[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA]

Oxidation of Hydrazine in Solution[1]

BY JOHN W. CAHN[2] AND RICHARD E. POWELL

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Non-equilibrium mixtures of ordinary hydrazine with hydrazine-N^{15} have been treated with a number of oxidizing agents, and the resulting N_2 analyzed by mass spectrometer. The N_2 arising from 4-electron oxidation is not isotopically randomized, but the N_2 from 1-electron oxidation is 50% randomized. The relative rates of 4-electron and 1-electron oxidation have been measured in the reaction of hydrazine with ferric ion. A reaction mechanism is proposed in which the first product of oxidation is a hydrazyl radical, which then suffers (a) further oxidation, (b) dismutation, or (c) dimerization.

The stoichiometry in the oxidation of aqueous hydrazine was worked out by Browne[3] and Bray[4] and their co-workers. They found three distinct reactions

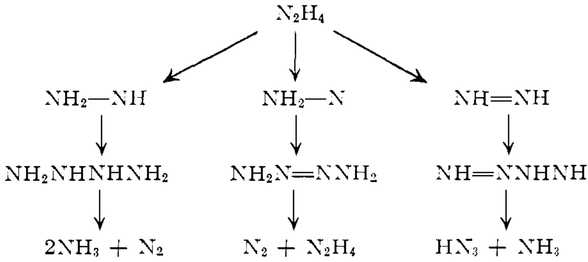
$$N_2H_5^+ = 4e^- + N_2 + 5H^+ \quad (1)$$

$$N_2H_5^+ = e^- + NH_4^+ + 0.5\ N_2 + H^+ \quad (2)$$

$$N_2H_5^+ = 2e^- + 0.5\ HN_3 + 0.5\ NH_4^+ + 2.5\ H^+ \quad (3)$$

For example, reaction 1 occurs when the oxidizing agent is acid iodate, neutral iodine or alkaline ferricyanide. Reaction 2 is approached by using ferric, ceric or manganic ion. Many oxidants give reactions 1 and 2 together. Reaction 3 is a major contributor when hydrazine is oxidized in hot, concentrated sulfuric acid with hydrogen peroxide.

The earlier investigators offered some speculations as to the mechanism of the reactions. Typical is the scheme of Kirk and Browne



which postulates a one-electron and two different kinds of two-electron primary oxidations, and involves six different hydronitrogen intermediates.[5] The data obtained in the present investigation lead to quite a different scheme.

For the first group of experiments reported here, a sample of hydrazine was synthesized from ammonia containing 63.0% of nitrogen of mass 15. To this was added a larger amount of ordinary hydrazine, and portions of the mixture were then oxidized by various oxidizing agents. The isotopic composition of the nitrogen produced was measured, to discover if it was statistically random as the mechanisms of Kirk and Browne would predict.[6]

The second experimental study reported is of the dependence of the stoichiometry of the reaction between hydrazine and ferric ion upon the concentrations of the reagents. From these data, a kinetic scheme can be set up for the oxidation.

Experimental

Synthesis of Isotopically-labeled Hydrazine.—The hydrazine was prepared by a small scale Raschig synthesis. Four millimoles of isotopically enriched ammonium nitrate (63.0 atom % N^{15}, purchased from Eastman Kodak Co.) was made alkaline with excess sodium hydroxide, and the ammonia distilled *in vacuo* into a reaction tube containing 10 cc. of water, 0.50 millimole of sodium hypochlorite and 200 mg. of gelatin. Reaction was allowed to proceed ten minutes at 80°. One millimole of ordinary hydrazine was added as a carrier, and the excess ammonia and hydrazine distilled off *in vacuo*. The yield of hydrazine was 11.5% based on ammonia consumed, which is about one half the yield obtainable in a large scale synthesis under the same conditions. Hydrazine was recrystallized from sulfuric acid, and used as solution of hydrazine sulfate.

