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BASIC STUDIES RELATING TO THE SYNTHESIS OF 1,1-DIMETHYLHYDRAZINE BY CHLORAMINATION

Final Report

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By

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The kinetics of important reactions in the proposed chloramination method for the manufacture of UDMH have been studied in anhydrous organic solvents. The studies yielded the rates for the formation of UDMH and the activation energy. However the use of the chloramination method in anhydrous organic solvents in the range 0°-30°C appears impractical because of the much higher rate found for the formation of an undesired subsequent reaction product, formaldehyde dimethylhydrazone.

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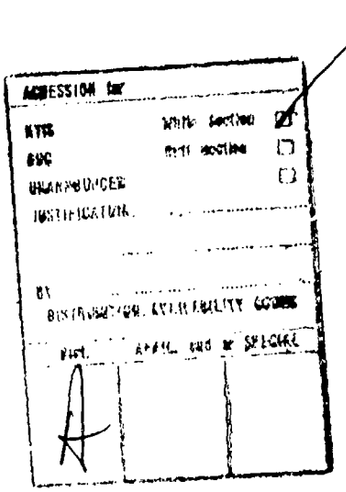
SUMMARY

Because of health hazzards associated with the previous method for the manufacture of the important liquid rocket fuel component, 1,1-dimethylhydrazine (UDMH), studies were carried out to determine the kinetics of formation of UDMH by an alternative process, the choramination of dimethylamine. The kinetics of undesirable side reactions which lower UDMH yields in the chloramination method were also investigated. The reaction between chloramine (NH_2Cl) and dimethylamine gives UDMH. Chloramine can react with the UDMH formed to give a variety of subsequent products, chiefly formaldehyde dimethylhydrazone. A stopped flow reaction system was assembled and used to measure the rate of formation of UDMH in anhydrous organic solvents (chiefly chloroform) in the temperature range 15°-30°C. Reaction rates and an activation energy of 9.8 kcal/mole were derived from these measurements. Bench-scale and modeling experiments showed that the reaction rate for the formation of the hydrazone is about 600 times that for the formation of UDMH at 0°C. The second order kinetics model for these consecutive reactions indicated and experiment showed that the concentration of UDMH quickly reaches a steady-state value while the yield of the hydrazone steadily increases with chloramine addition. The large-scale production of UDMH in anhydrous organic solvents by chloramination of dimethylamine does not appear feasible at practical temperatures because of the low ratios (<.3) UDMH to hydrazone obtained in these experiments.



Introduction:

Unsymmetrical dimethylhydrazine (UDMH) is an important fuel component of some liquid propellants used in military and space agency rockets. Some typical fuels which contain UDMH are[1]:

Aerozine 50:	50.0% UDMH
	50.0% Hydrazine
MAF-1:	39.0% UDMH
	49.9% Diethylenetriamine
	10.1% acetonitrile
	1.0% water
MAF-4:	60.0% UDMH
	40.0% Diethylenetriamine

Until recently, UDMH had been economically produced by the nitrosation of dimethylamine and hydrogenation of the nitroso intermediate to UDMH.

$$(CH_3)_2NH \xrightarrow[H_2O]{HNO_2} (CH_3)_2\,NNO \xrightarrow[H_2O]{H_2/Pd} \text{UDMH}$$

The concentration of UDMH in the final solution is 20-40% and it is distilled from this solution in the presence of sodium hydroxide. The overall yield is good. The favorable economics of this process are due, in part, to the high concentration of UDMH obtained which makes distillation costs relatively low. Unfortunately, the intermediate, N-nitrosodimethylamine, has proven to be very toxic and a probable human carcinogen. Accordingly, its use and worker exposure has been severely limited by the Occupational Safety and Health Administration. These restrictions have led to the abandonment of the nitroso process for the manufacture of UDMH. In the search for a new manufacturing process, investigators have examined a process developed by Sisler and co-workers[2-8] which involves the chloroamination of amines as summarized in the following equations:

$$2NH_3(g) + Cl_2(g) \longrightarrow NH_2Cl(g) + NH_4Cl(s) \qquad (1)$$

$$NH_2Cl + 2(CH_3)_2NH \longrightarrow (CH_3)_2\,NNH_2 + (CH_3)_2\,NH_2^+\,Cl^- \qquad (2)$$

Yields as high as 71% UDMH have been realized in neat dimethylamine (DMA) at low temperatures and at low chloramine (CA) concentrations. As the chloramine concentration (or moles of chloramine added) increases there is a marked decrease in product yield due to a rapid reaction between UDMH and chloramine which leads to a number of undesirable side products.

$$(CH_3)_2NNH_2 + NH_2Cl \longrightarrow \text{side products} + HCl \qquad (3)$$

These side products are mainly:

tetramethyltetrazene, $(CH_3)_2\ N - N = N - N\ (CH_3)_2$ (TMT),

2,2-dimethyltriazanium chloride $(CH_3)_2N(NH_2)_2^+\ Cl^-$ (DMTC) and

Formaldehyde dimethylhydrazone $(CH_3)_2N\text{-}N = CH_2$ (FDMH).

Tetramethyltetrazene is believed to arise from oxidation of UDMH to form a diazene (DMZ) intermediate which quickly dimerizes.

$$(CH_3)_2NNH_2 + NH_2Cl \longrightarrow (CH_3)_2\overset{+}{N} = \bar{N} + NH_4Cl \qquad (4)$$

$$2(CH_3)_2\overset{+}{N} = \bar{N} \longrightarrow (CH_3)_2N - N = N - N(CH_3)_2 \qquad (5)$$

The mechanism for the formation of formaldehyde dimethylhydrazone is still under scrutiny but is believed to be the rearrangement of diazene according to the equation:

$$2(CH_3)_2\overset{+}{N} = \bar{N} \longrightarrow (CH_3)_2\overset{+}{N} = N - CH_3 + CH_3 - N = N^- \qquad (6)$$

$$\downarrow -H^+ \qquad \downarrow +H^+$$

$$\begin{matrix} CH_3 \\ \diagdown \\ \quad N - N = CH_2 \\ \diagup \\ CH_3 \end{matrix} \qquad \{CH_3 - N = N - H\} \downarrow \; CH_4 + N_2$$

2,2-Dimethyltriazanium chloride can be visualized as a simple nucleophilic attack on chloramine by the disubstituted nitrogen of UDMH.

$$(CH_3)_2NNH_2 + ClNH_2 \longrightarrow (CH_3)_2N(NH_2)_2^+ Cl^- \qquad (7)$$

During 1974 and 1975, the Propellant Chemistry Branch, of the White Oak Laboratory, Naval Surface Weapons Center, made an extensive investigation of the experimental conditions for the best yield for Reactions 1 and 2[9]. This work showed that the hydrazone was a particularly troublesome by-product since this product can occur in relatively large amounts and cannot be separated from UDMH by conventional distillation procedures. It was further shown that low concentrations of chloramine, low reaction temperatures, well-stirred reaction solutions, large excesses of dimethylamine and low final concentrations of UDMH all favor the elimination of this contaminant.

During 1974-1975, the Martin-Marietta Corporation, Denver Division, made an extensive study of the Sisler chemistry and its application to the production of hydrazine fuels. Of particular significance to our studies, they measured the reaction rates of Equations (2) and (3) under anhydrous conditions. In these experiments, dilute ammonia solutions of chloramine were added to liquid dimethylamine or UDMH at low temperatures (-46° to -60°C) and at low chloramine/amine mole ratios (DMA/CA ∿1000 to 4000, UDMH/CA ∿500 to 700). The rate of reaction of chloramine was determined from the rate of increase of conductivity due to the formation of chloride ions. Pseudo first order reaction rates were obtained as functions of temperature. These data yielded the important result that the activation energy of Equation (2) (9.6 kcal/mole) is less than that of (3) (14.5 kcal/mole) and therefore the undesired reaction (3) becomes increasingly significant with increasing temperature. Under their conditions, the two rate constants were found to be about equal at -70°C.

It is evident that reaction variables in the Sisler process for the synthesis of hydrazines will need to be carefully optimized if the process is to be successfully applied to the large-scale production of UDMH or monomethyl hydrazine.

In order to provide the reaction rate and mechanism data needed for the selection of proper conditions for scale-up, a joint program between the University of Florida and the Naval Surface Weapons Center, White Oak Laboratory was initiated in September 1975. The main thrust of the NSWC/WOL effort has been to determine the rates of reactions (2) and (3).

In order to measure the rates of reactions (2) and (3) at temperatures of practical importance, a stopped-flow apparatus was designed and assembled. In this device two reactant solutions can be very rapidly mixed (mixing time <10 msec) and the concentrations of reactants and products subsequently measured as functions of time by a fast-response infrared non-dispersive spectrometer.

This report describes the application of the stopped-flow apparatus to reaction (2) and the results of a series of reactions which were carried out on a bench scale in order to determine final reaction products and the relative rates of reactions (2) and (3).

