characterization of the solution species, and such studies are in progress.
(36) Related phosphido complexes are described in several publications: R. Hayter, *Inorg. Chem.*, **2**, 1031 (1963); R. G. Hayter and L. F. Williams, *ibid.*, **3**, 613 (1964); R. G. Hayter, *J. Am. Chem. Soc.*, **86**, 823 (1964); *ibid.*, **88**, 4376 (1966); R. E. Dessy, A. L. Rheingold, and G. D. Howard, *ibid.*, **94**, 746 (1972).
(37) G. Huttner, H.-D. Müller, A. Frank, and H. Lorenz, *Angew. Chem., Int. Ed. Engl.*, **14**, 705 (1975).
(38) P–N bond rotation barriers determined in these studies include: $(Me_2N)_2P$, 14.6 kcal/mol; $[(i\text{-}Pr)_2N]_2P$, 11.1 kcal/mol.[7]

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Pyrolysis and Hydrolysis of 2,2-Dimethyltriazanium Chloride

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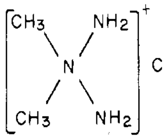
The purification, hydrolysis, and pyrolysis of 2,2-dimethyltriazanium chloride are discussed. The gas chromatography data indicate that the pyrolysis products in a helium atmosphere are NH_4Cl, N_2, $(CH_3)_2NN{=}CH_2$, and small amounts of $(CH_3)_2NNH_2$ and $(CH_3)_2NN{=}NN(CH_3)_2$. Under vacuum, with or without solid NaOH, the products are NH_4Cl, N_2, $(CH_3)_2NN{=}CH_2$, and trace amounts of $(CH_3)_2NN{=}NN(CH_3)_2$ but no $(CH_3)_2NNH_2$. The ultraviolet spectroscopy data for the hydrolysate of $(CH_3)_2N(NH_2)_2Cl$ in 0.5–2.0 N KOH solution indicate that $(CH_3)_2NN{=}CH_2$ is the major product. The value of λ_{max} for $(CH_3)_2NN{=}CH_2$ is pH dependent and shifts toward shorter wavelengths with increased pH. The rate of formation of $(CH_3)_2NN{=}CH_2$ follows approximately first-order kinetics with respect to $(CH_3)_2N(NH_2)_2Cl$. The mechanisms for the formation of various pyrolysis and hydrolysis products of $(CH_3)_2N(NH_2)_2Cl$ are discussed. The melting point of $(CH_3)_2N(NH_2)_2Cl$ has been corrected; the new value is 124 °C with decomposition.

Introduction

One potential process for the synthesis of 1,1-dimethylhydrazine is the liquid-phase[1-3] chloramination of dimethylamine. One of the byproducts of the chloramination is 2,2-dimethyltriazanium chloride,[4-9] $[(CH_3)_2N(NH_2)_2]Cl$. It has been shown that the latter substance is formed by the reaction between the 1,1-dimethylhydrazine and chloramine.[10-13]

Giordano and Sisler[14] have also obtained dimethyltriazanium chloride by the chloramination of trimethylhydrazine. Dimethyltriazanium chloride is reported to be stable in air and in neutral aqueous solutions.[15] It can be recrystallized[10] from boiling ethanol, acetone, diethyl ether, or acetonitrile. In a recent report Giordano, Palenik, and Sisler[16] have shown the structure of 2,2-dimethyltriazanium chloride to be



analogous to the structure of $[N(CH_3)_4]Cl$.

Although 2,2-dimethyltriazanium chloride is among the first known stable alkyl compounds which contain a single bonded chain of more than two nitrogen atoms, it is an undesirable byproduct in the synthesis of unsymmetrical dimethylhydrazine, $(CH_3)_2NNH_2$, by chloramination of dimethylamine. It was, therefore, the object of this study to determine the thermal and hydrolytic stabilities of 2,2-dimethyltriazanium chloride, to determine the various products formed by its pyrolysis and hydrolysis, and to determine the reaction mechanisms for the formation of the various products from the pyrolysis or hydrolysis. This information would be useful in optimizing the yield of unsymmetrical dimethylhydrazine from the chloramination of dimethylamine.

