PHYSICAL AND INORGANIC CHEMISTRY

[DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Radiolysis of Aqueous Solutions of Hydrazine[1,2]

BY H. A. DEWHURST AND MILTON BURTON

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In the radiolysis of air-free hydrazine solutions with Co^{60} gammas at room temperature, 100 e.v. yields are substantially independent of hydrazine concentrations above 2×10^{-2} M; the values are $G(-N_2H_4) = G(NH_3) \simeq 5.2$; $G(N_2) = G(H_2) = 2.5$. The latter are more reliable and are theoretically equal to one-half the $G(-N_2H_4)$ and $G(NH_3)$ values. The more reliable values give $G_w(H) + G_w(OH)$, the total 100 e.v. yield of free radicals from water, equal to 5.0 at pH 2, in agreement with Sworski's value 4.90. From data on radiolysis in presence of hydrogen peroxide $G_w(H_2) = 0.42$ at pH 2, in agreement with Sworski. The calculated relative rate constants for the reactions $N_4H_6 + H_2O_2 \rightarrow N_2 + N_2H_4 + 2H_2O$ (16) and $N_4H_6 \rightarrow N_2 + 2NH_3$ (4) are given by $k_{16}/k_4 = (3.5 \pm 2) \times 10^2$ l. mole^{-1}. For the reactions $H + H_2O_2 \rightarrow H_2O + OH$ (15) and $H + N_2H_5^+ \rightarrow H_2 + N_2H_4^+$ (11), calculation gives $k_{15}/k_{11} \sim 2 \times 10^3$.

1. Introduction

Numerous investigations of the radiation chemistry of water and dilute aqueous solutions are consistent with the view that the earliest detectable products ensuant on the primary physical effect include hydrogen atoms, hydroxyl radicals, hydrogen and hydrogen peroxide.[3-5] The reactions producing these earliest detectable products are generally written

$$H_2O \rightsquigarrow H + OH \qquad (R)$$

$$2H_2O \rightsquigarrow H_2 + H_2O_2 \qquad (F)$$

$$2H_2O \rightsquigarrow 2H + H_2O_2 \qquad (E)$$

and are currently employed to represent the separable stoichiometric processes.

Hydrogen atoms and hydroxyl radicals react rapidly with many solutes. Studies of the kinetics of these reactions have resulted in estimates of the 100 e.v. yield for radical production, for a long time identified with R.[6-11] Production of the molecular products, hydrogen and hydrogen peroxide (presumed to be "primary" in the sense that they are thought to be produced in the ion track itself) has also been studied by many workers and been used to calculate the yield G_F under irradiation by different bombarding particles as well as in a variety of solutions.[3] Certain discrepancies in measured values of $G_F(H_2O_2)$ and $G_F(H_2)$ ultimately led to the conclusion that a third reaction (E) was necessary for consistent treatment of the results.[5,12]

In general, the notion developed that for a specific type of irradiation (*e.g.*, Co^{60} gammas, such as used in this work), the various values G_R, G_F, G_E are invariant and not susceptible to the character or amount of solute in a low concentration range. Recently, however, Sworski has shown that this idea is incorrect and that those yields (if they have any special significance) are quite susceptible to the nature and concentration of solute in a surprisingly low range of concentration; *e.g.*, 10^{-5} M for Br^- ion.[13] We accordingly employ the nomenclature, $G_W(H)$, $G_W(OH)$, $G_W(H_2)$ and $G_W(H_2O_2)$ where the G values refer to the earliest detectable yield of the specific product from water itself (hence the subscript w), without any implications of a particular mechanism.[14]

In the work herein reported we have studied the effect of a very powerful reducing agent, *i.e.*, hydrazine, on the radiolysis of water with particular attention to possible significance for the various G_W values.

2. Experimental

2.1 **Materials.**—The water was purified by distillation from acid dichromate, followed by distillation from alkaline permanganate and collected in a Pyrex receiver. The water still was flushed with steam each time it was used and the first third of the distillate rejected. Water purity was checked on several occasions for possible organic impurities by the ferrous sulfate-chloride technique.[15]

Solutions of known hydrazine concentration were prepared with hydrazine sulfate, Eastman Kodak No. 575. J. T. Baker C.P. 30% hydrogen peroxide was used without further purification. Ferrous ammonium sulfate (J. T. Baker C.P.) and sulfuric acid (J. T. Baker analyzed reagent) were also used without further purification.

