Though there is probably some adsorption of solute at the glass–liquid interface, calculations show that the amount of butyl alcohol necessary to form a monomolecular layer over the interior of the capillary is negligible compared to the amount of alcohol in the capillary at the beginning of the period of calculation. Since much of the glass–liquid interface would be covered with alcohol prior to the period of calculation, this error is largely eliminated by the methods of calculation.

Stearn, Irish and Eyring[8] list a value of D for butyl alcohol of 0.88×10^{-5} cm.²/sec.

In a further study of diffusion by this method, a capillary length of 0.50 cm. was used while the bulk concentration at the lower end of the capillary was varied. Preliminary observations indicated that the rate of change in concentration at the hypothetical plane was nearly proportional to the bulk concentration. There was observed a slight tendency for the ratio (change in concn.)/(bulk concn.) to increase with bulk concentration. This seems indicative of a small increase in the diffusion coefficient as the over-all average concentration in the capillary increases. This tendency was also noted in the original determinations of diffusion coefficient.

Another preliminary study was made using a bulk concentration of 0.01482 weight per cent. and varying the length of the diffusion column from one determination to another. It was observed that within experimental error the change in concentration at the hypothetical plane was inversely proportional to the square of the capillary length involved in the diffusion process.

The agreement of the experimental results of these preliminary studies with predicted results indicates that either or both the length of column, or the bulk concentration may be varied within limits dictated by experimental technique, without invalidating determinations of diffusion coefficients.

The practical and theoretical aspects of this method are being further explored. It would seem that it should be applicable to the many and varied types of molecules which show surface activity in water or in other solvents. A slight modification should permit the study of diffusion of vapors from the vapor side of the interface.

LINCOLN 8, NEBRASKA RECEIVED JUNE 19, 1950

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[8] Stearn, Irish and Eyring, *J. Phys. Chem.*, **44**, 990 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Reaction of Nitrous Acid with Diaminoguanidine in Acetic Acid Media. Isolation and Structure Proof of Reaction Products[1]

BY EUGENE LIEBER AND DEWEY ROBERT LEVERING

The reaction of diaminoguanidine with one and two molar proportions of nitrous acid in acetic acid media has been studied. Tetrazolyl azide, in the form of its alkali salt is the only solid isolable product, the structure being established by degradation, synthesis and infrared absorption. The preparation and properties of pure tetrazolyl azide are described. With two molar proportions of nitrous acid the yield of tetrazolyl azide varies from 20 to 77%, the yield increasing with decrease in concentration of the reagents. A gaseous decomposition product, comprising equal quantities of nitrogen and nitrous oxide, accompanies the diazotization reaction, the amount of gas increasing with increase in concentration of reagents. The reaction of diaminoguanidine with one molar proportion of nitrous acid in acetic acid yields chiefly unreacted starting material, a small yield (0.5 to 6.0%) of tetrazolyl azide and gaseous decomposition products.

Introduction

Diaminoguanidine, $HN{=}C(NHNH_2)_2$, was first prepared almost fifty years ago by Stollé[2,3] and the method improved by Pellizzari and Gaiter.[4] Two other methods are mentioned in the literature.[5,6] However, none of these methods of preparation is very satisfactory and a different one is referred to in this paper. These few communications on the preparation of diaminoguanidine, its salts and a few selected derivatives comprise the only studies carried out on this compound.

The reactions of nitrous acid with aminoguanidine, $H_2NC({=}NH)NHNH_2$, in strong acid media and in neutral and acetic acid media have been summarized in a review article on aminoguanidine and related substances by Lieber and Smith.[7]

The study of the reaction of nitrous acid with diaminoguanidine in strong acid, weak acid and neutral media is currently under investigation in this laboratory. The purpose of this work is the preparation and reactions of high nitrogen-containing compounds. This paper reports the results of the reaction in weak acid solution.