Experimental Section

Materials. The 2,2-dimethyltriazanium chloride used in this study was prepared and purified by procedures described in the literature.[10,11,16] Its ^{1}H NMR spectrum showed ammonium chloride as an impurity although its melting point agreed with that reported in literature.[10,11] It was, therefore, further purified by dissolving 0.781 g in 30 mL of anhydrous ethanol at room temperature and recrystallizing it by adding an acetone–ether mixture (90 mL of acetone, 300 mL of ether) at −4 °C. The material obtained by this procedure melted at 124 °C (with decomposition) and showed no ammonium chloride impurity in its ^{1}H NMR spectrum or its infrared spectrum. The dimethylhydrazones of formaldehyde[17] ($(CH_3)_2NN{=}CH_2$) and tetramethyl-2-tetrazene[18] ($(CH_3)_2NN{=}NN(CH_3)_2$) were prepared by methods found in the literature. These compounds were analyzed by gas–liquid chromatography and nuclear magnetic resonance spectroscopy to ascertain that they were free from appreciable amounts of contaminants. Unsymmetrical dimethylhydrazine, $(CH_3)_2NNH_2$, of 95% purity was obtained from the Naval Surface Weapons Center, White Oak Laboratory. It was refluxed and distilled[11] over solid potassium hydroxide in a nitrogen atmosphere before use. The product so obtained invariably contained formaldehyde dimethylhydrazone. The amount of the hydrazone was determined and an appropriate correction was applied when it was necessary. Chloramine was prepared by the reaction of ammonia and chlorine in a nitrogen atmosphere in a gas phase reactor of the type described by Sisler and Mattair.[19] The chloramine content was determined[11] by shaking a measured sample with potassium iodide in 1 N acetic acid solution and titrating the liberated iodine with standard thiosulfate solution. The solvents used were dried and distilled over appropriate drying agents in a nitrogen atmosphere and were stored under dry conditions. The reagents and the buffers were ACS reagent grade and were used as supplied.

Spectra. Ultraviolet spectra were obtained with a Beckman DB spectrophotometer. A hydrogen lamp was used for wavelengths less than 340 nm and a tungsten lamp for the longer wavelengths. The measurements were made in matched quartz cells (with less than 1% of transmittance difference). The infrared spectra of solid samples (in pressed KBr pellets and liquid samples placed between KBr plates) were recorded with a Beckman IR-10 spectrometer. The ^{1}H NMR spectra of solutions of the samples in $CDCl_3$ or $Me_2SO\text{-}d_6$ were recorded with a Varian Model A-60 A NMR spectrometer using tetramethylsilane as an internal standard.

Analyses. All pH measurements were made with a Corning Model 12 Research pH meter using an Orion Model 91-01-00 pH electrode and Coleman Model 3-711 standard calomel reference electrode. The pH meter was standardized by using ACS grade buffers (pH 10.00 and 6.86) immediately before use. The instrument drift was less than 0.05 pH unit/h. A Perkin-Elmer Model 810 gas chromatograph equipped with twin 12 ft by $^1/_8$ in. E-20 Carbowax KOH 5% columns and a thermal conductivity detector was used for gas–liquid chro-

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Table I. Pyrolysis of $[(CH_3)_2N(NH_2)_2]Cl$ between 135 and 600 °C

interface temp, °C	100	residue, %	41.9
sample wt, mg	4.3	He flow rate, mL/min	27
residue wt, mg	1.8	column temp, °C	100

final temp, °C	pyrolysis interval, s	products
135	10	no product
150	10	no product
200	10	FDMH
225	10	N_2, UDMH,[b] FDMH,[c] unknown
250	10	N_2, UDMH, FDMH
275	10	N_2, FDMH
300	10	N_2, FDMH
350	10	N_2, UDMH, FDMH, unknown
400	10	N_2, UDMH, FDMH
500	5	N_2, ether,[a] UDMH, FDMH
600	2	no product

[a] Ether was used in the recrystallization of $[(CH_3)_2N(NH_2)_2]Cl$. [b] UDMH = $(CH_3)_2NNH_2$. [c] FDMH = $(CH_3)_2NN{=}CH_2$.

matography. An internal standard was used to relate the peak areas to the percent of compounds of interest.[20] Helium was used as the carrier gas.

Pyrolysis of Dimethyltriazanium Chloride in a Helium Atmosphere. For the pyrolytic study of dimethyltriazanium chloride in a helium atmosphere a Pyroprobe-100 supplied by Chemical Data Systems was used. The Pyroprobe-100 is a solid-state pyrolyzer, which essentially consists of three major parts: the interface, the pyroprobe, and the electrical control system. The interface was mounted on the injector port of the gas chromatograph column where it became an extension of the injector port. The interface was also used as the pyroprobe holder. Since the carrier gas enters through the interface, the atmosphere inside the interface and the column was the same, viz., helium. The temperature of the interface was maintained at 100 °C. The pyroprobe used in this study had a platinum spiral sample holder with a probe seal and an extension cable connected to the electrical control system. The weighed samples of dimethyltriazanium chloride were placed in the platinum spiral on the pyroprobe. The pyroprobe was then inserted into the interface and sealed. The sample was allowed to stay in the interface for a minimum of 10 min to allow the air and moisture to be purged from the interface and the column. By use of the electrical control, the final pyrolysis temperature, the duration of pyrolysis, and the rate of reaching the final temperatures were adjusted as desired. At the desired time the run button was pressed to start the pyrolysis. The volatile pyrolysis products were carried into the analytical gas chromatograph column with the carrier gas and were identified by comparing their retention times with the retention times of the known substances. The weights of the solid residues that remained in the sample tube were determined and percentages of residue remaining were calculated. The solid residues were shown to be NH_4Cl by their infrared spectra.[21] The results of the pyrolysis of the same sample of dimethyltriazanium chloride between 135 and 600 °C are listed in Table I and the results of the pyrolysis of different samples of this substance at various temperatures are listed in Table II. The schematics of the pyroprobe and gas chromatograph system are shown in Figure 1.