Electrolytic hydrogen and prepurified nitrogen (Mathieson Co.) were used in the preparation of known gas mixtures for calibration of the Pd tube. For hydrazine analysis p-dimethylaminobenzaldehyde (Eastman Kodak, No. 95) was used as received. The solid reagent was stable in contact with laboratory air for about six months; thereafter, it turned green and was of no use for quantitative analysis.

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[2] Paper presented before the Division of Physical and Inorganic Chemistry at the national meeting of the American Chemical Society, March 29, 1954.

[3] H. A. Dewhurst, A. H. Samuel and J. L. Magee, *Radiation Research*, 1, 62 (1954).

[4] A. O. Allen, *Disc. Faraday Soc.*, **12**, 79 (1952).

[5] A. O. Allen, *Radiation Research*, 1, 85 (1954).

[6] A. O. Allen, *J. Phys. Colloid Chem.*, **52**, 479 (1948).

[7] A. O. Allen, C. J. Hochanadel, J. A. Ghormley and T. W. Davis, *J. Phys. Chem.*, **56**, 575 (1952).

[8] C. J. Hochanadel, *ibid.*, **56**, 587 (1952).

[9] E. J. Hart, *ibid.*, **56**, 594 (1952).

[10] F. S. Dainton and E. Collinson, *Disc. Faraday Soc.*, **12**, 212 (1952).

[11] T. J. Sworski, *J. Chem. Phys.*, **21**, 375 (1953).

[12] F. S. Dainton and H. C. Sutton, *Trans. Faraday Soc.*, **49**, 1011 (1953).

[13] T. J. Sworski, THIS JOURNAL, **76**, 4687 (1954).

[14] This nomenclature was originally suggested by C. J. Hochanadel and J. A. Ghormley (private communication). In the symbolism of Hart reactions (1), (2) and (3) correspond to reactions (R), (F) and (E) of Allen. In Hart's symbolism G_1 = the number of water molecules decomposed in reaction R, etc. In Allen's symbolism the reference is to the number of product molecules produced. We may note the following equivalencies.

This paper	Hart	Allen
$G_W(H_2)$	$^1/_2G_2$	G_F
$G_W(H)$	$G_1 + G_3$	$G_R + G_E(H)$
$G_W(H_2O_2)$	$^1/_2G_2 + {}^1/_2G_3$	$G_F + G_E(H_2O_2)$
$G_W(OH)$	G_1	G_R

[15] H. A. Dewhurst, *Trans. Faraday Soc.*, **48**, 905 (1952).

All the glassware used in the preparation and irradiation of solutions was cleaned with hot nitric acid (Baker reagent) followed by steaming and finally rinsing with the purified water.

Alkaline *p*H's were adjusted with sodium hydroxide (Merck) and measured with a Beckman glass electrode (no. 290E) and Model G *p*H meter. The *p*H meter was standardized with appropriate standard buffer solutions.

2.2 Apparatus.—Solutions were deaerated by the high vacuum technique previously described,[16] and were irradiated at a temperature of ~25° with γ-rays from an approximately 300 curie (Co^{60}) source of the Ghormley–Hochanadel type.[17] A specially designed brass source and sample positioner was used to ensure reproducible geometry. Dosimetry measurements were made with standard ferrous sulfate solutions and the amount of energy absorbed in the solutions calculated using $G(Fe^{2+} \rightarrow Fe^{3+}) = 15.8$.[18]

Irradiation vessels supplied with a glass break-seal for gas analysis were made of Pyrex glass. New irradiation vessels were pre-irradiated for at least 24 hours. The volume ratio, (gas phase)/(liquid phase), was approximately unity.

2.3 Analytical.—Gas was analyzed for H_2, O_2 and N_2 using a high-vacuum micro technique employing a specially designed Pd tube and constant volume mercury diffusion pumps for transfer of gas.[19] The Pd tube was heated electrically to a temperature of ~425°. The apparatus was designed so that H_2 could be collected and measured independently of other components thus providing a useful check on the analysis. Calibration of the Pd tube with known mixtures of H_2 and N_2 showed the existence of a systematic error in the analysis; *i.e.*, the H_2 was not transferred quantitatively by the Pd tube. The calibration was found to be independent of total gas pressure and reproducible to ±1% (standard deviation).