Oxidation Procedure and Isotopic Analysis.—Portions of hydrazine sulfate solution and of the desired oxidizing agent were pipetted into a small flask with a partitioned bottom. After the contents were frozen and the flask put onto the vacuum line and evacuated, the reactant solutions were allowed to come to the desired temperature and then mixed by rotating the flask. The reaction temperature was 25°, except with ferric ion where it was 80°. After the reaction had subsided, the solution was frozen and the gas pumped into a sample bulb with a Toepler pump. Isotopic analysis was carried out on a Consolidated ratio-type mass spectrometer. We are indebted to Professor C. C. Delwiche for the mass spectrometric analyses. The following oxidizing agents were used: *Iodate*, IO_3^- 0.017 *M*, H^+ 2 *M*, $N_2H_5^+$ 0.02 *M*; *Ferricyanide*, $Fe(CN)_6^{---}$ 0.067 *M*, OH^- 0.8 *M*, N_2H_4 0.02 *M*: *Ceric*, Ce^{+4} 0.04 *M*, H_2SO_4 0.8 *M*, $N_2H_5^+$ 0.013 *M*; *Ceric with cupric*, Ce^{+4} 0.057 *M*, Cu^{++} 0.057 *M*, H_2SO_4 0.8 *M*, $N_2H_5^+$ 0.018 *M*; *Permanganate*, MnO_4^- 0.0605 *M*, H_2SO_4 0.18 *M*, $N_2H_5^+$ 0.03 *M*; *Ferric*, Fe^{+++} 0.54 *M*, $N_2H_5^+$ 0.03 *M*; *Ferric with cupric*, same as preceding, but with Cu^{++} 0.066, 0.13, or 0.92 *M*; *Peroxysulfate*, $S_2O_8^{--}$ 0.12 *M*, H_2SO_4 6.8 *M*, $N_2H_5^+$ 0.06 *M*. In all cases the stoichiometry of the oxidation was determined by suitable titration of the excess oxidizing agent.

Stoichiometry of the Reaction of Hydrazine with Ferric Ion.—Reaction mixtures were made from stock solutions of hydrazine sulfate and of ferric sulfate (or ferric ammonium sulfate) adjusted to the desired *p*H. In all experiments the ferric was present in large excess. Reaction was allowed to proceed at 50° for several days, since the theoretical treatment of the data required that the reaction be substantially

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[1] This work constitutes part of a thesis submitted by John W. Cahn to the Graduate School of the University of California in partial fullfilment of requirements for the degree of Ph.D., 1952.

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[3] A. W. Browne, THIS JOURNAL, **27**, 551 (1905); A. W. Browne and F. F. Shetterly, *ibid.*, **29**, 1305(1907); **30**, 53 (1908); **31**, 221 (1909); **31**, 783 (1909); C. F. Hale and H. W. Redfield, *ibid.*, **33**, 1353 (1911); C. F. Hale and V. E. Nunez, *ibid.*, **33**, 1555 (1911); A. W. Browne and A. R. Overman, *ibid.*, **38**, 285 (1916); R. E. Kirk and A. W. Browne, *ibid.*, **50**, 337 (1928); A. G. Houpt, K. W. Sherk and A. W. Browne, *Anal. Chem.*, **7**, 54 (1935).

[4] W. C. Bray and E. J. Cuy, THIS JOURNAL, **46**, 858 (1924); E. J. Cuy and W. C. Bray, *ibid.*, **46**, 1786 (1924); E. J. Cuy, M. E. Rosenberg and W. C. Bray, *ibid.*, **46**, 1796 (1924); E. J. Cuy, *ibid.*, **46**, 1810 (1924).

[5] For a discussion see Chap. 6 of L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951.

[6] Subsequent to the completion of this investigation, an isotopic study of hydrazine oxidation has been published by W. C. E. Higginson and D. Sutton, *J. Chem. Soc.*, 1402 (1953). Since our experimental results and our interpretation are in close agreement with theirs, we can let a brief presentation of our isotopic study suffice. From the study of the products of oxidation of hydrazine by ferric ion, we obtain some additional data concerning the mechanism, which the isotopic study does not reveal.

complete. To determine the stoichiometry, the ferrous produced was titrated with permanganate.

