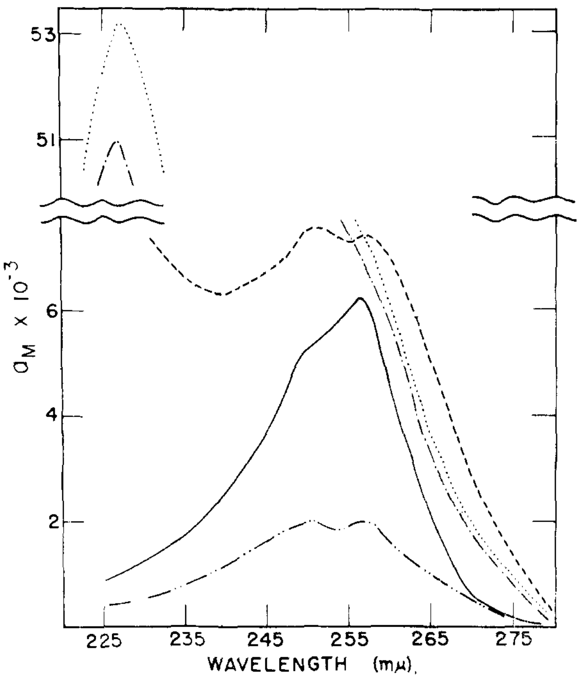

Fig. 2.—Absorption spectra of pyridine and of pyridine compounds in acetonitrile: - · - · - ·, pyridine; ———, $PyHClO_4$; - - - -, Py_2IClO_4; . . . . ., $PyHICl_2$; - · · · -, PyICl.

sorptivity of ICl_2^-. It is seen that this value agrees closely with that obtained for the BP-$HICl_2$ complex.

On the other hand, the iodine monochloride complex again yields variable molar absorptivities, varying from 45,000 to 51,000 at 227 mμ, but the variations seem to be much less pronounced than in the case of BP. Continuous variation method on the pyridine–iodine monochloride system in the 300–400 mμ region gave a series of sharp maxima at a 1:1 mole ratio of reacting species. Since, in this case, the molar absorptivity of the positive iodine complex with pyridine is known, it is possible to estimate the absorbance due to the ICl_2^- ion alone.

At 227 mμ, the molar absorptivity for a 4.3×10^{-5} *M* solution of Py·ICl is 44,400, calculated on the basis of the ICl_2^- ion. At this wave length, Py_2I^+ has a molar absorptivity of 8,500 which leaves 35,900 for the molar absorptivity of ICl_2^-. These results indicate that we have a dissociation of the Py·ICl complex according to

$$2\text{P·yICl} \rightleftarrows Py_2I^+ + ICl_2^-$$

and that in 4.3×10^{-5} *M* solution it occurs to the extent of ~ 70%.

Numerous spectrophotometric studies have been done in the past on solutions of iodine in pyridine.[15] Although in some cases evidence was obtained that the triiodide ion was formed in such systems, in general, it was assumed that the absorption was due to the PyI^+ ion. It seems from the results obtained in this investigation that two molecules of pyridine are coördinated to the positive iodine. The fact that positive iodine can have a coördination number of two is confirmed by the existence of such compounds as $Py_2{\cdot}IClO_4$, $Py_2{\cdot}INO_3$, etc.[10] Because of the time-dependent change in the absorption spectra of solutions containing iodine monochloride, exact quantitative calculations of the equilibria constants for the reactions described in this report seem to be impossible at the present time. The reasons for this change are now being investigated in this Laboratory.

Acknowledgment.—The authors wish to thank Mr. W. A. Deskin, Mr. R. H. Rygg and Mr. F. B. Stute for keeping them supplied with iodine monochloride and purified acetonitrile throughout this investigation.

[15] (a) G. Kortum and H. Wilski, *Z. physik. Chem.*, **202**, 35 (1953); (b) R. Zingaro, C. A. VanderWerf and J. Kleinberg, THIS JOURNAL, **73**, 88 (1951); (c) J. Kleinberg, E. Colton, J. Sattizahn and C. A. VanderWerf, *ibid.*, **75**, 447 (1953); (d) C. Reed and R. S. Mulliken, *ibid.*, **76**, 3869 (1954).

