has been noted. It has been shown that this zone behaves like the conduction film assumed to exist around a heated body.

3. It has been shown that the diameter of the mist-free zone is dependent on the wire temperature.

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STUDIES ON HYDRAZINE. THE AUTO-OXIDATION

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The strength of dilute solutions of hydrazine hydrate decreases rapidly in the presence of air. It has been shown[1] that this is due to oxidation by atmospheric oxygen. The reaction between oxygen and hydrazine has been studied also by Browne and Shetterly[2] who passed oxygen and ozone through hot hydrazine solutions, acid, neutral and alkaline. They found no products except nitrogen and in one case a trace of hydronitric acid. The oxidation of hydrazine in the presence of platinum black has been studied quite extensively[3] but this procedure as will be shown removes one of the principal products of the reaction. It is possible, though the evidence is conflicting, that platinum black also effects a catalytic decomposition of hydrazine. None was able to find a mathematical expression for the rate at which the hydrazine is oxidized.

The present work represents a study of the rate of oxidation of hydrazine hydrate in dilute solution by pure oxygen and by air. One of the most interesting developments was the discovery that considerable quantities of hydrogen peroxide are formed in the reaction. This is, of course, a concomitant of many auto-oxidations but hydrazine is a very powerful reducing agent and under some conditions at least reacts readily with peroxide. The presence of peroxide is of particular interest because it interferes seriously with many methods of determining hydrazine. In addition to this the velocity of oxidation under the conditions adopted has been found to follow a simple mathematical expression over a wide range of concentration, temperature and alkalinity.

Experimental Part

(1) **Procedure.**—The apparatus consists of an inverted Erlenmeyer flask into the mouth of which is fitted, by a ground joint, a Jena Gooch crucible containing a medium porous fritted glass disk through which oxygen may be passed into the solution. A hole made in what was formerly the bottom of the flask serves for the introduction of the

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[1] Bray and Cuy, THIS JOURNAL, **46**, 1786 (1924).

[2] Browne and Shetterly, *ibid.*, **31**, 790 (1909).

[3] Tanatar, *Z. physik. Chem.*, **40**, 475 (1902); **41**, 37 (1902); Purgotti and Zanichelli, *Gazz. chim. ital.*, **34**, I, 57 (1904); Gutbier and Neundlinger, *Z. physik. Chem.*, **84**, 203 (1913).

stirrer and for the withdrawal of samples. The reactions are carried out at constant temperature. For the work described here, the interior of the flask was coated with paraffin, as was also the stirrer. The solution was stirred at a constant rate just sufficient to ensure uniformity of concentration; too rapid stirring drew the bubbles of oxygen into the stirrer. In some runs stirring was omitted for periods of thirty minutes at a time with no noticeable effect. It was, however, necessary at the start. Oxygen passed through at the rate of five liters per hour as measured by a calibrated flowmeter. Some runs were made at 6.5 liters per hour but no difference was found. Too rapid flow of gas causes an unduly large loss of hydrazine by volatilization.

At the beginning of a run, water and sodium hydroxide (total volume 100 cc.) were introduced into the reacting vessel and saturated with oxygen. The proper amount of hydrazine hydrate (Eastman Kodak Company 50% solution) was added and after one minute a sample (2 cc.) was withdrawn for analysis. At further intervals of five minutes or more samples were withdrawn alternately for the determination of hydrazine and peroxide. Hydrazine was determined by the iodic acid method.[4] Peroxide interferes seriously with this method and must be removed. Both hydrazine and peroxide are reducing agents but peroxide is also an oxidizing agent so the following procedure was adopted, after trial. The sample of hydrazine containing peroxide is run into 6 *N* sulfuric acid and a few drops of sulfurous acid added. The peroxide is destroyed and so far as could be detected under these conditions the hydrazine is unaffected. The solution was boiled for five to ten minutes to remove excess sulfur dioxide and the hydrazine determined as usual. A test (containing no peroxide, however) went as follows:

Sample of hydrazine sulfate, cc.	H_2SO_3, cc.	HIO_3, cc.	$Na_2S_2O_3$, cc.
2.00	1.0	10.00	5.45
2.00	0.0	10.00	5.45

Peroxide could always be detected if present since the final starch–iodine end-point is not permanent if peroxide is present. Peroxide was determined as follows, though no great precision can be claimed for the method. The sample (2 cc.) was run into 3 cc. of 6 *N* sulfuric acid in a glass-stoppered flask and carbon dioxide passed through for at least five minutes to remove oxygen from the solution and flask. Potassium iodide was added and after standing for ten to fifteen minutes the liberated iodine was titrated with 0.005 *N* thiosulfate. In the presence of acid of this concentration hydrazine should react so slowly with iodine that the error would be negligible. Tests by this method on peroxide solutions of known concentration with and without hydrazine proved its suitability.