Results and Discussion

I. Isotopic Study.—The results of the isotopic study are displayed in Fig. 1. After each experiment, the number of equivalents of oxidizing agent consumed per mole of hydrazine, n, was measured. Since there was no appreciable hydrazoic acid among the oxidation products (except in one experiment which was specifically designed to favor its production), the fraction of N_2 arising from one-electron oxidation was $(4 - n)/(2 + n)$ the remaining N_2 arising from four-electron oxidation. The isotopic composition of the N_2 always corresponded to a mixture of N_2 whose composition was identical with that of the hydrazine ("unrandomized") with N_2 whose atoms had the statistical distribution ("randomized"), so the isotopic composition is reported as the percentage of the randomized gas in the mixture. In a typical set of experiments, 1 part of isotopically enriched hydrazine was mixed with 44.85 parts of ordinary hydrazine (0.36% N^{15}), to give an over-all enrichment of 1.70% N^{15}. The composition of unrandomized nitrogen was then 0.867% $N_2{}^{30}$, 1.767% $N_2{}^{29}$, 97.4% $N_2{}^{28}$; of randomized nitrogen 0.030% $N_2{}^{30}$, 3.40% $N_2{}^{29}$, and 96.6% $N_2{}^{28}$.

The oxidation with oxidizing agents which give exclusively four-electron oxidation (acid iodate, alkaline ferricyanide), yielded N_2 which was unrandomized. Therefore, in this reaction all four hydrogen atoms must be removed from a single hydrazine molecule. The bimolecular mechanism of Kirk and Browne is untenable.

Although there is no oxidizing agent which gives exclusively one-electron oxidation of hydrazine, there are many which give simultaneously four-electron and one-electron oxidation. We have here added to the range of such oxidizing agents by the addition of cupric ion to ceric or ferric ion, increasing concentrations of cupric ion resulting in a greater proportion of four-electron oxidation. We shall return later to the probable mode of action of cupric ion in the oxidation. As the data in Fig. 1 show, the extent of isotopic randomization is just proportional to the fraction of N_2 produced by one-electron oxidation, and a short extrapolation leads to the conclusion that the N_2 from the one-electron oxidation is 50% randomized.

If the one-electron oxidation proceeds through an intermediate tetrazane, NH_2-NH-NH-NH_2, in which the terminal amino groups crack off to become ammonia, and the central nitrogen atoms end up as N_2, the expected randomization would be 100%. If, however, the tetrazane loses one terminal amino group to yield triazene (the unsaturated hydronitrogen analogous to propylene, HN=N—NH_2), which can then tautomerize prior to the loss of the second amino group, the randomization would be 50% as found experimentally. The intermediate N_3H_3 could not be cyclotriazane (NH-NH-NH, analogous to cyclopropane), for this would lead to nitrogen 66.7% randomized.

A reaction scheme consistent with the isotopic data follows. For the sake of definiteness, we have written the reactions with Fe^{+++} as the oxidizing agent, but the same sort of reaction mechanism is proposed for all the oxidizing agents we have investigated.

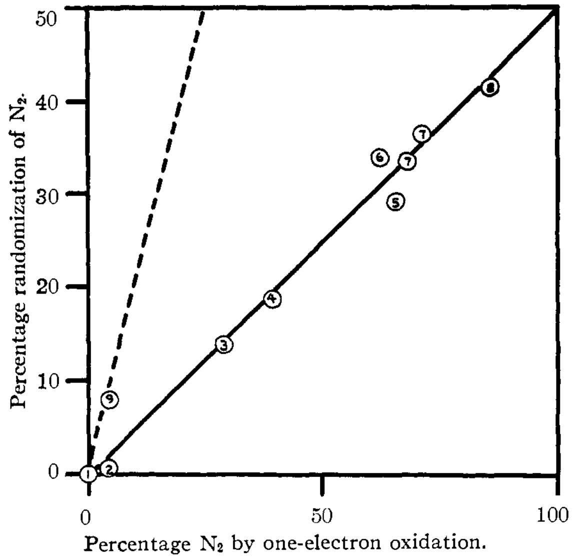

Fig. 1.—Isotopic randomization of N_2 from oxidation of hydrazine, key: 1, iodate or ferricyanide; 2, ferric with 0.92 M cupric added; 3, ferric with 0.13 M cupric added; 4, ferric with 0.066 M cupric added; 5, ferric; 6, ceric with cupric added; 7, permanganate; 8, ceric; 9, peroxysulfuric acid.