Reaction with Two Mole Proportion of Nitrous Acid.—When diaminoguanidine nitrate (I) is treated with two moles of nitrous acid in acetic acid solution, the only isolatable product is potassium or sodium tetrazolyl azide (II) depending upon whether potassium or sodium nitrite is the source of nitrous acid. The same compound (II) is obtained when buffered acetic acid is the reaction medium.

Pure potassium tetrazolyl azide precipitates in the form of lustrous white plates when ether is added to a solution of it in acetone. Potassium tetrazolyl azide is very soluble in water, alcohol and acetone but it is insoluble in benzene, carbon tetrachloride and ether. This azide salt (II) is *extremely sensitive* to pressure, friction or heat and must be handled with care and in small amounts. Very small amounts (less than 0.01 g.)

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[1] Abstracted from a portion of the thesis submitted by Dewey Robert Levering to the Graduate School of the Illinois Institute of Technology in partial fufillment for the Ph.D. degree.

[2] R. Stollé and K. Hofmann, *Ber.*, **37**, 4524 (1904).

[3] R. Stollé, *J. prakt. Chem.*, **75** [2] 423 (1907).

[4] G. Pellizzari and A. Gaiter, *Gazz. chim. ital.*, **44**, IIA, 72 (1914).

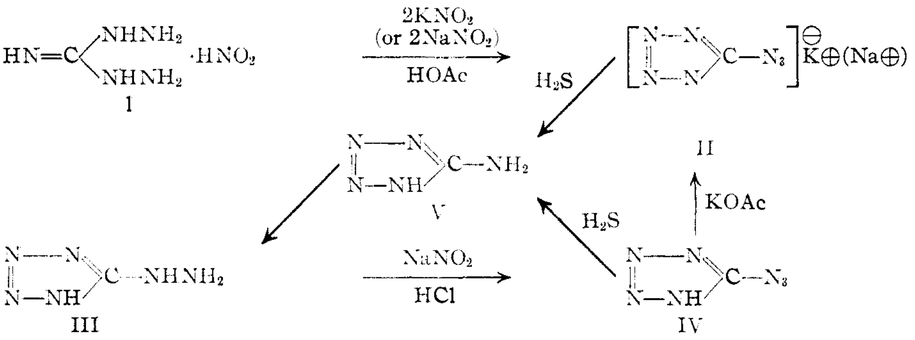
[5] R. Stollé and K. Krauch, *J. prakt. Chem.*, **88**, 306 (1913).

[6] R. Phillips and J. F. Williams, THIS JOURNAL, **50**, 2465 (1928).

[7] E. Lieber and G. B. L. Smith, *Chem. Rev.*, **25**, 213 (1939).

explode violently with a great shattering force. The crude solid when diluted with inert material (inorganic salts) is stable in the presence of acetic acid. However, when the azide is separated from these salts by extraction it will explode spontaneously if traces of acetic acid are present, even in acetone solution, but is stable in aqueous or alcoholic solution. It is essential therefore that *all traces of acetic acid be removed* before the azide is separated from its inert diluents. If small portions of the acetone solution explode, a detonation can be prevented by *immediately quenching with water*. The procedure for the isolation of the product, as described in the experimental part, was worked out after many trials and not a few explosions.

The structure of the reaction product was established by independent synthesis, and by reduction to 5-aminotetrazole (V) a known compound.[8] The cycle of reactions are shown in the equations



Tetrazolyl azide (IV) has never been satisfactorily characterized as such, although it has been reported and analyses for certain of its derivatives have been carried out.[9,10] The properties described by Thiele[8] for the tetrazolyl azide isolated by them did not correspond to those observed for the compound prepared in this laboratory. Accordingly proof that the compound obtained by their method is actually tetrazolyl azide was needed.

