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THE SYNTHESIS AND FLASH PHOTOLYSIS OF 1-PROPANEAZOETHANE

THESIS

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Master of Science

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Preface

I have presented in this thesis the preliminary phases of a research effort to determine certain kinetic constants. Included in these phases was the synthesis of a radical source which, I believe, is unique and I hope that it will prove of some interest to researchers in this field.

In a report such as this the confusion of chemical nomenclature presents itself. I have tried to eliminate some of this confusion by frequently inserting the structural formula of a compound after its name.

During the course of my investigation I have received help from people too numerous to mention, but I wish specifically to acknowledge my indebtedness to Dr. L. Spialter, Dr. J. Futrell, and Dr. G. John for their advice and guidance, and finally to my wife for her patience and understanding.

The history of kinetic investigation is a history of mistakes and subsequent modifications, and I must accept the responsibility for those errors that may be found in this report.

William A. Rush

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Abstract

The relative rate constants for the reactions between ethyl and n-propyl free radicals are required for radiolysis calculations. The preliminary phases of an investigation to determine these constants have been completed and are contained in this report.

1-Propaneazoethane ($C_2H_5NNC_3H_7$) was selected as the source of free radicals. Since it had not previously been made, a synthesis was devised and accomplished. The compound was decomposed by exposure to high energy bursts of ultraviolet radiation from a flashtube. This decomposition resulted in the formation of nitrogen, ethyl free radicals, and propyl free radicals. A reaction scheme for the radicals was proposed and equations for the relative rate constants, in terms of product concentrations, derived. The product concentrations were then determined by gas chromatography, but the initial results are too sparse and scattered to permit substantiated calculation of the constants.

THE SYNTHESIS
AND FLASH PHOTOLYSIS
OF 1-PROPANEAZOETHANE

I. Introduction

Efforts have been made by the personnel of the Aeronautical Research Laboratory, Wright-Patterson Air Force Base, to calculate the quantitative effects of radiation on simple hydrocarbons in the vapor phase (Ref 6; Ref 7). One of the difficulties encountered in these calculations was the lack of kinetic data on the reactions between different alkyl free radicals (molecules containing one or more unpaired electrons). The purpose of this report is to present the results of an investigation into the reactions between ethyl and n-propyl free radicals.

For a system containing a single species of radicals, $HA\cdot$, in thermal equilibrium, the two most important reactions that may be expected are recombination and abstraction of a hydrogen atom (termed disproportionation in the case of like radicals) thus:

$$2HA\cdot \rightarrow HAH + A \text{ (disproportionation)}$$

$$2HA\cdot \rightarrow HAAH \text{ (recombination)}$$

The rate of these reactions may be expressed, using kinetic theory for second order reactions, by the following equations:

$$R(HAH) = R(A) = k_a(HA\cdot)^2$$

$$R(HAAH) = k_r(HA\cdot)^2$$

where R is the rate of change with time, the bracketed quantities are the concentrations as functions of time, and k_a, k_r are the reaction rate constants for the abstraction and recombination reactions. It is these constants, or their ratios (relative rate constants), that are required for radiolysis calculations.

This report will present the initial phases of a research effort to determine the relative rate constants for the reactions between ethyl and n-propyl free radicals. The phases that shall be covered are: the synthesis of a source of radicals, the flash photolysis of the source, and the analysis of the products by gas chromatography. Also presented will be the use of the product analyses to calculate the relative rate constants and the initial results obtained. The investigation, however, was limited to the vapor phase and ambient temperatures.

To accomplish our ultimate objective it was obvious that a sequence of problems would have to be solved. First, a means of obtaining the radicals would have to be found. Next, a reaction scheme would have to be developed so that the necessary data could ascertained. And, finally, the experimental procedure to obtain the data would have to be devised.

1-Propaneazoethane ($C_2H_5NNC_3H_7$) was selected for the source of radicals and photodissociation for the means of obtaining them. This method of splitting a normal molecule to obtain radicals is not new and both ethyl and propyl radicals have been obtained by this method from their respective aldehydes (R-CO), ketones (RCOR), mercury (R_2H_g), and azo compounds (R-N = N-R). Our kinetic investigation required that the rate of formation of both the ethyl and propyl free radicals be known, at least relative to each other. Practically, we could accomplish this if both radicals were released simultaneously from a single molecule. Ethyl propyl ketone ($C_2H_5COC_3H_7$) and ethyl propyl mercury ($C_2H_5H_gC_3H_7$) presented themselves as possibilities. Unfortunately, it has been shown that ketones frequently yield directly, on decomposition, other products besides the desired radicals and carbon monoxide (Ref 17:9). The mercury compounds, on the other hand, had the disadvantage that the mercury released in the reaction can act as a photosensitizing agent and cause other reactions (Ref 3:110). In contrast to these sources, studies of the azo compounds had indicated that simultaneous formation of the radicals and nitrogen occurs, though stepwise decomposition has been observed infrequently (Ref 4:3629). The nitrogen, which is not a photosensitizing agent, would further provide a measure of the decomposition and, consequently, the radicals released.

These factors indicated that 1-propaneazoethane would be a satisfactory source of radicals, if it could be obtained. A search of the formula indexes of Chemical Abstracts, Beilsteins Handbuch Der Organischen Chemie, and numerous organic chemistry texts uncovered no mention of the compound. Indeed, one author felt such a compound might undergo rearrangement to a hydrazone (Ref 13:265). However, the synthesis of 1-propaneazoethane was undertaken and completed.

To obtain a sufficient number of radicals for study from the source it was necessary to expose it to very high intensity bursts of ultraviolet radiation. This method is known as flash photolysis.

Since the synthesis was independent of the kinetic investigation, it is presented first in a separate section. Next, in the flash photolysis section, the theory necessary to propose a reaction scheme is developed and a reaction scheme presented. The attendant kinetic equations are then used as a basis to determine what data is required for the determination of the relative rate constants. The procedure used in the investigation to determine the necessary data is next set forth, followed by the calculations and results. A discussion of the results and conclusions then terminate the report.

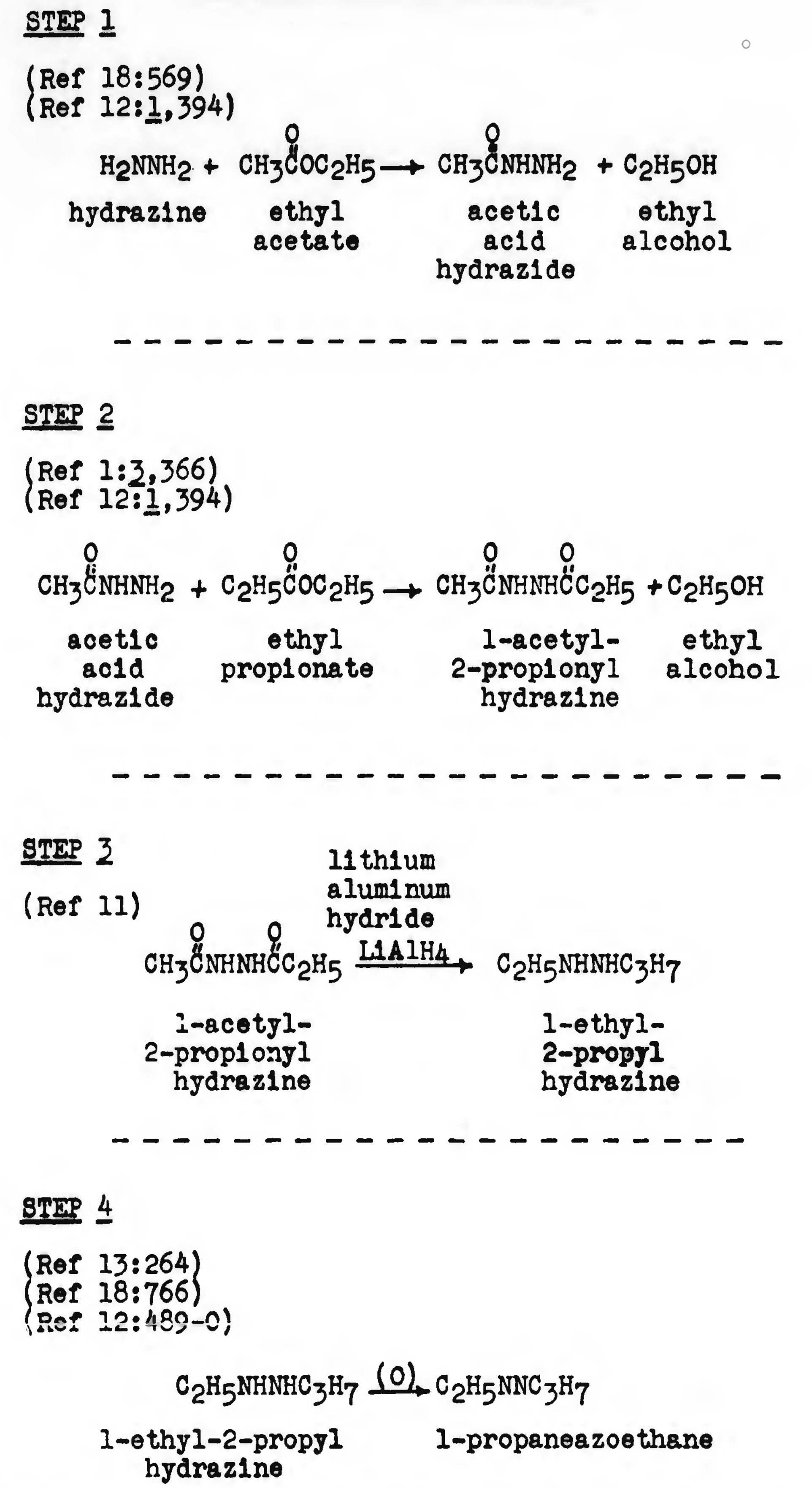


Figure 1
Initial Synthesis Scheme

STEP 1

(Ref 18:569)
(Ref 12:1,394)

$$H_2NNH_2 + CH_3\overset{O}{\overset{\|}{C}}OC_2H_5 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}NHNH_2 + C_2H_5OH$$

hydrazine + ethyl acetate → acetic acid hydrazide + ethyl alcohol

---

STEP 2

(Ref 1:3,366)
(Ref 12:1,394)

$$CH_3\overset{O}{\overset{\|}{C}}NHNH_2 + C_2H_5\overset{O}{\overset{\|}{C}}OC_2H_5 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}NHNH\overset{O}{\overset{\|}{C}}C_2H_5 + C_2H_5OH$$

acetic acid hydrazide + ethyl propionate → 1-acetyl-2-propionyl hydrazine + ethyl alcohol