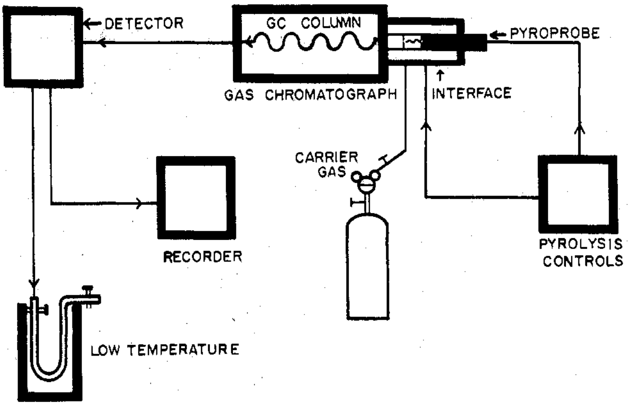

Figure 1. Schematics of the pyroprobe gas chromatograph system.

Pyrolysis of Dimethyltriazanium Chloride under Vacuum. Known weights of solid 2,2-dimethyltriazanium chloride and solid NaOH were pyrolyzed through the temperature range 100–185 °C over a 30-min period and the volatile pyrolysis products condensed in a thoroughly degassed dry ether–toluene mixture (100 mg of toluene/100 mL of ether) cooled by liquid nitrogen. The ether–toluene solution of the pyrolysis products was then examined by gas chromatography. The pyrolysis products were identified by comparing their retention times with those of known substances under similar conditions. The various products and their quantities obtained are listed in Table III. A white residue remained in the reaction flask and was shown by its infrared spectrum to be ammonium chloride[21] when no sodium hydroxide was used. The pressure caused by the pyrolysis products generally dropped to half of its original value when the products were cooled to liquid-nitrogen temperature. Although the identities of the noncondensable gases were not determined in these experiments, we believe, on the basis of experimental results on the pyrolysis of dimethyltriazanium chloride in helium atmosphere, this gas to be nitrogen. Some products other than formaldehyde dimethylhydrazone and tetramethyltetrazene were detected in the gas chromatographic analysis; the identities of these were not established.

Hydrolysis of Dimethyltriazanium Chloride in Aqueous Base. For an estimation of the amount of formaldehyde dimethylhydrazone

Table II. Pyrolysis of $[(CH_3)_2N(NH_2)_2]Cl$ at 350 and 400 °C

interface temp, °C	100	column temp, °C	100
He flow rate, mL/min	24		

sample wt, mg	residue wt, mg	% wt of residue	final temp, °C	interval times, s	products
5.5	2.8	50.9	350	2	N_2, CH_4, ether,[a] $(CH_3)_2NNH_2$, $(CH_3)_2NN{=}CH_2$, one unknown[b]
5.6	3.3	58.9	350	2	N_2, ether, $(CH_3)_2NN{=}CH_2$, and two unknowns
4.1	3.4	82.9	400	5	N_2, ether, $(CH_3)_2NNH_2$, $(CH_3)_2NN{=}CH_2$, $(CH_3)_2NN{=}NN(CH_3)_2$, and two unknowns
4.6	3.4	73.9	400	5	N_2, CH_4, ether, $(CH_3)_2NNH_2$, $(CH_3)_2NN{=}CH_2$, $(CH_3)_2NN{=}NN(CH_3)_2$, and two unknowns

[a] Ether was used for recrystallization. [b] One of the unknowns in substantial amount.

