous solutions of barium nitrate and perchlorate. Properties of these salts are given in Table 1.

TABLE 1. PHYSICAL PROPERTIES OF 2,2-DIMETHYLTRIAZANIUM NITRATE AND PERCHLORATE

	$(CH_3)_2N(NH_2)_2ClO_4$	$(CH_3)_2N(NH_2)_2NO_3$
MP	195 to 196 C (dec.)	124 to 125 C (dec.)
Density (g/ml)	1.5	1.4
Impact Sensitivity	10 to 15 in.-lb	>250 in.-lb
DTA (air)	endotherm 35 C exotherm 130 C	Very complex

ATTEMPTED PREPARATION OF 2,2-DIMETHYLTRIAZANIUM BISULFATE

Unsuccessful attempts were made to prepare 2,2-dimethyltriazanium bisulfate. When equimolar amounts of 1,1-dimethylhydrazine and hydroxylamine-O-sulfonic acid were brought together at either 0 C or ambient temperature, an extremely unstable solid (rapid ambient temperature decomposition) was formed. The final solid isolated was methanol-insoluble, possessed no oxidizing property, and was shown to be $(NH_4)_2SO_4$. This was the first evidence obtained which indicated that the stability of the triazanium cation could be influenced by the nature of the anion.

ATTEMPTED AMINATION REACTIONS OF MONOMETHYLHYDRAZINE

In view of the demonstration of NH_2OSO_3H as an efficient aminating agent for $(CH_3)_2NNH_2$, the behavior of this reagent toward monomethylhydrazine was investigated. Because of the previous knowledge gained from preparation of 2,2-dimethyltriazanium sulfate, most of the reactions conducted between NH_2OSO_3H and CH_3NHNH_2 were run at a 1:1 mole ratio, respectively. When the reaction was conducted in methanol at 0 C, an exothermic reaction was observed accompanied by gross gassing. A methanol-immiscible, unstable liquid, which gassed continuously, was formed. This material was finally converted to a methanol-insoluble solid which was identified as $(NH_4)_2SO_4$ by elemental and infrared analyses. Similar results were obtained when equimolar quantities of the reactants were used. When the reaction was conducted under vacuum conditions, N_2, $(CH_3)_2NH$, and ammonia were identified as the volatile products. The reaction which occurred was due to oxidation rather than amination of monomethylhydrazine.

Amination of monomethylhydrazine with chloramine was also attempted. It was anticipated that the reaction of chloramine might be more favorable than NH_2OSO_3H inasmuch as the process would not be occurring in the presence of, or giving rise to an acid-containing species. However, the same type of reaction occurred between NH_2Cl and CH_3NHNH_2, i.e., oxidation of the hydrazine, as was observed with NH_2OSO_3H.

STRUCTURE AND CHEMISTRY OF $N_3H_7SO_4$

A compound of empirical composition $N_3H_7SO_4$ results from the reaction of N_2H_4 and NH_2OSO_3H (Ref. 9 and 10). This product has previously been designated as triazanium bisulfate on the basis of its elemental analyses only. Because a compound of the above empirical composition could result from either of two reactions (Eq. 1 and 2), the structure of the product was investigated by two instrumental techniques for more conclusive identification.

$$NH_2OSO_3H + N_2H_4 \longrightarrow N_3H_6^+\ HSO_4^- \tag{1}$$

$$NH_2OSO_3H + N_2H_4 \longrightarrow N_2H_5^+\ H_2NSO_4^- \tag{2}$$

$N_3H_7SO_4$ is not stable at ambient temperature, but can be stored at -78 C without decomposition. Thermal decomposition of the material at ambient temperature appeared to follow the equation:

$$2N_3H_7SO_4 \longrightarrow N_2H_4 \cdot H_2SO_4 + (NH_4)_2SO_4 + N_2 \tag{3}$$

Attempts were made to convert the purported triazanium bisulfate to its sulfate by several chemical reactions. These reactions were conducted because it was postulated that the presence of the bisulfate ion might be affecting the stability of the triazanium ion. This postulate was based on the fact that the 2,2-dimethyltriazanium cation was unstable in acidic media (Ref. 6), and attempts to isolate 2,2-dimethyltriazanium bisulfate were unsuccessful.

Structure of $N_3H_7SO_4$

Determination of the structure of $N_3H_7SO_4$ was attempted by nmr and ir spectroscopy. Meaningful nmr spectral analysis of the material was not possible because of rapid decomposition of its aqueous solutions, and its insolubility in all other solvents tested. Infrared spectral analyses of the product did provide sufficient data to suggest its identity was the triazanium salt.

Based on the premise that the material of empirical composition $N_3H_7SO_4$ was either $N_2H_5^+\ O_4SNH_2^-$ or $N_3H_6^+\ HSO_4^-$, its ir spectrum in Nujol* was compared with those of

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*The sample decomposed when a KBr pellet was prepared for ir measurements.

N_2H_5Cl and $NaSO_4NH_2$ (Table 2). The differences in the spectra were sufficient to indicate the absence of both $N_2H_5^+$ and $NH_2SO_4^-$ ions.