The primary reaction product, whose production will be the rate-determining step, is taken to be hydrazyl radical

$$N_2H_5{}^+ + Fe^{+++} \xrightarrow{k_1} Fe^{++} + N_2H_3 + 2H^+ \quad (4)$$

A dimerization step will then lead to tetrazane

$$2N_2H_3 \xrightarrow{k_2} NH_2\text{—}NH\text{—}NH\text{—}NH_2 \quad (5)$$

which undergoes the relatively fast reactions

$$NH_2\text{—}NH\text{—}NH\text{—}NH_2 \longrightarrow NH_3 + HN{=}N\text{—}NH_2 \quad (6)$$

$$HN{=}N\text{—}NH_2 \rightleftarrows NH_2\text{—}N{=}NH \quad (7)$$

$$N_3H_3 \longrightarrow NH_3 + N_2 \quad (8)$$

Instead of dimerizing, the hydrazyl radical can be oxidized further

$$N_2H_3 + Fe^{+++} \xrightarrow{k_4} Fe^{++} + HN{=}NH + H^+ \quad (9)$$

The diazene (HN=NH) suffers rapid oxidation to N_2. The reaction sequence proposed in reactions 4–9 is identical with that given by Higginson and Sutton.[4] An additional reaction, whose existence is not demanded by the isotopic results but by the relative kinetic results given in the following section, is the dismutation of two hydrazyl radicals, also giving diazene

$$2N_2H_3 \xrightarrow{k_3} HN{=}NH + N_2H_4 \quad (10)$$

Although cupric ion does not react at an appreciable rate with hydrazine in acid solution, nor change the rate of oxidation of hydrazine by ferric ion, its presence greatly increases the relative amount of four-electron oxidation. This observation suggests that the reaction

$$N_2H_3 + Cu^{++} \xrightarrow{k_5} Cu^+ + HN{=}NH + H^+ \quad (11)$$

is relatively fast. The cuprous ion is, of course, reoxidized to cupric by the Fe^{+++} or other strong oxidizing agent present. The relatively high reaction rate of cupric ion with free radicals, in the present system hydrazyl radicals, has also been observed with HO_2 radicals, in the enhancement by cupric ion of the oxidation of hydrogen peroxide by ferric ion.[7]

If hydrazoic acid were formed in the oxidation, and subsequently oxidized to N_2, the isotopic randomization would be that indicated by the dotted line in Fig. 1.[8] Since the experimental points are not in the neighborhood of this line, none of the oxidizing agents used produced any significant amount of hydrazoic acid, even as a transitory intermediate. An exception must be made for peroxysulfuric acid, which was used under conditions closely duplicating those of Browne and Shetterly (1909) to give a considerable quantity of hydrazoic acid as an isolable product. This oxidation gave N_2 which was 8.2% randomized. We did not obtain a complete analysis of all our products in this oxidation, but if we accept Browne and Shetterly's data, which appear to be entirely reliable, the products from our oxidation were 0.182 mole of HN_3, 0.238 mole of NH_3, and 0.580 mole of N_2 per mole of hydrazine. After deducting the number of equivalents of oxidizing agent necessary to form the HN_3 and an equimolal amount of NH_3, these figures lead to a value of $n = 3.72$ equivalents per mole of hydrazine, which corresponds to an apparent 4.8% of N_2 by the one-electron oxidation. In this particular reaction mixture, therefore, the isotopic results indicate that the N_2 arising from other than the four-electron oxidation came from hydrazoic acid as an intermediate, and, within the accuracy of our data, exclusively from hydrazoic acid. This means that no significant amount of N_2 was produced by the successive cracking of tetrazane and triazene, reactions 6–8. It is not possible to say now whether the explanation is that tetrazane or triazene is more stable toward cracking in the strongly acid solution, or merely that one of them is rather rapidly oxidized to hydrazoic acid in this reaction mixture. The splitting off of the NH_3 may either precede or follow the oxidation step, *i.e.*, the immediate precursor of hydrazoic acid may be either tetrazane or triazene. In either case the net reaction would be