The concentration of sodium hydroxide was varied from 0.0 to 0.46 *M*, the initial concentration of hydrazine from 0.07 to 0.27 *M* and the temperature from 20 to 25 and 30°. Air was used in place of oxygen only to determine the effect of oxygen pressure, as the rate of oxidation was much more rapid with pure oxygen. Runs were made in the presence of ammonia, hydronitric acid, hydrogen peroxide and sand, and with various rates of stirring and oxygen flow.

In the light of the results of Browne and Shetterly it was thought that hydronitric acid might be present but none could be found, though the tests are extremely sensitive. The solution also gave a negative test for nitrite and nitrate. Peroxide was shown to be present by the ether–dichromate test and also by the color reaction with titanium sulfate. The gases were tested for hydrogen with a palladium absorption tube but none could be found. In the early part of the work a small amount of ammonia was found in the more alkaline solutions. The amount was so small that it was not tested for in later runs.

An entirely different procedure was also used, shaking the solution in a bottle in

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[4] Bray and Cuy, THIS JOURNAL, **46**, 858 (1924).

the presence of oxygen, and the results are apparently of a different character. This report deals only with the bubbling method.

(2) **Results.**—In Fig. 1 is shown a series of characteristic curves for the auto-oxidation of hydrazine and the accompanying curves for the formation of peroxide. Data for some of the curves are given in Table I. For the sake of brevity the major part of the results is merely summarized (Table II).

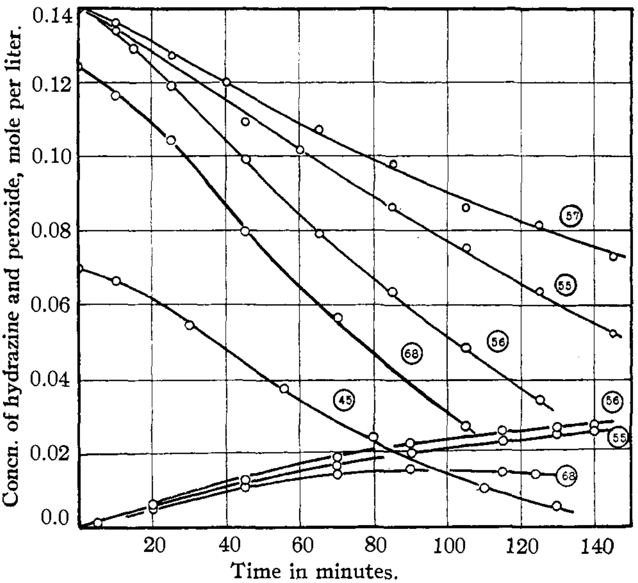

Fig. 1.—Oxidation of hydrazine and formation of peroxide. Upper curves, concn. of hydrazine; lower curves, concn. of peroxide. (57), NaOH = 0.00 *N*; (55), NaOH = 0.46 *N*; (56), NaOH = 0.15 *N*; (68), NaOH = 0.03 *N*; (45), NaOH = 0.03 *N*; Temp. = 20° in Run (45), 25° in others.

TABLE I

CALCULATION OF VELOCITY CONSTANT FOR THE AUTO-OXIDATION OF HYDRAZINE

$$k = \frac{1}{(t_2 - t_1)(1 - 1/n)} \left(C_1^{(1 - 1/n)} - C_2^{(1 - 1/n)}\right)$$

Expt. 68

NaOH, 0.03; Temp., 25°

t	*C*	*k*
25 (t_1)	0.1038	...
35	.0920	0.0036
45	.0802	.0038
55	.0700	.0037
65	.0602	.0038
75	.0512	.0038
85	.0425	.0039
105	.0274	.0039

Expt. 57

NaOH, 0.00; Temp., 25°

t	*C*	*k*
25 (t_1)	0.1275	...
45	.1162	0.0016
65	.1065	.0016
85	.0970	.0015
105	.0880	.0015
125	.0805	.0015
145	.0740	.0014