---

STEP 3

(Ref 11)

$$CH_3\overset{O}{\overset{\|}{C}}NHNH\overset{O}{\overset{\|}{C}}C_2H_5 \xrightarrow[\text{}]{\substack{\text{lithium}\\ \text{aluminum}\\ \text{hydride}\\ LiAlH_4}} C_2H_5NHNHC_3H_7$$

1-acetyl-2-propionyl hydrazine → 1-ethyl-2-propyl hydrazine

STEP 4

(Ref 13:264)
(Ref 18:766)
(Ref 12:489-0)

$$C_2H_5NHNHC_3H_7 \xrightarrow{(O)} C_2H_5NNC_3H_7$$

1-ethyl-2-propyl hydrazine → 1-propaneazoethane

II. The Synthesis of 1-Propaneazoethane

Nomenclature

The system used to name the compounds synthesized in this investigation is that adopted by Chemical Abstracts in 1945 (39: 5817-9). However, when compounds reported in the literature are referred to, the author's name is usually used.

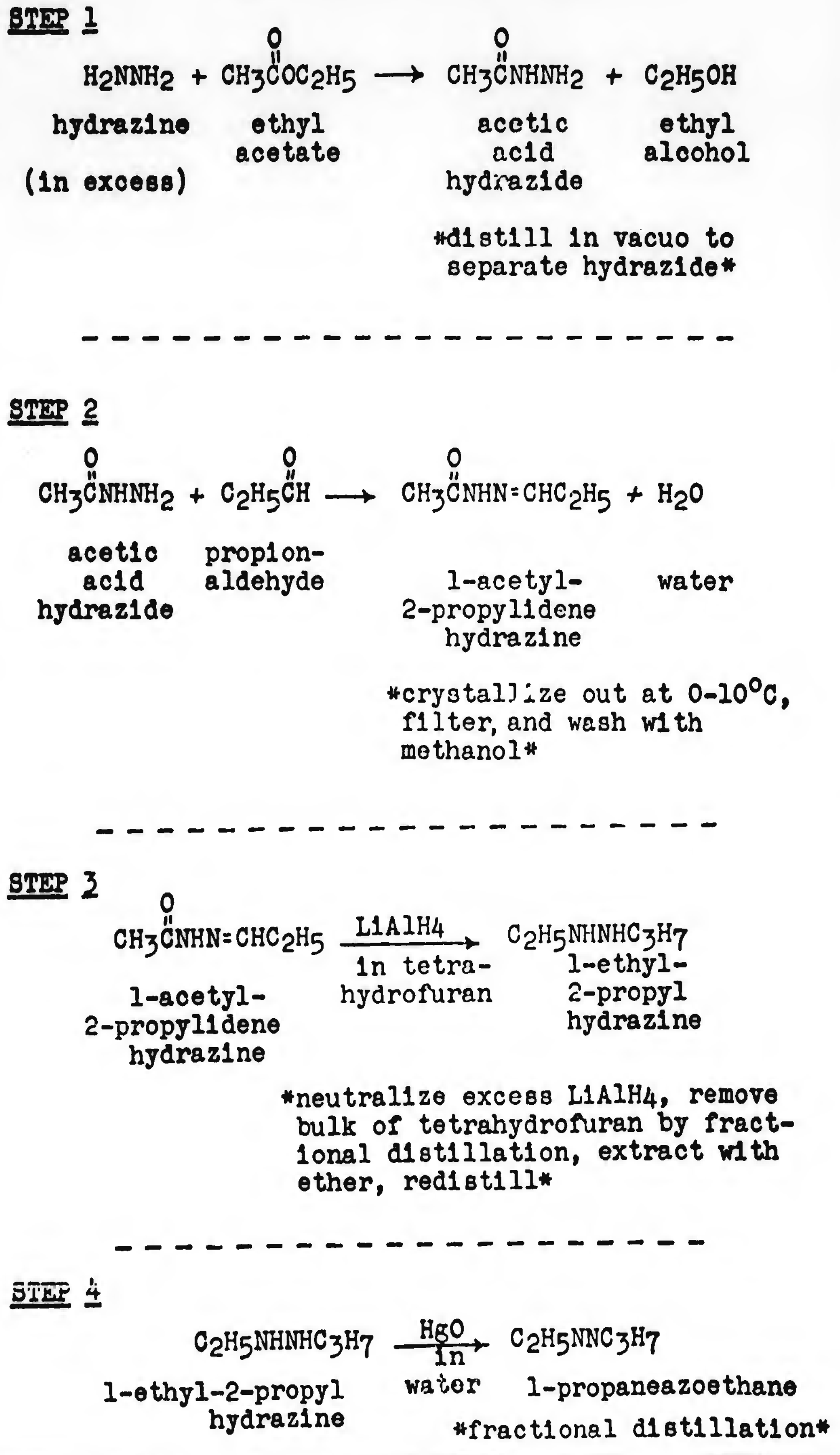
Formulation of the Synthesis Scheme

In general, the formulation of a synthesis begins with a proposed sequence of reactions that end with the desired product. The approach used to formulate this synthesis was to start with 1-propaneazoethane and work backwards until a step using commercially available materials was reached. General class reactions, as presented in the Organic Chemistry Texts referenced in Fig 1, were adapted to our purpose for the initial reaction scheme. Since a reaction step might fail, alternative steps were added where possible. Finally, the literature was searched for specific details of the reactions using our compounds or homologs. To conserve time, experimentation was begun almost concurrently with the reaction-detail search.

The Initial Synthesis Scheme

The basic scheme devised is presented in Fig 1 on the facing page. Other basic schemes may be devised from the syntheses reported by Ramsperger (Ref 14) and the Renaud-Leitch team (Ref 15).

Figure 2
Final Synthesis Scheme



STEP 1

$$H_2NNH_2 + CH_3\overset{\overset{O}{\|}}{C}OC_2H_5 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}NHNH_2 + C_2H_5OH$$

hydrazine (in excess)	ethyl acetate	acetic acid hydrazide	ethyl alcohol

distill in vacuo to separate hydrazide

STEP 2

$$CH_3\overset{\overset{O}{\|}}{C}NHNH_2 + C_2H_5\overset{\overset{O}{\|}}{C}H \longrightarrow CH_3\overset{\overset{O}{\|}}{C}NHN{=}CHC_2H_5 + H_2O$$

acetic acid hydrazide	propionaldehyde	1-acetyl-2-propylidene hydrazine	water

crystallize out at 0-10°C, filter, and wash with methanol

STEP 3

$$CH_3\overset{\overset{O}{\|}}{C}NHN{=}CHC_2H_5 \xrightarrow[\text{in tetrahydrofuran}]{LiAlH_4} C_2H_5NHNHC_3H_7$$

1-acetyl-2-propylidene hydrazine	in tetrahydrofuran	1-ethyl-2-propyl hydrazine

neutralize excess $LiAlH_4$, remove bulk of tetrahydrofuran by fractional distillation, extract with ether, redistill

STEP 4

$$C_2H_5NHNHC_3H_7 \xrightarrow[\text{water}]{HgO \text{ in}} C_2H_5NNC_3H_7$$

1-ethyl-2-propyl hydrazine	in water	1-propaneazoethane

fractional distillation

This initial reaction scheme, however, had to be modified when the reaction to obtain 1-acetyl-2-propionyl hydrazine could not be accomplished. The effort made consisted of refluxing stoichiometric quantities of acetic acid hydrazine and ethyl propionate for four hours. Rather than continue efforts in this direction, experimentation was began with an alternative reaction for 1-acetyl-2-propylidene hydrazine.

The Final Synthesis Scheme

The reaction for 1-acetyl-2-propylidene hydrazine was successful and this compound was used in place of 1-acetyl-2-propionyl hydrazine in the final synthesis scheme. This scheme is presented in Fig 2 with the basic operations that were involved. It may be observed that the substitution of different esters and aldehydes leading to other mixed alkyl azo compounds appears feasible.