Results and Discussion:

Over thirty runs of the chloramine dimethylamine reaction in chloroform have been made at chloramine concentrations in the range 0.1 - 0.4M and at temperatures from 15° to 30° dimethylamine/chloramine ratios varied from 5.2 to 17.6. For all runs, changes in concentrations with time were determined by measuring the infrared intensity at 1590 cm^{-1}. Figure 1 shows the measured transmittance data at 1590 cm^{-1} as a function of time for a typical run. While the 512 data points digitally recroded for this experiment show high noise, it is evident that a well-defined smooth curve can be drawn through them.

All reactants and products of reaction (2) contribute to the change in absorption at 1590 cm^{-1} (A_{1590}) according to the equation:

$$A_{1590} = \ln(I_o/I) = l \times (8.47\{\Delta DMA\} + 15.13\ \{\Delta CA\} + 49.5\ \{UDMH\} + 49.1\ \{DMACl\}) \quad (8)$$

Where I_o is the transmission at time zero, I the transmission at any subsequent time, l is the cell length, {DMACl} and {UDMH} are the concentrations of the products, dimethylammonium chloride and UDMH, and {ΔDMA} and {ΔCA} are the changes in the concentrations of the reactants, dimethylamine and chloramine.

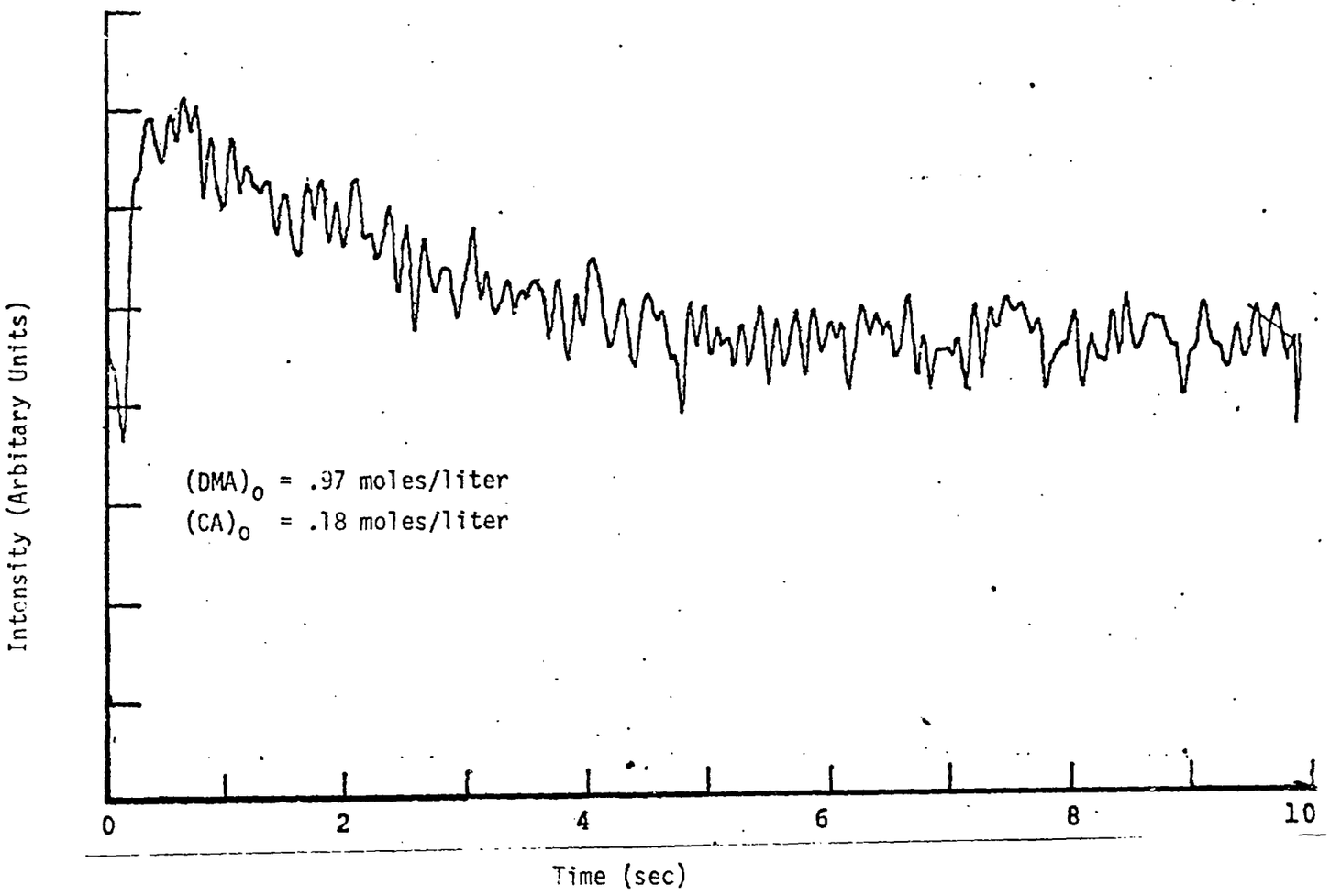


Figure 1

Infrared Intensity as Function of Time

The coefficients of the concentrations are the molar absorption coefficients in M^{-1} cm^{-1}. Assuming that the measured A_{1590} is proportional to the rate of change of the chloramine concentration, i.e. that the reaction is pseudo-first order, we have determined the rate constants of Table I from a set of measurements at various temperatures. The activation energy derived from these rates is 9.8 kcal/mole. This result compares favorably with the 9.6 kcal/mole found by the Martin-Marietta workers.

Table I

Pseudo-First Order Reaction Rates

Run No.	Temperature (^oC)	Rate (sec^{-1})	$t_{1/2}$ (sec)
18	27.7	.500	1.4
22	20.2	.352	2.0
23	15.4	.246	2.8

As will be discussed below, the yields of UDMH were very low in these reactions and the change in absorbance was effectively a measure of the concentration of the hydrochloride salt. The yield of dimethylammonium chloride determined from the absorbance was about the theoretical based on chloramine and agreed with the yields obtained in the bench-scale experiments. The nature of the species causing the change in absorbance at 1590 cm^{-1} is not important for first order analysis. All we need to assume is that the change in absorbance is a measure of the rate of the reaction between chloramine and dimethylamine and that this reaction controls the rate of formation of the salt.

We had based our design of the kinetics experiments on reaction rates for reactions (2) and (3) which were estimated from the low temperatures experiments of the Martin-Marietta workers. From their activation energies the estimated ratio of the reaction rates is 22.5 at 0^oC and the estimated UDMH to side-product final yield ratio is about 1.6 at DMA/CA = 8.5.

However in the final products flushed from the fast reaction cell, we noted some gas bubbles (CH_4) but were unable to detect any UDMH. These findings led us to carry out a series of larger scale reactions at the bench in order to

measure final product concentrations. At low UDMH yields, the final absorbances in the kinetics measurements give only the yield of dimethylammonium chloride. Other products need to be measured in separate experiments. These experiments generally involved the reaction of DMA in solution with a less concentrated solution of CA at $0^{o}C$ and then analysis of the final products by gas chromatography.

In one such experiment, Experiment A, 3.75 mmoles of CA in 15 cm^3 of chloroform were added in 0.125, 0.25 or .5 mmole increments to a 15 cm^3 chloroform solution containing 49.5 mmoles of DMA. After the equilibration of each addition, a sample was withdrawn for gas chromatographic analysis. The yields of FDMH and UDMH so measured are given in Figure 2. Note that the yield of UDMH rises to a maximum value quite early in the addition sequence while the concentration of FDMH increases nearly linearly with chloramine added. The fall-off of the yields of UDMH and decrease of the rate of increase of UDMH yield will be discussed later. They are results of some subsequent slower decompositions presumed to be not related to the chemistry of (2) - (6). If we then neglect these later effects, Figure 2 shows that UDMH quickly reaches a steady-state concentration, while FDMH steadily increases with addition of chloramine. This behavior is typical of consecutive reactions in which a product of the first becomes a reactant in the second. Quite evidently, the steady-state concentration of UDMH is independent of the final DMA/CA ratio and depends only the relative rates of (2) and (3).

In order to determine the relative reaction rates from these data, reaction rates equations were set up for reactions (2), (4), (5), (6) and for:

$$(CH_3)_2NH + HCl \longrightarrow (CH_3)_2\overset{+}{N}H_2Cl^- \qquad (7)$$

Reaction (2), the formation of UDMH and reaction (4), the formation of the intermediate subsequent product are assumed to be the rate controlling reactions for the formation of UDMH and side products.