$$NH_2{-}NH{-}NH{-}NH_2 \longrightarrow 2e^- + NH_3 + HN_3 + 2H^+ \quad (12)$$

which in the light of the present work is more plausible than the dimerization of diazene proposed by Kirk and Browne.

II. Oxidation by Ferric Ion.—A preliminary kinetic study of the reaction between $N_2H_5^+$ and Fe^{+++} showed it to be first order with respect to each, but no detailed study was pursued, since the study of the rate-determining step gives no information about the fast subsequent reactions 5, 9 and 10, in which we were particularly interested. However, an investigation of the variation of stoichiometry with reagent concentration permits an assignment of relative rates to those fast reactions. The derivation of the necessary mathematical equations, on the basis of the reaction scheme given in the previous section, follows. In the derivation the concentration of Fe^{+++} is regarded as constant, since it was in large excess in our experiments.

In the technique used, oxidation was allowed to proceed until substantially all of the hydrazine was consumed. The total amount of N_2 produced by the four-electron oxidation, $N_2{}^4$, and the total amount of N_2 produced by the one-electron oxidation, $N_2{}^1$, bear to one another the relation

$$\frac{N_2{}^4}{N_2{}^1} = \frac{k_3 \int_0^{\infty} (N_2H_3)^2 dt + k_4(Fe^{+++}) \int_0^{\infty} (N_2H_3) dt}{k_2 \int^{\infty} (N_2H_3)^2 dt} \quad (13)$$

The steady-state concentration of hydrazyl radicals is given by the solution of the equation

$$0 = k_1(Fe^{+++})(N_2H_5^+) - 2(k_2 + k_3)(N_2H_3)^2 - k_4(Fe^{+++})(N_2H_3) \quad (14)$$

The net rate of disappearance of hydrazine is

$$d(N_2H_5^+)/dt = -k_1(Fe^{+++})(N_2H_5^+) + k_3(N_2H_3)^2 \quad (15)$$

From these three equations, after rather a lot of algebraic manipulation, the desired result is obtained. It is

$$\frac{N_2{}^4}{N_2{}^1} = r + (2 + r)\frac{2W(1 + r)/(1 + 1.5r) - \ln(1 + W)}{W^2(1 + r)/(1 + 1.5r) - W + \ln(1 + W)} \quad (16)$$

where

$$r = k_3/k_2, \text{ and} \quad (17)$$

$$W = \frac{1}{2} \times \frac{(1 + r/2)}{1 + r}\left[\sqrt{1 + 8(1 + r)\frac{k_1k_2(N_2H_5^+)_0}{k_4{}^2(Fe^{+++})}} - 1\right] \quad (18)$$

It is convenient to determine experimentally not the relative production of N_2 by the two stoichiometries, but n, the number of equivalents of oxidizing agent per mole of hydrazine, which is given by

$$n = 4\,\frac{0.5 + N_2{}^4/N_2{}^1}{2 + N_2{}^4/N_2{}^1} \quad (19)$$

The comparison of experimental results with equations 16–19 is much easier than might appear from their length, since n is really dependent on only one experimental variable, the ratio of initial hydrazine concentration to ferric ion concentration, $(N_2H_5^+)_0/(Fe^{+++})$. Only two numerical parameters enter, namely r and $k_1k_2/k_4{}^2$, and the latter only as a multiplier of the concentration ratio. For a given value of r, a value of n readily can be computed for each value of the group $(k_1k_2/k_4{}^2)(N_2H_5^+)_0/(Fe^{+++})$ which we shall for brevity call Z. A graph of n against the logarithm of Z can then be prepared, and this can be compared with a graph of the experimental values of n against the logarithm of $(N_2H_5^+)_0/(Fe^{+++})$. If the theory is consistent with the experimental results, the two curves can be made to coincide by a displacement along the logarithmic axis.