The First Reaction to Obtain Acetic Acid Hydrazide

Literature Basis. Details of the reaction are contained in the literature (Ref 16, Band II: 191). Essentially ethyl acetate is added to an excess of hydrazine hydrate, refluxed for several days, and then distilled in vacuo. The distillation is performed at low pressure because the hydrazide rearranges at 180°C. Purification may be accomplished by recrystillization from chloroform with either methyl alcohol or absolute ether.

Experimental Procedure. Ethyl acetate (215 g) was added slowly with stirring to an excess (679 g) of anhydrous hydrazine (the use of anhydrous hydrazine allowed elimination of the reflux period).

Table I

Analysis of 1-Acetyl-2-Propylidene Hydrazine

	Found (1 determination)	Expected
% C	52.28	52.61
% H	8.58	8.83
% O	14.86	14.02
% N	24.31	24.54
Molecular Weight (by ebullioscopic method using benzene)	160	114.15

Huffman Analytical Laboratory
Sample No. RLS-631
AF Contract 33 616 6742

The compounds reacted, with some evolution of heat, to form acetic acid hydrazide. A fractional distillation was used to separate the product from solution. The distillation was performed at atmospheric pressure until the temperature rose to 115°C. Then the remainder of the distillation was carried out in vacuo (24-31 mm). The hydrazide was collected in three fractions, 141-150°C & 27 mm (108 g), 150-160°C & 26 mm (43.5 g), and 160-165°C & 26 mm (10 g). Reported value (Ref 16, Band II: 191) bp 129°C & 18 mm. The melting points of the respective fractions were 49-62°C, 51-62°C, and 54-65°C. The melting point reported in the literature (ibid.) is 67°C.

Discussion. While the purity, as indicated by the melting points, was not high it was felt that purification could be reserved for the products of later reactions, and recrystallization from chloroform was not attempted. However, structural confirmation of the product was obtained from an infra-red spectra. In the preparation of the nujol mull for the spectra it was found that the hydrazide was hygroscopic.

The Second Reaction to Obtain 1-Acetyl-2-Propylidene Hydrazine

Literature Basis. Migrdichian (Ref 12, 1: 153) indicates, in general, that this reaction should be possible. In addition, the reaction of propionaldehyde (C_3H_6O) with hydrazine to form propylideneazine ($C_3H_6 = NN = C_3H_6$) has been reported (Ref 15). With the 1-position protected on our compound ($CH_3CONHNH_2$), the proposed reaction with propionaldehyde to obtain 1-acetyl-2-propylidene ($CH_3CONHN = C_3H_6$) appeared highly feasible.

Experimental Procedure. Propionaldehyde (106 g) was slowly added to acetic acid hydrazide (133 g). Evolution of heat occurred and a clear solution resulted. The solution was kept overnight in the refrigerator and a slurry formed. This was filtered, washed with methanol (20 ml, then 10 ml), and dried in the vacuum oven to obtain 132 g (64% yield) of 1-acetyl-2-propylidene hydrazine. The melting point was found to be 72-75°C. Similar runs without cooling resulted in a lower yield of large crystals with a melting point of 75-77°C. A crystal sample was analyzed with the results presented in Table I. It was also found that the product could be recrystallized from methanol using a dry-ice bath.

Discussion. The results of the analysis are in good agreement with the expected values with the exception of the molecular weight. However, the ebullioscopic molecular weight method is based on the assumption that the test material has a negligible vapor pressure at the boiling point of the solvent. As this was not the case, the high result was to be expected. The infra-red spectra was obtained using a nujol mull. The absorption points of the spectra agreed with those expected and purification by recrystallization was not performed.

The Third Reaction to Obtain 1-Ethyl-2-Propyl Hydrazine

Literature Basis. The reduction of 1-acetyl-2-isopropylidene hydrazine ($CH_3CO\text{-}NHN = CCH_3CH_3$) to obtain 1-ethyl-2-isopropyl hydrazine has been reported by Kratzl and Berger (Ref 9). They used lithium aluminum hydride ($LiAlH_4$) as the reducing agent and methylal or tetrahydrofuran (THF) as vehicles. While they reported the use of methylal resulted in higher yields than THF, methylal was not available and THF had to be used as our vehicle. Essentially their procedure was followed. For our compound this consisted of refluxing 1-acetyl-2-propylidene hydrazine ($CH_3CO\text{-}NHN = CHC_2H_5$) with lithium aluminum hydride in THF, neutralizing the excess hydride, extracting the product, and separating by fractional distillation. Precautions were taken, of course, with lithium aluminum hydride to prevent conflagration.

Experimental Procedure. An argon atmosphere was maintained throughout all of the following operations and, where mixing was required, a magnetic stirrer was used. Freshly dried and distilled tetrahydrofuran (700 ml) was slowly added to lithium aluminum hydride(58 g). The mixture was stirred and refluxed for 10 minutes to put the hydride in solution. Then the mixture was cooled below 10°C in an ice bath. A solution of 1-acetyl-2-propylidene hydrazine (71 g) and tetrahydrofuran (300 ml) was slowly added (duration of 1 hour) to the reaction mixture (with stirring). During the addition, the temperature was kept below 20°C. Next, the mixture was refluxed for 30 minutes and then cooled in an ice bath. A water (110 ml) solution of tetrahydrofuran (200 ml) was slowly added (duration of 2 hours) with stirring. During this addition, the temperature was kept below 60°C. Under the same conditions, 10N potassium hydroxide (100 ml) was next added and followed by 110 ml of water. The mixture was refluxed for 10 minutes to assure hydride neutralization and then cooled to room temperature.

To separate the product, the liquid was decanted from the white residue and distilled to remove the major portion of tetrahydrofuran (900 ml). The remaining solution was placed in a liquid-liquid extractor and the residue washings (300 ml ether and 400 ml water) added. Additional ether (50 ml) was added and extraction performed for four hours. The ether-product solution was dried over sodium sulfate (85 g) and distilled. The fraction, boiling from 94.5°C to 134°C was collected, again dried, and redistilled in a microdistillation unit. 1-Ethyl-2-propyl hydrazine (18.7 g) was collected from 128°C to 130.5°C & 752 mm for 29.5% yield.

Discussion. The product was noted to be susceptible to oxidation (turning yellow on exposure to air in less than an hour) but the argon atmosphere prevented this during the synthesis procedure. The low yield was predicted by Kratzl and Berger (Ref 9) but probably could be improved somewhat with more elaborate procedures. Moreover, it is quite possible that the next step in our synthesis scheme could be performed in the ether solution. However, since 1-ethyl-2-propyl hydrazine had not been found in a brief literature search, it was felt the physical properties were of interest. Therefore, it was isolated, as described, rather than left in solution with ether.

The infra-red spectra was obtained and the refractive index determined ($N_D^{25} = 1.4225$). This compared favorably with the indicies reported for the bracketing compounds of 1,2-diethyl hydrazine ($N_D^{20} = 1.4205$) and 1,2-dipropyl hydrazine ($N_D^{20} = 1.4287$) (Ref 15). The boiling point of our compound (128-130.5°C) also falls between that of the bracketing compounds (106-107°C and 149.5-150°C) (ibid.) and above, as expected, that of 1-ethyl-2-isopropyl hydrazine (116-118°) (Ref 9).

The Fourth Reaction to Obtain 1-Propaneazoethane

Literature Basis. The oxidation of aromatic hydrazine derivatives to their azo compounds using either sodium dichromate or cupic chloride has been accomplished (Ref 13: 264; Ref 18: 766). However, Renaud and Leitch have reported the oxidation of symmetric alkyl hydrazines to their azo compounds using mercuric oxide (Ref 15). Their method was felt the most applicable and it was used to accomplish this reaction. This procedure consisted of adding a water solution of the hydrazine to a water mixture of mercuric oxide and then separating the product by fractional distillation.

Experimental Procedure. A water (35 ml) solution of 1-ethyl-2-propyl hydrazine (10.35 g) was prepared. However, the solubility

Table II

Analysis of 1-Propaneazoethane

	Expected	Found (1 determination)
% C	59.95	59.13
% H	12.08	11.77
% N	27.97	27.69
Mol.Wt.*by Vapor Density	100.16	114

*Determined at 95.6°
At 99° the sample
appeared to decompose
and gave a molecular
weight of 79.2