In addition to the absence of the characteristic bands for $N_2H_5^+$ and $NH_2SO_4^-$, the observed ir absorption bands for $N_3H_7SO_4$ also supported the triazanium structure. The highest NH stretching frequency reported for the NH_2 group in $N_2H_5^+$ is at 3261 cm^{-1} (Ref. 11), but $N_3H_7SO_4$ exhibited a strong absorption at 3330 cm^{-1} which must also be due to a NH_2 stretching vibration. The shift to higher frequency can be attributed to differences in the dipole moments of $N_2H_5^+$ and $N_3H_6^+$ ions. In the former case, one positive charge is delocalized over two nitrogen atoms, while in the latter case, the same charge is distributed over three nitrogen atoms. This difference in the charge distribution will result in changes in the N-H dipoles, and consequently, the vibrational frequencies.

Evidence for the presence of the HSO_4^- ion was also obtained by a comparison of the ir spectrum of $N_3H_7SO_4$ with those of ammonium, sodium, and potassium bisulfates (Ref. 12). Strong absorption bands are present in the spectra of the latter three compounds at 850-880 cm^{-1}, 1035-1075 cm^{-1}, and 1160-1280 cm^{-1}. The $N_3H_7SO_4$ also exhibited absorption bands in these regions (Table 2). On the basis of these results, $N_3H_7SO_4$ appears to be triazanium bisulfate.

Chemistry of Triazanium Bisulfate

Unsuccessful attempts were made to convert triazanium bisulfate to its sulfate and perchlorate. The attempts to prepare the sulfate included the reaction of N_2H_4 and NH_2OSO_3H in the presence of $LiOCH_3$, N,N-dimethylaniline, and reaction of the bisulfate with ammonia.

When the reaction of N_2H_4 and NH_2OSO_3H was run in methanol in the presence of $LiOCH_3$ (Eq. 4 and 5), the product isolated was $LiHSO_4 \cdot 2N_2H_4$.

$$LiOCH_3 + NH_2OSO_3H \overset{CH_3OH}{\not\longrightarrow} LiSO_4NH_2 + CH_3OH \qquad (4)$$

$$LiSO_4NH_2 + NH_2OSO_3H + 2N_2H_4 \overset{CH_3OH}{\not\longrightarrow} (N_3H_6)_2SO_4 + LiHSO_4 \qquad (5)$$

Isolation of this product occurred whether methanolic solution of $LiOCH_3$ and N_2H_4 were added to NH_2OSO_3H in methanol, or N_2H_4 was added to a methanolic solution of $LiOCH_3$ and NH_2OSO_3H. Presumably, the preferred reactions were:

$$LiOCH_3 + NH_2OSO_3H \longrightarrow LiHSO_4 + NH_2OCH_3 \qquad (6)$$

$$LiHSO_4 + 2N_2H_4 \longrightarrow LiHSO_4 \cdot 2N_2H_4 \qquad (7)$$

The use of N,N-dimethylaniline as an acid acceptor was next attempted. Reaction of this amine with NH_2OSO_3H is reported to occur only at elevated temperatures and, consequently, no interference of the amination of N_2H_4 was expected. A precipitate

TABLE 2. COMPARISON OF INFRARED ABSORPTION MAXIMA (CM^{-1})

N_2H_5Cl	$NaSO_4NH_2$	$N_3H_7SO_4$
3261 (s)	3325 (s)	3330 (s)
3150 (s)	3255 (s)	3100 (s)
3034 (s)	1580 (s)	2625 (s)
2950 (s)	1285 (s)	1605 (s)
2903 (s)	1225 (s,b)	1540 (s)
2716 (s,b)	1140 (s,b)	1275 (s)
2602 (s)	1072 (s)	1105 (s)
1970 (m)	1000 (m)	1045 (s)
1638 (m)	905 (s)	970 (s)
1584 (m)	795 (s)	888 (s)
1500 (s)	615 (m)	758 (s)
1417 (m)		612 (s)
1246 (s)		579 (m)
1124 (s)		554 (m)
1101 (s)		453 (s)
973 (s)		

was formed immediately on addition of a cold methanolic solution of N_2H_4 and $(CH_3)_2NC_6H_5$ to NH_2OSO_3H. The product was identified as triazanium bisulfate by ir and melting point. Similar results were obtained when N_2H_4 was added to a mixture of NH_2OSO_3H and $(CH_3)_2NC_6H_5$ in methanol.

2,2-Dimethyltriazanium chloride is soluble in and does not react with liquid ammonia; however, when an attempt was made to carry out the reaction represented by Eq. 8, a violent decomposition occurred on contact of the solid with ammonia.

$$2N_3H_7SO_4 + 2NH_{3(\ell)} \xrightarrow{?} (N_3H_6)_2SO_4 + (NH_4)_2SO_4 \qquad (8)$$

Finally, the reaction of N_2H_4 and $NaSO_4NH_2$ in methanol was investigated. The reaction produced a methanol-insoluble product shown to be $(NH_4)_2SO_4$.

The next series of experiments were conducted to prepare triazanium perchlorate from its bisulfate. Efforts were made to conduct a metathetical reaction of the bisulfate and $Ba(ClO_4)_2$. The reaction, as expressed by Eq. 9,

$$2N_3H_6HSO_4 + Ba(ClO_4)_2 \longrightarrow 2N_3H_6ClO_4 + BaSO_4 + H_2SO_4 \qquad (9)$$

yields an undesirable coproduct, H_2SO_4, which would be expected to accelerate the decomposition of any triazanium perchlorate formed. Reactions therefore were performed also in the presence of the requisite amount of base to neutralize the amount of acid expected.