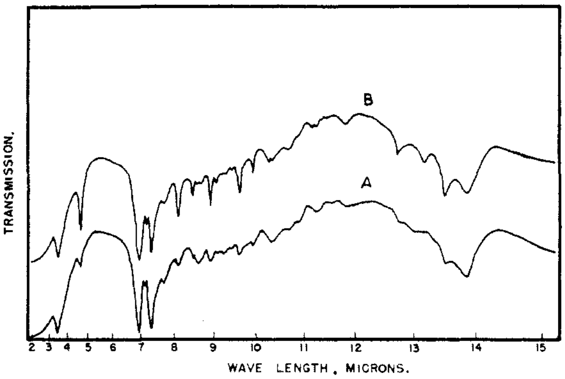


Fig. 1.—Infrared absorption spectra of potassium tetrazolyl azide: A, prepared from diaminoguanidine nitrate; and B, prepared by independent synthesis.

Pure tetrazolyl azide (IV) is much less sensitive to shock than its alkali salts (II) and much heavier impacts are required to detonate it. The presence of the azide group[11] was established by infrared absorption studies and reduction with hydrogen sulfide. Infrared curves of several known azides were obtained (Table I) and compared with that of tetrazolyl azide (IV). The azide band has been assigned as 4.67 μ by Randall and coworkers.[12] Such a band was obtained in all the known azides and in tetrazolyl azide (Table I). The reduction of tetrazolyl azide (IV) by hydrogen sulfide gave 5-aminotetrazole (V). This procedure has been shown to give amines from azides, first by Thiele[8] who reduced guanyl azide nitrate to guanidine and later by Hantzsch,[13] Turrentine,[14] and Hart.[15]

The characterization of the potassium (or sodium) tetrazolyl azide (II), derived from diaminoguanidine (I) was completed by converting tetrazolyl azide (IV) to its potassium salt by treatment with potassium acetate (IV to II). Comparison of the infrared absorption spectra of the products prepared by both methods (Fig. 1) shows the two to be identical.

The explosive nature of the alkali salts of tetrazolyl azide made the direct determination of the yield very difficult and dangerous.[16] The best estimates obtainable, using a concentration of 20 millimoles of diaminoguanidine nitrate in about 40 ml. of water, was 25 to 40%. The observation that a gas was evolved in

TABLE I

SUMMARY OF FREQUENCIES

Compound	Wave length, μ				
Potassium tetrazolyl azide					
(1) from diaminoguanidine	4.69	8.1	8.5	8.9	9.6
(2) from tetrazolyl azide	4.69	8.1	8.5	8.9	9.6
Sodium azide	4.70				
Tetrazolyl azide					
(3) from tetrazolylhydrazine	4.65	7.9	8.45	9.1	9.6
Guanyl azide nitrate[8]	4.68	6.0			

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[8] J. Thiele, *Ann.*, **270**, 1 (1892).

[9] J. Thiele and H. Ingle, *ibid.*, **287**, 233 (1895).

[10] K. A. Hofmann, H. Hock and R. Roth, *Ber.*, **43**, 1087 (1910).

[11] Thiele's (ref. 9) proof for the presence of the azide group comprised treating his compound for several hours with strong KOH, acidifying and distilling off the hydrazoic acid which was characterized only by the appearance of the silver salt and the odor of the hydrazoic acid.

[12] H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 51.

[13] A. Hantzsch and A. Vagt, *Ann.*, **314**, 339 (1900).

[14] Turrentine, THIS JOURNAL, **34**, 285 (1912).

[15] C. V. Hart, *ibid.*, **50**, 1922 (1928).

[16] On one occasion approximately 0.1 g. of II was being filtered when it exploded violently, due to the force of suction, completely shattering the Buchner funnel. At no time were more than 30 mg. of II handled in any one experiment.

the reaction, coupled with the fact that a large amount of starting material was still unaccounted for made an examination of the reaction for by-products desirable.