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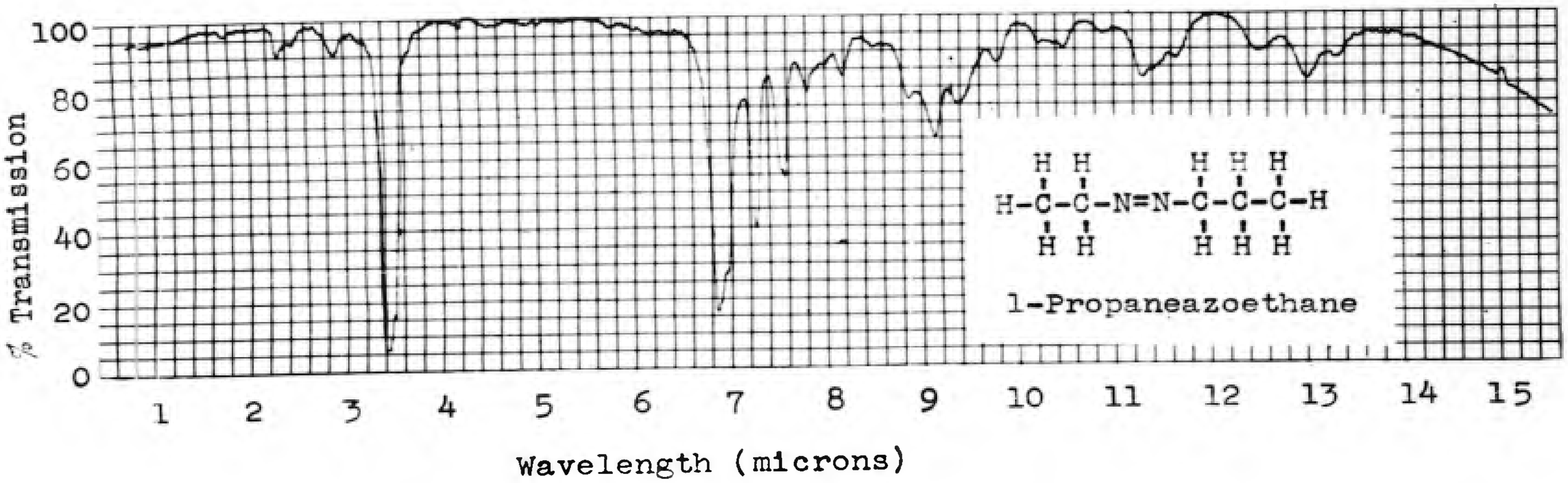
of the hydrazine was not high enough for all of it to dissolve, and some remained in a small layer on top of the water. The solution (including the hydrazine layer) was slowly added, with stirring, to a mixture of water (65 ml) and yellow mercuric oxide (32.5 g). A dark green precipitate of mercury and mercurous oxide resulted. The mixture was then distilled directly, and the fraction boiling from 72.5°C to 74°C & 739 mm collected (8.33 g, probably water azeotrope). This was dried over sodium sulfate and redistilled. Product (pale yellow liquid) was collected from 84-88°C. Subsequent analysis by gas chromatography with an apiezon L column indicated a purity of 96%. Another drying and redistillation was then performed and product collected from 83-85°C & 745 mm. Analysis, again by gas chromatography, indicated a purity of 99.6%. A sample was submitted to an independent laboratory for ultimate analysis and determination of the molecular weight.

Discussion. The analysis results, as presented in Table II, are in good agreement with those expected, with the exception of the molecular weight. However, the vapor density method assumes ideal behavior and the results are usually high (Ref 5: 10). The molecular weight determination does show, though, that a dimer was not formed.

The infra-red spectra was obtained and is presented in Fig 3. Some of the major absorption points may be seen to occur at 3.45, 6.85, 7.25, and 7.55 microns. The 3.45 wavelength absorption is,



Purity: BP 83-85°C
Phase: Liquid
Thickness: 0.025 mm
Date: 20 Jan 61
Operator: W. Rush

Prism: NaCl
Resolution: 9.27
Response: 1
Gain: 5.5
Speed: 4
Suppression: 0

Figure 3
Infra-red Spectra

of course, due to the carbon-hydrogen bonding. Evidence that rearrangement to a hydrazone had not occurred is manifested by the absence of absorption in the 5.92-6.1 micron range (Ref 2: 226). The absorption range due to azo bonding ($-N=N-$) has not as yet been definitely established, but the spectra compares favorably to that of 2,2'-azoisobutane $[(CH_3)_3CN=NC(CH_3)_3]$ which exhibits absorption at 3.3, 6.7, 7.25, 7.9, and 8.2 microns (Ref 10: Fig 1).

The refractive index was determined ($N_D^{22.5} = 1.3957$) and found to agree with the indices of the bracketing compounds of azobisethane ($C_2H_5N=NC_2H_5$, $N_D^{20} = 1.3852$) and azobispropane ($C_3H_7N=NC_3H_7$, $N_D^{20} = 1.4053$) as reported by Renaud and Leitch (Ref 15). A rough prediction of the boiling point may be made by taking the geometric mean of the boiling point of azobisethane (58°C) and azobispropane (113.5°C) (ibid.). This is 81°C and the boiling point found (83-85°C & 745 mm) is resonably close to this prediction.

Consideration of the synthesis method, the analysis results, and the physical properties leave little doubt that the compound synthesized is 1-propaneazoethane.

III. The Flash Photolysis of 1-Propaneazoethane

Theory

As previously discussed in the introduction, the exposure of 1-propaneazoethane to ultraviolet radiation may be expected to cause decomposition and the subsequent formation of ethyl free radicals, n-propyl free radicals, and nitrogen. The free radicals may then be expected to quickly dissipate any excess energy in collision with undissociated molecules and the walls of the container until they react with each other by combination or hydrogen abstraction. Other reactions are possible between 'hot', or energetic, radicals but it has been shown that methyl radicals produced by photolysis do not normally have an enhanced reactivity owing to the inheritance of surplus energy from the initial photolytic act (Ref 17: 66) and it shall be assumed that our radicals will exhibit similar behavior. Radical-product molecule reactions are also possible, but the energy requirements are higher than radical-radical reactions, and they should be negligible at low product concentrations. Based on these assumptions the following reaction scheme is proposed:

$$C_2H_5 - N = N - C_3H_7 \xrightarrow{h\nu} C_2H_5\cdot + N_2 + C_3H_7\cdot \qquad (0)$$

$$2C_2H_5\cdot \longrightarrow C_2H_4 + C_2H_6 \qquad (1)$$

$$2C_2H_5\cdot \longrightarrow C_4H_{10} \qquad (2)$$

$$2C_3H_7\cdot \longrightarrow C_3H_6 + C_3H_7 \qquad (3)$$

$$2C_3H_7\cdot \longrightarrow C_6H_{14} \qquad (4)$$

$$C_2H_5\cdot + C_3H_7\cdot \rightarrow C_2H_6 + C_3H_6 \qquad (5)$$

$$C_2H_5\cdot + C_3H_7\cdot \rightarrow C_2H_4 + C_3H_8 \qquad (6)$$

$$C_2H_5\cdot + C_3H_7\cdot \rightarrow C_5H_{12} \qquad (7)$$

The rate of formation of the products may be expressed using second order kinetics by:

$$R(C_2H_4) = k_1(C_2H_5\cdot)^2 + k_6(C_2H_5\cdot)(C_3H_7\cdot) \qquad (8)$$

$$R(C_2H_6) = k_1(C_2H_5\cdot)^2 + k_5(C_2H_5\cdot)(C_3H_7\cdot) \qquad (9)$$

$$R(C_3H_6) = k_3(C_3H_7\cdot)^2 + k_5(C_2H_5\cdot)(C_3H_7\cdot) \qquad (10)$$

$$R(C_3H_8) = k_3(C_3H_7\cdot)^2 + k_6(C_2H_5\cdot)(C_3H_7\cdot) \qquad (11)$$

$$R(C_4H_{10}) = k_2(C_2H_5\cdot)^2 \qquad (12)$$

$$R(C_5H_{12}) = k_7(C_2H_5\cdot)(C_3H_7\cdot) \qquad (13)$$

$$R(C_6H_{14}) = k_4(C_3H_7\cdot)^2 \qquad (14)$$

where R is the rate of change, or derivative, with respect to time, and the bracketed quantities are the concentrations as functions of time. The subscripts of the reaction rate constants (k's) indicate which of the seven reactions (Eqs 1-7) they are associated with.

The primary objective is to obtain the relative rate constants for the mixed reactions (Eqs 5, 6, 7). From equations (8) - (14) the following expressions may be derived (see appendix A) for the desired constants:

$$k_5/k_7 = \frac{C_2H_6 - (k_1/k_2)C_4H_{10}}{C_5H_{12}} = \frac{C_3H_6 - (k_3/k_4)C_6H_{14}}{C_5H_{12}} \tag{15}$$

$$k_6/k_7 = \frac{C_2H_4 - (k_1/k_2)C_4H_{10}}{C_5H_{12}} = \frac{C_3H_8 - (k_3/k_4)C_6H_{14}}{C_5H_{12}} \tag{16}$$

where C_2H_6, C_4H_{10} etc. refer to the concentrations present. Two independent expressions then exist for each relative rate constant to check the consistency of any experimental data.

Required Data. The relations derived for k_5/k_7 and k_6/k_7 may be satisfied by the product concentrations relative to pentane. A relation for k_5/k_6 may, of course, be obtained but it will require knowledge of the absolute product concentration. Since gas chromatography will be the method of analysis, the relative concentrations will be the ratios of corrected peak areas and these may be determined more precisely than the absolute concentrations.

For the purpose of analysis, relatively high product concentrations are desirable. On the other hand, at high product concentrations, radical-product molecule reactions will become significant. Therefore, it will be necessary to obtain and examine samples of lower and lower product concentrations that are still consistent with analysis limitations. These samples may be obtained by flashing a different number of times. As long as radical-molecule reactions are not occurring, and the quantity of 1-propaneazoethane has not appreciably diminished, each flash should result in the same quantity of products as a previous flash. Even if the quantity of azo compound is diminished, the ratio of product concentrations should remain the same as that of previous flashes. Therefore a plot of the number of flashes versus the ratio of two products should result in a straight line parallel to the ratio axis until radical-molecule reactions become significant.

A knowledge of k_1/k_2 and k_3/k_4 is also required to satisfy Eqs (15) and (16). These two ratios are the relative rate constants for the ethyl free radical system alone and the propyl free radical system alone. Values from the literature of $(k_1/k_2) = 0.14$ and $(k_3/k_4) = 0.25$, (Ref 8) shall be used for our calculations. However, even these values, particularly k_3/k_4, have not been established beyond question and are subject to future change.