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[7] W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 462, 591 (1951).

[8] Calculated on the assumption that N_2 arising from the oxidation of HN_3 will be 66.7% randomized. This percentage randomization is expected if the oxidation of HN_3 proceeds through an intermediate N_6, whether linear or cyclic, or if the oxidation proceeds by cleavage into N_2 + N fractions, both of which eventually yield N_2.

Of course, the theoretical computation must be repeated for several values of r, and that one chosen which best fits the experimental data. It will be noted that r, which is the ratio of dismutation rate to dimerization rate for hydrazyl radicals, determines the limiting stoichiometry at very small concentrations of ferric. In fact, we were driven to include dismutation in the reaction scheme by the observation that the limiting stoichiometry always gives n greater than one, no matter how dilute the oxidizing agent or what its chemical nature. It is entirely plausible that hydrazyl radicals, like alkyl radicals, should be subject to dismutation. The value of r which best agrees with our data at 50° is 0.15, and in Fig. 2 the theoretical curve for n as a function of Z has been drawn for $r = 0.15$.

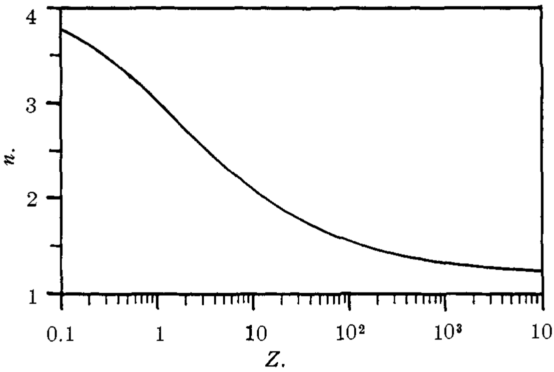

Fig. 2.—Theoretical relation between stoichiometry and the hydrazine-to-ferric concentration ratio.

After preliminary experiments had verified that a tenfold increase in ferric ion did produce the same change in stoichiometry as a tenfold decrease in hydrazine concentration, the ratio of reactants was systematically varied over a wide range. The smallest concentration of ferric used was 0.015 M, the greatest 0.73 M; the smallest concentration of hydrazine was 0.0008 M, the greatest 0.08 M. Runs were carried out at hydrogen ion concentrations of 0.017, 0.16, 0.80 and in 3.5 M sulfuric acid. In Fig. 3, these experimental results have been plotted along with the theoretical curve, and the corresponding values of the numerical parameters are given in Table I.

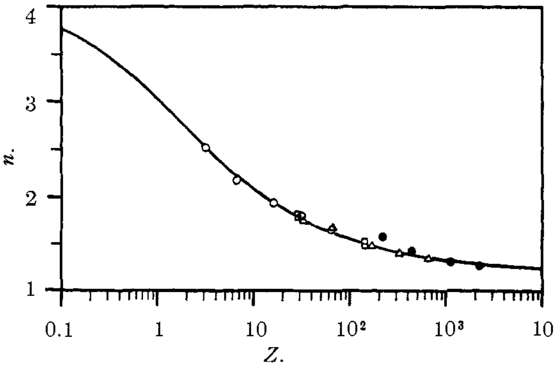

Fig. 3.—Comparison of experiment with theory, for key, see text.

The dependence of the ratio of rate constants upon acidity suggests that both FeOH^{++} and Fe^{+++} species are acting as oxidizing agents, with the hydrolyzed species playing the major role except at very high acidity. However, our data on the effect of acidity are not extensive enough to compare quantitatively the reactivity of the two species.