IOWA CITY, IOWA

[CONTRIBUTION FROM THE INORGANIC CHEMISTRY BRANCH, CHEMISTRY DIVISION, U. S. NAVAL ORDNANCE TEST STATION]

Alkylhydrazines. I. Formation of a New Diazo-like Species by the Oxidation of 1,1-Dialkylhydrazines in Solution

BY WILLIAM R. MCBRIDE AND HOWARD W. KRUSE

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It has been found that 1,1-dialkylhydrazines react with alkali halates and halogens in acidic media to form a new class of diazo-like compounds, $R_2N^+{=}N^-$, which exhibit remarkable stability as their conjugate acids, $R_2N^+{=}NH$, but in neutral or basic solution immediately dimerize to form tetraalkyltetrazenes, $R_2NN{=}NNR_2$. For example, the oxidation of 1,1-dimethylhydrazine with iodine or bromine in neutral or weakly basic solution at 0° involves a two-electron change and produces tetramethyltetrazene in essentially quantitative amounts. In acidic solution at 0° the reaction of 1,1-dimethylhydrazine with potassium iodate or bromate consumes two equivalents of oxidant and forms a diazo-like compound which can be either reconverted quantitatively by stannous chloride to 1,1-dimethylhydrazine or converted quantitatively to tetramethyltetrazene by careful neutralization of the freshly prepared acidic solutions at low temperatures. Evidence for the formation of this class of diazo-like compounds is interpreted on the basis of the present experimental data and related to the previously postulated reactions for the oxidation of hydrazine itself. Application of this species to preparative chemistry is discussed briefly.

Introduction

Although the mechanism for the oxidation of hydrazine in solution has been partially established from experiments with isotopically distinguished nitrogen and kinetic studies,[1,2] no concerted effort has been directed toward the elucidation of the oxi-

[1] W. C. E. Higginson and P. Wright, *J. Chem. Soc.*, 1551 (1955).

[2] J. W. Cahn and R. E. Powell, THIS JOURNAL, **76**, 2568 (1954).

dation of alkylhydrazines. Earlier work on the potentiometric titration of numerous derivatives of hydrazine with potassium iodate in both hydrochloric and sulfuric acid solutions led to a partial characterization of the oxidation as to the effect of the degree and kind of substitution on the stoichiometry.[3] More recently, the titration of 1,1-dimethylhydrazine with various oxidizing agents was studied in order to obtain an unequivocal procedure for the analysis of 1,1-dialkylhydrazines.[4] Certain anomalies of the work suggested that only a complete investigation of the oxidation of 1,1-dialkylhydrazines in solution would resolve the apparent discrepancies. This paper is the first of a series concerned with the properties and reactions of alkylhydrazines. The scope of this paper[5] is limited to certain related aspects in the formation and stability of the new class of diazo-like compounds, and the interpretation of the experimental evidence presented for their existence.

Experimental

Materials.—Commercial 1,1-dimethylhydrazine (Westvaco) was purified by fractional distillation through a four-foot column packed with glass helices. 1,1-Diethyl- and 1,1-di-*n*-propylhydrazines were prepared by reduction of the corresponding nitrosodialkylamines with lithium aluminum hydride in ether.[6] The dialkylhydrazines were purified by converting them to the oxalate salts by precipitation from ether solution. These salts were then recrystallized from 95% ethanol. The dialkylhydrazines were recovered as the free bases from the oxalates by treatment with saturated sodium hydroxide solution and distillation. They were then dried with barium oxide and redistilled.

Stable salts of 1,1-dimethylhydrazine prepared included the oxalate, $(CH_3)_2NNH_2 \cdot H_2C_2O_4$, m.p. 143° (reported m.p. 142–143°),[7] the sulfate, $[(CH_3)_2NNH_2]_2 \cdot H_2SO_4$, m.p. 105°, and the picrate, $(CH_3)_2NNH_2 \cdot (NO_2)_3C_6H_2OH$, m.p. 146–147° (reported m.p. 146–147°).[3] The sulfate is hygroscopic and somewhat difficult to prepare in an anhydrous condition.

For handling small quantities of the salts or the free bases, acidified stock solutions were prepared from which aliquots were withdrawn. In this manner difficulties from air oxidation were prevented.

Tetramethyltetrazene was prepared by the oxidation of 1,1-dimethylhydrazine with mercury(II) oxide[8] in ether solution and was purified by distillation from barium oxide. The picrate derivative, $(CH_3)_2NN{=}NN(CH_3)_2 \cdot (NO_2)_3C_6H_2OH$, melted at 76–77° with decomposition.

All other materials used in this investigation were reagent grade and were used without further purification.

Spectrophotometric Studies.—All measurements were made with a Cary Model 11 MS recording spectrophotometer using 1-cm. cells.