Table III. Pyrolysis Products of $[(CH_3)_2N(NH_2)_2]Cl$ under Vacuum

mmol of $[(CH_3)_2N(NH_2)_2]Cl$	mol of NaOH/mol of $[(CH_3)_2N(NH_2)_2]Cl$	mmol of total $(CH_3)_2NN{=}CH_2$ formed	mmol of total $(CH_3)_2NN{=}NN(CH_3)_2$ formed
0.33	0	0.042	0.009
0.42	31.0	0.132	0.002
0.13	15.0	0.003	trace
0.22	1.8	0.048	0.009
0.28	300.0	0.053	0.003
0.23	11.0	0.057	0.030

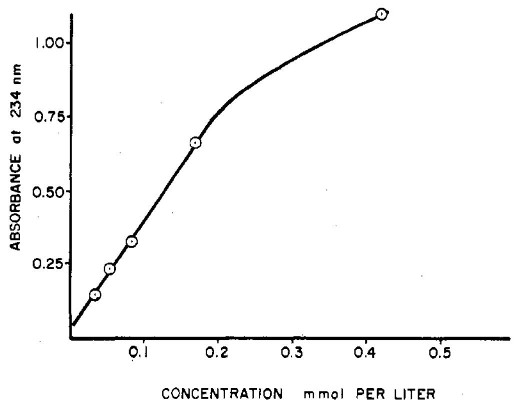

Figure 2. Absorbance at wavelength 234 nm and near pH 13.8 vs. concentration of $(CH_3)_2NN{=}CH_2$.

Table IV. Hydrolysis of $[(CH_3)_2N(NH_2)_2]Cl$ in 1 N KOH as Function of $[(CH_3)_2N(NH_2)_2]Cl$ Concentration Determined by UV Spectrophotometry at 234 nm

mmol of $[(CH_3)_2N(NH_2)_2]Cl$/L	mmol of $(CH_3)_2NN{=}CH_2$/L
0.30	0.05
0.60	0.12
0.90	0.14
1.50	0.23
3.00	0.37

Table V. λ_{max} of $(CH_3)_2NN{=}CH_2$ and $[(CH_3)_2N(NH_2)_2]Cl$ Solutions as a Function of pH

solution	pH	λ_{max}
0.4×10^{-3} M FDMH[a] in 1 N KOH + 3.0 mL 5 N NaOH	13.90	230
0.4×10^{-4} M FDMH in 1 N KOH + 1.5 mL 5 N NaOH	13.89	235
0.4×10^{-4} M FDMH in 1 N KOH	13.75	238
0.4 mmol FDMH in 1 N KOH + HCl	11.40	240
DMTC[b] in 1 N KOH	13.79	234
DMTC in 1 N KOH + HCl	13.40	237
DMTC in 1 N KOH + HCl	11.25	240

[a] FDMH = $(CH_3)_2NN{=}CH_2$. [b] DMTC = $[(CH_3)_2N(NH_2)_2]Cl$.

formed in the KOH–dimethyltriazanium chloride reaction, standard solutions of the hydrazone in 1 N KOH solution and in water were prepared. The pH values of these solutions were adjusted by titrating them with 5.0 N NaOH solution to the same pH as that of the reaction solutions. This titration yielded solutions with ultraviolet spectra closely resembling those of the reaction mixtures. The wavelength of maximum absorbance was consistently between 234 and 236 nm as in the case of the reaction solutions. A plot of absorbance at 234 nm vs. hydrazone concentration is shown in Figure 2. This plot was used to determine the hydrazone concentrations of the various reaction mixtures.

Hydrolysis of Dimethyltriazanium Chloride in 1 N KOH as a Function of Dimethyltriazanium Chloride Concentration. The solutions of dimethyltriazanium chloride were prepared by dissolving known amounts in 1 N KOH solution. The various products obtained by the hydrolysis were analyzed by using a Beckman DB spectrophotometer and the calibration curve in Figure 2. The results are summarized in Table IV. The only product identified was the hydrazone.

Hydrolysis of Dimethyltriazanium Chloride in Aqueous Base—Ultraviolet Analysis. The solutions of dimethyltriazanium chloride were prepared by dissolving known amounts (0.1–1.0 mg/mL) in KOH solutions with pH values higher than 11. Reference solutions of unsymmetrical dimethylhydrazine and the dimethylhydrazone of formaldehyde were prepared in the range of 2.6×10^{-5} to 4.2×10^{-4} M. Solutions of these two substances were also prepared in a pH 10.00 buffer (borate, K_2CO_3, and KOH). The solutions were analyzed by ultraviolet spectrophotometry (400–230 nm) using a Beckman DB spectrophotometer. The results of the various measurements are listed in Table V.

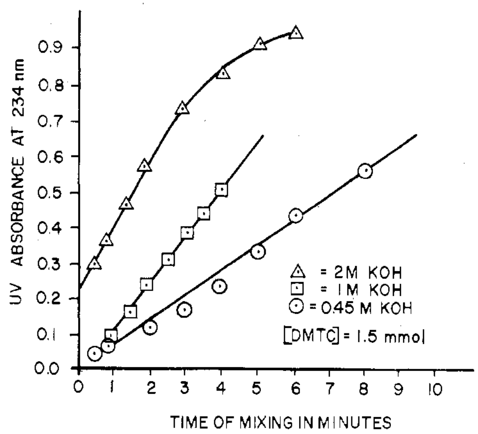

Figure 3. Hydrolysis of $[(CH_3)_2N(NH_2)_2]Cl$ (DMTC) in aqueous base.