In the absence of base, the addition of solid $N_3H_6HSO_4$ to a cooled aqueous solution of $Ba(ClO_4)_2$ resulted in gross gassing. Addition of $N_3H_6HSO_4$ to an aqueous, turbid mixture of $Ba(ClO_4)_2$ and NaOH did not result in isolation of the desired perchlorate. Gassing was noted both during the initial reaction and concentration of the filtrate.

Reaction of $(CH_3)_2NCl$ and N_2H_4

The reaction of chloramine, NH_2Cl, with unsymmetrically substituted hydrazines yields the corresponding 2,2-dialkyl-substituted triazanium chloride. As a possible approach for the synthesis of 1,1-dimethyltriazanium chloride, isomeric with the known 2,2-dimethyl derivative, the reaction of N,N-dimethylchloramine and N_2H_4 was studied.

$$(CH_3)_2NCl + N_2H_4 \longrightarrow (CH_3)_2NNH_2NH_2Cl \qquad (10)$$

The only reaction observed under varying experimental conditions was the oxidation of hydrazine. Vacuum line experiments were conducted in toluene, and the volatile products were identified as N_2, $(CH_3)_2NH$ and trace amounts of ammonia. The solid products of the reaction were found to be hydrazinium and dimethylammonium chlorides. Based on the nature and amounts of products isolated, the reaction is expressed by Eq. 11.

$$2(CH_3)_2NCl + 2N_2H_4 \longrightarrow N_2 + N_2H_5Cl + (CH_3)_2NH + (CH_3)_2NH_2Cl \qquad (11)$$

Reaction of $(CH_3)_2NCl$ With $(CH_3)_2NNH_2$

Although some oxidation of $(CH_3)_2NNH_2$ occurred during its reaction with NH_2Cl (Ref. 3), the principal reaction involved amination of the hydrazine to form 2,2-dimethyltriazanium chloride. N,N-Dimethylchloramine, on the other hand, was observed to behave solely as an oxidizing agent toward $(CH_3)_2NNH_2$ in a fashion similar to that observed for hydrazine. Vacuum line experiments showed that the volatile products were N_2, NH_3, and $(CH_3)_2NH$; no satisfactory stoichiometry for this reaction was derived.

Two possible explanations are offered for failure to synthesize a tetramethyltriazanium chloride from $(CH_3)_2NNH_2$ and $(CH_3)_2NCl$. First, a Fisher-Hirschfelder model of the tetramethyltriazanium ion exhibited restricted rotation of the adjacent $N(CH_3)_2$ groups. Second, because NH_2Cl does oxidize $(CH_3)_2NNH_2$, $(CH_3)_2NCl$ should be an even better oxidizer because of the inductive effect of the methyl group (the chlorine becomes more positive).

1,1-DIMETHYLTRIAZANIUM BISULFATE

The methyl derivatives of hydroxylamine-O-sulfonic acid are weaker oxidizing agents than the parent compound (Ref. 13). The methyl groups by virtue of their inductive effect (I_s^+) increase the electron density on the nitrogen atom and render it more basic (less oxidizing in this case). Thus, the methylhydroxylamine-O-sulfonic acids were expected to be less oxidizing toward hydrazines than the corresponding chloramines.

Reaction of equimolar amounts of $(CH_3)_2NOSO_3H$ and N_2H_4 in absolute methanol gave a product after 72 hours that analyzed as $C_2H_{11}N_3SO_4$. The melting point of the product was 136 to 137 (dec.), and it showed neither hygroscopicity nor instability at ambient temperature. Aqueous solutions of the product were unstable, however. Infrared spectra (Table 3) of the product exhibited a strong absorption band at 3335 cm^{-1}, which is attributed to a NH_2 stretching frequency. Based on the reasoning previously presented, the product is considered to be 1,1-dimethyltriazanium bisulfate, $(CH_3)_2NNH_2NH_3^+\ HSO_4^-$.

Reaction With Barium Perchlorate

Although $(CH_3)_2NNH_2NH_3^+\ HSO_4^-$ did not decompose in aqueous methanol as vigorously as the unsubstituted compound in water, only decomposition products were isolated from its reaction with $Ba(ClO_4)_2$.

REACTION OF $(CH_3)_2NOSO_3H$ AND METHYLHYDRAZINES

The preparation of $(CH_3)_2NNH_2NH_3^+\ HSO_4^-$ demonstrated that $(CH_3)_2NOSO_3H$ acted as an amination agent toward N_2H_4. A series of experiments was subsequently performed to determine if a similar reaction could be obtained with 1,1-dimethylhydrazine and monomethylhydrazine. The products obtained from the reaction of $(CH_3)_2NNH_2$ and CH_3NHNH_2 with $(CH_3)_2NOSO_3H$ were noncrystallizable oils.

TABLE 3. INFRARED ABSORPTION MAXIMA FOR $(CH_3)_2NNH_2NH_2^+HSO_4^-$*

CM^{-1}	Intensity
3335	s
3195	s
2905	s
2595	w
1610	m
1550	m
1500	m
1460	m
1435	m
1270	s,b
1220	s,b
1085	s
1060	s
1002	m
965	s
935	m
830	s,b
790	m
725	w
625	s
583	s
570	s

*KBr pellet.