Table I (*Concluded*)

t	*C*	*k*	*t*	*C*	*k*
Expt. 45 NaOH, 0.03; Temp., 20°			Expt. 62 NaOH, 0.03; Temp., 25°		
20 (t_1)	0.0620	...	15 (t_1)	0.2562	...
30	.0545	0.0032	35	.2170	0.0041
40	.0475	.0032	55	.1820	.0040
50	.0410	.0032	75	.1475	.0041
70	.0285	.0033	95	.1155	.0042
90	.0182	.0033	115	.0850	.0043
110	.0107	.0033			
130	.0062	.0033			

Table II

Summary of Experimental Data on Auto-oxidation of Hydrazine at 25°

Expt.	Orig. concn. of hydrazine, mole/liter	Concn. of NaOH	Peroxide present when 0.05 mole of N_2H_4 is oxidized	*k*	Remarks
52	0.1392	0.03	0.013	0.0037	
54	.1398	.03	.013	.0038	
60	.0672	.03	.012	.0042	
62[a]	.2646	.03	.013	.0041	
68[a]	.1243	.03	.012	.0038	6 months after 52–54
69	.1243	.03	.012	.0033	0.015 *M* NH_3 present
70	.1232	.03	.011	.0038	0.015 *M* NH_3 present
71	.1232	.03	.012	.0038	0.0001 *M* HN_3 present
53	.1232	.012	.012	.0039	
74	.1436	.012	.010	.0035	6 months after 53
58	.1398	.15	.019	.0032	
56	.1398	.15	.018	.0034	
55	.1398	.46	.018	.0021	
59	.1398	.46	.018	.0022	
57[a]	.1398	.00	.022	.0015	
76	.1263	.03	.011	.0020	1 g. Ottawa sand added
45[a]	.0699	.03	.014	.0032	Temp., 20°
46	.1398	.03	.010	.0056	Temp., 30°
64	.1366	.03	.002	.0042	0.0167 *M* H_2O_2 present
44	.0699	.46	(.020)	.0013	Temp., 20°
63	.1398	.03	Extrap. (.009)	$-dc/dt$ = .0002	Air instead of O_2

[a] Full data in Table I.

(3) **Discussion.** (a) **The Effect of Hydrazine Concentration.**—The curves all show for the oxidation of hydrazine a characteristic double inflection, with a period of "induction" at the beginning followed by a rapid change of slope, after which they assume a slight concavity to the horizontal axis. After the first period of irregular change all, covering a fourfold increase in hydrazine concentration, may be formulated by the equa-

tion developed by Bodenstein[5] for certain gas reactions and adapted by MacInnes[6] to a heterogeneous reaction in solution whose rate is governed by the adsorption of the reactants, or diffusion

$$-\frac{dC}{dt} = k\cdot C^{\frac{1}{n}}$$

Since it is not possible to begin the calculations with zero time, it is necessary to calculate the constants from point to point or better to adopt some one point as a basis. In either case

$$k = \frac{1}{(t_2 - t_1)\,(1 - 1/n)}\,(C_1^{(1 - 1/n)} - C_2^{(1 - 1/n)})$$

A value of 2 for "n" proved to satisfy the conditions satisfactorily over the whole range of temperature and concentration. It might be expected that a different value would be required at different temperatures, but a similar small variation of "n" with temperature has been noted in another similar heterogeneous reaction.[7] A certain drift should be expected in these constants because there is unavoidably some loss of hydrazine by volatilization. This is a variable quantity depending upon duration of experiment and alkalinity of solution but present in all cases. Rough experiments using hydrogen instead of oxygen indicated a maximum loss of 2% an hour. This being a heterogeneous reaction it was difficult to obtain results which agreed as closely as 2% and no correction was made for the loss. Duplicates run at periods of three to six months agreed in quite a satisfactory manner, as may be seen from the tables.