The method chosen for the determination of the explosive alkali salt of tetrazolyl azide (II) comprised its reduction by hydrogen sulfide to the more stable 5-amino-tetrazole (V), which was isolated and weighed. The volume of gaseous products evolved in the diazotization process, after scrubbing with 50% aqueous potassium hydroxide, was collected and measured. The composition of the gas was determined by mass spectrometric and infrared absorption techniques. The mass spectrometric analysis showed the presence of approximately *equal volumes* of nitrogen and nitrous oxide. The presence of nitrous oxide was readily confirmed by the infrared absorption spectra of the evolved gas. Infrared spectra of the evolved gas without potassium hydroxide scrubbing were similar, an accentuation of the nitrous oxide bands being obtained. The results of the gas evolution studies are summarized in Table II which is in the nature of a "diaminoguanidine balance" for the reaction. The total diaminoguanidine accounted for is based on the number of millimoles of nitrogen and 5-aminotetrazole recovered. All of the reactions summarized in Table II are based on the reaction of diaminoguanidine with two molar proportions of nitrous acid in the presence of the required amount of acetic acid. Due to the fact that only small quantities of 5-aminotetrazole were handled in these experiments, it is probable that the diaminoguanidine balances are low by about 10%. The inorganic salts accompanying these reactions contained small unknown amounts of 5-aminotetrazole which could not be recovered. The results of these experiments bring out the important fact that the amount of gaseous decomposition products *increases markedly* as the concentration of the reagents in the reaction mixture increases. The practical results of these studies indicated that the yields of isolated 5-aminotetrazole (IV) were highest in the more dilute solutions, and repetition of these reactions using large quantities of diaminoguanidine nitrate (0.05 mole) gave average yields of 5-aminotetrazole of 77%.

TABLE II

DIAMINOGUANIDINE BALANCE

Reaction[a]		Products			Total diaminoguanidine accounted for	
Millimoles diaminoguanidine[b]	Ml. H_2O used	Nitrogen millimoles[e]	5-Aminotetrazole[c] Millimoles	Yield, %	Millimoles	Per cent.
1.1	40	0.17	0.48	43.7	0.65	59.1
2.0	40	0.38	0.46	23.0	0.84	42.0
3.0	40	0.53	0.91	30.3	1.44	40.0
4.0	40	0.73	2.25	56.3	2.98	74.5
7.3	40	+2.2[d]	2.62	35.9	+4.82	+68.9
2.0	120	0.16	1.47	73.5	1.63	81.5

[a] Reaction of diaminoguanidine with two molar proportions of nitrous acid at 0°. [b] As the nitrate salt. [c] At the completion of the gas evolution the reaction was allowed to stand at 5° for 24 hours and then reduced with hydrogen sulfide. [d] This represents the complete capacity of the gas buret, the evolved gas was still rapid at this point. [e] One-half the total volume of gas measured.

Reaction with One Mole Proportion of Nitrous Acid.—The reaction of diaminoguanidine nitrate (I) with one molar proportion of nitrous acid in acetic acid media resulted chiefly in the recovery of the diaminoguanidine to the extent of 80 to 95% and the isolation of a small quantity of potassium tetrazolyl azide (II). Because of the small quantity of potassium tetrazolyl azide involved, the exact yield was difficult to determine. However, by using the reduction technique yield values up to 6% tetrazolyl azide were obtained for the one mole nitrous acid reaction. This, together with the recovered diaminoguanidine, gave a practically complete material balance.

Experimental[17]

Diaminoguanidine Nitrate (I).—This compound was prepared from thiosemicarbazide according to a procedure adapted from the preparation of N-alkyl-N′-aminoguanidines[18] and developed at the U. S. Naval Ordnance Test Station, Inyokern, China Lake, California. (Private communication.)

Anal. Calcd. for $CH_8O_3N_6$: N, 55.26. Found: N, 54.90.[19]

Reaction of Diaminoguanidine Nitrate with Nitrous Acid. A. Buffered Acetic Acid: 1. Potassium Tetrazolyl Azide (II).—A solution of 3.04 g. (0.02 mole) of diaminoguanidine nitrate, 1.47 g. (0.015 mole) of potassium acetate and 1.74 g. (0.029 mole) of glacial acetic acid in 30 ml. of water was prepared and cooled to 0° (some solid reprecipitated). A solution of 3.74 g. (0.044 mole) of potassium nitrite in 10 ml. of water was added slowly keeping the temperature at 0–5°. The solution thus obtained was allowed to stand in an ice-box for two to four days. It was then evaporated nearly to dryness under vacuum (water aspirator) and in a stream of pure nitrogen.[20] Long, white, prismatic needles of potassium nitrate were filtered off and washed with ethanol.[21] An additional small amount of potassium nitrate came out of the filtrate on the addition of alcohol and was also filtered off. The filtrate was evaporated to dryness on a *steam-bath* and the yellow solid obtained was washed with absolute ether to remove the acetic acid and then extracted with acetone. The residue consisted of salts and was discarded.