TABLE I

Symbol in Fig. 3	Concn. of H^+, M	k_1k_2/k_4^2
Open circles	0.017	280
Squares	0.16	1200
Filled circles	0.80	13,000
Triangles	3.5 (H_2SO_4)	4,000

The general agreement between the predicted and observed effects is satisfactory. The point which should be emphasized most strongly is that ferric ion is neither a "four-electron-type" nor a "one-electron-type" of oxidizing agent toward hydrazine, but can cover almost the whole range from one extreme to the other, depending on its concentration and that of the hydrazine. Since there is no reason to doubt that the same behavior is to be found for other oxidizing agents, the classification of the oxidizing agents into groups according to the products they form with hydrazine would appear to be of limited usefulness.

The reaction of cupric ion with hydrazyl radical is readily incorporated into the kinetic scheme, the mathematical result being unchanged except that the group Z has now become

$$\frac{k_1k_2(\mathrm{Fe}^{+++})(\mathrm{N_2H_5}^+)_0}{[k_4(\mathrm{Fe}^{+++}) + k_5(\mathrm{Cu}^{++})]^2}$$

If for a particular mixture of ferric ion and hydrazine the Z-value is measured without cupric and then with cupric ion (call the latter measurement Z_{Cu}), the relative rate constants for ferric and cupric can be computed from the relation

$$\sqrt{\frac{Z}{Z_{\mathrm{Cu}}}} - 1 = \frac{k_5\,(\mathrm{Cu}^{++})}{k_4\,(\mathrm{Fe}^{+++})} \qquad (20)$$

Figure 4 displays the results of a set of such oxidations with increasing additions of Cu^{++}, at pH 0.6 and 50°. At this acidity, cupric ion is seen to oxidize hydrazyl radicals 1200 times as fast as does ferric ion.

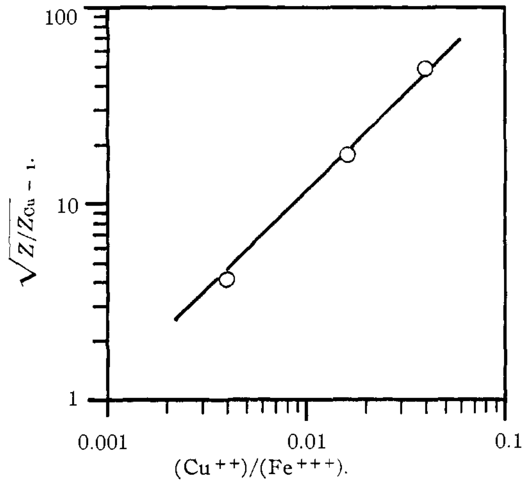

Fig. 4.—Relative reaction rates of cupric and ferric ions with hydrazyl radicals.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Preparation of Hydrazine from Urea and *t*-Butyl Hypochlorite[1]

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The use of *t*-butyl hypochlorite as an oxidizing agent and as an N-chlorinating agent has been extended to urea. It has been demonstrated that *t*-butyl hypochlorite and urea react in alkaline solution to form hydrazine. The yield of hydrazine is dependent upon (a) the mole ratio of urea to *t*-butyl hypochlorite, (b) the presence of alkali, and (c) the use of an inhibitor such as gelatin. Experimental conditions are similar to those which have been found previously to govern the formation of hydrazine from *t*-butyl hypochlorite and ammonia. It has been shown spectrophotometrically that N-chlorourea is the initial product of reaction between urea and *t*-butyl hypochlorite.

Introduction

It is well-known from prevous investigations[2-9] that urea and alkali hypochlorites can react in alkaline solution to form hydrazine. Of the two commercial processes used for the preparation of hydrazine in this country, one employs urea as the starting material in place of ammonia. Since it was observed in a previous investigation[1] that *t*-butyl hypochlorite and ammonia react to form hydrazine, the use of this organic hypochlorite as an oxidizing agent and as an N-chlorinating agent has been extended to urea. It has been found that *t*-butyl hypochlorite reacts with urea in alkaline solution to form hydrazine. The yield of hydrazine is dependent upon three factors: (a) the mole ratio of urea to *t*-butyl hypochlorite, (b) the presence of alkali and (c) the use of an inhibitor such as gelatin.