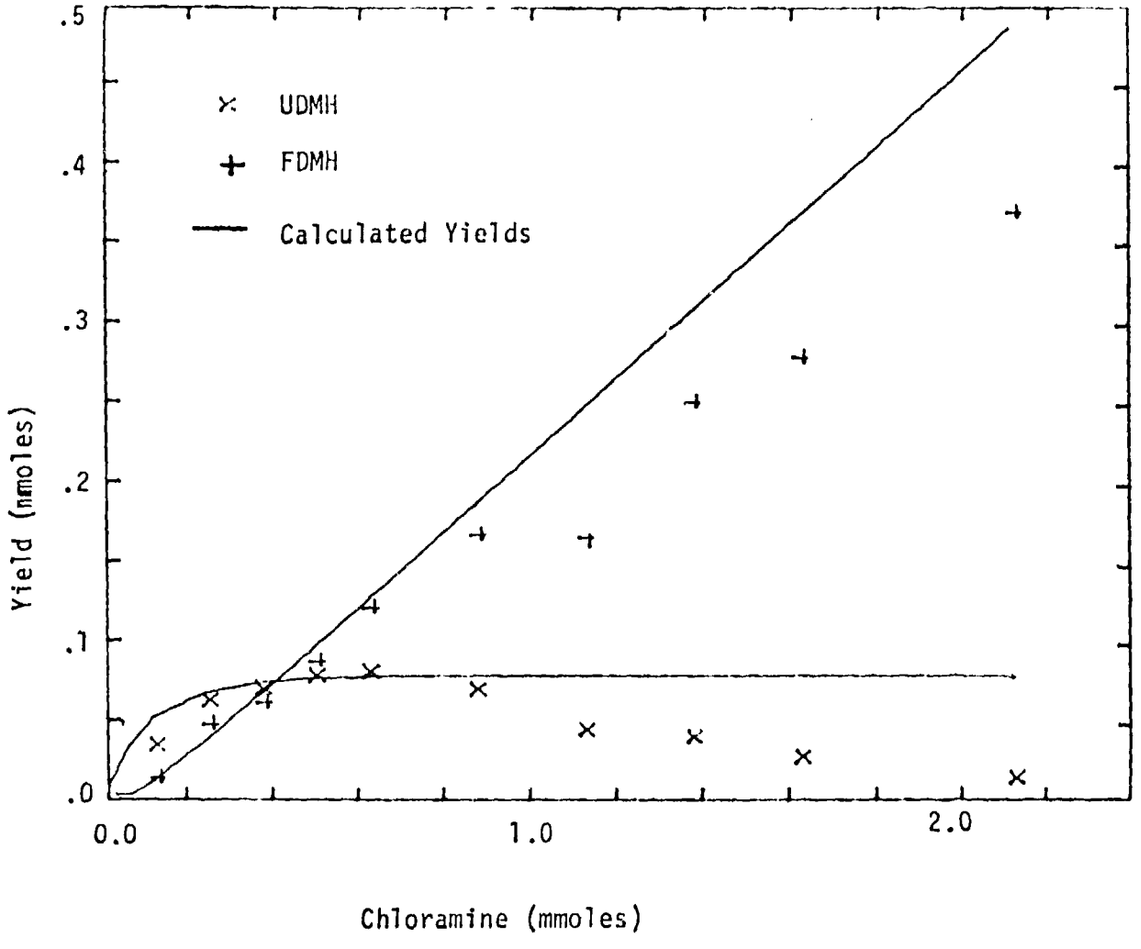


Figure 2: Yields in Experiment A

The equations yield the following rate equations:

$$d\{DMA\}/dt = -k_1\{DMA\} \times \{CA\} - k_5\{DMA\} \times \{HCl\} \quad (10)$$

$$d\{CA\}/dt = -k_1\{DMA\} \times \{CA\} - k_2\{UDMH\} \times \{CA\} \quad (11)$$

$$d\{UDMH\}/dt = k_1\{DMA\} \times \{CA\} - k_2\{UDMH\} \times \{CA\} \quad (12)$$

$$d\{DMZ\}/dt = k_2\{UDMH\} \times \{CA\} \quad (13)$$

$$d\{HCl\}/dt = +k_1\{DMA\} \times \{CA\} + k_2\{UDMH\} \times \{CA\} - k_5\{DMA\} \times \{HCl\} \quad (14)$$

$$d\{DMACl\}/dt = k_5\{DMA\} \times \{HCl\} \quad (15)$$

$$d\{TMT\}/dt = k_3\{DMZ\}^2 \quad (16)$$

$$d\{FDMH\}/dt = k_4\{DMZ\}^2 \quad (17)$$

At time zero, all concentrations are zero except {CA} and {DMA} which are, of course, known from analysis. A solution is not known for the general case involving second order consecutive reactions such as (2) and (4). Consideration of the other reactions makes the mathematics even more intractable. However, equations (10)-(17) are easily integrated numerically to give values for all concentrations at any time.

Our objective was to model experiments such as A in order to estimate k_2/k_1. Equations involving the other rate constants k_3, k_4 and k_5 have been included to control the stoichiometry. These rates are assumed to be fast enough so that they do not affect k_2/k_1. With these assumptions, we have integrated this set of simultaneous first order differential equations with a modified Runge-Kutta procedure for various k_2/k_1 ratios. The results for Experiment A are compared in Figure 2 to the measured yields of UDMH and TDMH. The agreement is good during the earlier phases of the reaction. Note that both the model and the experimental data show that significant amounts of the hydrazone are produced even in the early phases of the reaction. The ratio of k_2/k_1 which best fits this experiment is about 600/1. For comparison,

Figure 3 is the calculated product yields for this experiment when the k_2/k_1 ratio as estimated from the Martin-Marietta data are used.

A series of experiments were carried out in dioxane as well as chloroform in which the entire chloramine solution (10 ml) was rapidly added to DMA solution (10 ml) rather than small increments as in Experiment A. These experiments were the bench-scale analogues of the stopped-flow experiments. The results of these experiments are given in Table II. The rapid mixing experiments which were carried out in chloroform solution gave no detectable amounts of UDMH and low yields of FDMH. The yield of TMT was comparable to the yields observed in other solvents. Repeated analyses of the reaction mixture after completion of the reaction showed a steady decrease in FDMH concentration and an increase in the amount of an unidentified product. Rapid mixing experiments in 1,4-dioxane gave very low yields of UDMH but about theoretical yields of FDMH. For reactions in dioxane, the final concentration of FDMH was stable with time as were the concentrations of UDMH and TMT. The mechanism of Equation (6) requires the formation of a mole of methane for every mole of FDMH formed. Methane was detected in good yield in the gas chromatographic analysis of the final reaction solution, but accurate results could not be obtained since methane tends to volatilize from the solution. However, the yield of methane was determined to be comparable to that of the hydrazone both in chloroform and dioxane solutions. This supports the mechanism of Equation (6) as the principal route for the formation of FDMH. In Experiment A, the yields of methane as determined from the gas chromatograms were proportional to the yields of FDMH as a function of the amount of chloramine added especially during the earlier phases of the reaction.

Note that in Table II, the yield of FDMH in the dioxane is above theoretical (i.e. 1/4 × CA). Netswander[10] has postulated that the high yields of FDMH result not from the mechanism of Equations (4) and (6) but from the following sequence of reactions:

$$NH_2Cl + HN(CH_3)_2 \longrightarrow H_2NN(CH_3)_2 + HCl$$

$$NH_2Cl + HN(CH_3)_2 \longrightarrow (CH_3)_2NCl + NH_3$$

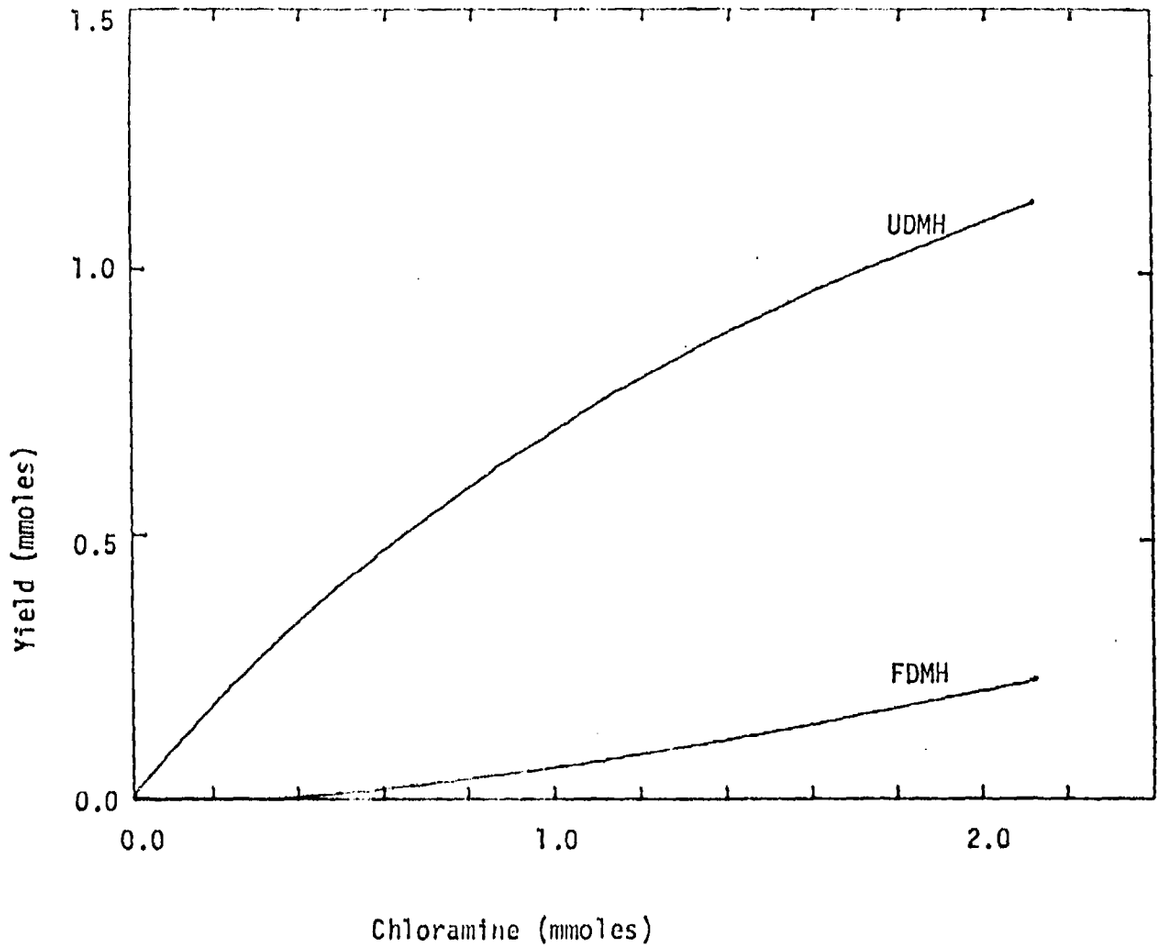


Figure 3: Calculated Yields in Experiment A From Extrapolated Rate Constants.

Table II

Reactants and Yields in Rapid Mixing Experiments

Run	Solvent	DMA (mmoles)	CA (mmoles)	UDMH (mmoles)	FDMH (mmoles)	TMT (mmoles)	Temp. °C
B	Dioxane	25.5	3.71	∿.002	1.54	.07	0
C	Chloroform	32	1.55	0	.06	.008	28
D	Chloroform	32	1.55	0	.025	.02	0
E	Dioxane	25.5	2.99	∿.004	.91	.026	5

$$(CH_3)_2\,NCl \longrightarrow CH_2 = N\text{-}CH_3 + HCl$$

$$CH_2 = N\text{-}CH_3 + H_2NN(CH_3)_2 \longrightarrow CH_2 = NN(CH_3)_2 + CH_3NH_2$$

This mechanism was supported by the detection of methylamine (no experimental details given). We were unable to test for methylamine as it is not separated from dimethylamine on our column.

The Neiswander mechanism requires only 2 moles of CA for each mole of FDMH formed and yields no methane. Our high yields for FDMH in the dioxane experiments may be indirect evidence for this reaction sequence. However, our estimation that the methane yield is comparable to the FDMH yield suggests that the mechanism of Equations (4) and (6) is the dominant one for the formation of FDMH. In any event, in the Neiswander reactions, the rate of formation of FDMH is proportional to the concentration of UDMH and the scheme Equations (10) - (17) would hold generally even if both reaction routes were followed. Among the many reactions involving the synthesis of UDMH done by the Martin-Marietta workers, three was similar to ours in that they were done in an anhydrous organic solvent. In these experiments, chloramine from the generator was collected in xylene and the resultant solution slowly added to liquid DMA at 0^{o} - 2^{o}C. Their DMA/CA mole ratios varied from 11 to 22. For these experiments, the final UDMH/FDMH ratios were in the range 0.3 to 0.4 and the yields of UDMH based on chloramine about 3%. At a DMA/CA ratio of about 22, Figure 3 shows a UDMH/FDMH ratio of about 0.3. This result also indicates a different rate of formation of FDMH in anhydrous organic solvents from that estimated from the rate at low temperatures in the liquid amomia-DMA solvent system.

Experimental:

Chemicals: Dimethylamine, ammonia, chlorine and nitrogen (Matheson, stated purity 99.0% min) were used without further purification. 1,1-dimethylhydrazine (UDMH) (Matheson Coleman and Bell, stated purity 99%) was distilled trap-to-trap, in a vacuum system before use. A gas chromatogram showed the purity to be at least 99.5%. Dioxane (Fisher certified) was used without further purification. Alcohol-free chloroform was obtained by treating reagent grade chloroform (Fisher) with concentrated sulfuric acid followed by successive washings with distilled water. The chloroform was finally dried over

anhydrous calcium chloride and distilled. The distillate proved to be alcohol-free by virtue of its infrared spectrum and could be stored in the dark for about 10 days with no noticeable decomposition.

General Procedures: The ^{1}H and ^{13}C nuclear magnetic resonance spectra were determined at 28°C in a Jeol JNM-PS-100 spectrometer in appropriate solvents using tetramethylsilane as an internal standard. The infrared spectra were recorded by menas of a Perkin-Elmer 421 grating spectrometer. Liquid samples were prepared as neat films between salt plates or dissolved in the appropriate solvent and analyzed in solution cells. Gas chromatographic measurements were performed at 80°C with a Perkin-Elmer Model 3920 instrument equipped with a flame ionization detector and a 12 ft x 1/8" O.D. stainless steel column packed with 5% KOH, 15% carbon wax 20M and 80% chromosorb P (NAW 30/60 mesh)[11] UDMH was identified qualitatively by the following tests.

(a) A sample solution was acidified with 6N hydrochloric acid. Potassium iodate (0.1N) was added dropwise. A dark brown discharge indicated the presence of a reducing agent.

(b) Several drops of 1% sodium pentacyanoammine-ferroate solution were added to one drop of the neutral test solution. The appearance of a cherry red color indicated the presence of UDMH[12].

Kinetic Measurements:

Apparatus: The need to study rapid reactions near and below room temperature leads to two requirements: A reactor is needed in which the reactants can be mixed in a time short compared to the reaction time and an analytical method is required which can follow the rapid concentration changes in real-time. The recent literature on the kinetics of fast reactions details several methods whereby the first requirement can be met[13]. For these solution kinetic studies on the Sisler process reactions, a reactor of the stopped flow type[14,15] seemed best suited. The design and operation of the reactor assembled for the UDMH studies is indicated schematically in Figure 4. In this reactor, the two solutions to be reacted are placed into the two filling syringes and are then loaded into the driven syringes. A force is abruptly and simultaneously applied to both syringes by the pneumatic cylinder. This forces the two solutions through the mixing section and the optical absorption cell into the stopping syringe