Absolute ether was added to the yellow acetone solution to the cloud point and allowed to stand. Fine cream-colored needles formed and were filtered, and the filtrates saved. These needles were dissolved in the minimum amount of acetone and reprecipitated by the addition of absolute ether. This time beautiful, shiny white plates of potassium tetrazolyl azide (II) were obtained. Further purification was effected in the same manner. By adding more absolute ether to the filtrates an additional amount of product was obtained.

Potassium tetrazolyl azide explodes violently when heated in a flame, giving a purple color. It will also explode when placed on a hot melting-point bar (60° or above), but when heated slowly it is stable to about 200° unless touched with a spatula. It can also be detonated by light pressure.

Anal. Calcd. for CN_7K: N, 65.74; K, 26.17. Found: N, 66.75; K, 25.66.

2. **Sodium Tetrazolyl Azide.**—The procedure described above for the preparation of the potassium salt was followed exactly except that sodium nitrite and sodium acetate were used. However, the difference in the solubility of some of the salts made it more difficult to purify this material. Shiny white plates were obtained and their properties were similar to those of potassium tetrazolyl azide.

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(17) All melting points are uncorrected.

(18) G. W. Kirsten and G. B. L. Smith, THIS JOURNAL, **58**, 800 (1936).

(19) Micro-analyses by Micro-Tech Laboratories, Skokie, Illinois.

(20) L. F. Fieser, THIS JOURNAL, **46**, 2639 (1924).

(21) If absolute ethanol or acetone is used, the resulting solutions tend to be explosive due to extraction of too large amounts of the inert salts.

Anal. Calcd. for CN_7Na: N, 73.89. Found: N, 72.73.

B. Reaction in Acetic Acid.—The procedure used for this reaction was similar to the procedure used for the buffered acetic acid reaction. In this case 0.02 mole of diaminoguanidine nitrate to 0.022 mole of glacial acetic acid was used. The infrared spectra of the products of the buffered acetic acid and the acetic acid reactions are identical.

Preparation of Potassium Tetrazolyl Azide (II) from Tetrazolyl Azide (IV): Tetrazolyl Azide (IV).—A solution of 2.3 g. (0.023 mole) of tetrazolyl hydrazine[9] (III) (*Anal.* Calcd. for CH_4N_6: N, 83.97. Found: N, 83.77) and 2 g. (0.029 mole) of sodium nitrite in 100 ml. of water was prepared. It was cooled to 5° and 5 ml. of concentrated hydrochloric acid was added. There was a small amount of gas evolution and the solution turned a cloudy yellow. The mixture was filtered and evaporated to dryness on a steam-bath. The light yellow plates thus obtained were extracted with acetone and the yellow acetone solution on evaporation to dryness at room temperature gave a yellow solid. This solid was heated with benzene and a brown oil formed on the bottom. When the benzene layer was decanted off and cooled, long white needles were obtained. The brown oil was discarded. The yield for two runs was 20–22%. When the brown oil was extracted with more benzene, the yield was raised to 45–48%. The white needles melted sharply without decomposition at 72–73° and exploded when heated in a flame or placed on a hot bar, 217° or over. Tetrazolyl azide (III to IV) is also obtained as fine white needles from chloroform and carbon tetrachloride. It is very soluble in water, absolute ethanol or absolute ether (Thiele[9] reported his product to be insoluble in ether).

Anal. Calcd. for CHN_7: N, 88.29. Found: N, 88.20.