The gas from an irradiated solution was removed over ethyl bromide mush (−119°) and pumped directly into a calibrated Saunders–Taylor apparatus.[20] The gas was then circulated over the hot Pd tube for determination of O_2 content and the H_2 separated by diffusion through the hot Pd tube. Mass spectrometric analysis of the gas evolved from irradiated solutions (in the absence of added H_2O_2) showed that the gas contained only H_2 and N_2.

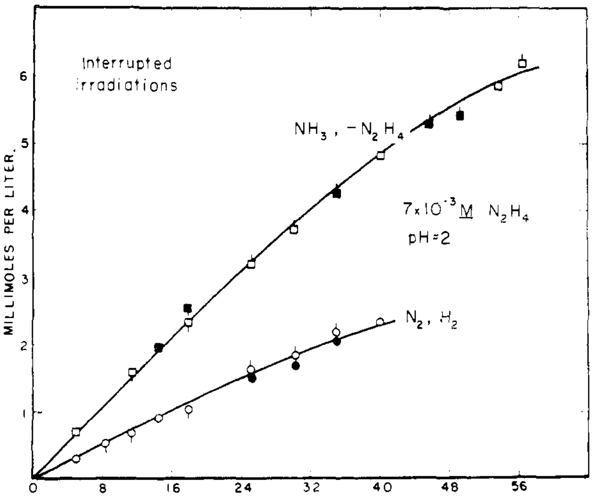

Fig. 1.—Yields of products and destruction of hydrazine as a function of irradiation time in aqueous solution originally 7×10^{-3} *M* in hydrazine at *p*H 2.0.

□, NH_3
■, $(-N_2H_4)$ irradiated 25.25 hr.; out 19.5 hr., then irradiation continued.
○, N_2
●, H_2
□, etc. irradiated 8.5 hr.; out 15.0 hr., then irradiation
■, continued.
Without flag, continuous irradiation.

The production of NH_3 was determined colorimetrically using Nessler reagent prepared according to the method of Beeghly.[21] Since hydrazine reacts with Nessler reagent it was destroyed by making the sample approximately 5 *N* in H_2SO_4 and adding an excess of KIO_3. The solution was made strongly alkaline and Nessler reagent added. The color develops immediately and was measured within five minutes with a Beckman spectrophotometer model DU at λ 410 mμ. The method was calibrated by preparing known mixtures of hydrazine and ammonium chloride. Blank analysis of the unirradiated solution was always made. The standard deviation of the ammonia analytical method was found to be ±3%.

The concentration of hydrazine was determined colorimetrically by the method of Pesez and Petit[22] as elaborated by Watt and Chrisp.[23] The reagent *p*-dimethylaminobenzaldehyde (Eastman Kodak, No. 95) was used as a 2% (weight) solution in ethanol. Since NH_4^+ ion was found not to influence the color development, the reagent was added directly to the irradiated solution which had been made 1.0 *N* in H_2SO_4. The color reached maximum intensity after approximately 10 minutes and was measured at λ 458 mμ. The spectrophotometer was calibrated with known concentrations of hydrazine prepared by solution of a weighed amount of hydrazine sulfate in purified water. The precision of the method was found to be ±3%.

3. Results

3.1 Effect of Hydrazine Concentration.—Figure 1 shows the results of a series of typical runs (at *p*H 2.0) in aqueous solution originally 7×10^{-3} *M* in hydrazine. The *G* values for hydrazine disappearance and ammonia production are equal (within the limits of experimental error) and approximately twice those of hydrogen or of nitrogen production, which are also very closely equal. The latter values are considered more reliable because they do not involve analytical difficulties peculiar to the former.

Similar groups of experiments were performed at a variety of hydrazine concentrations from 2×10^{-4} *M* to 10^{-1} *M* and in the *p*H range 1 to 13. In the initial portion of each experiment, while the hydrazine concentration remains practically constant, the yields of product per unit time are constant. In each case, the initial slope gives the initial *G* value. Figure 2 shows a plot of such *G* values for *p*H 2; they are constant above 2×10^{-2} *M* hydrazine but fall off markedly at lower concentrations. On any reasonable basis one would expect these values to extrapolate to zero at zero hydrazine concentration but such an effect is not observed in the range of concentration studied; presumably at very low hydrazine concentrations the *G* values would approach zero and indicate that the reaction is first order in hydrazine at low concentration just as it is zero order in hydrazine above 2×10^{-2} *M*.