REACTION OF CH_3NHOSO_3H WITH HYDRAZINES

N-Methylhydroxylamine-O-sulfonic acid was investigated as an aminating agent for both N_2H_4 and $(CH_3)_2NNH_2$. In contrast to $(CH_3)_2NOSO_3H$, the monomethyl derivative did not give rise to an isolable triazanium salt in either case. In the reaction with N_2H_4, the only solid product obtained was $(N_2H_4)_2 \cdot H_2SO_4$, while with $(CH_3)_2NNH_2$ oxidation of the hydrazine occurred and $(NH_4)_2SO_4$ was the only solid product isolated.

PREPARATION OF $CH_3SO_2ONH_2$

It was shown that both NH_2OSO_3H and $(CH_3)_2NOSO_3H$ aminated N_2H_4 to give triazanium salts which varied in their thermal stability. Aqueous solutions of both salts also decomposed, and the instability of these materials was attributed to the presence of the acidic bisulfate ion. Therefore, it was decided to investigate an aminating agent for N_2H_4 which (1) would not give rise to an acidic anion, and (2) would not serve as an oxidizing agent for N_2H_4. Hydroxylamine esters of the type RSO_2ONH_2 appeared to satisfy these requirements.

A search of the literature did not reveal a preparative method for RSO_2ONH_2 compounds. The first approach to synthesis of $CH_3SO_2ONH_2$ was based on a reaction analogous to that used for preparation of NH_2OSO_3H:

$$CH_3SO_2Cl + NH_2OH \cdot HCl \longrightarrow CH_3SO_2ONH_2 + 2HCl \qquad (12)$$

No evidence was obtained for a reaction.

The method which proved to be a successful one was based on the reaction:

$$CH_3SO_3H + NH_2OH \longrightarrow CH_3SO_2ONH_2 + H_2O \qquad (13)$$

Reaction of equimolar amounts of CH_3SO_3H and NH_2OH in methanol yielded a colorless solid which melted at 149 to 151 C. Analyses of the material were consistent with the composition given.

Reaction With N_2H_4

The reaction of hydrazine and $CH_3SO_2ONH_2$ was conducted at ambient temperature for 16 hours with no evidence of gassing during the first 2 hours of observation. After this reaction time, a colorless solid was isolated by addition of diethylether to the clear solution. Recrystallization of this product from a 2:1 ethanol-methanol solution yielded a material melting at 77 to 79 C (dec.).

The reaction product decomposed under the conditions used for preparation of KBr pellets for ir measurements in the same manner as previously observed for $N_3H_6HSO_4$. Suitable ir spectra were obtained in Nujol, however, and the absorption maxima observed in the NH region are compared with those of $N_3H_6HSO_4$ in Table 4.

TABLE 4. COMPARISON OF INFRARED ABSORPTION MAXIMA (CM^{-1})

$N_3H_6HSO_4$	$N_3H_6SO_3CH_3$
3320	3340
3260	3255
3200	3145
3125	2600
2625	1625
1590	1575
1525	1530

Similarities in the infrared spectra are apparent, and it is concluded that both are triazanium salts.

Triazanium methylsulfonate was markedly more stable than the analogous bisulfate. Whereas the bisulfate underwent rapid decomposition in the solid state at ambient temperature, no observable differences in the infrared spectrum of the methylsulfonate were observed at ambient temperature during a period of 10 days.

Reaction of $N_3H_6SO_3CH_3$ and $Ba(ClO_4)_2$

Conversion of triazanium methylsulfonate to the perchlorate by metathetical reaction with $Ba(ClO_4)_2$ was performed in methanol and methanol-ethanol mixtures. The slight solubility of the coproduct $Ba(SO_3CH_3)_2$ in alcohols resulted in less than quantitative recovery of this material when the reaction was conducted in either methanol or methanol-ethanol solutions. The best yield (77 percent) of $Ba(SO_3CH_3)_2$, as the insoluble fraction, was obtained when the reaction was conducted in a 5:2 mixture of ethanol and methanol.

The alcohol-soluble product was recovered by concentration of the filtrate from the above reaction. Multiple recrystallizations of the product from ethanol finally provided a material which gave a clear melt at 78 to 80 C. Infrared spectra of this solid in Nujol exhibited the following principal bands in the NH region: 3350, 3300, 3250, 3155, 2600, 1600, and 1540 cm^{-1}. Characteristic absorptions for the ClO_4^- ion were also present.

Elemental analyses of the recrystallized product were: C, 0.77; H, 4.67, N, 24.54 percent. The small amount of carbon found was attributed to the presence of the impurity $Ba(SO_3CH_3)_2$. If it is assumed that the product consisted only of $Ba(SO_3CH_3)_2$ and $N_3H_6ClO_4 \cdot H_2O$, the amount of $Ba(SO_3CH_3)_2$ (based on the carbon analysis) was 8.6 mole percent. For a mixture of 8.6 mole percent $Ba(SO_3CH_3)_2$ and

94.4 mole percent $N_3H_6ClO_4 \cdot H_2O$, the expected analyses are: C, 0.77; H, 4.55; N, 22.9 percent. Attempts to dehydrate this material were unsuccessful. Thermal treatment of the assumed mixture at temperatures below 50 C in vacuum gave only decomposition products.