The standard curve for a sample of tetramethyltetrazene (which was purified as noted previously, redistilled over barium oxide, and weighed in ampoules by a procedure similar to that noted elsewhere[9]) was obtained as follows: a 0.0759-g. sample was dissolved in an aqueous solution adjusted to a *p*H of approximately 11 by the addition of 2 ml. of 0.1 *N* sodium hydroxide, and diluted to 100 ml. To suitable aliquots (1–5 ml.) were added 2 ml. of 0.1 *N* sodium hydroxide and the solution diluted to 100 ml.; the resulting solution was scanned in the region of 3500 to 2000 Å. The molar absorbancy indexes, a_M, for the two peaks of maximum absorption in the ultraviolet at 2480 and 2770 Å. are, respectively, 5280 and 7156 in units of 1000 cm.²/mole. In acidic solution, the conjugate acid of tetramethyltetrazene exhibits a maximum absorption at 2360 Å. (a_M = 8920). The present work extends the reported spectra[10] for tetramethyltetrazene in aqueous solution to 2000 Å. In Fig. 1 several curves illustrate the variation of the absorption of tetramethyltetrazene as a function of *p*H. Two isosbestic points exist at 2100 and 2600 A. Essentially no further change is noted in solutions either more acidic than *p*H 3.34 or more basic than *p*H 8.89. The application of this spectrophotometric technique to the determination of the pK_b gave a value of 7.80 at 25° which was in excellent agreement with the value obtained potentiometrically.

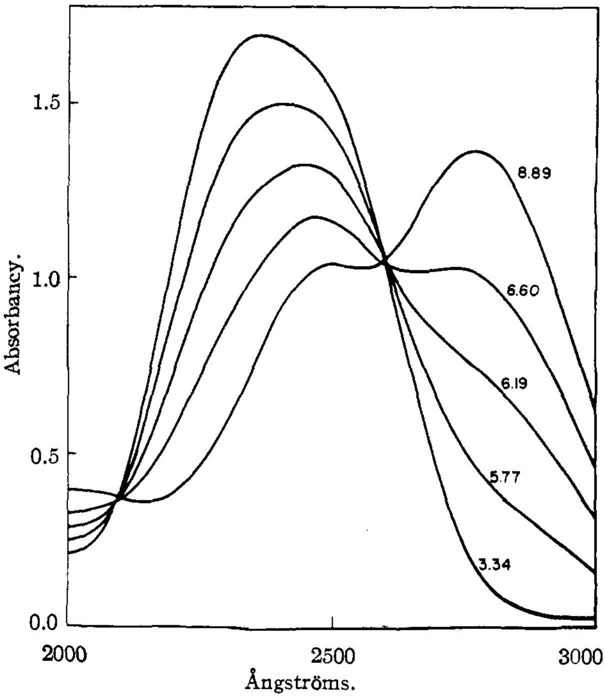

Fig. 1.—Ultraviolet absorption spectra of tetramethyltetrazene as a function of *p*H in aqueous solution at 25°: tetramethyltetrazene = 1.92×10^{-4} *M*; *p*H was adjusted with either 0.1 *N* NaOH or HCl immediately prior to scanning; data were obtained with a Cary recording spectrophotometer, model 11MS, using 1-cm. cells.

1,1-Dimethylhydrazine was characterized quantitatively by its conversion to formaldehyde-1,1-dimethylhydrazone which exhibits a maximum absorption at 2360 Å. (a_M = 5190). The detailed procedure for the application of this technique is to be described elsewhere.[11] Suitable aliquots of a standard solution are added to a reagent consisting of a buffer (which is adjusted so that the final *p*H of the solution is between 6.7 and 7.3) and an excess of formaldehyde to dimethylhydrazine corresponding to a mole ratio of about 20 to 1. Under these conditions the resulting solution is stable for periods of approximately 24 hours although in a more acidic solution the hydrazone hydrolyzes rapidly.

These techniques are applicable, in general, to other 1,1-dialkylhydrazines.

Oxidation of 1,1-Dialkylhydrazines with Halogens.—For the most part, the oxidation of 1,1-dialkylhydrazines with halogens in neutral or weakly basic aqueous solution conforms to the equation

$$2R_2NNH_2 + 2X_2 + 4OH^- \longrightarrow R_2NN{=}NNR_2 + 4H_2O + 4X^- \quad (1)$$

A typical experiment for the oxidation of 1,1-dimethylhy-

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[3] W. R. McBride, R. A. Henry and S. Skolnik, *Anal. Chem.*, **25**, 1042 (1953).

[4] L. M. Hall and H. W. Kruse, unpublished results.