Irrespective of the yields, the ratios of *G* values of the various products remain constant.

Data obtained at other *p*H values were not so extensive, but similar trends with hydrazine concentration were observed.

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(16) H. A. Dewhurst, *Trans. Faraday Soc.*, **49**, 1174 (1953).

(17) J. A. Ghormley and C. J. Hochanadel, *Rev. Sci. Instr.*, **22**, 473 (1951).

(18) R. M. Lazo, H. A. Dewhurst and M. Burton, *J. Chem. Phys.*, **22**, 1370 (1954).

(19) The authors are grateful to F. H. Krenz and T. J. Hardwick, Atomic Energy of Canada, Ltd., Chalk River Laboratories, for details of the Pd tube and gas analysis apparatus.

(20) K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, **9**, 616 (1941).

(21) H. F. Beeghly, *Ind. Eng. Chem., Anal. Ed.*, **14**, 137 (1942).

(22) M. Pesez and A. Petit, *Bull. soc. chim. France*, 122 (1947).

(23) G. W. Watt and J. D. Chrisp, *Anal. Chem.*, **24**, 2006 (1952).

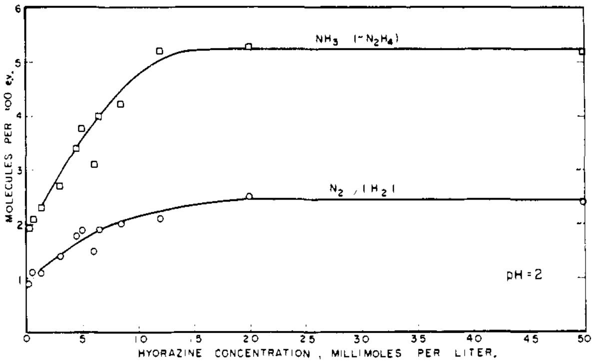

Fig. 2.—100 e.v. yields in aqueous hydrazine solution as a function of initial hydrazine concentration at *p*H 2.0: □, NH_3; O, N_2.

3.2 Interrupted Irradiation.—At one time in the course of the work it was suspected that free-radical products of radiolysis of water might interact with some relatively persistent intermediate to establish the observed rate. An intermittency effect was therefore sought. Figure 1 includes data which clearly shows the absence of such effect for two cycles of interruption and exposure. One set of data is for continuous exposure; a second is for 8.5 hours of exposure, followed by 15.0 hours "darkness," followed by further irradiation to give the total exposure indicated on the abscissa; the third is for 25.25 hours irradiation, followed by 19.5 hours "darkness," followed by irradiation to give the total exposure indicated. All the data lie on approximately the same lines irrespective of the irradiation cycle.

3.3 Effect of Products.—Figure 3 shows the results of a series of experiments on the effect of added hydrogen (pressure ~400 mm., corresponding to ~4×10^{-4} *M*) on the course of radiolysis in 2.5×10^{-4} *M* hydrazine at *p*H 2. The results are similar to those obtained in the absence of hydrogen.

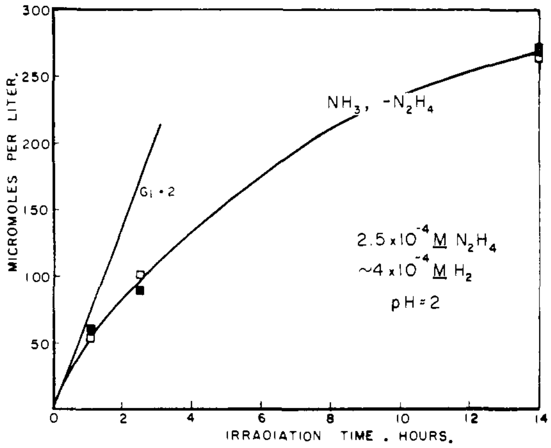

Fig. 3.—Effect of added hydrogen (~400 mm. pressure; *i.e.*, ~4×10^{-4} *M*) on yields of ammonia and nitrogen in radiolysis of 2.5×10^{-4} *M* hydrazine at *p*H 2.0: □, NH_3; ■, $(-N_2H_4)$.

Figure 4 shows that 0.02 *M* ammonium sulfate has no significant effect on radiolysis of 2.9×10^{-3} *M* hydrazine at *p*H 2.