Reaction of $N_3H_6SO_3$ and $Ca(NO_3)_2$

Attempts to prepare triazanium nitrate were unsuccessful. The reaction of $N_3H_6SO_3CH_3$ and $Ca(NO_3)_2$ was performed in methanol-ethanol, and a crude product was obtained melting at 56 to 58 C. When this material was treated with warm ethanol, an immiscible oil was formed in addition to a soluble solid fraction. Neither of these fractions analyzed as the desired triazanium nitrate.

Reaction of $CH_3SO_2ONH_2$ and Methyl Hydrazines

Attempts were made to effect a reaction between $CH_3SO_2NH_2$ and the hydrazines CH_3NHNH_2 and $(CH_3)_2NNH_2$. In the former case, only oils were isolated. 1,1-Dimethylhydrazine gave, only after an extended reaction time, 1,1-dimethylhydrazinium methylsulfonate, apparently due to alcoholysis of $CH_3SO_3ONH_2$ and subsequent reaction of the CH_3SO_3H formed with $(CH_3)_2NNH_2$.

RECOMMENDATION FOR FUTURE WORK

This research effort has resulted in a method for preparing unsubstituted triazanium salts. Although the stability of these salts appeared to be related to the nature of the anion, it was apparent that the methylsulfonate and perchlorate monohydrate salts have reasonable stability at ambient temperature. Additional work is warranted to determine if other salts can be prepared and characterized for future naval applications.

EXPERIMENTAL DETAILS

GENERAL

All solution preparations were conducted in a nitrogen-filled dry box. In general, solutions of the aminating agent were prepared in a three-neck, round-bottom flask fitted with a dropping funnel, water condenser, and immersion thermometer. Stirring was effected magnetically. After the apparatus was removed from the dry box, the hydrazine was added to the aminating agent at 0 to 5 C. Workup of the reaction mixture was then performed in a nitrogen atmosphere.

Vacuum line experiments were conducted by vacuum condensation of the hydrazine into a degassed solution of the aminating agent. The mixture was then warmed to 0 to 5 C and reaction allowed to occur in this temperature range.

All infrared spectra were recorded on a Perkin-Elmer Infracord, Model 337. Melting points given are uncorrected. Elemental analyses were performed by Elek Microanalytical Laboratories, Torrance, California.

PREPARATION OF $[(CH_3)_2N(NH_2)_2]_2SO_4$

A typical large-scale preparation of 2,2-dimethyltriazanium sulfate was conducted as follows utilizing 97.9 percent pure NH_2OSO_3H prepared from the reaction of chlorosulfonic acid and hydroxylamine hydrochloride (Ref. 14). 1,1-Dimethylhydrazine (100g, 1.67 moles) was dissolved in absolute methanol (210 ml), and this solution was added dropwise to a suspension of NH_2OSO_3H (95.7 g, 0.83 mole) in absolute methanol (300 ml) cooled to 0 C. After addition of approximately one-half of the $(CH_3)_2NNH_2$, a clear solution was obtained. Continued addition of the hydrazine caused a solid to precipitate. The mixture was stirred for an additional 15 minutes, the precipitate filtered and vacuum dried. The weight of the solid recovered was 64.4 g (0.26 mole), or a 63-percent yield based on the NH_2OSO_3H used.

<u>Analysis</u>. Found: C, 19.33; H, 8.30; N, 33.87. Calculated for $[(CH_3)_2N(NH_2)_2]_2SO_4$: C, 19.35; H, 8.12; N, 33.85.

PREPARATION OF $(CH_3)_2N(NH_2)_2ClO_4$

Anhydrous $Ba(ClO_4)_2$ (0.5074 g, 1.51 mmoles) was dissolved in 10 ml of deionized water and added with stirring to a solution of $[(CH_3)_2N(NH_2)_2]_2SO_4$ (0.3561 g, 1.43 mmoles) dissolved in 10 ml of deionized water. The mixture was filtered through a tared filter funnel and the precipitate washed twice with 5-ml portions of deionized water. The precipitate was dried to constant weight at 110 C, and 0.3496 g (1.50 mmoles) of $BaSO_4$ was recovered. The filtrate was concentrated on a Rotary Evaporator using a 35-C water bath, and 0.513 g of a colorless solid was recovered. The crude product was dissolved in 20 ml of 95 percent ethanol, at approximately 35 C, and a small amount of insoluble material removed by filtration. Diethyl ether (60 ml) was then added to the filtrate and the precipitated solid filtered. After vacuum drying, the recovered solid amounted to 0.466 g (2.65 mmoles), or a 93 percent yield of 2,2-dimethyltriazanium perchlorate. The material melted at 196 C with violent decomposition.

Analysis. Found: C, 13.20; H, 5.65; N, 23.58. Calculated for $(CH_3)_2N(NH_2)_2ClO_4$: C, 13.68; H, 5.74; N, 23.93.

PREPARATION OF $(CH_3)_2N(NH_2)_2NO_3$

2,2-Dimethyltriazanium nitrate was prepared from the sulfate (0.913 g, 3.63 mmoles) and $Ba(NO_3)_2$ (0.9481 g, 3.63 mmoles) in 20 ml of water similar to the method described for preparation of the perchlorate. The weight of the dried $BaSO_4$ was 0.8667 g (3.71 mmoles), and the weight of crude solid product recovered from the filtrate was 0.992 g. The product was recrystallized from a 3:1 mixture of diethylether and ethanol and 0.952 g (7.0 mmoles), or a 96 percent yield, was obtained. The recrystallized product melted between 124 and 125 C.