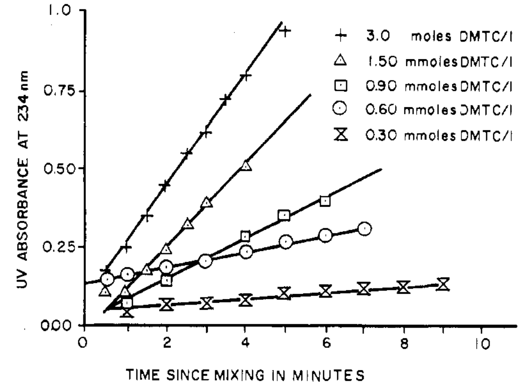

Figure 4. Absorbance at 234 nm of $[(CH_3)_2N(NH_2)_2]Cl$ solutions of various concentrations in 1 N KOH solution vs. time after mixing.

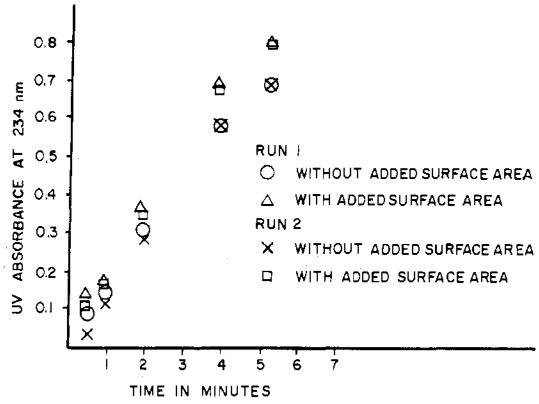

Figure 5. Effect of surface area on the hydrolysis of $[(CH_3)_2N(NH_2)_2]Cl$ in aqueous KOH solutions.

Kinetic Studies of the Hydrolysis of Dimethyltriazanium Chloride in Aqueous Base. The rate of formation of formaldehyde dimethylhydrazone in the solutions of dimethyltriazanium chloride in potassium hydroxide was studied by monitoring the change in absorption of the solution at 234 nm. A 1-mL aliquot of solution of appropriate concentration was pipetted into an ultraviolet cell. Into this cell was injected 2.0 mL of potassium hydroxide solution of appropriate concentration. The mixing time was less than 5 s. The sample holder of the spectrophotometer was enclosed in a water jacket and the temperature was maintained at 25 °C. The changes in ultraviolet absorption with time at various potassium hydroxide concentrations and at a fixed concentration of the triazanium salt are shown in Figure 3. The final concentration of the hydrazone measured 0.5–1 h after mixing was the same for all concentrations of KOH. Similar experiments were performed with a single potassium hydroxide concentration (at 1.5 N KOH) and various initial dimethyltriazanium chloride concentrations. These results are shown in Figure 4.

In one series of experiments half of the reaction cell was filled with broken glass to test the effect of surface area on the rate of reaction. The results obtained in these studies were identical within the limits of the experimental error with those obtained in the absence of added surface (Figure 5). The three experiments performed in 1.0 N KOH with no broken glass yielded lines with slopes of 0.165 ± 0.002 (arbitrary units) and the two experiments performed with added broken glass yielded slopes of 0.167 ± 0.01 (arbitrary units).

Hydrolysis of Dimethyltriazanium Chloride in Oxygen-Free 0.67 N KOH. The 250-mL portions of deionized water and 1.0 N KOH were purged of dissolved oxygen by passing nitrogen gas through the solutions for 16 h. The two solutions were connected in series, with the water first to saturate the nitrogen and minimize the evaporation of 1 N KOH solution. Less than 5% evaporation of the potassium hydroxide solution was observed. Several 15-mg samples of the triazanium chloride were weighed out and placed in a glovebag which was purged with nitrogen for 16 h. These samples were then dissolved in 15 mL of oxygen-free water and treated with 30 mL of oxygen-free 1 N KOH. The final concentrations of the triazanium chloride and hydroxide ions were thus 0.0030 and 0.67 M, respectively. Samples of these solutions were analyzed on the gas chromatograph 5, 10 and 60 min after mixing. All mixing was carried out in the nitrogen atmosphere of the glovebag, and all samples were taken with gastight syringes which had been previously cleaned with oxygen-free water. In all cases the only product observed was formaldehyde dimethylhydrazone.