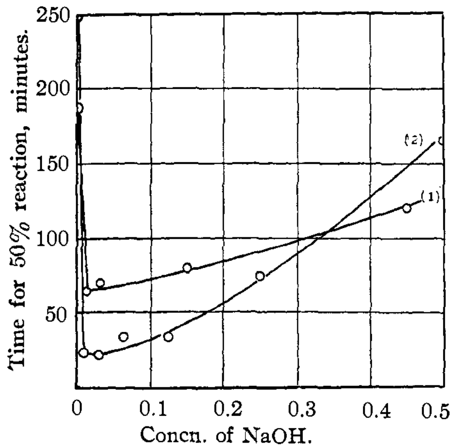

Fig. 2.—Comparison of effect of NaOH on auto-oxidation of hydrazine (1) and on the catalysis of hydrogen peroxide by colloidal platinum (2).

(b) **The Effect of OH⁻ Concentration.**—The effect of increasing the hydroxyl-ion concentration is first to accelerate oxidation and then to retard it. The maximum rate of oxidation is found when the sodium hydroxide concentration is 0.01–0.03 *M*. An interesting coincidence occurs here. Inspection of Fig. 2 shows that the effect of sodium hydroxide on this reaction is practically the same as its effect on the catalysis of hydrogen peroxide by colloidal platinum.[8] It is difficult to ascribe this effect to some

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[5] Stock and Bodenstein, *Ber.*, **40**, 570 (1907).

[6] MacInnes, This Journal, *36*, 878 (1914).

[7] Sieverts and Peters, *Z. physik. Chem.*, 91, 199 (1916).

[8] Bredig and Müller von Berneck, *ibid.*, **31**, 258 (1899).

particular part of the phenomenon, because the maximum rate of oxidation is attended by a minimum formation of peroxide (see paragraph c). Whether the smaller amount of peroxide is present at this concentration (NaOH = 0.01–0.03 *M*) because this represents the optimum condition for the decomposition of peroxide (Fig. 2) is not certain. It is fairly certain, however, that the amount of peroxide present is the resultant of two reactions, one of formation and one of decomposition, since in some cases the amount passes through a maximum and decreases (see Run 68, Fig. 1).

A possible explanation of the effect of sodium hydroxide on the oxidation is this. The molecule N_2H_4 may be the oxidizable material. Low concentrations of NaOH serve to repress the ionization of hydrazine hydrate, thus increasing the concentration of the N_2H_4 molecules. It also combines with the peroxide formed. High concentration may alter conditions such as hydration, association, etc., so as to reduce the actual number of reactive molecules. It might be thought that the formation of peroxide would reduce the hydroxyl-ion concentration to an extent sufficient to affect the course of the reaction. A rough calculation shows this not to be the case.

$$\frac{N_2H_5^+ \times OH^-}{N_2H_4} = 1.5 \times 10^{-6}$$

In a solution where NaOH = 0.03 *M*, as a first approximation then

$$\frac{N_2H_5^+}{N_2H_4} = 5 \times 10^{-5}$$

The hydrazine is practically un-ionized. At the end of two hours the peroxide concentration was about 0.015 *M*. Assuming that the sodium salt is not hydrolyzed, the effective OH^- is still 0.015 and the ratio is

$$\frac{N_2H_5^+}{N_2H_4} = 1 \times 10^{-4}$$

Since the molecule is presumably the reactive form, this difference in ratio can have no detectable effect on the reaction from the standpoint of hydrazine concentration.

(c) **The Effect of Peroxide Concentration.**—It has not been found possible to formulate any satisfactory expression for the increase of peroxide with time, probably because it is the difference between formation and decomposition. Run 76 in which standard Ottawa sand was added shows a lower amount of peroxide than usual, substantiating this theory. The amount of peroxide varies with the initial concentration of hydroxyl ion almost in inverse ratio to the rate of oxidation, *i. e.*, slow oxidation, high peroxide and *vice versa* as may be seen by comparing companion curves in Fig. 1. It does not necessarily follow that the peroxide is low because it is reacting or has reacted with hydrazine, thereby accelerating the rate, because when air is used instead of oxygen, the rate of oxidation falls to one-fifth, but the amount of peroxide does not decrease accordingly. In Run 64, however, in which 0.0167 *M* peroxide was added at the start, the oxidation seems to run slightly faster, but the interesting thing is that the peroxide formed in the run is less than 30% the normal amount formed in a similar run with no added peroxide.