[5] W. R. McBride and H. W. Kruse, presented before the Physical and Inorganic Division at the 129th National Meeting of the American Chemical Society at Dallas, Texas, April 8–13, 1956.

[6] H. Zimmer, L. F. Audrieth, M. Zimmer and R. A. Rowe, THIS JOURNAL, **77**, 790 (1955).

[7] R. A. Rowe and L. F. Audrieth, *ibid.*, **78**, 563 (1956).

[8] E. Renouf, *Ber.*, **13**, 2169 (1880).

[9] G. W. Watt and D. M. Sowards, THIS JOURNAL, **76**, 4742 (1954).

[10] G. Kortüm, *Z. physik. Chem.*, **B50**, 361 (1941).

[11] W. R. McBride and W. M. Ayres, to be published.

drazine with a standard iodine solution was carried out as follows: to 40 ml. of solution which was 0.02 *N* in hydrochloric acid concentration and contained 0.0416 g. of 1,1-dimethylhydrazine was added 0.5–1.0 g. of magnesium hydroxide. While the solution was maintained at 0–5° and blanketed with nitrogen, 0.0818 *N* iodine solution was added dropwise. The end-point could be detected either with or without the addition of starch indicator. The required volume of titrant was 17.15 ml. (theory for a two-electron change, 16.91 ml.). The final solution was diluted to 100 ml. (*p*H 9.63) and a 5-ml. aliquot withdrawn from a centrifuged sample of the solution. The aliquot was treated with 2 ml. of 0.1 *N* sodium hydroxide and diluted to 100 ml. The corrected absorbancy values at 2770 Å. for two analyses were 1.240 and 1.237 (theory 1.239).

Similar results were obtained when oxidations with iodine were performed in the presence of excess calcium carbonate. Analytical procedures for the oxidation of 1,1-dialkylhydrazines with iodine are discussed elsewhere.[7,12] In experiments with bromine and chlorine solutions, the optimum conversions to tetramethyltetrazene were 97 and 47%, respectively. In addition to spectrophotometric identification, the tetramethyltetrazene formed in the halogen oxidations was characterized by comparison of the melting points and X-ray powder patterns of the picrate derivatives with picrate derivatives of tetramethyltetrazene prepared according to the method of Renouf.[8]

The disposition of the iodine in the oxidation of 1,1-dimethylhydrazine was determined as follows: 2.25 g. of iodine in 50 ml. of anhydrous ether was added slowly to 1.60 g. of 1,1-dimethylhydrazine in 50 ml. of anhydrous ether cooled to 0° under a nitrogen atmosphere. The white precipitate of 1,1-dimethylhydrazine hydroiodide was filtered, washed with ether and dried to constant weight, yield 3.20 g. (theory 3.34), m.p. 140–141° dec. (authentic sample, m.p. 145–146° dec.). The identity was further confirmed by X-ray powder patterns which were identical for both the authentic sample and that prepared by the oxidation of 1,1-dimethylhydrazine. Tetramethyltetrazene picrate, m.p. 77–77.5° dec., was semi-quantitatively isolated in approximately 80% yield in accordance with the equation

$$6(CH_3)_2NNH_2 + 2I_2 \longrightarrow (CH_3)_2NN{=}NN(CH_3)_2 + 4(CH_3)_2NNH_2{\cdot}HI \quad (2)$$

In a separate experiment in which piperidine (a stronger base than 1,1-dimethylhydrazine) was used in a greater than 2:1 mole ratio to 1,1-dimethylhydrazine, the reaction proceeded in a manner equivalent to eq. 1; conversion to piperidine hydroiodide was 98% and to tetramethyltetrazene at least 77%.

Oxidation of 1,1-Dialkylhydrazines with Alkali Halates.—A representative experiment for the oxidation of 1,1-dimethylhydrazine with potassium bromate in hydrochloric acid solution was carried out as follows: sixty ml. of a solution 6 *N* in hydrochloric acid contained 0.03918 g. of 1,1-dimethylhydrazine cooled and maintained at 0–5°, was titrated dropwise with 0.1000 *N* potassium bromate by procedures described.[3,12] On the addition of one drop of excess oxidant the potential changed from about 0.60 to 0.78 v. The volume of titrant used was 13.11 ml. (theory 13.04 ml.). The resulting solution was diluted to 100 ml. and kept at 0°. A 5-ml. aliquot was removed from this standard solution, diluted to 100 ml., and immediately scanned in the ultraviolet region between 3500 and 2000 Å. (curve I, Fig. 2). An additional aliquot was removed from the standard solution, adjusted to a *p*H about 11 with a sodium hydroxide solution, and diluted to 100 ml. This solution was scanned in a similar fashion as before (curve II, Fig. 2). A 50-ml. aliquot was withdrawn from this latter solution, the *p*H adjusted to about 1, subsequently diluted to 100 ml., and the solution scanned (curve III, Fig. 2). The conversion to tetramethyltetrazene from curve II, Fig. 2 was 87%. Conversions from a series of experiments ran as high as 97%.