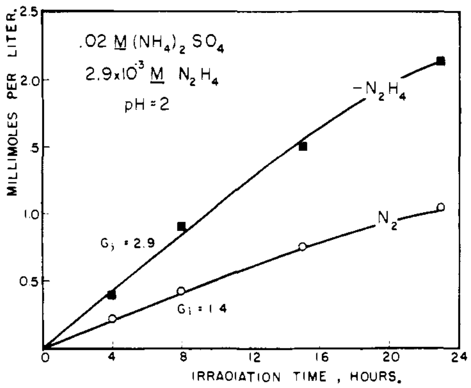

Fig. 4.—Effect of 0.02 *M* ammonium sulfate on radiolysis of 2.9×10^{-3} *M* hydrazine at *p*H 2.0: ■, $(-N_2H_4)$; O, N_2.

The only other stable product which might possibly intercede in the reaction is nitrogen. However, it is known from a variety of experiments[24] to be too stable to enter into reaction with the radicals involved in radiolysis of water.

3.4 Effect of *p*H.—Figure 5 shows the effect of *p*H on the 100 e.v. yields in 5×10^{-3} *M* hydrazine. Nitrogen and hydrogen yields are equal within experimental error over the *p*H range from 0.3 to 12.3; $G(NH_3)$ is twice as great as $G(N_2)$ and equal within experimental error to $G(-N_2H_4)$. However, the values change markedly, being approximately constant in the range up to *p*H 8 and dropping off rather rapidly at the higher values.

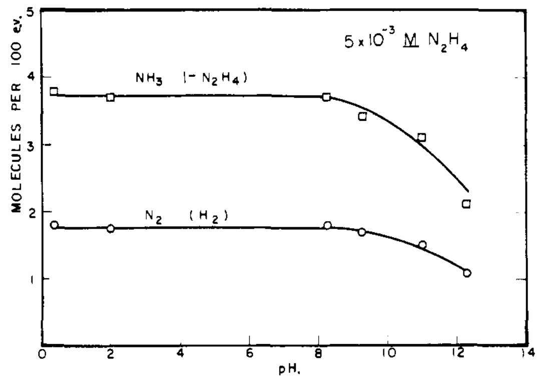

Fig. 5.—Effect of *p*H on 100 e.v. yields in radiolysis of 5×10^{-3} *M* hydrazine as a function of *p*H: □, NH_3; O, N_2.

3.5 Effect of Hydrogen Peroxide.—At *p*H 2 in the concentration range studied (up to 10^{-2} *M*), hydrogen peroxide does not oxidize 2×10^{-2} *M* hydrazine in a thermal reaction. However, Fig. 6 shows that it has a rather considerable and sharply different effect on the various *G* values. The $G(N_2)$ values are constant at ~2.5; *i.e.*, the same value obtained in the absence of hydrogen peroxide. The value of $G(H_2)$ is greatly affected. With hydrogen peroxide absent the measured $G(H_2)$ is 2.5; in 2×10^{-5} *M* hydrogen peroxide $G(H_2)$ is 1.1, drops to ~0.42 in 10^{-3} *M* hydrogen peroxide and remains constant at that value up to 10^{-2} *M*.

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[24] *Cf.* G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, Inc., New York, N. Y., 1939, p. 280.

On the other hand, although $G(\mathrm{NH_3})$ is approximately constant at ~5.2 (equal approximately to $2 \times G(\mathrm{N_2})$) independent of hydrogen peroxide up to 6×10^{-4} *M*, it drops rapidly at higher concentrations. The data on $G(-\mathrm{H_2O_2})$, *i.e.*, the 100 e.v. yield of hydrogen peroxide disappeared, are consistent with the other yields. Decrease in decomposition of hydrazine to yield ammonia is matched by increased decomposition of the peroxide.

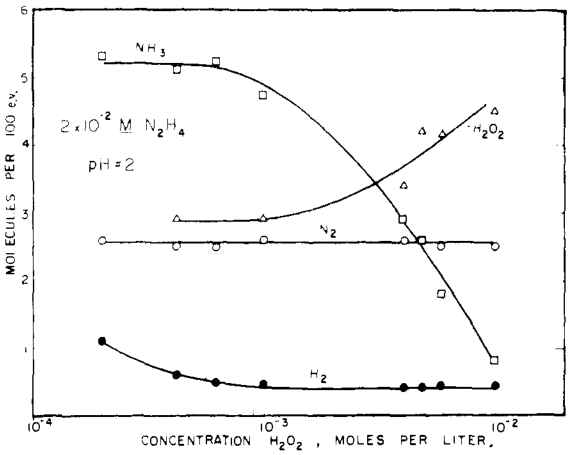

Fig. 6.—Effect of initially introduced hydrogen peroxide on yields of radiolysis of 2×10^{-2} *M* hydrazine at *p*H 2.0: □, $\mathrm{NH_3}$; ○, $\mathrm{N_2}$; ●, $\mathrm{H_2}$; △, $(-\mathrm{H_2O_2})$.