As judged by the amount of peroxide formed when 0.05 mole of hydrazine has been oxidized, see Col. 4, Table II, it seems probable that in the absence of NaOH the ratio Moles peroxide formed/Moles hydrazine oxidized = 1:2. In the presence of low OH^- (0.012–0.03) the ratio is 1:4 and in strong NaOH (0.15–0.46) the ratio is 1:3. Since, however, different time intervals are required in the several cases for this amount of oxidation, no very close distinctions may be drawn. It should be stated that the formation of peroxide is not a function of this apparatus or procedure. It is formed by simple exposure of an alkaline solution of any hydrazine salt, or hydrazine hydrate, on a watch glass to air, though, of course, not so rapidly as with pure oxygen.

(d) **The Temperature Effect.**—In 0.03 *N* NaOH, *k* for the oxidation increases from 0.0032 at 20° to 0.0056 at 30°, giving a coefficient of 1.75 for this ten-degree interval. This corresponds more closely to that of a chemical reaction at a surface than to a diffusion process.[9]

(e) **The Active Surface.**—The data so far obtained indicate, therefore, a reaction at a surface, but it is not certain what this surface may be. The walls and stirrer were coated with paraffin, upon which very little reaction would be expected. The fritted glass disk falls under suspicion, but addition of sand which should increase such surface cuts the velocity in half. The bubbles of oxygen were extremely fine but they passed through the solution rather rapidly. The temperature coefficient and indeed the expression for the velocity constant correspond to a micro-, rather than macro-heterogeneous reaction, so it is possible that this is a reaction catalyzed by dust particles.[10] In preliminary experiments it was found that variously prepared samples of hydrazine sulfate gave very great differences in rate, most easily explained by this same hypothesis.

(f) **The Effect of Oxygen Pressure.**—When air was used the rate was so slow that the curve was practically a straight line after an initial drop. The slope of this line was 0.0002 as compared with a slope of 0.00107 for a similar solution using oxygen. This ratio is within the limit of experimental error 1:5. In other words, the reaction rate is directly proportional to the partial pressure of oxygen. A 30% increase in oxygen flow above that ordinarily used had no detectable effect on the rate of oxidation.

(g) **The Effect of Added Impurities.**—Ammonia (0.015 *M*) was added in two runs. No effect could be noted. Two runs with small amounts of hydronitric acid added likewise showed no difference from the ordinary. These two substances were added because they are the most common prod-

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[9] Denham, *Z. physik. Chem.*, **72**, 687 (1910).

[10] Rice, THIS JOURNAL, **48**, 2909 (1926).

ucts of oxidation of hydrazine with the exception of nitrogen itself. Qualitatively it was found that the reaction, like other auto-oxidations, is affected by substances like acetanilide, aniline, hydroquinone, etc.

Summary

1. The auto-oxidation of hydrazine in alkaline solution has been studied by the procedure of passing oxygen through a fritted glass disk into the solution.

2. With this procedure the reaction is heterogeneous and the rate may be expressed by the equation $-dC/dt = k \times p_{O_2} \times C^{1/n}$, being governed by the rate of adsorption of hydrazine on the active surface.

3. Hydrogen peroxide is formed under all conditions when hydrazine in dilute alkaline solution is exposed to the action of oxygen.

4. The rate of oxidation passes through a maximum, in the presence of sodium hydroxide, with increasing concentration of hydroxide. The optimum concentration corresponds with that for the maximum rate of decomposition of hydrogen peroxide by colloidal materials, indicating that the auto-oxidation is also a micro-heterogeneous reaction.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

OZONIZATION AND INTERACTION OF OXYGEN WITH NITROGEN UNDER ALPHA RADIATION

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The following experiments were made about three years ago as a part of our general study of chemical reactions produced by alpha rays. Detailed publication[3] was delayed in the hope that the work could be made more complete in certain respects. Recent results of others for the same reactions, but using high-speed cathode rays, which will be fully discussed later, indicate that maximum yields per ion pair can be approached only with such high rates of gas flow and with such low intensity of discharge that it appears uninviting to attempt with alpha radiation to push farther in either of these directions than has already been done. The results given here for the formation of oxides of nitrogen, although rather incomplete, represent the first ionic yields to be reported for this important reaction.

Ozonization.—The production of ozone is studied both in pure oxygen and in mixtures with nitrogen. This was begun as a continuation

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[2] Research Chemist, Atmospheric Nitrogen Corporation, Syracuse, New York.

[3] Brief mention was made of the results in "Chemical Effects of Alpha Particles and Electrons," Chemical Catalog Co., New York, 1928, 2d ed., pp. 83 and 92.