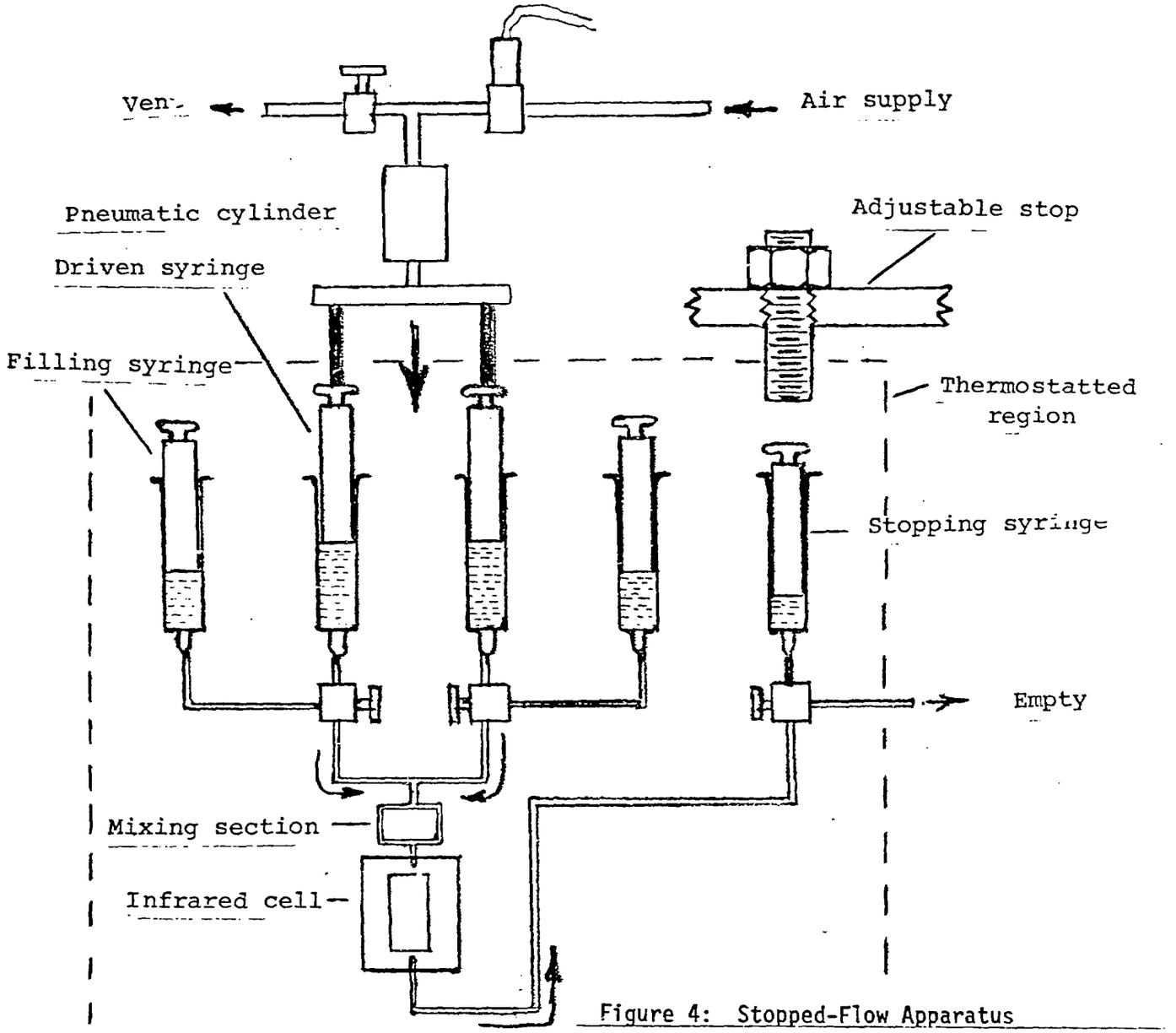


Figure 4: Stopped-Flow Apparatus

which forces the piston of the syringe upward. When the stopping piston hits the stop, the flow is suddenly arrested, a freshly mixed solution exists in the optical cell and the absorption measurements of the concentrations of the reactants and products begin. The flow rate is at a maximum just before the sudden stop so that the age of the mixed solution depends on this peak velocity and the volume of the system between the point of mixing and the cell. In our apparatus, at the driving rates used so far, the age of the mixed solution is about 10 msec or less based on the time to travel from the first mixing Tee to the center of the cell. The upper limit to the driving rate has not been determined. Because of finite mixing rates, the mixing may not be complete until quite near the cell. This effect of course reduces the age of the mixed solution but introduces some uncertainty in the average age. The five syringes are housed in a large aluminum block that can be heated or cooled over the range -40 to +100°C. The cooling is achieved by passing a stream of cold nitrogen gas through the block and infrared cell holder and then through a copper coil surrounding the block. The block and holder are insulated with styrofoam. Because of the high heat capacity of the apparatus relative to the nitrogen stream good temperature regulation can be achieved by manual control of the nitrogen flow rate. The cold nitrogen is obtained from liquid nitrogen boil-off. To prevent moisture condensation on the cell and cell holder, the nitrogen stream is vented into the spectrometer to maintain a dry atmosphere around the moisture-sensitive parts. Heating is achieved by a circulating constant temperature fluid.

For reasons of sensitivity, selectivity and availability, an infrared spectrometirc method was chosen for the real-time analysis of the reacting mixtures. A spectrometer which had previously been set up for some air pollution studies and modified for this work is shown skematically in Figure 5. The major change required was an increase in the chopping frequency from 50 hz to 1250 hz to give the instrument the needed faster response. This spectrometer scans the spectrum by rotation of a circular variable band-pass filter wheel. While the resolution of the instrument is low ($\lambda/\Delta\lambda$ = 65), the energy throughput is high and the instrument has a very good signal/noise ratio. With the time constant of the electrical filtering in the amplifier at 30 msec, the signal-to-noise ratio in the 1600 cm^{-1} region is better than 300:1. Thus low concentrations or small absorption changes can be measured more accurately than on a conventional spectrometer. Two variable filters are available-one covering the range

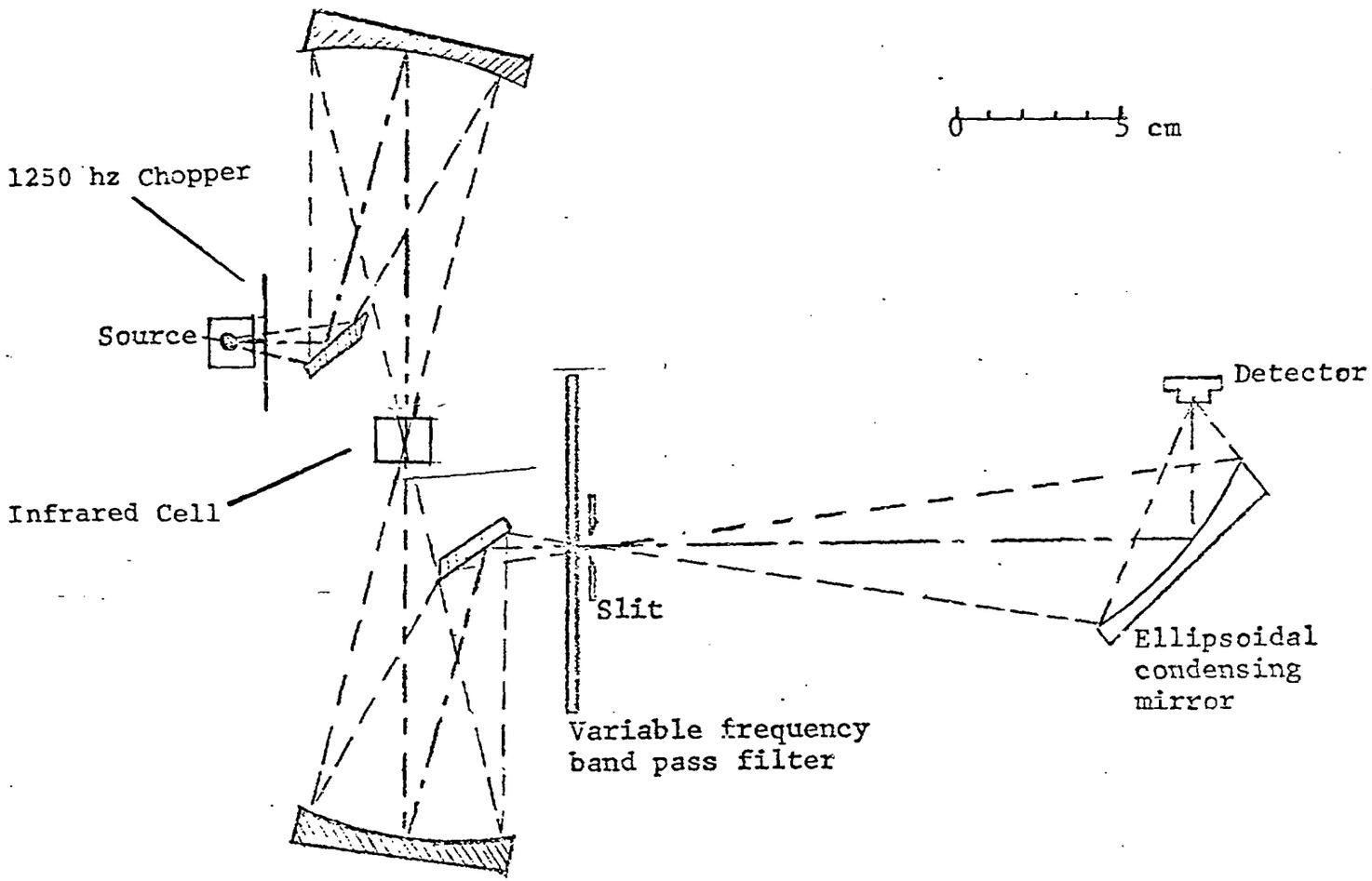


Figure 5: Infrared Spectrometer

4-8μm (2500-1250 cm^{-1}) and the other 8-14.5μm (1250-690 cm^{-1}). When measuring concentrations, the filter can be held fixed at an absorption frequency and the time-rate of change of absorption monitored.

Figure 6 shows the circuits for the spectral and timing signals. The chopped infrared radiaition is received by a pyroelectric detector of the high sensitivity glycine sulfate type (Barnes Engineering Corp., Model T-300). The AC signal from the detector is demodulated without preamplification by a lock-in amplifier (Princeton Applied Research Model 122) whose reference frequency is generated by a LED-phototransitor system at the chopper blade. Some noise is generated by oscillations in the angular velocity of the belt-driven chopper but this noise can be minimized by careful tuning of the lock-in amplifier using an oscilloscope.

The demodulated amplified output of the lock-in amplifier is fed to an analogue-to-digital converter on an PDP/8E minicomputer. When the stopping syringe piston hits the stop, a switch is closed and the signal from this switch is also digitized to indicate the starting time of the reaction. A displacement transducer of the linear variable differential transformer type is connected to the stopping syringe piston. The signal from this transducer is digitized to give the velocity of the piston. The three channels of data are acquired, stored on magnetic tape cartridge and printed out under the control of a machine language program. The data are subsequently read back in for analysis by various BASIC language programs.