It had been shown previously that monochloramine is the first product of reaction between *t*-butyl hypochlorite and ammonia. It has now been demonstrated, spectrophotometrically, that N-chlorourea is the initial reaction product from urea and *t*-butyl hypochlorite.

Experimental

Materials Used.—The urea employed was Merck and Co., Inc., U. S. P. material. *t*-Butyl hypochlorite was prepared[10] and analyzed as described previously.[1] Standard potassium iodate was prepared by dilution of the required amount of the reagent grade chemical. Sodium thiosulfate solution was standardized against the potassium iodate solution, starch being used as the indicator. The inhibitor was Schaar pure gelatin powder.

Proof of Hydrazine Formation and Method of Analysis for Hydrazine.—The formation of hydrazine from urea and *t*-butyl hypochlorite was demonstrated by the isolation and identification of salicylalazine, m.p. 215–216°, uncor. (lit.[11] 214°). Hydrazine was determined quantitatively by the indirect iodate method.[12] It was found that *t*-butyl alcohol did not interfere in this procedure.

Evidence for the Formation of N-Chlorourea from *t*-Butyl Hypochlorite and Urea.—In 50 ml. of distilled water there was dissolved 0.35 g. of urea (5.8 mmoles). Two ml. of 0.346 *M* *t*-butyl hypochlorite (0.69 mmole) in *t*-butyl alcohol was introduced and the homogeneous solution allowed to stand at room temperature (*ca.* 25°) for two days. The absorption spectrum of a portion of this reaction mixture was determined with the Cary recording spectrophotometer, a maximum being observed at 2450 Å., ϵ 244. From Fig. 1 it is readily apparent that the absorbing species cannot be urea, *t*-butyl hypochlorite or dichlorourea.[13] It is conceivable that the peak might have been due to monochloramine, possibly formed by a hydrolysis reaction. This possibility is immediately obviated, however, since monochloramine has a molecular extinction coefficient of 416 at 2450 Å.[14]

Experimental Procedure.—The procedures used in the studies designed to evaluate the effect of the mole ratio of urea to *t*-butyl hypochlorite, the effect of alkali, and the use of an inhibitor were essentially the same. In studies on the yield of hydrazine as a function of the urea to *t*-butyl hypochlorite ratio, the following method was followed. Each of six erlenmeyer flasks was charged with 200 mg. of gelatin and predetermined quantities of water. The mixture was allowed to stand overnight to bring about solution of the gelatin. A 3-necked, 500-ml. flask equipped with a condenser and a stirrer was mounted on a steam-bath. Before each run, 50 ml. of 3.16 *N* sodium hydroxide solution and 3.160 g. of urea were introduced into the reaction vessel along with the aqueous gelatin solution. Then the calculated amount of 0.428 *M* *t*-butyl hypochlorite (in *t*-butyl alcohol) was added and the mixture heated under reflux and stirring for 20 minutes on the steam-bath. The resulting solution was cooled, made up to 250 ml. and a 50-ml. aliquot withdrawn and analyzed quantitatively for hydrazine by the indirect iodate method. The results are depicted graphically in Fig. 2.

To evaluate the effect of the NaOH/urea ratio (see Fig. 3), a constant mole ratio of 12.3 was chosen for the urea/*t*-BuOCl, and varying amounts of aqueous sodium hydroxide solution were employed. In the absence of base, no hydrazine could be detected. However, the presence of an oxidizing species (presumably N-chlorourea) could be demonstrated after the standard heating period of 20 minutes. Some experiments were carried out in which the mole ratio of urea to *t*-butyl hypochlorite was held constant at 1. No hydrazine could be detected when the ratio of sodium hydroxide to urea was also 1. An oxidizing species was again shown to be present. When the ratio NaOH/urea

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