Procedure

General Outline. A sample of 1-propaneazoethane was purified by gas chromatography. Standard vacuum techniques were then used to fill quartz sample bottles with the vapor. The bottles were then exposed to a sufficient number of flashes of ultraviolet radiation to cause measurable decomposition. Using the vacuum rack and a toepler pump, the vapor in each sample bottle was split into two portions, and analyzed by the gas chromatograph using different columns. Peak areas for the nitrogen and the seven products were obtained and corrected for their differences in thermal conductivity. After correction, the areas were proportional to the quantities present.

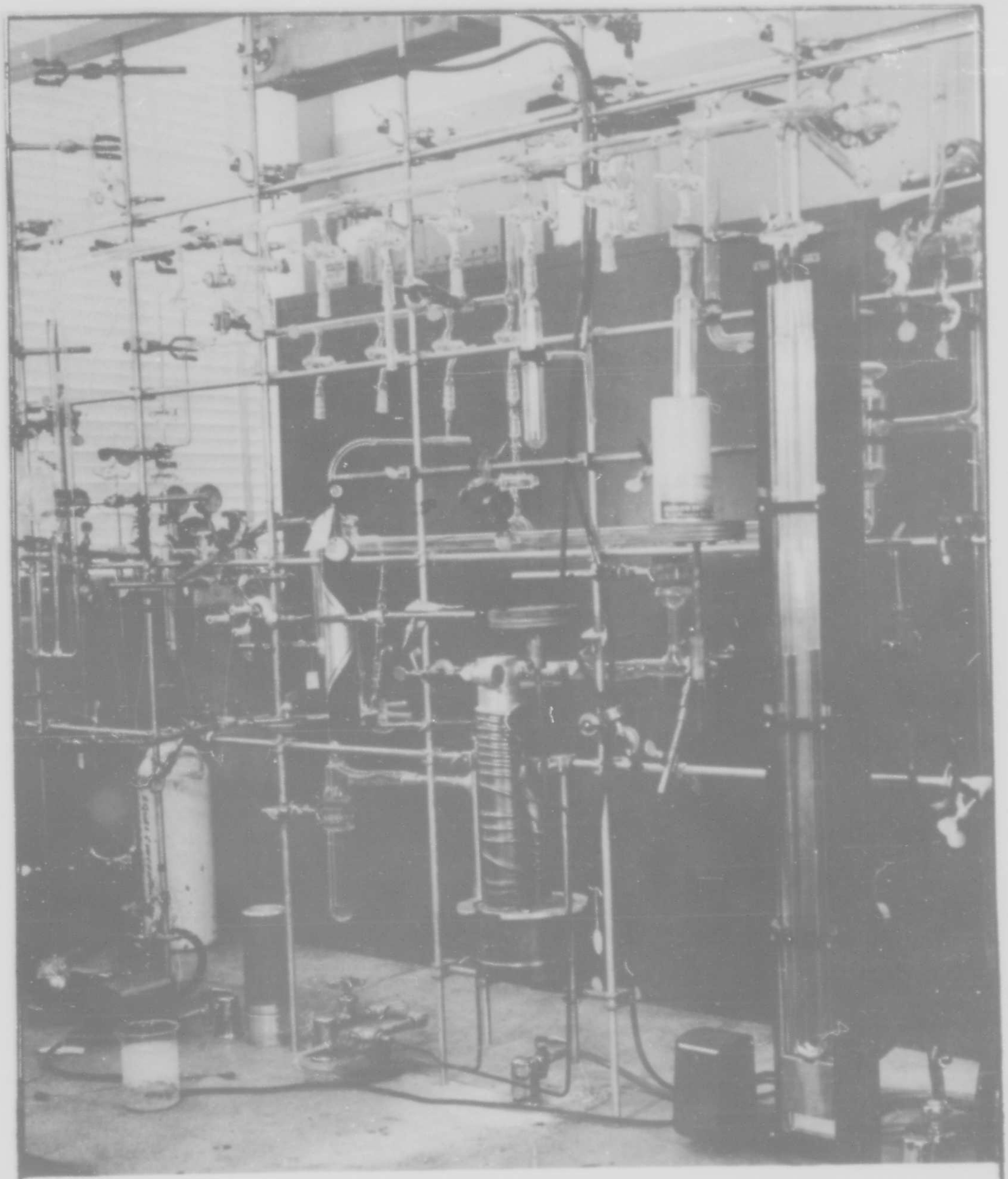


Figure 4
Photograph of the Vacuum Rack

Equipment. A Burrell gas chromatograph, Kromo-Tog model K-2, was used for the purification and analysis. Columns used in conjunction with the chromatograph were a 2.5 m-polyethylene glycol-on-chromosorb w column, a 8 m-hexadecane-on-firebrick column, a 2.5 m-hexamethylphosphoramide-on-firebrick column (HMPA) and a 1 m-molecular sieve (Type 5A) column.

Sample handling was accomplished on a laboratory-built vacuum rack. A GE flashtube (FT-524, Xenon filled) was used in conjunction with a laboratory-constructed electrical circuit to obtain the flashes of ultraviolet radiation.

Purification of 1-Propaneazoethane. To accomplish purification, a column and operating conditions had to be determined that would cause sufficient separation of the impurities from the azo compound. Trial runs indicated that bareco wax, apiezon L, hexadecane, HMPA, and tricresyl phosphate columns were unsatisfactory. However, a polyethylene glycol column operating at 40-50°C and 50 ml/mm He flow was found adequate. Unfortunately, only a small analytical column with a maximum capacity of 75λ, before flooding, was available. It was estimated that 1 ml was required to fill the vacuum rack manifold and 18 runs were accomplished to obtain this quantity. The run procedure was to inject the sample (75λ) into the column with a syringe and collect it at the end of the column in a cold trap (dry-ice-trichloroethylene bath) when the azo peak appeared on the instrument recorder chart.

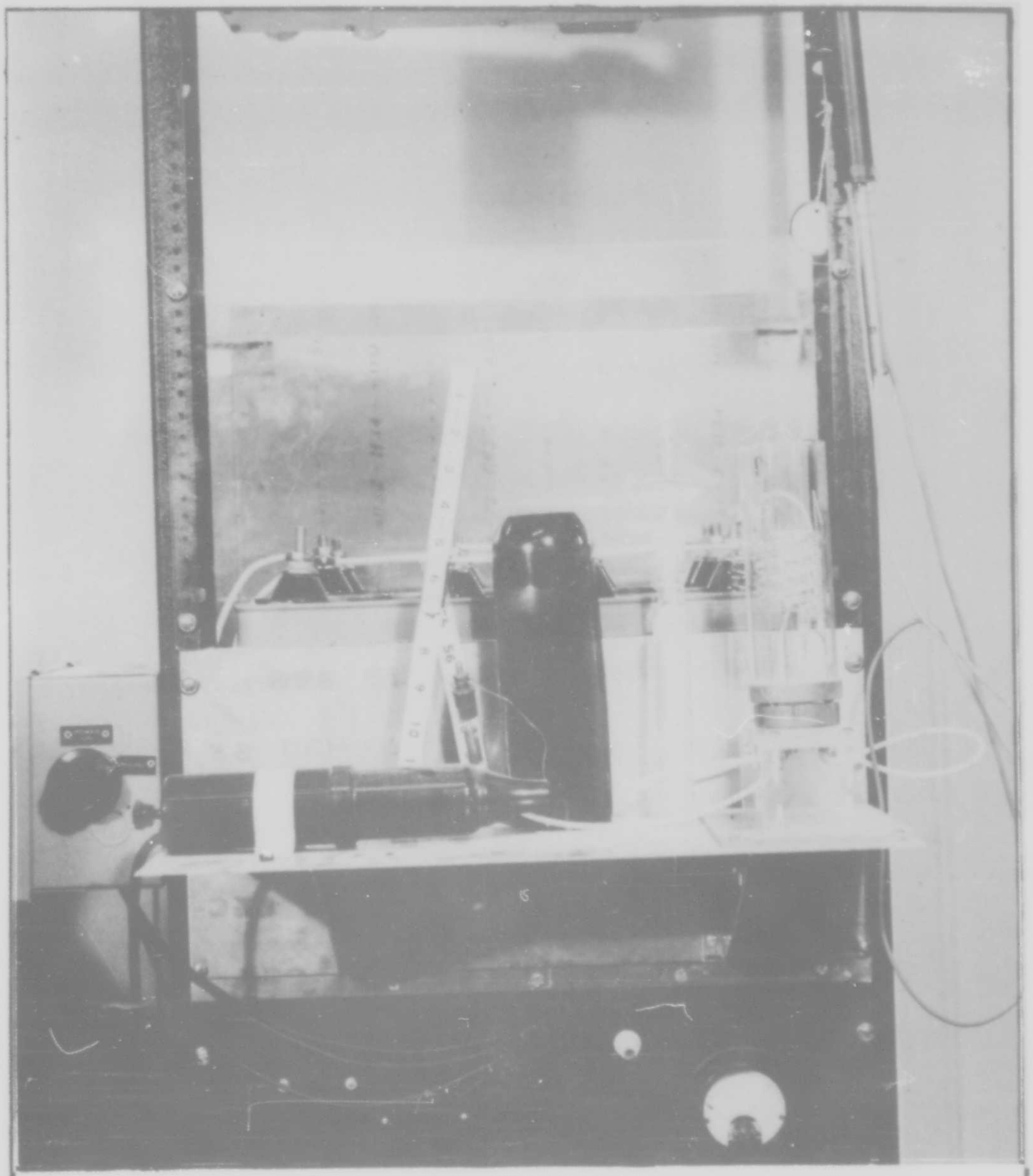


Figure 5
Photograph of the Flashtube Equipment

Sampling Pre-Flash. A photograph of the vacuum rack (containing the manifold, manometer and toepler pump) is shown in Fig 4. The trap containing the purified azo compound was connected to another trap on the manifold. The azo compound was then frozen with liquid nitrogen, the manifold evacuated, and the sample distilled (and degassed) by moving the nitrogen bath to the trap on the manifold. The manifold was then isolated from the vacuum side and the azo compound allowed to evaporate and fill the quartz sample bottles connected to the manifold. The vapor pressure and temperature were recorded, the quartz vessels closed, and the remaining azo compound frozen out in the trap.