Results and Discussion

2,2-Dimethyltriazanium chloride as prepared and purified by the procedure described in the literature[10,11] contains a small amount of NH_4Cl as an impurity and melts at 134–135.5 °C. However, by use of a modified method of recrystallization, the ammonium chloride was eliminated and the melting point was decreased to 124 °C. (The presence of ammonium chloride causes the melting point of dimethyltriazanium chloride to rise.[11])

The products of the solid-state pyrolysis of the triazanium salt under vacuum with or without NaOH as analyzed by gas chromatography showed mainly the hydrazone, a small amount of tetramethyltetrazene, and trace amounts of some unidentified products. A large amount of nitrogen gas was also obtained. However, no dimethylhydrazine or chloramine was detected. From the data listed in Table III it is apparent that no simple relationship exists either between the amount of the triazanium salt pyrolyzed and the amount of the hydrazone and tetramethyltetrazene formed or between the amount of NaOH taken and the amount of the hydrazone and tetramethyltetrazene detected. On the other hand, the pyrolysis of the triazanium salt using the Pyroprobe-100 in a helium atmosphere (Tables I and II) gave dimethylhydrazine and tetramethyltetrazene in small amounts and formaldehyde dimethylhydrazone and nitrogen gas in large amounts. Two other unidentified products were also detected in small amounts. On the basis of the results of these two series of experiments, we believe that dimethyldiazine ($(CH_3)_2{}^+N{=}N^-$) is formed as a result of the dissociation of $(CH_3)_2N(NH_2)_2Cl$ either in two steps[8,22,23] (eq 1, 2) or in one step (eq 3). In

$$(CH_3)_2N(NH_2)_2Cl \rightarrow (CH_3)_2NNH_2 + NH_2Cl \qquad (1)$$

$$(CH_3)_2NNH_2 + NH_2Cl \rightarrow (CH_3)_2\overset{+}{N}{=}\overset{-}{N} + NH_4Cl \qquad (2)$$

$$(CH_3)_2N(NH_2)_2Cl \rightarrow (CH_3)_2\overset{+}{N}{=}\overset{-}{N} + NH_4Cl \qquad (3)$$

either case the dimethyldiazine produced reacts further to give tetramethyltetrazene[24] and $(CH_3)_2NN{=}CH_2$[8,22,23] as shown by eq 4 and 5, respectively. In the pyrolysis of the triazanium chloride in a helium atmosphere all the products except NH_2Cl and CH_4 were identified in variable amounts. The reason CH_4 was not detected is the fact that the retention times of CH_4 and N_2 are very close to each other, methane being slower by less than one-tenth of a minute. Chloramine is too reactive to be detected on the gas chromatograph.

$$2(CH_3)_2\overset{+}{N}{=}\overset{-}{N} \rightarrow (CH_3)_2NN{=}NN(CH_3)_2 \qquad (4)$$

$$2(CH_3)_2\overset{+}{N}{=}\overset{-}{N} \rightarrow (CH_3)_2NN{=}CH_2 + CH_4 + N_2 \qquad (5)$$

The interesting fact to note here is that no dimethylhydrazine was detected when the pyrolysis of the triazanium salt was carried out under vacuum, whereas some was found when the pyrolysis was carried out in a helium atmosphere. One can explain this difference in terms of the experimental conditions in the two series of experiments. In the former series the $(CH_3)_2NNH_2$ and NH_2Cl (if formed) by the pyrolysis remained in the reaction zone and had a chance to react to give NH_4Cl, N_2, $(CH_3)_2NN{=}NN(CH_3)_2$, $(CH_3)_2NNH_2$, and CH_4 whereas, in the latter situation, the opportunity for such reaction was reduced since $(CH_3)_2NNH_2$ and NH_2Cl would be carried away from the reaction zone by the flow of helium and separated in the gas chromatography column.

Ultraviolet absorption spectrophotometry was found to be a satisfactory method for the quantitative analysis of formaldehyde dimethylhydrazone in aqueous solution. However, several problems were encountered in the use of this technique. The absorption maximum of an aqueous solution of the pure hydrazone is between 234 and 240 nm. Basic solutions have a strong absorption at 222 nm associated with the solvent. Even at 234 to 240 nm there is some background absorption by the solvent. Use of 1 N KOH as a reference solution in the double-beam spectrophotometer partially alleviated this problem but the apparent wavelength of maximum absorbance remained highly pH dependent.

The reaction mixture of dimethyltriazanium chloride and potassium hydroxide solutions exhibits a similar absorption to that of the hydrazone but at a somewhat shorter wavelength (230–235 nm). This difference is caused by a difference in pH of the solutions (Table V). It can be seen that the spectra in the two solutions have quite similar absorption maxima at the same pH. Particularly striking is the shift to 240 nm of the triazanium salt–reaction solution at pH 11.25 and the shift to the shorter wavelength (232–230 nm) of the hydrazone with the addition of more base.