3.6 Bromide Addition.—Addition of potassium bromide in the concentration range 4.3×10^{-4} to 10^{-3} *M* at *p*H 2 had no perceptible effect on the yields of products from 1.5×10^{-3} and 5.7×10^{-3} *M* hydrazine solutions. When air-free potassium bromide solutions (concentration 4.3×10^{-3} *M* at *p*H 2) were irradiated in the absence of hydrazine, four experiments gave $G_\mathrm{W}(\mathrm{H_2}) = 0.42 \pm 0.02$.

4. Discussion

4.1 Primary Chemical Reactions.—At the concentrations employed in this study the primary reactions are in the water itself and correspond to those necessary to yield the R, F and E reactions. Because the work of Sworski[13] now clearly shows that the yields of these reactions are not invariant, it is convenient to represent the combination of primary processes by the expression

$$\mathrm{H_2O} \rightsquigarrow \mathrm{H,\ OH,\ H_2,\ and\ H_2O_2} \qquad (\mathrm{O})$$

where

$$2G_\mathrm{W}(\mathrm{H_2}) + G_\mathrm{W}(\mathrm{H}) = 2G_\mathrm{W}(\mathrm{H_2O_2}) + G_\mathrm{W}(\mathrm{OH}) \qquad (\mathrm{I})$$

All other reactions in the radiolysis of hydrazine solutions must be considered as ensuant on the over-all reaction (O).

4.2 Secondary Processes in Absence of Hydrogen Peroxide.—The simplest scheme which can be written for basic solution to explain the stoichiometry of hydrazine decomposition is

$$\mathrm{H + N_2H_4 \longrightarrow N_2H_3 + H_2} \qquad (1)^{25}$$

$$\mathrm{OH + N_2H_4 \longrightarrow N_2H_3 + H_2O} \qquad (2)$$

$$\mathrm{2N_2H_3 \longrightarrow N_4H_6} \qquad (3)$$

$$\mathrm{N_4H_6 \longrightarrow N_2 + 2NH_3} \qquad (4)^{26}$$

On the basis of these reactions

$$G(-\mathrm{N_2H_4}) = G_\mathrm{W}(\mathrm{H}) + G_\mathrm{W}(\mathrm{OH}) \qquad (\mathrm{II})$$

The reaction

$$\mathrm{OH + H_2 \longrightarrow H + H_2O} \qquad (5)$$

does not require special consideration since the total effect represented in relationship (II) is not thereby affected.

The work of Hart, Gordon and Hutchinson[27] indicates that the reaction

$$\mathrm{OH + OH^- \longrightarrow O^- + H_2O} \qquad (6)$$

is important at $p\mathrm{H} > 8$. Thus, the probability of reaction (2), as well as of all other reactions involving OH, is affected by *p*H. Decrease in the various yields, $G(-\mathrm{N_2H_4})$, etc., at high *p*H (see Fig. 5) is consistent with this requirement and at the same time indicates, as Hart, Gordon and Hutchinson have suggested, that $\mathrm{O^-}$ is not an effective oxidizing agent. Presumably, however, the reaction

$$\mathrm{O^- + H + aq \longrightarrow OH^-{\cdot}aq} \qquad (7)$$

competes favorably with reaction (1).