Tetramethyltetrazene, tetraethyltetrazene and tetra-*n*-propyltetrazene were prepared in convenient amounts by the oxidation of the respective 1,1-dialkylhydrazine in acid solution with potassium bromate, neutralization, ether extraction and purification by vacuum distillation from barium oxide. The yield of pure compound recovered varied from 60 to 90%.

Anal. Calcd. for $C_4H_{12}N_4$: N, 48.23. Found: N, 47.93, 48.05. Calcd. for $C_8H_{20}N_4$: N, 32.53. Found: N, 32.91, 32.56. Calcd. for $C_{12}H_{28}N_4$: N, 24.53. Found: N, 24.53, 24.68.

Decomposition of the Diazo-like Species in Acid Solution.—Earlier work on the titration of 1,1-dimethylhydrazine indicated that on standing, oxidized solutions decomposed to form at least one product capable of reacting further with potassium iodate.[4] This continued consumption of oxidant as a function of time was measured in a preliminary manner using potassium iodate and potassium bromate in experiments at 0° and 25 ± 0.3°. Solutions were prepared containing 0.0784 g. of 1,1-dimethylhydrazine in 40 ml. of 11 *N* hydrochloric acid and were titrated potentiometrically with 0.1 *N* solutions of the oxidants in about a two-minute period. At constant intervals thereafter, the solutions were reoxidized to the potential corresponding to the initial endpoint of the titrations. The data presented for the potassium iodate titrations at 0 and 25° in Fig. 3 show the remarkable stability of the product of the two-electron oxidation of 1,1-dimethylhydrazine and the increase in the rate of its decomposition with increasing temperature. The results of the experiments with potassium bromate agreed with the results shown in Fig. 3 within experimental error. Similar experiments at other acid concentrations indicated that the rate of consumption of oxidant (beyond the two-electron change) decreased as the concentration of the hydrochloric acid was increased, *i.e.*, the stability of the diazo-like species was increased with increasing acidity.

Reduction of the Diazo-like Species with Stannous Chloride in Acid Solution.—A 1.530-g. sample of 1,1-dimethylhydrazine was added with cooling to 40 ml. of 6 *N* hydrochloric acid, the solution cooled to 0° and oxidized with potassium bromate to a two-electron change using the potentiometric procedure to detect the end-point. Stannous chloride was added as a solid in slight excess to that calculated on the basis of the 1,1-dimethylhydrazine. The solution was treated with a large excess of sodium hydroxide and distilled under vacuum. The drying procedure was repeated several times with sodium hydroxide and finally with barium oxide. The reconversion to 1,1-dimethylhydrazine on the basis of the gravimetric separation of the oxalate was about 88%.

Typical data for a spectrophotometric analysis in the reconversion to 1,1-dimethylhydrazine is as follows: potentiometric titration of 1,1-dimethylhydrazine with 0.1000 *N* potassium bromate at −5° required 26.13 ml. (theory 26.06 ml.). After the addition of a slight excess of stannous chloride, the subsequent analysis of the formaldehyde 1,1-dimethylhydrazone corresponded to 98.2% recovery of 1,1-dimethylhydrazine.

Similar data were obtained from a potentiometric titration which utilized a standard solution of stannous chloride in the reduction. This reaction is the basis of a titrimetric procedure for the analysis of 1,1-dimethylhydrazine in the presence of other derivatives of hydrazine such as methylhydrazine or hydrazine itself.[13]

Under comparable conditions tetramethyltetrazene is *not* reduced by stannous chloride to 1,1-dimethylhydrazine.

Discussion

Previously, Fischer[14] had demonstrated that two equivalents of mercury(II) oxide were consumed in the oxidation of 1,1-diethylhydrazine although the corresponding yield of tetraethyltetrazene was not determined accurately. In the present work the tetraalkyltetrazenes formed by the halogen oxidation of the respective dialkylhydrazine were determined quantitatively in basic solution by spectrophotometric procedures utilizing the absorption of these compounds at approximately 2480 and 2770 Å. Although the yield was quantitative with iodine as the oxidant and nearly quantitative with bromine, with chlorine the yield was much lower. In acidic solution the conjugate acid of these 2-tetrazenes exhibits maximum absorption at approx-

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(12) H. W. Kruse and W. R. McBride, to be published.