Sample bottles were filled on three occasions but, because it was discovered that the azo compound attacks vacuum grease, the last two runs were cut before thermal equilibrium to minimize air leakage.

The Flash-Photolysis. The quartz sample bottles (labeled A, B, and C) contained a piece of gold foil and were constructed with an outer jacket. One is shown in the picture of the flash apparatus, Fig. 5. The jacket was filled with water to absorb those wavelengths which would affect any traces of water vapor that might remain in the sample. The gold foil was present to amalgamate with any mercury vapor picked up from the vacuum rack and thereby eliminate the possibility of mercury photosensitization.

The prepared sample bottle was placed inside the spiral glass flash tube and a blue glass cover (for eye protection) was placed over the flash tube. Then the condensor bank was charged to 4000 volts and discharge initiated by turning on the tesla coil briefly.

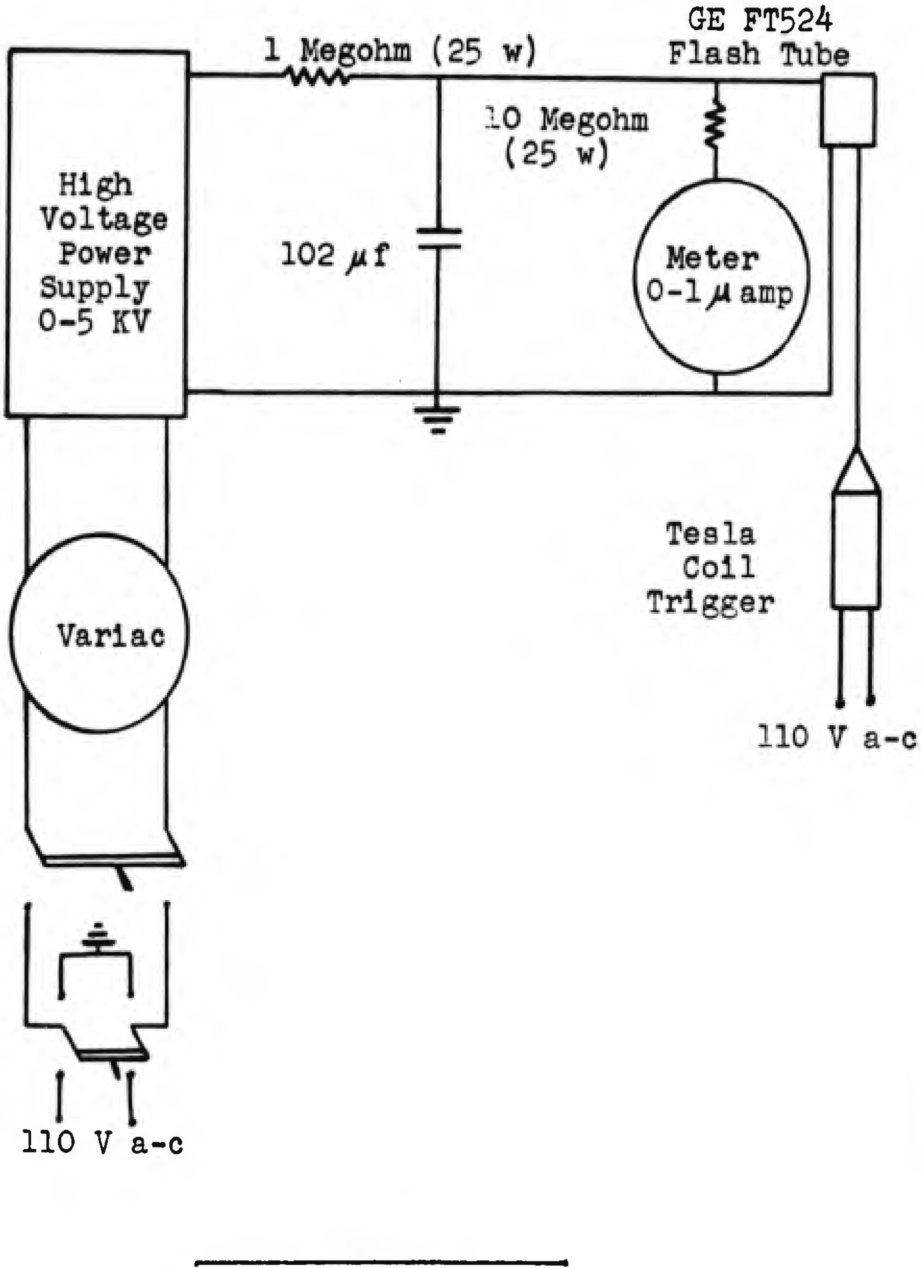
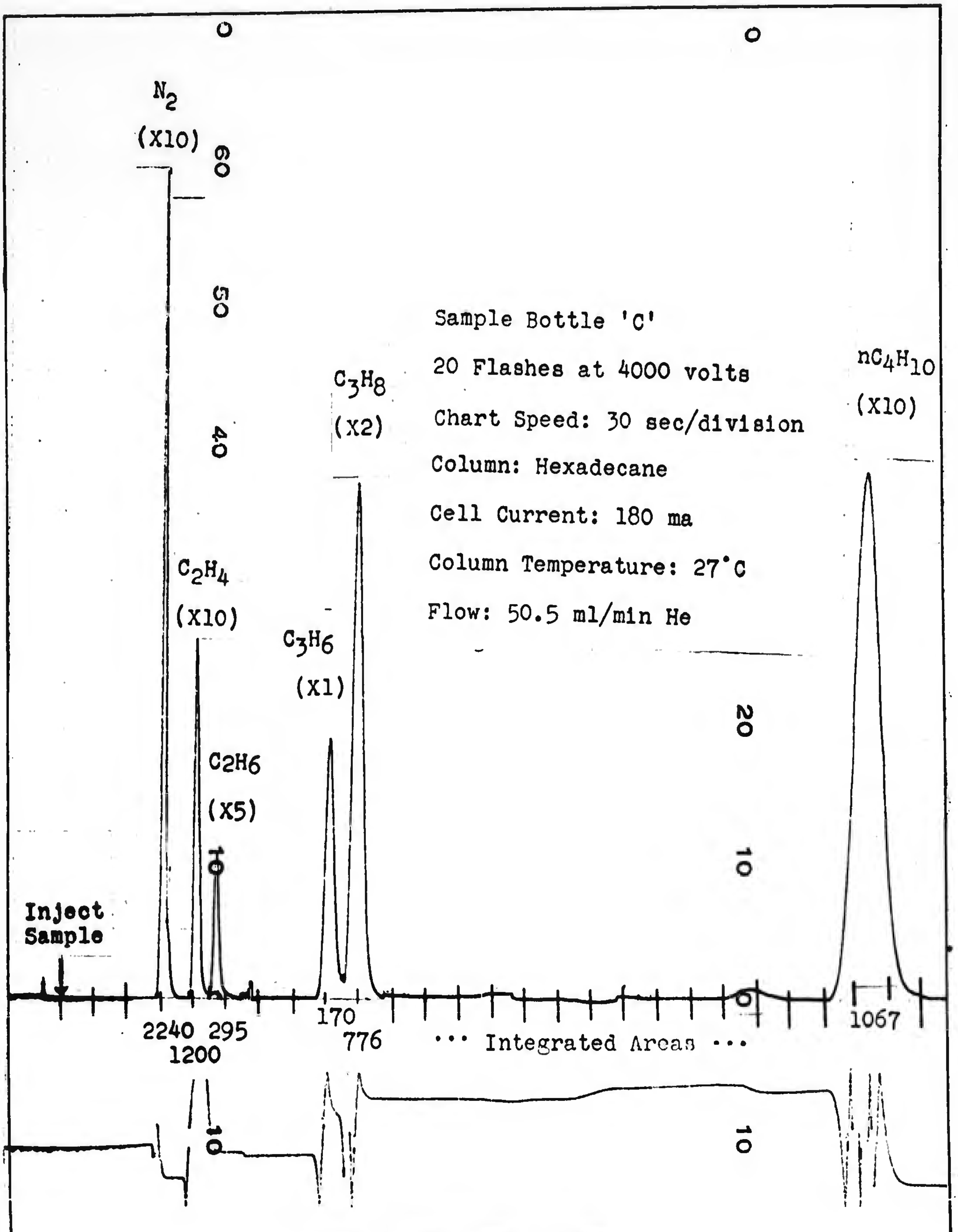


Figure 6
Flash Tube Circuit

A component wiring diagram is shown in Fig 6. Initial runs were made using 20 and 10 flashes to insure measurable product. On the basis of the results further runs were made at 10 and 5 flashes. Throughout the course of the second series of runs the noise of tube discharge was peculiar, and it was subsequently found that a connection to the flash tube from the condensor bank was melting through.