On the basis of the ultraviolet measurements of the hydrolysis products of dimethyltriazanium chloride and the comparison of them with the ultraviolet absorption of various possible products of the hydrolysis, the possibility of tetramethyltetrazene as the reaction product can be ruled out. The absorption spectrum of tetramethyltetrazene is rather distinctive[18] and contains two peaks—one at 248 nm and the other at 277 nm. No such absorptions were detected in the hydrolysis products of the triazanium salt. A weak absorbance at 280 nm was observed when the solutions were allowed to stand for a long period of time. It is not clear whether this long wavelength "tail" results from some other absorption or from a trace amount of tetramethyltetrazene.

The principal product of the hydrolysis of dimethyltriazanium chloride in aqueous base is the dimethylhydrazone of formaldehyde. The ultraviolet analysis, particularly the similarity in pH dependence of the spectra of the hydrazone and the reaction products of dimethyltriazanium chloride, supports this conclusion (Table V). In addition, the gas chromatography analysis of the samples of the hydrolysis products showed a peak with retention time 5.5 min (the retention time of pure hydrazone under similar conditions is 5.5 min). This is also consistent with the formation of the hydrazone. There was initially some confusion as to the identity of the product because another suspected product, methanol, has a similar ultraviolet absorption and its retention time on the gas chromatography (5.3 min) is close to that of the hydrazone. Addition of a quantity of methanol to the reaction mixture produced a new peak in the chromatograph whereas the addition of the hydrazone only enhanced the intensity of the peak which was already present. This also supported the identification of the reaction product as the hydrazone.

The rate of formation of the hydrazone from the triazanium salt was studied by monitoring the change in ultraviolet absorbance with time. By use of Beer's law, absorbance was taken as proportional to the concentration of the hydrazone. Therefore, the plots of absorbance vs. time are indicative of the change in concentration of the hydrazone with time. These results are shown in Figure 3. It can easily be seen that increasing the concentration of the hydroxide and holding the triazanium salt concentration at 1.5×10^{-3} M speed up the formation of the hydrazone but the results fit no simple kinetic scheme. The results of similar experiments with a constant potassium hydroxide concentration and $[(CH_3)_2N(NH_2)_2]Cl$ concentrations of 3.0×10^{-3}, 1.5×10^{-3}, 0.9×10^{-3}, 0.6×10^{-3}, and 0.3×10^{-3} M are shown in Figure 4. By use of two independent techniques,[25] these data show the rate of formation of the hyrazone to be approximately first order in $[(CH_3)_2N(NH_2)_2]Cl$ with a pseudo-first-order rate constant of $(2.8 \pm 0.5) \times 10^{-3}$ s^{-1}. The addition of extra surface does not affect the rate of reaction (Figure 6).

From the limiting absorbances of the solution usually obtained 0.5–1 h after mixing, one can obtain the final concentration of formaldehyde dimethylhydrazone in the reaction mixture (Table IV). In general the amount of the hydrazone obtained accounted for approximately 33% of the triazanium salt initially used. The rest of the salt gives products which were not detected by ultraviolet spectroscopy or by gas chromatography.

The only clearly identified product of the hydrolysis of dimethyltriazanium chloride in basic aqueous solutions obtained in these experiments was the dimethylhydrazone of formaldehyde. There is evidence that some other unidentified gaseous products were also formed. Utvary[15] has suggested that the hydrolysis of dimethyltriazanium chloride is a complex process and proposed the formation of dimethylhydrazine and dimethylamine as possible hydrolysis products. We analyzed our reaction mixtures by both ultraviolet spectroscopy and gas chromatography. Dimethylhydrazine is transparent in the ultraviolet, but there is no difficulty in identifying it by gas chromatography. Hydrolysis of the triazanium salt was performed in oxygen-free KOH solution under an oxygen-free atmosphere to avoid possible oxidation of dimethylhydrazine by oxygen;[26] yet no dimethylhydrazine was detected in the hydrolysis products. Attempts to identify dimethylamine as a salt of picric acid were also unsuccessful. In absence of any external oxidizing agent, the absence of dimethylhydrazine and dimethylamine leads to the following two conclusions: either the hydrolysis of the triazanium salt takes place as shown via

$$(CH_3)_2N(NH_2)_2^+ \rightarrow (CH_3)_2\overset{+}{N}{=}\overset{-}{N} + NH_4^+ \qquad (6)$$

$$2(CH_3)_2\overset{+}{N}{=}\overset{-}{N} \rightarrow (CH_3)_2NN{=}CH_2 + N_2 + CH_4 \qquad (7)$$

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O \qquad (8)$$

or it follows a path shown by

$$(CH_3)_2N(NH_2)_2^+ + OH^- \rightarrow (CH_3)_2NNH_2 + NH_2OH \qquad (9)$$

$$(CH_3)_2NNH_2 + NH_2OH \rightarrow (CH_3)_2\overset{+}{N}{=}\overset{-}{N} + NH_3 + H_2O \qquad (10)$$

In either instance the dimethyldiazine produced would be expected to react to give[9,10,24] the hydrazone. The observed odor of NH_3 and the other gaseous products detected are consistent with the proposed mechanism.