Analysis. Found C, 17.35; H, 7.17; N, 39.70. Calculated for $(CH_3)_2(NH_2)_2NO_3$: C, 17.39; H, 7.30; N, 40.56.

REACTION OF CH_3NHNH_2 AND $ClNH_2$

Chloramine, NH_2Cl, was formed by the reaction of NH_3 and Cl_2 (Ref. 15), and a standard solution of the aminating agent in diethylether was prepared. A solution of monomethylhydrazine (0.320 g, 7.0 mmoles) in diethylether (50 ml) was treated with an etheral solution (85 ml) of $ClNH_2$ (7.4 mmoles) at 0 C. An immediate precipitate (0.26 g) was formed which was shown by ir to be NH_4Cl.

REACTION OF CH_3NHNH_2 and NH_2OSO_3H

The amounts of reactants used and the weight of methanol-insoluble solid product obtained are given in Table 5. All reactions were conducted in absolute methanol at 0 C. The solid product possessed no oxidizing power toward acidic iodide, did not melt below 250 C, and its ir spectra was identical to that of $(NH_4)_2SO_4$.

TABLE 5. CH_3NHNH_2/NH_2OSO_3H REACTION IN ABSOLUTE METHANOL

NH_2OSO_3H, mmoles	CH_3NHNH_2, mmoles	CH_3OH, milliliters	Reaction Time, hours	Weight of Product, g
19	38	30	1	1.0
20	34	25	1	0.53
33	33	150	1	0.2
33	33	30	4	2.73

$N_3H_7SO_4$ AND ITS REACTIONS

$N_3H_7SO_4$ was prepared in 71 to 73 percent yield as described in Ref.9. Identification of the material was made on the basis of its published ir spectrum and mp (59 C, dec.).

Reaction in the Presence of $LiOCH_3$

A methanolic solution of $LiOCH_3$ was prepared by the reaction of LiH and CH_3OH. The solution's $LiOCH_3$ content was determined by standard acid-base analysis. To a solution of NH_2OSO_3H (10.4 mmoles) in 35 ml of cold CH_3OH, was added a methanolic solution (20 ml) containing N_2H_4 (11 mmoles) and $LiOCH_3$ (5.3 mmoles). A precipitate formed immediately. After 1 hour, the precipitate was filtered and dried at ambient temperature (weight, 0.88 g; theoretical for $LiHSO_4 \cdot 2N_2H_4$ is 0.89 g).

A methanolic solution (60 ml) of NH_2OSO_3H (10.4 mmoles) and $LiCH_3$ (5.3 mmoles) was added at 0 C to 11 mmoles of N_2H_4 dissolved in methanol (20 ml). A precipitate formed immediately. Filtration of the solid, followed by vacuum drying,gave 0.87 g of $LiHSO_4 \cdot 2N_2H_4$.

Identification of $LiHSO_4 \cdot 2N_2H_4$ was made by comparing its ir spectrum with that obtained from an authentic sample of the compound. Addition of benzaldehyde to an acidic solution of the salt gave a yellow precipitate. Recrystallization of this derivative from 95 percent ethanol gave yellow needles melting between 91 and 93 C. Benzalazine, the product formed by reaction of hydrazine and benzaldehyde, has a mp of 93 C.

Reaction in the Presence of $(CH_3)_2NC_6H_5$

A methanolic solution (50 ml) containing $(CH_3)_2NC_6H_5$ (16 mmoles) and N_2H_4 (31 mmoles) was added dropwise to a cold methanolic solution (100 ml) of NH_2OSO_3H (32 mmoles). The precipitate that immediately formed was filtered after 1 hour, and dried in vacuo. The solid (3.31 g or 71 percent yield) was identified as $N_3H_7SO_4$ by its mp (59 C) and ir spectrum.

The same proportions of reactants were used in a second experiment. In this experiment, N,N-dimethylaniline and NH_2OSO_3H were dissolved in methanol (100 ml) at 0 C and a methanolic solution of N_2H_4 was then added. The insoluble product was filtered and vacuum-dried, and 3.36 g (73 percent yield) of $N_3H_7SO_4$ was recovered.

Reaction with $Ba(ClO_4)_2$

To 20 ml of water cooled to 10 C and containing a mixture of $Ba(ClO_4)_2$ (0.696 g, 2.07 mmoles) and NaOH (0.156 g, 3.9 mmoles), was added solid $N_3H_6HSO_4$ (0.572 g, 3.95 mmoles). Gassing was observed on dissolution of the bisulfate, and the initially turbid solution of $Ba(ClO_4)_2$ and NaOH became more opaque until a precipitate was formed. During filtration of the solid and concentration of the filtrate, gassing continued. The recovered solid did not give the characteristic absorption bands for a triazanium derivative.

$N_2H_4/NaOSO_3NH_2$ Reaction

Sodium hydroxylamine-O-sulfonate was prepared by taking a suspension of NaOH (21 mmoles) in CH_3OH (40 ml) and adding enough water to give a clear solution.

The solution of NaOH was then added to one of NH_2OSO_3H (20 mmoles) dissolved in 50 ml of cold methanol. Addition of benzene (50 ml) precipitated $NaOSO_3NH_2$. A yield of 81 percent of the dried product was obtained.