Spectral considerations: The kinetics of the reaction between dimithylamine and chloramine was followed by measuring the time-rate of change of absorbance of the product concentrations, Equation (8). Since concentration measurements in the 1% range were needed a thick absorption cell (0.5 mm) was used. For studies in the 0-3% range three infrared absorption frequencies (1590, 1305 and 1050 cm^{-1}) of UDMH or dimethylammonium chloride were located which could be used depending on the choice of solvent. Three solvents, chloroform, carbon tetrachloride and tetrachloroethylene were surveyed for spectral consideration. All bands are readily measurable in tetrachloroethylene and all but the 1590 cm^{-1} band in carbon tetrachloride. The 1590 cm^{-1} is readily measurable in chloroform and useful measurements can be made at the 1305 cm^{-1}

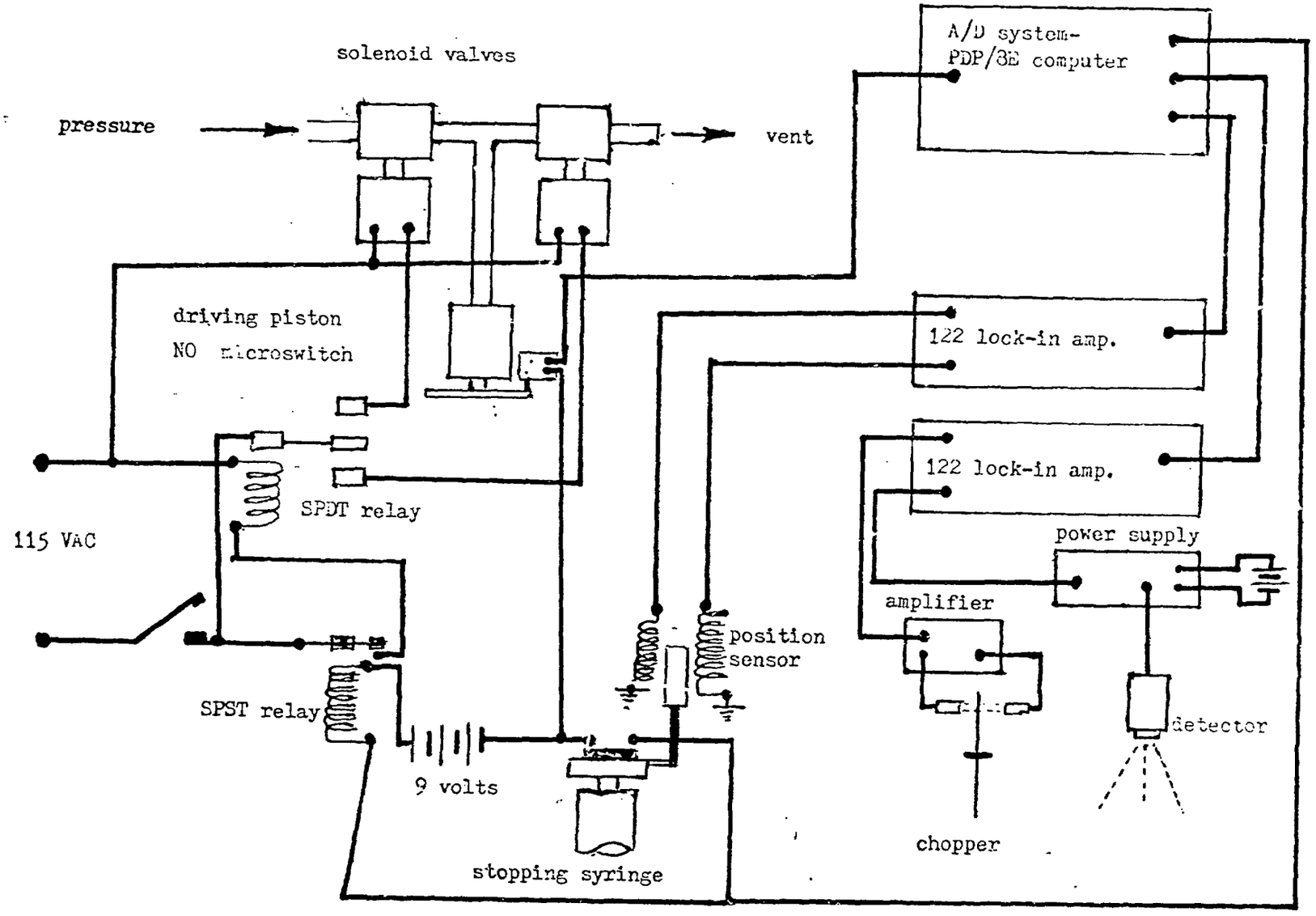


Figure 6: Control, timing and signal processing systems.

band despite some obscuration by the solvent. Interference from reactants and side products was also considered (Equation (8)). Dimethylammonium chloride is vertually insoluble in carbon tetrachloride and tetrachloroethylene. Formation of an insoluble salt in the absorption cell could give use to light scattering leading to erroneous results. For this reason chloroform was chosen as the solvent.

Preparation of Chloramine: Chloramine was prepared by the reaction of ammonia and chlorine in a flow reactor (Figure 7) similar to that of Sisler and others[2,8,9,10]. The chlorine is first mixed with nitrogen and this stream is then mixed with ammonia. Typical gas ratios are 1:4:4 = Cl_2:N_2:NH_3. The reacted gas stream is filtered through glass wool to remove ammonia chloride formed during reaction and bubbled through solvent. Excess ammonia is removed by application of vacuum to the solution.

Analysis of $ClNH_2/HCCl_3$ Solutions: A known volume of chloramine solution was dissolved in 20 ml of distilled water in a 125 ml erlenmyer flask. The test solution was acidified with 20 ml of 6N hydrochloric acid then treated with 15 ml of 10% potassium iodide solution. The liberated iodine was titrated with 0.1N sodium thiosulfate that had been standardized against NBS potassium dichromate. When the yellow color of the iodine became faint, 5 ml of starch solution was added and titrated until the blue color disappeared.

Stability of Chloramine in Chloroform: During the preparation, storage and handling of $ClNH_2/HCCl_3$ solutions, a marked decrease in chloramine concentration was observed with the formation of insoluble NH_4Cl. Since it is essential to know the chloramine concentration at the start of a kinetic run, the extent of chloramine decomposition was determined over an extended period of time. The $ClNH_2/HCCl_3$ solution was titrated at convenient time intervals and the results shown graphically in Figure 8. The initial decomposition is quite rapid yielding a cloudy suspension of insoluble NH_4Cl. This instability presents two problems: (1) change in $ClNH_2$ concentration prior to and during data collection, (2) the possible blockage of tubing by precipitated ammonium chloride in the stopped-flow apparatus.