Potassium Tetrazolyl Azide (II).—A solution of 0.35 g. (0.0031 mole) of tetrazolyl azide (IV) and 0.35 g. (0.0036 mole) of potassium acetate in 20 ml. of water was heated gently for a few minutes. The solution was cooled and extracted with ether to remove the acetic acid formed. The layers were separated and potassium chloride was added to the aqueous layer. The solution was evaporated to dryness on a steam-bath. White crystals were obtained and were extracted with acetone. Addition of absolute ether to the solution precipitated the product as shiny white plates. Its explosive properties were similar to those of the compound prepared from diaminoguanidine nitrate. Comparison of the infrared absorption spectra of these compounds (Fig. 1) showed them to be the same.

Anal. Calcd. for CN_7K: K, 26.17. Found: K, 26.06.

Reduction of Potassium Tetrazolyl Azide (II) and Tetrazolyl Azide (IV) to 5-Aminotetrazole (V): A. Reduction of Product (II) from Diaminoguanidine Nitrate.—A stream of hydrogen sulfide was bubbled through a solution of 0.2 g. (0.0013 mole) of (II) in 12 ml. of water for 15 minutes. The solution became cloudy immediately due to the formation of colloidal sulfur. The mixture was heated to coagulate the sulfur and then filtered. The filtrate was acidified with dilute nitric acid and concentrated to about 1 ml. White plates in 80% yield were obtained. Upon recrystallization from water long white prisms of 5-aminotetrazole were obtained, m. p. 199° (reported[8] 199°). The product was dried over phosphorus pentoxide under vacuum prior to analysis. A similar procedure with IV gave the same substance in 70% yield.

Anal. Calcd. for CH_3N_5: N, 82.35. Found: N, 83.07.

Measurement of Gaseous Decomposition Products.—The apparatus used for conducting the diazotization reaction and simultaneously collecting and measuring the volume of gaseous decomposition products was essentially that described by Siggia and Lohr.[22] The reaction was carried out in an atmosphere of carbon dioxide and the gaseous decomposition products were swept by a stream of carbon dioxide to a 100-ml. azotometer where it was collected over 50% potassium hydroxide.

To determine the extent of tetrazolyl azide formation, a stream of hydrogen sulfide gas was passed through the reaction mixture, after removal from the gas-collecting device. The 5-aminotetrazole was isolated, as described above, and weighed. Table II summarizes the data obtained.

Synthetic Method for 5-Aminotetrazole (IV).—A solution of 7.60 g. (0.05 mole) of diaminoguanidine nitrate and 3.3 g. (0.055 mole) of glacial acetic acid in 1900 ml. of water was prepared and cooled to 5°. A solution of 7.60 g. (0.11 mole) of sodium nitrite in 100 ml. of water was added slowly maintaining the temperature at 5 to 10°. The solution was allowed to stand at 5° overnight. Hydrogen sulfide was then bubbled through until no more sulfur precipitated out. The volume of the solution was reduced to 50 ml. and cooled. White crystals of 5-aminotetrazole weighing 3.85 g. resulted, m.p. 198–199°. This was a yield of 74.8%. A second preparation gave a 79.8% yield.

For analysis a portion of the product was recrystallized from water and dried in vacuum over phosphoric anhydride.

Anal. Calcd. for CH_3N_5: N, 82.33. Found: N. 82.18.

Reaction of Diaminoguanidine Nitrate with One Mole Proportion of Nitrous Acid.—A solution of 3.04 g. (0.02 mole) of diaminoguanidine nitrate and 1.32 g. (0.022 mole) of glacial acetic acid in 40 ml. of water was heated to 50°. A solution of 1.64 g. (0.02 mole) of sodium nitrile in 10 ml. of water was added slowly, while maintaining the temperature at 50°. Gaseous decomposition products were evident. After 40 minutes reaction at 50°, the solution was cooled to room temperature and 4.24 g. (0.04 mole) of benzaldehyde was added with stirring. A large amount of curdy white precipitate formed. It was filtered and washed, first with water and then with ether to remove excess benzaldehyde. Upon two recrystallizations from water very fine cotton-white needles of dibenzaldiaminoguanidine nitrate were obtained; yield 5.22 g. (80%), m.p. 210 to 212° (reported,[4] 211 to 212°). A mixed melting point with an authentic sample prepared from diaminoguanidine nitrate showed no depression.