Post-Flash Sampling. The quartz sample bottle was connected to the toepler pump on the vacuum rack and a portion of the sample pumped into the evacuated burette. The pressure and volume were recorded and the sample portion forced, by a mercury column, into a gas chromatograph sampling bottle. Sometimes the sample could be split into more than the two parts required for complete analysis, and this made a few additional tests and analysis reruns possible.

Analysis of the Products. The sample bottle was connected to the chromatograph. The connecting legs were then evacuated and filled with helium. Next, the sample was cut into the main stream to the column and the time noted on the recorder chart. The hexadecane column separated, and was used to determine: N_2 (including O_2), C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_{10} and CO_2. An example chromatogram is shown in Fig 7. An integrator attachment to the recorder traced out the areas of the peaks on the bottom of the chromatogram. The HMPA column was used to determine C_5H_{12} and C_6H_{14}. In addition, this column also separated: N_2 (including O_2), $C_2H_4 + C_2H_6$, C_3H_6, C_3H_8, C_4H_{10}, and CO_2. The areas of these peaks were used when a product area on a hexadecane column run could not be determined because of an



Sample Bottle 'C'

20 Flashes at 4000 volts

Chart Speed: 30 sec/division

Column: Hexadecane

Cell Current: 180 ma

Column Temperature: 27°C

Flow: 50.5 ml/min He

Figure 7

Example Chromatogram

improper scale-attenuation setting. In addition to these tests, two samples were run on a molecular sieve column; one to determine if oxygen was present, and the other (using N_2 carrier gas and reversed polarity) to determine if hydrogen was present. At low product concentrations the sensitivity of the instrument was increased by raising the detector cell current to the maximum (218 ma).

Calculations and Results

The peak areas, as obtained from the chromatograph, were corrected to account for the difference in the detector sensitivity to different gases*, using butane as a basis. This was accomplished by multiplying the peak areas by the following correction factors**: C_2H_4 - 1.54, C_2H_6 - 1.45, C_3H_6 - 1.20, C_3H_8 - 1.2, C_4H_{10} - 1.0, C_5H_{12} - 0.91, C_6H_{14} - 0.82, CO_2 - 1.15, N_2 - 4.57. The CO_2 and N_2 factors were obtained from absolute concentration calibrations and are not as reliable as the others. It was also necessary to convert the sample size run on the HMPA column to the sample size run on the hexadecane column. This was done by multiplying by the ratio of the butane peak areas. Still another correction had to be applied to samples run at a high detector cell current (218 ma). A factor of 0.591** was used to convert these to the usual cell current (180 ma).

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*The detector measures changes in the thermal conductivity of the flow stream.

**These factors were previously determined by the laboratory and the data is recorded in ARDC notebook 16520, pp. 68, 90.

Table III

Corrected Peak Areas

	Samples Filled Pre-flash to: 59.7mm Hg at 24°C			Samples Filled Pre-flash to: 51.2mm Hg at 19.8°C **		Samples Filled Pre-flash to: 42mm Hg at 19.3°C	
Compound	Sample A 20 Flashes pv = 81.7 (ml-cm Hg)	Sample B* 10 Flashes pv = 246 (ml-cm Hg)	Sample C 20 Flashes pv = 104 (ml-cm Hg)	Sample A 10 Flashes pv = 108 (ml-cm Hg)	Sample C 5 Flashes pv = 103 (ml-cm Hg)	Sample A 5 Flashes pv = 85 (ml-cm Hg)	Sample C 5 Flashes pv = 93 (ml-cm Hg)
N_2	13486	12780	10220	5260	unknown	2510	2830
C_2H_4	1800	6125	1848	82.0	68.2	34.6	58.1
C_2H_6	479	2015	428	103.7	61.6	28.3	59.1
C_3H_6	178	504	204	88.7	51.0	25.5	36.9
C_3H_8	840	2320	931	112.9	65.2	34.7	61.0
C_4H_{10}	920	2500	1067	393	201.5	88.0	175
C_5H_{12}	600	1440	754	1319	527	123.3	318
C_6H_{14}	150	trace	253	not Detd.	not Detd.	not Detd.	not Detd.
O_2	494	no test	no test	no test	no test	no test	no test
CO_2	none	none	none	none	none	27.2	42.9
% Azo Compound Decomposed	21.2	16.7	15.9	6.9	3.1	1.2	2.4

* no hydrogen present
** Flashtube connection melting through

Determined by gas chromatography at
the Aeronautical Research Laboratory,
Wright-Patterson Air Force Base: Jan 1960

The final corrected peak areas, proportional to the quantities present, are presented in Table III. Due to the variance in areas, scale attenuations, and shifting base lines, an estimate of limit of error could not be made.

The percentage azo compound that was decomposed was calculated on the basis of a carbon material balance using a factor* of 493 integrator units per micromole of gas. An example calculation is presented in Appendix B.

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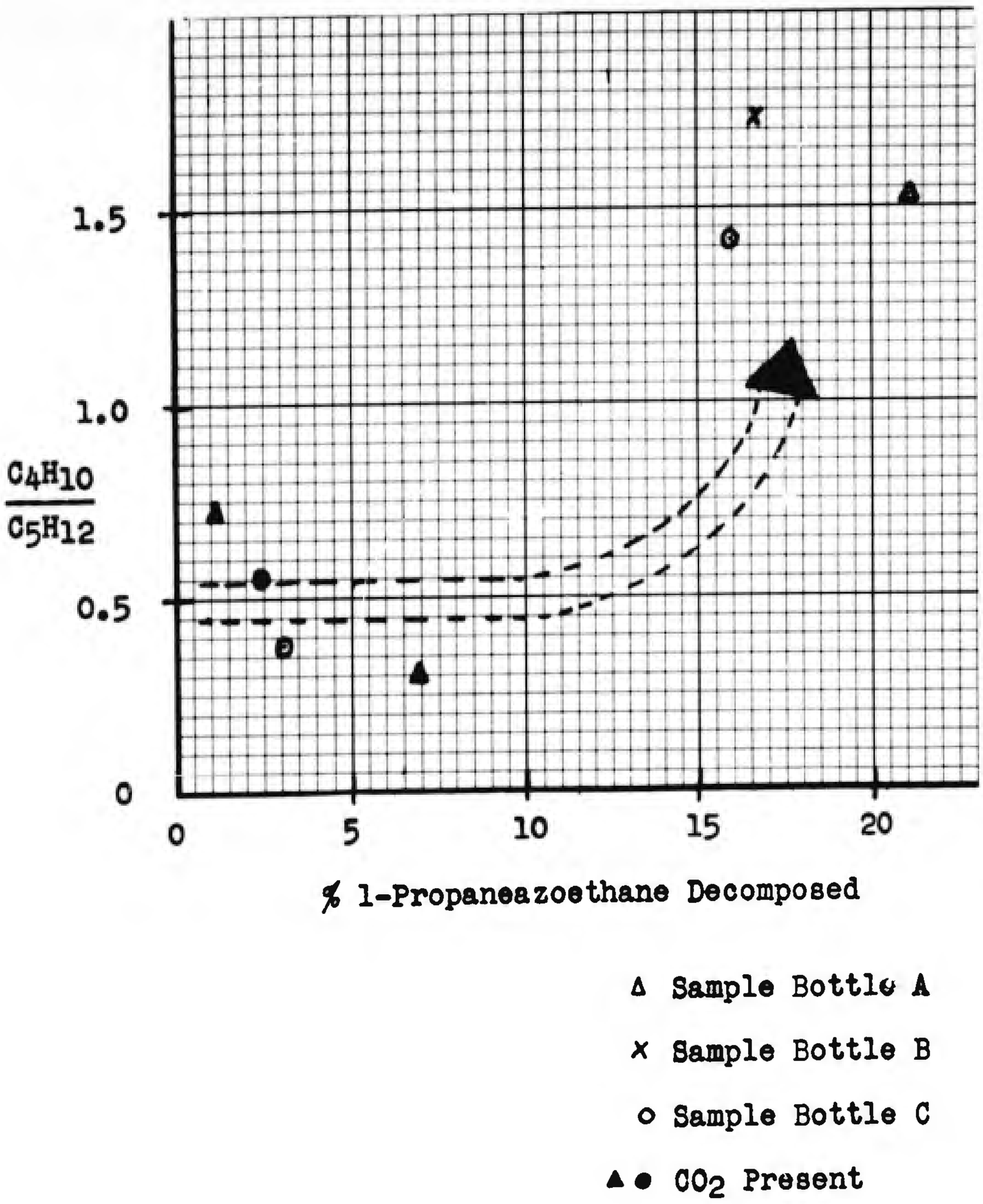
*These factors were previously determined by the laboratory and the data is recorded in ARDC notebook 16520, p. 68.