It has been suggested that in acid solution ($p\mathrm{H} < 2$) H atoms produced in reaction (O) enter the reaction[28]

$$\mathrm{H + H^+{\cdot}aq \rightleftharpoons H_2^+{\cdot}aq} \qquad (8)$$

so that reaction of $\mathrm{H_2^+}$ with hydrazine, as well as with $\mathrm{H_2O_2}$ produced in reaction (O), must be considered. Under the conditions of this work, $\mathrm{H_2}$ and $\mathrm{H_2O_2}$ so produced do not react with hydrazine. Judging from the hydrolysis constant,[25] the hydrazine itself is, however, affected by the acidity so that

$$\mathrm{N_2H_4 + H^+ \longrightarrow N_2H_5^+} \qquad (9)$$

A reaction such as

$$\mathrm{H_2^+ + N_2H_5^+ \longrightarrow H_2^+ + N_2H_4^+ + H} \qquad (10)$$

requires close approach of two positive charges. The fact is that the results are represented adequately by the scheme 1, 2, 3, 4 over the entire *p*H range, although reactions 1 and 2 are certainly inconsistent with the reality of reaction 9. A simple view is that the reaction

$$\mathrm{H + N_2H_5^+ \longrightarrow H_2 + N_2H_4^+} \qquad (11)$$

competes rather favorably with reaction (8)[29] and that the reaction

$$\mathrm{N_2H_4^+ + aq \longrightarrow N_2H_3 + H^+{\cdot}aq} \qquad (12)$$

ensues. For acid solution instead of reaction 2 we write simply

$$\mathrm{OH + N_2H_5^+ \longrightarrow H_2O + N_2H_4^+} \qquad (13)$$

The scheme in acid solution is then 11, 13, 12, 3, 4.

Decrease in yields at low hydrazine concentrations is probably a manifestation of competition between reactions such as 11, 13 (or 1, 2) and reactions like

$$\mathrm{H + OH \longrightarrow H_2O} \qquad (14)$$

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[25] The hydrolysis constant for $\mathrm{N_2H_4 + H_2O \rightarrow N_2H_5^+ + OH^-}$ is $\sim 10^{-6}$ (*cf.* L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, 1951, p. 156). Thus, at *p*H values ≥ 9, the $\mathrm{N_2H_4}$ is substantially in the molecular form.

[26] Reaction 4 is in reality a two-step process; *cf.* W. C. E. Higginson and D. Sutton, *J. Chem. Soc.*, 1402 (1953); J. W. Cahn and R. E. Powell, This Journal, **76**, 2568 (1954).

[27] E. J. Hart, S. Gordon and D. A. Hutchinson, *ibid.*, **75**, (1953).

[28] J. Weiss, *Nature*, **165**, 728 (1950).

[29] *Cf.* H. A. Schwarz, J. P. Losee, Jr., and A. O. Allen, This Journal, **76**, 4693 (1954), who suggest that the reaction $\mathrm{H + I_2 \rightarrow H^+ + I^- + I}$ competes favorably with reaction (8).

At high hydrazine concentrations ($>2 \times 10^{-2}$ *M*) the free H and OH produced in reaction O disappear exclusively by processes involving destruction of N_2H_4 so that it follows that

$$G(NH_3) = G(-N_2H_4) = G_W(H) + G_W(OH) \qquad (III)$$

According to Sworski,[13] at *p*H 2 the latter sum = 4.90. Our values for $G(NH_3) = G(-N_2H_4)$ are $\sim$5.2. On the basis of the same mechanism

$${}^1/_2G(NH_3) = G(H_2) = G(N_2) \qquad (IV)$$

in fair agreement with the experimental data which show $G(H_2) = G(N_2) = 2.5$. Since the latter values are considered more reliable, we note that $G_W(H) + G_W(OH)$ so calculated $= 2 \times 2.5$ or 5.0, in agreement with Sworski.

4.3. Effect of Hydrogen Peroxide.—The effects of added hydrogen peroxide are adequately represented by the scheme

$$H + H_2O_2 \longrightarrow H_2O + OH \qquad (15)$$

followed by the acid sequence 11, 13, 12, 3, 4 and an over-all reaction

$$N_4H_6 + H_2O_2 \longrightarrow 2H_2O + N_2 + N_2H_4 \qquad (16)$$

When the hydrogen peroxide concentration becomes sufficiently high, reaction 15 takes over as the only fate of H atoms so that reaction 11 is eliminated and $G(H_2)$ becomes identical with $G_W(H_2)$. Figure 6 shows that this situation occurs at H_2O_2 concentration $\geq 10^{-3}$ *M*. The value $G(H_2) = G_W(H_2) = 0.42 \pm 0.03$ in reasonable agreement with Sworski's value 0.42 at *p*H 2 and our own value of 0.42 for $G(H_2)$ in bromide solutions. Schwarz, Losee and Allen[29] give 0.45 while the data of Miller and Wilkinson[30] give $G_W(H_2) = 0.52$.