The filtrate was extracted with ether three times to remove excess benzaldehyde and then treated with hydrogen sulfide as described in the previous reduction experiments. Yield of 5-aminotetrazole was 0.13 g. (6%). Examination of the mother liquors yielded only inorganic salts.

Other experiments in which diaminoguanidine nitrate was treated with one molar proportion of nitrous acid under the conditions described above and in the temperature range of 5 to 40°, yielded 90 to 95% of the starting material and only traces of tetrazolyl azide (0.5 to 2.0%).

Infrared Spectra.—The infrared absorption spectra were measured for us by Lorna J. Patterson of the Armour Research Foundation, in a Perkin-Elmer Spectrometer Model 12C. The sample in Nujol slurry, was contained in a sodium chloride cell. Modified (removal of CO_2 and H_2O bonds) tracings are reproduced in full in Fig. 1. The Nujol bands are at 3.5, 6.95, 7.3 and 13.85 μ. The spectral data for the gaseous decomposition products are summarized in Table III. As can be observed, all of the strong and medium bands given for nitrous oxide are found in the unknown gas. The mass spectrometer

TABLE III

SPECTRAL DATA: COMPARISON OF ABSORPTION FREQUENCIES (WAVE NUMBERS) OF N_2O AND UNKNOWN GAS

From Herzberg for N_2O^b	Unknown gas	From Herzberg for N_2O^b	Unknown gas
579 m.	692 w.	1867 w.	
589 v.s.	743 w.	2223 v.s.	2223^a v.s.
	935 w.	2461 m.	2500^a w.
	970 w.	2563 m.	2563^a m.
1167 m.	1163^a w.	2798 w.	2858 w.
	1189 w.	3365 w.	2983 w.
1285 v.s.	1283^a w.	3481 m.	3505^a m.
	1308 v.s.	4419 w.	
		4734 w.	

[a] N_2O absorption bands. [b] v.s., very strong; m., medium; w., weak.

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[22] S. Siggia and L. G Lohr, *Anal. Chem.*, **21**, 1202 (1949).

analysis[23] showed the presence of 49.9% nitrogen and 50.1% nitrous acid.

Solubility of Nitrous Oxide in Potassium Hydroxide Solution.—In order to correct the mass spectrometer analysis for the solubility of nitrous oxide in 50% potassium hydroxide solution under the conditions used for the measurement of the volume of the gaseous decomposition products, measured volumes of pure nitrous oxide were bubbled through the azotometer (in the absence of carbon dioxide). The average loss of the nitrous oxide after bubbling through approximately 110 ml. of 50% potassium hydroxide solution was 2.15%.

Acknowledgment.—The interest and support of the U. S. Naval Ordnance Test Station, China Lake, California, under Research Contract N 1235-61517, Task Order No. 1 is gratefully acknowledged.

CHICAGO, ILLINOIS RECEIVED OCTOBER 30, 1950

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[23] By Consolidated Engineering Corporation, Pasadena, California.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Rearrangement in the Reaction of 2,3,4-Trimethyl-3-pentanol with Hydrochloric Acid; Chlorination of 2,3,4-Trimethylpentane[1]

BY HERBERT C. BROWN AND ROSLYN SILBER FLETCHER[2]