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Registry No. $[(CH_3)_2N(NH_2)_2]Cl$, 13166-44-4; $(CH_3)_2NN{=}CH_2$, 2035-89-4.

References and Notes

(1) G. M. Omietanski, A. D. Kelmers, R. W. Shellman, and H. H. Sisler, *J. Am. Chem. Soc.*, **78**, 3874 (1956).
(2) H. H. Sisler and A. D. Kelmers, U.S. Patent 792741 (March 26, 1958).
(3) H. H. Sisler and A. D. Kelmers, British Patent 792741 (March 26, 1958).
(4) "The Sisler Process for the Manufacture of Hydrazine Fuels, Summary Status Report of the Development", NOS Indian Head, Md., May 1975.
(5) W. McQuistion, G. A. Carpenter, J. R. Wardell, and G. B. Wilmot, "Basic Studies Relating to the Synthesis of 1,1-Dimethylhydrazine and Monomethylhydrazine by Chloramination", Annual Report, NSWC White Oak Laboratories, Silver Spring, Md., Sept 1, 1975–Aug 31, 1976.
(6) W. McQuistion, R. E. Bowen, G. A. Carpenter, and G. B. Wilmot, "Basic Studies Relating to the Synthesis of 1,1-Dimethylhydrazine and Monomethylhydrazine by Chloramination", Semiannual Progress Report, NSWC Wite Oak Laboratories, Silver Spring, Md., March 1977.
(7) W. McQuistion, R. E. Bowen, and G. B. Wilmot, "Basic Studies Relating to the Synthesis of 1,1-Dimethylhydrazine and Monomethylhydrazine by Chloramination", Annual Report, NSWC White Oak Laboratories, Silver Spring, Md., Oct 1, 1976–Sept 30, 1977.
(8) H. H. Sisler, "Basic Studies Relating to the Synthesis of Unsymmetrical Dimethylhydrazine and Monomethylhydrazine by Chloramination", Progress Report to the AFOSR, University of Florida, Gainesville, Fla., April 1, 1976–Nov 30, 1977.
(9) Harry H. Sisler and Milap A. Mathur, Proceedings of the Conference on Environmental Chemistry of Hydrazine Fuels, Tyndall AFB, Sept 13, 1977.
(10) K. Utvary and H. H. Sisler, *Inorg. Chem.*, **5**, 1835 (1966).
(11) K. Utvary and H. H. Sisler, *Inorg. Chem.*, **7**, 698 (1968).
(12) S. E. Frazier and H. H. Sisler, *Inorg. Chem.*, **11**, 1223 (1972).
(13) K. Utvary, H. H. Sisler, and P. Kitzmantel, *Monatsh. Chem.*, **100**, 401 (1969).
(14) Thomas J. Giordano and Harry H. Sisler, *Inorg. Chem.*, **16**, 2043 (1977).
(15) K. Utvary, *Monatsh. Chem.*, **99**, 1483 (1968).
(16) Thomas J. Giordano, Gus J. Palenik, and Harry H. Sisler, *Inorg. Chem.*, **15**, 751 (1976).
(17) J. B. Class, J. G. Aston, and T. S. Oakwood, *J. Am. Chem. Soc.*, **75**, 2937 (1953).
(18) W. E. Bull, J. A. Seaton, and L. F. Audrieth, *J. Am. Chem. Soc.*, **80**, 2516 (1958).
(19) Robert Mattair and H. H. Sisler, *J. Am. Chem. Soc.*, **73**, 1619 (1951).
(20) H. M. McNair and E. J. Bonelli, "Basic Gas Chromatography, Varian Aerograph", Walnut Creek, Calif., 1969, Chapter VII.
(21) K. Nakomoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed., Wiley-Interscience, New York, 1970, p 108.
(22) K. Utvary, private communication.
(23) Harry H. Sisler, Milap A. Mathur, and R. Greengard, in preparation.
(24) H. H. Sisler, R. M. Kren, and K. Utvary, *Inorg. Chem.*, **8**, 2007 (1969).
(25) S. W. Benson, "The Foundations of Chemical Kinetics", McGraw-Hill, New York, 1960, pp 75–85.
(26) Milap A. Mathur and Harry H. Sisler, in preparation.