Since disappearance of H in reaction 15 is accompanied by production of an identical amount of OH, rate of production of the intermediate N_4H_6 is not affected by H_2O_2 concentration. At high H_2O_2 concentration ($>2 \times 10^{-3}$ *M*) reaction 16 begins to compete with reaction 4 as a path of disappearance of N_4H_6. Since N_2 is produced in both reactions, the value $G(N_2)$ is unaffected by H_2O_2 concentrations while the value $G(NH_3)$ must fall when reaction 16 predominates. At very high H_2O_2 concentration, $G(NH_3)$ goes to zero.[31] Thus, the scheme suggested is consistent with the results.

The data satisfy the requirement that

$$G(NH_3)_{max} - G(NH_3) = G(-H_2O_2) - G(-H_2O_2)_{min} \qquad (V)$$

although inaccuracy in the determination of $G(-H_2O_2)$ at very low concentration prevents an exact balance.

4.4. Kinetics of Radiolysis in Presence of Hydrogen Peroxide.—Reactions occurrent in radiolysis of acid hydrazine solution in presence of hydrogen peroxide may be adequately summarized by the scheme

$$\begin{array}{lr} H_2O \rightsquigarrow H, OH, H_2, H_2O_2 & (O) \\ H + H_2O_2 \rightsquigarrow H_2O + OH & (15) \\ H + N_2H_5^+ \longrightarrow H_2 + N_2H_4^+ & (11) \\ OH + N_2H_5^+ \longrightarrow H_2O + N_2H_4^+ & (13) \\ N_2H_4^+ \longrightarrow N_2H_3 + H^+ & (12) \\ 2N_2H_3 \longrightarrow N_4H_6 & (3) \\ N_4H_6 \longrightarrow N_2 + 2NH_3 & (4) \\ N_4H_6 + H_2O_2 \longrightarrow N_2 + N_2H_4 + 2H_2O & (16) \end{array}$$

Reaction 8 is omitted since in order to justify such a scheme its rate r_8 must be assumed much less than the rate r_{11}.

By the usual steady-state treatment, equations may be obtained for ratios of rate constants as

$$\frac{k_{16}}{k_4} = \left\{\frac{2G(N_2)}{G(NH_3)} - 1\right\}\frac{1}{[H_2O_2]}\ \text{l. mole}^{-1} \qquad (V)$$

$$\frac{k_{15}}{k_{11}} = \frac{[N_2H_5^+]\{G_W(H) + G_W(H_2) - G(H_2)\}}{[H_2O_2]\{G(H_2) - G_W(H_2)\}} \qquad (VI)$$

For high concentrations of hydrogen peroxide, $[H_2O_2]$ may be treated as unaffected by reaction O. Use of the data of Fig. 6 for the $[H_2O_2]$ range above 10^{-3} gives $k_{16}/k_4 = (3.5 \pm 2) \times 10^2$ l. mole^{-1}. An alternative treatment of the kinetic relationships gives

$$\frac{1}{G(NH_3)} = \frac{k_{16}}{k_4[G_W(H) + G_W(OH)]} \times (H_2O_2) + \frac{1}{G_W(H) + G_W(OH)} \qquad (VII)$$

Plot of the $1/G(NH_3)$ data against H_2O_2 concentration yields a value of the intercept = 0.16.[32] The slope of the line so obtained gives $k_{16}/k_4 = 3 \times 10^2$ l. mole^{-1}. The magnitude of this ratio indicates rather high stability of the intermediate N_4H_6.

The data for $[H_2O_2]$ above 10^{-3} are not useful for calculation of k_{15}/k_{11} but the extrapolated value for such concentrations (using the Sworski value[13] for $G_W(H)$) is $\sim 2 \times 10^3$. These ratios of rate constants are for the radiolysis conducted at approximately 25°.

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[30] N. Miller and J. Wilkinson, *Trans. Faraday Soc.*, **50**, 690 (1954).

[31] At H_2O_2 concentration approaching that of N_2H_4, the reaction $OH + H_2O_2 \rightarrow HO_2 + H_2O$ begins to compete with reaction 13 and chain decomposition of H_2O_2 (with concomitant O_2 production) sets in. This reaction is considered more fully in a later paper.

[32] The corresponding value $G_W(H) + G_W(OH) = 6.3$ may be compared with the value 5.0 obtained from the value of $G(N_2) + G(H_2)$.