Hydrazine (11 mmoles) dissolved in CH_3OH (25 ml) was added to a cold solution of $NaOSO_3NH_2$ (11 mmoles) in CH_3OH (50 ml). After 1 hour, the insoluble product was filtered and vacuum-dried. The product Na_2SO_4 weighed 0.84 g.

REACTIONS OF $(CH_3)_2NCl$

Toluene or diethyl ether solutions of $(CH_3)_2NCl$ were prepared by oxidation of $(CH_3)_2NH_2Cl$ with Chlorox solutions (Ref. 16). After drying, the organic phase was assayed for $(CH_3)_2NCl$ content by standard iodometric titrations.

Reaction of $(CH_3)_2NCl$ and N_2H_4

Several ambient pressure reactions were conducted between $(CH_3)_2NCl$ and hydrazine in toluene, diethyl ether, and methanol-diethyl ether solutions. The experimental results described are those obtained in toluene under vacuum conditions.

Hydrazine (0.2550 g, 8.0 mmoles) was condensed onto a degassed toluene solution of $(CH_3)_2NCl$ (6.0 mmoles). The reaction mixture was stirred at 0 to 5 C, and a total of 3.19 mmoles of nitrogen was obtained. The reaction mixture was fractionated at -45, -78, and -196 C, and 2.06 mmoles of $(CH_3)_2NH$ (containing a trace of ammonia) were recovered in the -196 C trap. The nonvolatile solid was then treated with 50 percent NaOH, and an additional 3.5 mmoles of $(CH_3)_2NH$ were recovered.

When the reaction of hydrazine (8.0 mmoles) and $CH_3)_2NCl$ (7.8 mmoles) was conducted in a 2: 1 mixture of methanol and diethyl ether, the solid that precipitated was N_2H_5Cl by ir and melting point (found, 90 to 91 C; literature value, 89 C). The weight of the recovered material corresponded to 2.6 mmoles of N_2H_5Cl.

Reaction of $(CH_3)_2NCl$ and $(CH_3)_2NNH_2$

A satisfactory material balance was not obtained from vacuum line experiments conducted on the titled reaction. For example, after addition of 7.8 mmoles of $(CH_3)_2NNH_2$ to 10 ml of a degassed toluene solution of $(CH_3)_2Cl$, 4.04 mmoles of nitrogen were collected. Vacuum line fractionation of the toluene solution at -45, -78, -95, and -196 C gave 1.2 mmoles of NH_3 [containing some $(CH_3)_2NH$] and 2.1 mmoles of $(CH_3)_2NH$ contaminated with a trace of NH_3. The solid product (0.20 g) was identified as $(CH_3)_2NH_2Cl$ by ir. Neither NH_4Cl nor N_2H_5Cl was apparently formed.

1,1-DIMETHYLTRIAZANIUM BISULFATE

N,N-Dimethylhydroxylamine-O-sulfonic acid was prepared in 76 percent yield by reaction of $(CH_3)_2NOH \cdot HCl$ (Ref. 17) and chlorosulfonic acid (Ref. 13). The purity of the $(CH_3)_2NOSO_3H$ was 100.1 percent based on base titration of the salt.

Reaction of N_2H_4 and $(CH_3)_2NOSO_3H$

N,N-Dimethylhydroxylamine-O-sulfonic acid (2.3 g, 16.3 mmoles) was dissolved in methanol (70 ml) and the solution cooled to 5 C. A solution of N_2H_4 (0.50 g, 15.6 mmoles) in CH_3OH (10 ml) was added to the aminating agent. No insoluble products or gassing was noted during 72 hours at ambient temperature. The reaction mixture was concentrated on a Rotary Evaporator and 2.61 g of a colorless solid was recovered. The product after recrystallization from ethanol melted at 136 to 137 C (dec.).

<u>Analysis</u>. Found: C, 14.10; H, 6.45; N, 24.05. Calculated for $(CH_3)_2NNH_2NH_2^+ HSO_4^-$: C, 13.87; H, 6.40; N, 24.27.

Reaction of $(CH_3)_2NNH_2NH_2HSO_4$ and $Ba(ClO_4)_2$

A methanolic solution (10 ml) of $(CH_3)_2NNH_2NH_2HSO_4$ (0.3556 g, 2.05 mmoles) was added at ambient temperature to 10 ml of a 90 percent CH_3OH solution of $Ba(ClO_4)_2$ (0.6889 g, 2.05 mmoles). The water-insoluble precipitate was filtered, and the filtrate was added to 100 ml of diethyl ether. The precipitated solid (0.29 g) did not melt completely below 190 C.

PREPARATION OF $CH_3SO_2ONH_2$

Methanesulfonic acid (14.8 g, 0.154 mole) prepared by hydrolysis of methanesulfonyl chloride, and shown to be 100.2 percent pure by acid-base titration, was dissolved in 150 ml of absolute methanol. Potassium hydroxide (8.69 g, 0.155 mole) was dissolved in 30 ml of hot absolute methanol and added to a solution of $NH_2OH \cdot HCl$ (10.7 g, 0.154 mole) in 120 ml of absolute methanol. The resulting slurry was cooled to 10 C, the KCl was removed by filtration, and the resulting filtrate was added to the solution of methanesulfonic acid. The mixture was allowed to stand for 1 hour and the methanol removed by vacuum distillation. The recovered solid (18.1 g) was recrystallized from a mixture of 25 ml of methanol and 125 ml of ethanol. The dried product amounted to 13.6 g and melted at 149 to 151 C.