(13) W. R. McBride and W. M. Ayres to be published.

(14) E. Fischer and H. Troschke, *Ann.*, **A199**, 294 (1879).

imately 2360 Å. as evidenced with tetramethyltetrazene, Fig. 1. This dependence of the absorption on pH allows a rapid determination of the pK_b of the respective tetraalkyltetrazenes.

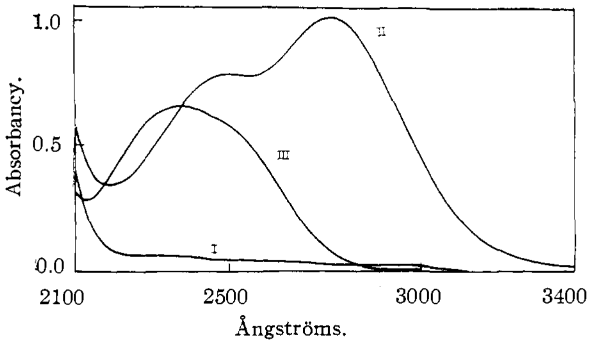

Fig. 2.—Spectrophotometric evidence for the diazo-like compound formed by the oxidation of 1,1-dimethylhydrazine with potassium bromate in acid solution. Curve I is a spectrum of the oxidized solution containing $3.26 \times 10^{-4}\ M$ diazo-like compound in 0.1 N HCl. Curve II is the spectrum of the solution after adjusting to pH 11. Curve III is the spectrum obtained when the solution from curve II is reacidified to pH 1 and diluted to twice its original volume.

In acidic solution at low temperatures the potentiometric titration of 1,1-dialkylhydrazines is stoichiometric and requires two equivalents of either potassium bromate or iodate; with potassium chlorate other conditions are required. Although tetramethyltetrazene might be the expected oxidation product, a solution of 1,1-dimethylhydrazine in hydrochloric acid freshly oxidized with potassium bromate at 0° does not exhibit the absorption at 2360 Å. characteristic of tetramethyltetrazene.

If, however, the acidic solution is carefully neutralized at low temperatures, tetramethyltetrazene is formed in nearly quantitative amounts; its reacidified solution now exhibits the characteristic absorption at 2360 Å., Fig. 2. If the initial oxidation product is allowed to stand for any period of time, decomposition occurs accompanied by gas evolution and one of the resulting products is again capable of consuming bromate or iodate, Fig. 3. Work is in progress to elucidate the nature of this decomposition reaction and to identify the products. This reaction appears to be first order and gives an approximate activation energy of 17 kcal. The rate of this decomposition is identical either in the presence or absence of the oxidizing agent, iodine monochloride. Moreover, the loss of this initial oxidation product may be followed by noting its decreased conversion to tetramethyltetrazene as the solution is aged at some constant temperature.

Preliminary data on the decomposition of tetramethyltetrazene in acidic medium indicate that the energy of activation is nearly 10 kcal. greater than that noted for the decomposition of the initial oxidation product. Furthermore, although tetramethyltetrazene is very slowly oxidized by either potassium iodate or bromate in acidic solution, its decomposition products consisting of dimethylamine, methylamine, nitrogen and formaldehyde[8] are not oxidized by either of these reagents in contrast to the species formed from the decomposition of the initial oxidation product of 1,1-dimethylhydrazine. In addition, tetramethyltetrazene is not reduced in acidic solution by stannous chloride to 1,1-dimethylhydrazine, whereas the initial oxidation product from the reaction of 1,1-dimethylhydrazine with the alkali halates and halogens is reconverted quantitatively by stannous chloride to 1,1-dimethylhydrazine. (The reduction of aromatic diazonium salts by stannous chloride in acidic solution is the customary method for obtaining the corresponding hydrazines.) Similar evidence demonstrates the generality of these reactions for other homologs of the 1,1-dialkylhydrazine series.