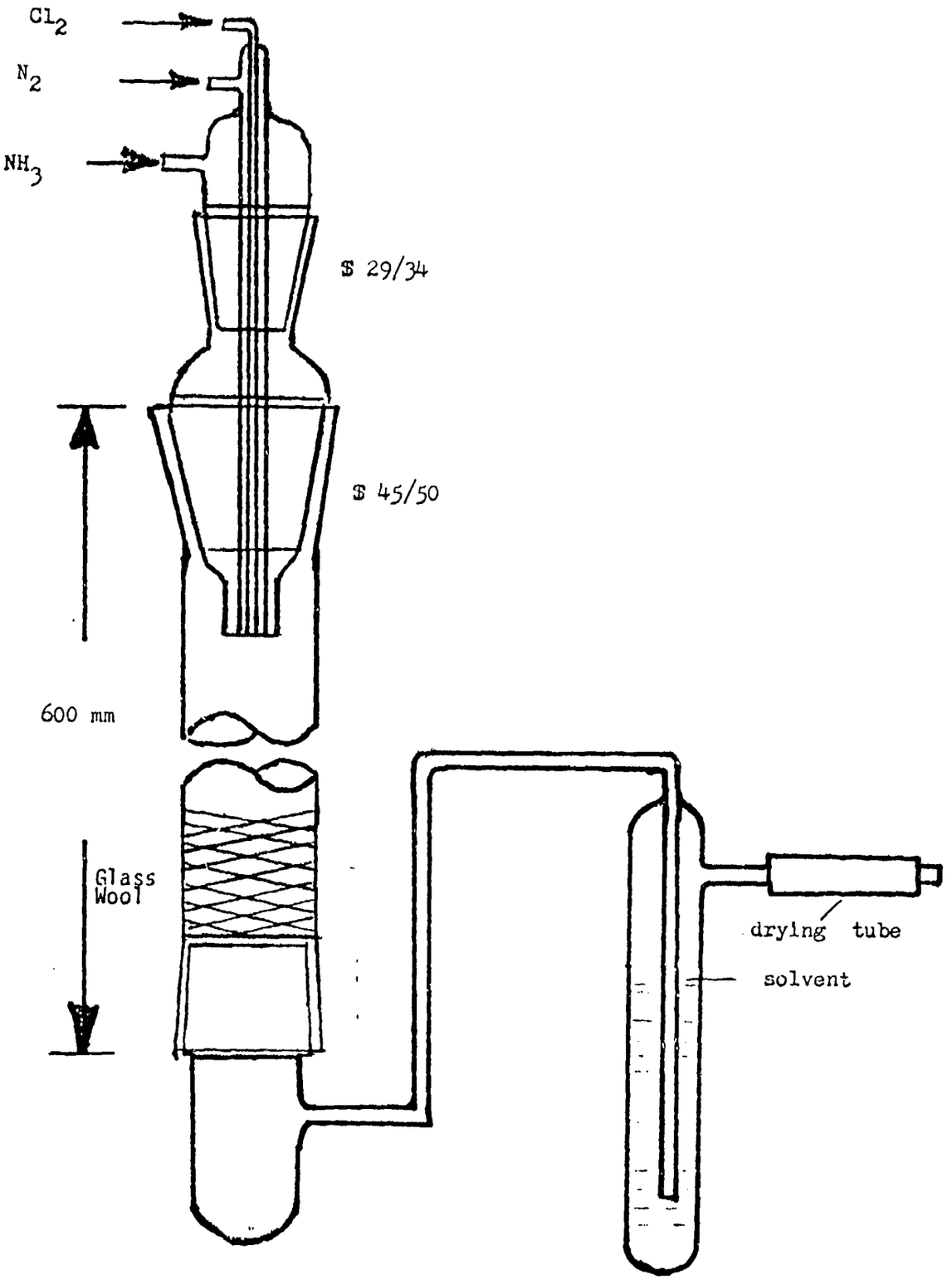


Figure 7: Chloamine Generator

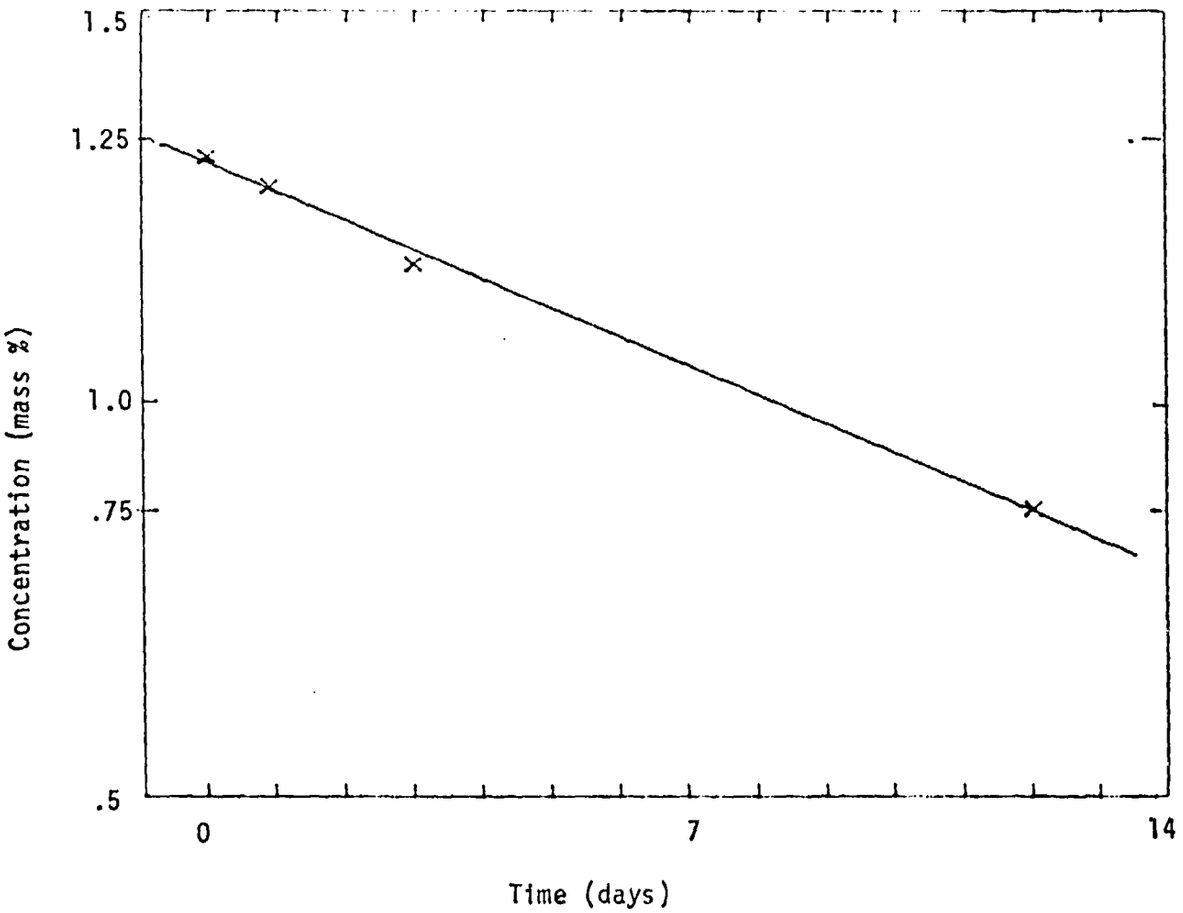


Figure 8: Stability of Chloramine in Chloroform at $4^{o}C$

During initial runs syringes containing $ClNH_2$ and reaction products had a tendency to stick between barrel and cylinder interface because of ammonium chloride formation. If chloramine solutions were allowed to remain in the system for extended periods of time difficulties were encountered in obtaining fast mixing rates and short stop times during collection of kinetic data.

The ammonium chloride problem is alleviated by filtration immediately before loading of the chloramine solution into the syringe and by not allowing the chloramine solutions to remain in the stopped-flow system for prolonged periods of time.

Preparation of Dimethylamine Solutions: A known volume of anhydrous dimethylamine (Matheson, 99% min) was passed through a trap containing solvent at ambient temperature. Prior to use the amine solution was treated with excess standard hydrochloric acid and back titrated with standard sodium hydroxide to the methyl red end-point. Concentrations approaching 4M dimethylamine were obtained.

Preparation of formaldehyde dimethylhydrazone: The formaldehyde hydrazone of UDMH was prepared by dropwise addition of UDMH to a well-stirred aqueous solution of paraformaldehyde and hydrogen chloride (10%) cooled in an ice bath. Excess KOH pellets were added to the reaction mixture and the hydrazone distilled through a short column (b.p. 70°C). A gas chromatogram showed only a single peak. The proton decoupled C^{13} NMR showed two peaks in the ratio of 2:1 which is consistant with the formula $(CH_3)_2$ N-N = CH_2.

Preparation of tetramethyltetrazene: Tetramethyl-2-tetrazene was prepared by the oxidation of 1,1-dimethylhydrazene with mercuric oxide at 0°C[16,17]. Ten (10) ml (7.914g; 0.131 mole) of 1,1-dimethylhydrazine (Matheson-Coleman Bell) was diluted with 25 ml of anhydrous ether in a 100 ml three-necked round bottomed flask fitted with a stirrer and a reflux-condenser and immersed in an ice bath. Yellow mercuric oxide (28.52g; 0.131 mole) was added slowly over a half hour period. The solution began to reflux in a few minutes and allowed to cool before more oxide was added. After 1 1/2 hours the reaction ceased imparting a yellow tinge to the resulting solution. After warming to room temperature with stirring the ether was separated from the aqueous layer which was extracted with ether. The etheral solutions were combined and the ether removed under vacuum leaving a light yellow liquid which distilled at 95°C and 210 mm Hg. The infrared and C^{13} NMR spectra were consistant with the formula $(CH_3)_2$ NN = $NN(CH_3)_2$.

Preparation of 2,2-dimethyltriazanium chloride[18,19]: UDMH (2.4 ml; 31 mmoles) was dissolved in 100 ml of chloroform in a 250 ml three necked round bottom flask fitted with stirrer, water condenser and additional funnel. Fifty (50) ml of 0.62M $ClNH_2/HCCl_3$ solution was added dropwise with stirring at 0°C. A white precipitate formed during addition of the $ClNH_2$. The resulting solution was allowed to warm to room temperature with stirring. The precipitate was filtered and digested for 10 minutes in 30 ml of absolute ethanol. 90 ml of acetone was added and the mixture boiled for an additional 15 minutes. 300 ml of anhydrous ether was added and the solution allowed to cool overnight. White hydroscopic crystals were filtered and dried under vacuum. A positive test with KI and a melting point of 135°C-d characterized the product as 2,2-dimethyltriazanium chloride, $(CH_3)_2N(NH_2)_2^+Cl^-$.

In an attempt to better understand the chemistry of the reaction sequence under investigation a series of bench top experiments were conducted in conjunction with the kinetic study. The experimental details for these reaction follow.