C_4H_{10}/C_5H_{12} as a Function of % 1-Propaneazoethane Decomposed

Figure 8

IV. Discussion of Results

The original plan of observing the variance of product-to-pentane-ratios with number of flashes had to be abandoned due to the melting flashtube connection. This invalidated the assumption of equal flashes and probably caused the complete scatter of data. Also, the presence of oxygen in one sample cast doubt on the significance of the nitrogen areas, since air leakage, post-flash, may well have occurred in the rest. However, it was still possible to calculate (without using N_2 areas) the % decomosition and use it in place of the number of flashes. A typical product (C_4H_{10})-to-pentane-ratio variance with % decomposition is presented in Fig. 8. The presence of CO_2 in the samples is evidence that air leakage occurred prior to flashing and again invalidates the nitrogen areas. Furthermore, since the CO_2 is a result of oxygen reacting with the radicals, doubt is cast on any product-to-pentane ratios obtained. However, there is some feeling among kineticists* that oxygen would scavange both our radicals with equal efficiency. If this is true, and there are still two good pieces of datum in the low conversion range, then the expected trend may be imposed on the data (indicated by the dotted curve Fig 8). While the data is too scattered to permit any conclusions, it is interesting to note the consistancy of the results obtained using the data of sample 'C' at low conversion. From eqs (15) and (16) we obtain for the two values per equation:

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*A private communication from Dr. J. Futrell, though he himself feels that there is insufficient evidence, as yet, to warrant any conclusion in this matter.

$$k_5/k_7 = 0.151 \cong 0.159$$

$$k_6/k_7 = 0.106 \cong 0.116$$

Gas chromatography was used as the only available means of analysis and it was not possible to determine if radical reactions with 1-propaneazoethane to form tetra alkyl hydrazines (four are possible) occurred. Therefore, substantiation of our reaction scheme is not yet possible, though mass spectrometer analysis can be expected to resolve the question.

The vital question of whether or not simultaneous decomposition takes place, also, can not be answered by the results of our investigation. Again, a mass spectrometer may be employed to answer this question because radicals will ionize, and may be observed, at lower ionizing currents than are required to ionize the products of the radical reactions. Should stepwise decomposition be occurring, the presence of the ·NN-R radical will enter into the reaction scheme and make the determination of the relative rate constants difficult, if not impossible.

V. Conclusions and Recommendations

A synthesis procedure for 1-propaneazoethane has been established and should be applicapable to other mixed alkyl azo compounds.

The data obtained from the kinetic investigation is inadequate to establish the validity of the proposed reaction scheme or permit justifiable calculation of the relative reaction rate constants.

However, further experimentation using 1-propaneazoethane as a radical source should result, if stepwise decomposition is not occurring, in the determination of the desired constants. It is recommended that the effort of future investigations be initially directed at determining whether or not step-wise decomposition occurs.

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Appendix A

The Derivation of the Relative Rate Constant Relations

The kinetic equations resulting from the proposed reaction scheme are

$$R(C_2H_4) = k_1(C_2H_5\cdot)^2 + k_6(C_2H_5\cdot)(C_3H_7\cdot) \tag{8}$$

$$R(C_2H_6) = k_1(C_2H_5\cdot)^2 + k_5(C_2H_5\cdot)(C_3H_7\cdot) \tag{9}$$

$$R(C_3H_6) = k_3(C_3H_7\cdot)^2 + k_5(C_2H_5\cdot)(C_3H_7\cdot) \tag{10}$$

$$R(C_3H_8) = k_3(C_3H_7\cdot)^2 + k_6(C_2H_5\cdot)(C_3H_7\cdot) \tag{11}$$

$$R(C_4H_{10}) = k_2(C_2H_5\cdot)^2 \tag{12}$$

$$R(C_5H_{12}) = k_7(C_2H_5\cdot)(C_3H_7\cdot) \tag{13}$$

$$R(C_6H_{14}) = k_4(C_3H_7\cdot)^2 \tag{14}$$

where R is the derivative with respect to time, the bracketed quantities are the concentrations as functions of time, the k's are the reaction rate constants, and the k subscript identifies the reaction the k is associated with.

Eqs (12), (13), and (14) on rearrangement become

$$\frac{R(C_4H_{10})}{k_2} = (C_2H_5\cdot)^2 \tag{15}$$

$$\frac{R(C_5H_{12})}{k_7} = (C_2H_5\cdot)(C_3H_7\cdot) \tag{16}$$

$$\frac{R(C_6H_{14})}{k_4} = (C_3H_7\cdot)^2 \tag{17}$$

Substitution for $(C_2H_5\cdot)^2$, $(C_2H_5\cdot)(C_3H_7\cdot)$, and $(C_3H_7\cdot)^2$ from Eqs (15), (16) and (17) into Eqs (8) through (11) result in

$$R(C_2H_4) = \frac{k_1}{k_2} R(C_4H_{10}) + \frac{k_6}{k_7} R(C_5H_{12}) \tag{18}$$

$$R(C_2H_6) = \frac{k_1}{k_2} R(C_4H_{10}) + \frac{k_5}{k_7} R(C_5H_{12}) \tag{19}$$

$$R(C_3H_6) = \frac{k_3}{k_4} R(C_6H_{14}) + \frac{k_5}{k_7} R(C_5H_{12}) \tag{20}$$

$$R(C_3H_8) = \frac{k_3}{k_4} R(C_6H_{14}) + \frac{k_6}{k_7} R(C_5H_{12}) \tag{21}$$

Because of the short flash duration, less than 250 μsec above 1/3 peak intensity (Ref 19: 54) at our operating conditions, it is not possible to measure the rates of product formation.

However, it is possible to determine the product concentrations at some time, t, later. Integrating Eqs (18)-(21) from zero time (start flash) to time, t, and applying the boundary condition that the concentration of products is zero at zero time, the following Eqs are obtained:

$$C_2H_4\Big|_t = \frac{k_1}{k_2} C_4H_{10}\Big|_t + \frac{k_6}{k_7} C_5H_{12}\Big|_t \tag{22}$$

$$C_2H_6\Big|_t = \frac{k_1}{k_2} C_4H_{10}\Big|_t + \frac{k_5}{k_7} C_5H_{12}\Big|_t \tag{23}$$

$$C_3H_6\Big|_t = \frac{k_3}{k_4} C_6H_{14}\Big|_t + \frac{k_5}{k_7} C_5H_{12}\Big|_t \qquad (24)$$

$$C_3H_8\Big|_t = \frac{k_3}{k_4} C_6H_{14}\Big|_t + \frac{k_6}{k_7} C_5H_{12}\Big|_t \qquad (25)$$

As the reactions have proceeded to completion in less than a fraction of a second after the end of the flash, the measured concentrations are independent of time. Rearrangement of Eqs (22)-(25) for k_5/k_7 and k_6/k_7 finally results in:

$$\frac{k_5}{k_7} = \frac{C_2H_6 - (k_1/k_2)C_4H_{10}}{C_5H_{12}} \qquad (26)$$

$$\frac{k_5}{k_7} = \frac{C_3H_6 - (k_3/k_4)C_6H_{14}}{C_5H_{12}} \qquad (27)$$

$$\frac{k_6}{k_7} = \frac{C_2H_4 - (k_1/k_2)C_4H_{10}}{C_5H_{12}} \qquad (28)$$

$$\frac{k_6}{k_7} = \frac{C_3H_8 - (k_3/k_4)C_6H_{14}}{C_5H_{12}} \qquad (29)$$

Appendix B

Calculation of % Decomposition

For Sample Bottle C at 20 Flashes:

Sample Size

$$PV = 104 \text{ ml-cm} \times 0.539 \, \frac{\text{micromole}}{\text{ml-cm}} = 56.0 \text{ micromoles}$$

Carbon Balance

Product	Peak Area ÷ 493	= micromoles	x $\frac{\text{micrograms carbon}}{\text{micromole}}$
C_2H_4	1848	3.750	90.0
C_2H_6	428	0.869	20.9
C_3H_6	204	0.414	14.9
C_3H_8	931	1.890	68.1
C_4H_{10}	1067	2.165	104.0
C_5H_{12}	754	1.528	91.7
C_6H_{14}	253	0.513	36.9
		11.129	426.5 micrograms total

$$\frac{426.5 \text{ micrograms carbon}}{60.05 \text{ micrograms carbon/micromole Azo decomposed}} = 7.1 \text{ micromoles decomposed}$$

quantity undecomposed = quantity sample-quantity N_2 - quantity products

= 56 - 7.10 - 11.13

= 37.77 micromoles

% Conversion

$$\% \text{ Conversion} = \frac{\text{amount decomposed}}{\text{amount undecomposed} + \text{amount decomposed}} \times 100$$

$$\% \text{ Conversion} = \frac{7.1}{37.77 + 7.1} \times 100 = 15.9\%$$

Vita

William A. Rush was born on [redacted] After graduation in 1951 from [redacted] he attended the University of Florida, Gainesville, Florida. In August 1955 he was graduated with the degree of Bachelor in Chemical Engineering and received his commission as Lieutenant in the USAF Reserve. From September 1955 to March 1956 he was employed with the Rocketdyne division of North American Aviation Inc. as a research engineer. He entered active duty in May 1956 and received his commission in the Regular Air Force in May 1960. Prior to attending the Air Force Institute of Technology he was assigned to the Missile Propellants and Chemical Laboratory, 6550th Field Maintenance Squadron, Patrick Air Force Base, Florida.

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This thesis was typed by Mrs. Judy A. Adams.