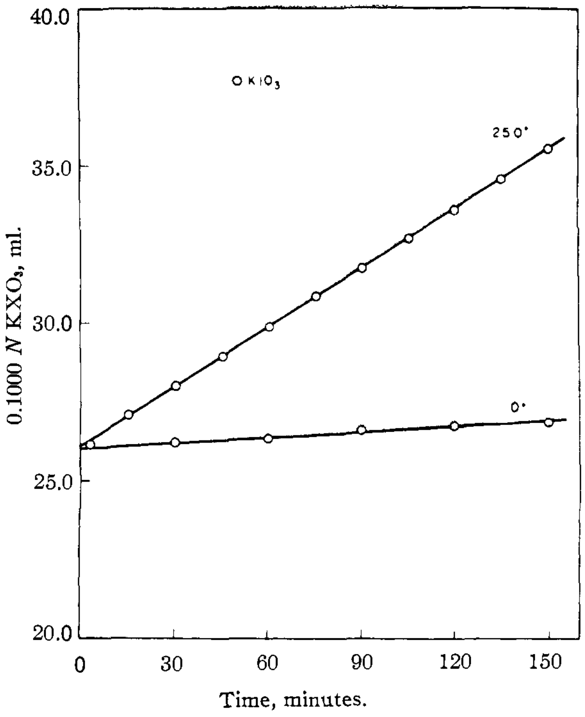

Fig. 3.—The rate of decomposition of the diazo-like compound, $(CH_3)_2N^+{=}N^-$, at an initial concentration of about $2 \times 10^{-2}\ M$ in 6 N HCl determined indirectly by the continued consumption of oxidant beyond the two-electron change.

The summation of the experimental evidence presently available suggests the following series of reactions

$$R_2NNH_3^+ \rightleftharpoons R_2N^+{=}NH + 2H^+ + 2e^- \quad (3)$$

$$R_2N^+{=}NH + OH^- \rightleftharpoons R_2N^+{=}N^- + H_2O \quad (4)$$

$$2R_2N^+{=}N^- \longrightarrow R_2NN{=}NNR_2 \quad (5)$$

Equation 3 represents the half reaction for the reversible oxidation of 1,1-dialkylhydrazines in acid solution to form the stabilized conjugate acid of the diazo-like compound whose basic form lacks suitable resonance stability as indicated in eq. 4 and immediately couples in an irreversible manner to form the tetraalkyltetrazene, eq. 5. These equations illustrate the mode of formation of mixed 2-tetrazenes such as 1,1-diethyl-4,4-dimethyltetrazene through the technique of separately oxidizing the corresponding 1,1-dialkylhydrazines in acid solution, mixing the solutions, and coupling through careful neutralization.[4]

By analogy, the oxidation of 1,1-dialkylhydrazines by halates and halogens in aqueous solution is plausibly explained by consideration of some aspects of the kinetics of the oxidation of hydrazine by iron(III) in acid solution.[1] The mechanism is represented as

$$\mathrm{Fe(III)} + \mathrm{N_2H_4} \rightleftarrows \mathrm{Fe(II)} + \mathrm{N_2H_3} + \mathrm{H^+} \quad (6)$$

$$\mathrm{Fe(III)} + \mathrm{N_2H_3} \rightleftarrows \mathrm{Fe(II)} + \mathrm{N_2H_2} + \mathrm{H^+} \quad (7)$$

$$2\mathrm{N_2H_3} \rightleftarrows \mathrm{N_4H_6} \quad (8)$$

$$2\mathrm{N_2H_3} \rightleftarrows \mathrm{N_2H_2} + \mathrm{N_2H_4} \quad (9)$$

the fast reaction, eq. 10, follows eq. 7 and 9

$$\mathrm{N_2H_2} \longrightarrow \mathrm{N_2} + 2\mathrm{H^+} + 2e^- \quad (10)$$

and the fast reaction, eq. 11, follows eq. 8

$$\mathrm{N_4H_6} \longrightarrow \mathrm{N_2} + 2\mathrm{NH_3} \quad (11)$$

The equations of Higginson and Wright were generalized to conform to the following discussion in which no conclusion is made with regard to the reverse reactions in eq. 6, 7, 8 and 9. The essential difference in the oxidation of the 1,1-dialkylhydrazines is that the oxidation ceases after the step corresponding to the formation of N_2H_2, eq. 7 and 9. However, the study with the oxidation of hydrazine and the present work substantiate the opinion that N_2H_2 or its present counterpart, $R_2N^+{=}N^-$, is the primary intermediate. Due to the stability of the conjugate acid of this counterpart, $R_2N^+{=}NH$, the rate-controlling reactions for the oxidation of 1,1-dialkylhydrazine are different than those for hydrazine.