Reaction between dimethylamine and chloramine in chloroform: Dimethylamine in chloroform (30 ml, 3.1M) was placed in a 100 ml three necked round bottom flask fitted with stirring bar, reflux condenser, additional funnel and dry N_2 flow. 30 ml of a 0.197 M chloramine/chloroform solution were added slowly with stirring at 30°C. The solution became warm and gas evolution was observed. After removal of solvent under vacuum the residue was distilled at ambient pressure and the fraction distilling at 62°C was collected. The distillate was mainly chloroform and one or possibly more unidentified side products, according to the infrared spectrum. Absorption bands did not correspond to any of the predicted side products. The residue was dissolved in 10 ml of chloroform then treated with 125 ml of ether producing 0.57g of a white crystalline compound. The infrared spectrum is identical to that of dimethylammonium chloride.

In a similar experiment 100 ml of 3.76M dimethylamine in chloroform was placed in a 500 ml three-necked round bottom flask fixed with stirring bar, reflux condenser, addition funnel and dry nitrogen flow. The flask was cooled at -30°C by means of a dry-ice/isopropanol bath and 100 ml of 0.414M

chloramine/chloroform solution was added dropwise with stirring. Stirring was continued for an additional half hour resulting in a clear solution. No precipitate was observed. The resulting solution gave a positive KI test and a negative KIO_3 test. The same test results were obtained after an additional hour of stirring at -30°C. Solvent and volatile products were removed by distillation at 60°C. The distillate give a positive KI test but on standing overnight it gave negative KI and KIO_3 tests. The residue was filtered, washed with ether and dried producing 4.00 g of dimethylammonium chloride.

An attempt was made to isolate the reaction product by treating the resulting clear solution from the reaction between dimethylamine and chloramine with 6N hydrochloric acid. The aqueous layer was treated with 3N KOH until basic. The resulting solution was analyzed by gas chromatography but failed to show any of the expected reaction products.

In a milder treatment of the resulting solution, solvent and volatile products were removed under vacuum at room temperature. Infrared analysis of volatile products showed no evidence for an appreciable concentration of UDMH. In a control experiment a solution of dimethylamine/chloroform/ UDMH analyzed clearly for UDMH as low as 0.03 M UDHM.

Inorder to simulate the mixing process in the stop-flow reactor for final product analysis, equal volumes of dimethylamine in chloroform and chloramine in chloroform were syringed simultaneously into a flask fixed with stirring bar and dry nitrogen flow. The resulting solution was immediately analyzed by gas chromatography (these are runs B-E of Table II). Similar reactions were carried out using dioxane as the solvent.

In a separate experiment, Experiment A, 15 ml of 3.3M dimethylamine in chloroformwere placed in a 50 ml three-necked flask fixed with stirring bar addition funnel and dry nitrogen flow. The flask was cooled to 0°C, nitrogen flow stopped and 15 ml of 0.25 M chloramine in chloroform was added in 0.5 ml increments over a two (2) hour period. The contents of the flask was analyzed after each addition by GLC.

Reaction between UDMH and chloramine in the presence of dimethylamine and dimethylammonium chloride: Dimethylammonium chloride (5.4 g, 66 mmoles),

75 ml of 3.76 M dimethylamine/chloroform and 5 ml (66 mmole) of UDMH were placed in a 100 ml three-necked round bottom flask fitted with a dropping funnel, a condenser and a stirring bar. Chloramine (75 ml of 0.888M in chloroform, 66 mmoles) was added dropwise with stirring at room temperature. No precipatate was observed but the solution became warm with gas evolution. After the final addition of chloramine a clear solution was obtained which gradually turned yellow.

Reaction between UDMH and chloramine in the presence of dimethylammonium chloride: Dimethylammonium chloride (2.1%, g, 26.6 mmoles) and UDMH (2.02 ml, 26.6 mmoles) were dissolved in 30 ml chloroform in a 100 ml three-necked round bottom flask fitted with a dropping funnel, a condenser and a stirring bar. Thirty (30) ml of 0.88M chloramine/chloroform was added dropwise with stirring at room temperature resulting in an exothermic reaction with the formation of a white precipetate.

In order to facilitate solvent removal and aid in product identification, the reaction between dimethylamine and chloramine was carried out in diethylether.

Reaction between dimethylamine and chloramine in diethylether: Twenty (20) ml of 2.3N dimethylamine in diethylether was placed in a 100 ml three-necked round bottom flask fitted with stirring bar, condenser, addition funnel and dry nitrogen flow. The flask was cooled to -40°C with dry ice/isopropanol. Twenty (20) ml of 0.77M $ClNH_2$ in diethylether was added dropwise with stirring. The mixture was stirred for 30 minutes at -40°C and allowed to warm to room temperature. Spot tests were negative for UDMH. The IR showed no bands characteristic of UDMH. A white precipatate characteristic of $(CH_3)_2NH_2^+Cl^-$ was observed but was not isolated. The solution was filtered and the ether distilled at 35°C, with a bath temperature not exceeding 42°C. The residue remaining after solvent removal was analyzed by IR but no bands characteristic of UDMH, FDMH or TMT were observed. The proton NMR showed one major peak characteristic of $N\text{-}CH_3$.

Conclusions:

1. The activation energy of formation of UDMH from chloramine and dimethylamine is 9.8 kcal/mole in agreement with earlier work.

2. The rate of formation of formaldehyde dimethylhydrazone is very high (~600X) compared to that of UDMH in anhydrous organic solvents at 0°C.

3. Comparison of our finding with those of other workers indicates that the relative rates of formation of these two products is much more favorable in aqueous or liquid ammonia solvent systems than in anhydrous organic solvents.

4. Since methane is produced concurrently with the hydrazone, our results support the mechanism of FDMH formation proposed by Sisler.

5. The alternative mechanism of FDMH proposed by Neiswander is supported only indirectly by our results. However, this mechanism cannot be ruled out as a concurrent route with a lower yield than the Sisler mechanism.

6. Both UDMH and FDMH are unstable in the reaction mixture when chloroform is used as a solvent.

7. If anhydrous organic solvent systems are used in the Sisler synthesis of UDMH, only low yields of UDMH and high yields of the hydrazone will result at least in the temperature range 0°C and above.

8. As a consequences of the consecutive reaction scheme for the formation of UDMH and FDMH and of the high ratio of the formation rate constant of FDMH to that of UDMH, the yield of UDMH will reach a low constant value early in the reaction. Any further additions of chloramine do not increase the UDMH yields.

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References:

1. Chemical Rocket/Propellant Hazards, Volume III, CPIA/194, AD 870259, July 1972.

2. The Synthesis of Chloramine by the Ammonia-Chlorine Reaction in the Gas Phase, Sisler, H. H., Neth, F., Drago, R. and Yancy, D., J. Am. Chem. Soc., 76, 3906-9 (1954).

3. Reactions of Chloramine with Primary and Secondary Amines, Omietanski, G., Kelmers, A. D., Shellman, R. W., and Sisler, H. H., J. Am. Chem. Soc., 78, 3874 (1956).

4. Substituted Hydrazines, Sisler, H. H., and Kelmers, A. D., U.S. Patent 2,806,851, August 17, 1957.

5. Chloramine Process, Sisler H. H., and Mattari, R., U.S. Patent 2,837,409, June 3, 1958.

6. The Reaction of 1,1-Dimethylhydrazine with Gaseous Chloramine, Utvary, K. and Sisler, H. H., Inorg. Chem., 7,698 (1968).

7. Reaction of Chloramine with 1,1-Dimethylhydrazine-Formation of Tetramethyl-2-Tetrazene, Sisler, H. H., Kren, R. M., and Utvary, K., Inorg. Chem., 8, 2007 (1969).

8. Process of Preparing Chloramine, Bernard Gruskin and Harry H. Sisler, U.S. Patent #3,488,164, 6 January 1970.

9. Process Development for the Manufacturer of Unsymmetrical Dimethylhydrazine, Mueller, K. F., Farncomb, R. E., Wagaman, K. L., McQuistion, W. E., Naval Surface Weapons Center, Tech. Report 78-98, 17 May 1978.

10. Amine Fuels Production Feasibility Demonstration, Williams, L. O., Neiswander, D. W., Howerton, M. T., Final Report, Contract F04701-74-C-0039, MCR-75-466, Martin Marietta Corp., Nov 1975.

11. H. H. Sisler, Personal Communication.

12. F. Feigl, "Spot Tests in Organic Chemistry", Elsevier Publishing Co., New York, 1960, p. 305.

13. Fast Reactions in Solution, E. F. Baldin, J. Wiley and Sons, New York (1964).

14. ibid, pp. 43-48.

15. R. M. Reich, Anal., Chem. 43 85A (1971).

16. Bull, W. E., J. A. Seaton and L. F. Audrieth, J. Am. Chem. Soc., 80, 2516 (1958).

17. E. Renouf, Ber., 13, 2169 (1880).

18. K. Utvary and H. H. Sisler, Inorg. Chem. 7, 698 (1968).

19. H. H. Sisler, et al, Inorg. Chem., 8, 2007 (1969).