Hydrochloric acid reacts at room temperature with 2,3,4-trimethyl-3-pentanol to give a product, presumably 3-chloro-2,3,4-trimethylpentane. However, hydrolysis of the product in 80% ethanol results in complex kinetic data which can be analyzed into two first order rate constants, $k_1^\alpha = 0.481$ hr.$^{-1}$ and $k_1^\beta = 0.0315$ hr.$^{-1}$. The product is therefore postulated to contain two components. The alpha component constitutes 22.9% of the reaction mixture; the beta, 77.1%. Photochemical chlorination of 2,3,4-trimethylpentane at 25° yields a product which also shows the existence of two isomeric tertiary chlorides: $k_1^\alpha = 0.460$ hr.$^{-1}$, $k_1^\beta = 0.0299$ hr.$^{-1}$. In this case the alpha component constitutes 33.1% of the reaction mixture; the beta, 66.9%. Assuming statistical chlorination of the available tertiary hydrogen atoms, the alpha component must be 3-chloro-2,3,4-trimethylpentane; the beta component, 2-chloro-2,3,4-trimethylpentane. The ratio of primary to tertiary substitution in the hydrocarbon is 1:3.7.

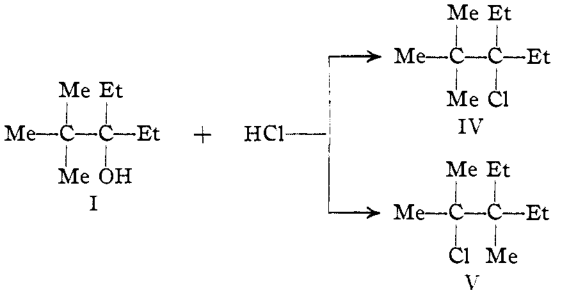
In an earlier investigation a series of twelve tertiary alkyl halides was prepared for examination of the postulated effect of steric strain on the rates of hydrolysis.[3] In the course of this study it was observed that the tertiary chlorides prepared from highly branched tertiary alcohols did not exhibit the simple first order kinetics usually observed in the solvolysis of tertiary halides.[4]

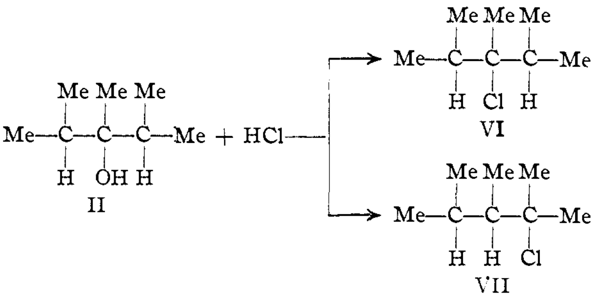
Thus the alkyl chlorides derived from 2,2-dimethyl-3-ethyl-3-pentanol (I) and from 2,3,4-trimethyl-3-pentanol (II) yielded rate data which could be analyzed into two simultaneous first order reactions. It was postulated that treatment of each of the highly branched tertiary alcohols with hydrochloric acid led to the formation of two different tertiary chlorides, the expected product (IV, VI) and a rearranged product (V, VII).

It was the purpose of the present investigation to study this phenomenon in more detail and to examine the validity of the proposed interpretation by establishing structures for the postulated isomeric halides.

Attempts to separate the isomeric tertiary chlorides into pure components offered great experimental difficulties. The isomers apparently boil quite close together. They are relatively unstable and cannot be subjected to long exposure to elevated temperatures such as are encountered in highly efficient fractionation columns. Classical methods of structure determination were therefore abandoned in favor of another, simpler approach—the photochemical chlorination of 2,3,4-trimethylpentane (III).

There is ample evidence that the chlorination of





aliphatic hydrocarbons does not lead to rearrangement of the carbon skeleton.[5] Therefore the chlorination of 2,3,4-trimethylpentane should yield the same two tertiary chlorides, 3-chloro- (VI) and 2-chloro-2,3,4-trimethylpentane (VII), previously postulated to be present in the product obtained from 2,3,4-trimethyl-3-pentanol.

Since the relative ease of chlorination of tertiary hydrogen atoms is essentially constant in paraffinic hydrocarbons,[6] the two chlorides should be present in the ratio VI : VII = 1:2. Thus, a study of the hydrolysis of the chlorinated product should indicate the presence of two tertiary chlorides whose rate constants should agree with those obtained

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[1] Chemical Effects of Steric Strains. V.

[2] Standard Oil Company (Indiana) Fellow at Purdue University, 1947-1949.

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