From the previous work with isotopically distinguished nitrogen, the reaction with oxidizing agents, such as iodic acid, which gave exclusively a four-electron oxidation yielded nitrogen which was unrandomized (with oxidizing agents, which gave a one-electron oxidation of hydrazine, 50% randomization of the nitrogen occurred).[2] Thus one uncertain aspect of the oxidation mechanism for 1,1-dialkylhydrazines is that no distinction can be observed for reactions analogous to eq. 6 and 7 since halates or halogens under the described conditions behave as poly-electron oxidants. For this reason eq. 8 and 9 would be negated due to the potential two-electron change in the initial oxidation of the 1,1-dialkylhydrazine. If it were conceivable to utilize a one-electron oxidant, the equilibria corresponding to the formation of tetraalkyltetrazanes (analogous to eq. 8) and the disproportionation of the oxidation product (comparable to N_2H_3 in eq. 9) to form 1,1-dialkylhydrazine and the diazo-like compound might be a reality. Due to the rapidity with which these authors claim the decomposition of N_2H_2, eq. 10, no representation of a dimerization similar to eq. 8 was postulated. In the present situation this comparable reaction, as given in eq. 5, becomes exceedingly important. At the present time no information is available to consider a reaction analogous to that expressed in eq. 11. The distinction of the present work with regard to that for hydrazine is thus best expressed by the class of compounds, $R_2N^+{=}N^-$, the stability of this class of compounds, as their conjugate acids, $R_2N^+{=}NH$, and their ability to couple in neutral or basic solution to form tetraalkyltetrazenes, $R_2NN{=}NNR_2$. Similarity of the proposed structures to the probable resonance hybrids for diazoalkanes, $R{=}N^+{=}N^-$, covalent azides, $RN{=}N^+{=}N^-$, and diazonium ions, $RN^+{\equiv}N$, is apparent.[15]

Consideration of free radical mechanisms in the oxidation reactions are eliminated on several grounds: the long half-life of the compound, its dependence on acid concentration for stability, and the isolation from solution of its perchlorate salt in mixture with silver iodide.[16]

Recent work[17] at this Laboratory has demonstrated that the diazo-like species may provide new and novel techniques in preparative chemistry. The oxidation product of 1,2-diamino-1,2-dimethylguanidine, under conditions outlined for the oxidation of 1,1-dialkylhydrazines with potassium bromate in acidic solution, on neutralization formed 1,4-dimethyl-5-iminotetrazole in 37% yield as identified by its phenylthiourea derivative. The oxidation is stoichiometric as anticipated by the present paper and the difference is attributed to intermolecular coupling in addition to the intramolecular reaction to form the corresponding tetrazole. Utilization of the reactive species formed by the oxidation of 1,1-dialkylhydrazines has not, as yet, been extended to other types of reactions although such an extension of this work should be both of theoretical and practical interest.

CHINA LAKE, CALIFORNIA

[15] It is interesting to note that S. H. Bauer, THIS JOURNAL, **69**, 3104 (1947), considered the configuration $N^-{=}N^+F_2$ for difluorodiazine on the basis of electron diffraction data. He stated, however, that such a structure was chemically untenable because compounds of the type $(CH_3)_2N^+{=}N^-$ had not yet been synthesized.

[16] The compound $[(CH_3)_2N{=}NH]ClO_4$ has been isolated in preliminary experiments by the reaction of iodine, silver perchlorate, and 1,1-dimethylhydrazine in anhydrous ether. R. I. Walter, *ibid.*, **77**, 5999 (1955), prepared highly colored triarylaminium perchlorates by a similar procedure. In contrast to his work, the only color observed during the reaction was the loss of iodine color and the formation of a white precipitate of the perchlorate salt and silver iodide which rapidly became yellow after filtration. This precipitate was washed several times with anhydrous ether until dry. (This material ignited on the hot plate to leave a silver iodide residue and was sensitive to impact.) An extract of the perchlorate salt with absolute methanol was made basic and the conversion to tetramethyltetrazene noted by the spectrophotometric technique. The reaction was in accordance with the equation

$$\mathrm{(CH_3)_2NNH_2} + \mathrm{I_2} + 2\mathrm{AgClO_4} \longrightarrow [\mathrm{(CH_3)_2NNH}]\mathrm{ClO_4} + 2\mathrm{AgI} + \mathrm{HClO_4}$$

The only color observed during any of the reactions was a transitory red color during the neutralization reactions and may be attributed to the species $(CH_3)_2N^+{=}N^-$, which probably exists in low concentration before coupling to tetramethyltetrazene.

[17] W. R. McBride, R. A. Henry and W. G. Finnegan, *J. Org. Chem.*, in press.