<u>Analysis</u>. Found: C, 10.75; H, 4.50; N, 12.31. Calculated for $CH_3SO_3ONH_2$: C, 10.81; H, 4.54; N, 12.61.

Reaction of N_2H_4 and $CH_3SO_2ONH_2$

Hydrazine (0.45 g, 14 mmoles) and $CH_3SO_2ONH_2$ (1.55 g, 14 mmoles) were dissolved in 40 ml of absolute methanol, and the mixture was reacted at ambient temperature for 16 hours. Diethylether (250 ml) was added to the solution to precipitate a colorless solid [1.40 g, mp 73 to 75 C (dec.)]. After recrystallization from a 2:1 ethanol-methanol solvent pair, the material melted at 77 to 79 C (dec.).

<u>Analysis</u>. Found: N, 30.44; H, 6.58; N:H, 3.00. Calculated for $N_3H_6SO_3CH_3$: N, 29.35; H, 6.34; N:H, 3.

Reaction of $N_3H_6SO_3CH_3$ and $Ba(ClO_4)_2$

Triazanium methylsulfonate (0.500 g, 3.5 mmoles) was dissolved in CH_3OH (30 ml) and treated with $Ba(ClO_4)_2$ (0.620 g, 1.85 mmoles) dissolved in CH_3OH (10ml). Turbidity developed within 1/2 minute, and a precipitate was slowly formed. The mixture was stirred at ambient temperature for 1 hour and filtered through a tared crucible. After drying, the precipitate weighed 0.322 g (calculated, 0.557 g). The filtrate was concentrated to dryness, and 0.88 g of a colorless solid was recovered. This solid was extracted with 30 ml of 2 :1 ethanol-methanol solution, and 0.53 g of a solid was recovered from the filtrate, melting at 61 to 63 C.

The reaction was repeated in a 5:2 ethanol-methanol mixture to minimize the solubility of $Ba(SO_3CH_3)_2$. A solution of triazanium methylsulfonate (0.403 g, 2.82 mmoles) was dissolved in a mixture of 40 ml of warm absolute methanol and 20 ml of methanol. A solution of $Ba(ClO_4)_2$ (0.479 g, 1.42 mmoles) in 10 ml of ethanol was added to give an immediate precipitate. After 1 hour of reaction, the precipitate (0.355 g; theo., 0.462) was removed by filtration. The filtrate yielded 0.525 g of a colorless solid (theo., 0.462 g), melting at 60 to 62 C.

An analytical sample was obtained by recrystallizing the crude product twice from 10 ml of warm ethanol. The recrystallized material melted at 78 to 80 C.

Analysis. Found: C, 0.77; H, 4.67; N, 24.34. Calculated for $N_3H_6ClO_4 \cdot H_2O$: H, 4.87; N, 25.39.

Calculations are presented in the text on the purity of the hydrated salt based on the assumption that the only impurity present was $Ba(SO_3CH_3)_2$.

REACTION OF CH_3NHOSO_3H AND HYDRAZINES

N-Methylhydroxylamine-O-sulfonic acid was prepared from 9.86 g of 98 percent pure $CH_3NHOH \cdot HCl$ (Aldrich Chemical Co.) in 94 percent yield by the preparative method of Ref. 13. A purity of 99.8 percent was indicated by titration with standard base to the phenolphthalein endpoint.

Reaction With Hydrazine

Hydrazine (0.70 g, 22 mmoles) was reacted with CH_3NHOSO_3H (2.624 g, 21 mmoles) in absolute methanol (50 ml) at 10 C. Gassing was noted, and a precipitate was formed. The colorless solid weighed 0.425 g after vacuum drying and melted at 108 to 110 C (dec.).

Analysis. Found: N, 33.74; H, 6.28. Calculated for $(N_2H_4)_2 \cdot H_2SO_4$: N, 34.55; H, 6.21.

The filtrate yielded a viscous liquid which was not identified.

Reaction With $(CH_3)_2NNH_2$

N-Methylhydroxylamine-O-sulfonic acid (2.56 g, 20 mmoles) was partially dissolved in absolute methanol (50 ml) and treated with $(CH_3)_2NNH_2$ (2.37 g, 39 mmoles) dissolved in CH_3OH (10 ml). The CH_3NHOSO_3H was completely dissolved during addition of the hydrazine. The reaction was continued for 16 hours after which a colorless solid (0.489 g), identified as $(NH_4)_2SO_4$ by ir, was collected. The filtrate yielded a viscous yellow liquid (3.79 g) which was not identified.

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13. ABSTRACT

Studies were conducted on the preparation and characterization of triazanium salts. A method was devised for synthesis of 2,2-dimethyltriazanium sulfate. The sulfate was converted to its perchlorate and nitrate by metathetical reactions. The isomer 1,1-dimethyltriazanium bisulfate was also prepared, but its conversion to the perchlorate was not successful. Triazanium bisulfate and methylsulfonate were prepared and characterized by ir spectroscopy. A hydrated triazanium perchlorate was apparently prepared, but attempts to obtain the anhydrous salt gave only decomposition products.

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