pure and dry hydrogen chloride under identical conditions is without effect upon them.[5] It seems significant in this connection that wet hydrogen chloride is likewise an active agent in corroding these same metals. It therefore seems more plausible to consider momentary recombination of ammonia, or water, with hydrogen chloride on the metallic surface, where both may possibly be absorbed with more readiness, with transient formation of the "onium" ion, which must be regarded as the active agent in causing reaction to take place.

That the reaction between "onium" salts and oxides at higher temperatures is considerably more complicated is self-evident. Here water is one of the products and its formation undoubtedly

(5) K. A. Hofmann, Hartmann and Nagel, *Ber.*, **58**, 808 (1925).

exerts a marked accelerating effect upon the course of the reaction.

Summary

1. Using a specially purified pyridinium hydrochloride it has been shown that this, as a typical "onium" salt, possesses acidic character in the fused state, reacting with metals and metallic oxides much as does hydrochloric acid in aqueous solution.

2. It has also been shown that many metallic chlorides are soluble in fused pyridinium hydrochloride and form stable low temperature melts. Such melts conduct the electric current with facility and in the case of tin, lead, arsenic, antimony, bismuth and mercury permit the electrodeposition of these metals.

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Studies of the Reducing Action of Mercury. I. The Formation of Hydrogen Peroxide in the Interaction of Mercury with Hydrochloric Acid in the Presence of Oxygen

BY N. HOWELL FURMAN AND W. M. MURRAY, JR.

Introduction

In the course of an investigation concerned with further applications of mercury as a reducing agent for certain ions in solutions containing hydrochloric acid, it was observed that a dilute hydrochloric acid solution, when shaken with mercury in the presence of air, acquires reducing properties as indicated by its reaction with ceric sulfate. A large amount of calomel is formed during the shaking of the mixture.

The reaction at room temperature of mercury, oxygen and water to yield oxides of mercury was noted by Fourcroy[1] and has been mentioned frequently in the older textbooks. It has also long been known that a dilute solution of hydrochloric acid attacks mercury in the presence of air, calomel being formed.

$$2HCl + 2Hg + O = Hg_2Cl_2 + H_2O \qquad (1)$$
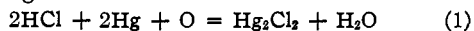
Such an equation was postulated by Berthelot[2] and has been assumed by other workers. These reactions of mercury and hydrochloric acid in the presence of oxygen were observed and discussed by McCay and Anderson[3] in their work on the

reduction of ferric chloride by mercury and also in a later paper by McCay[4] on the reduction of quinquivalent antimony.

Schönbein[5] and Voit[6] reported the formation of "ozon" when mercury is shaken with water and dilute acids in the presence of air. It is now known that the "ozon" to which these workers so frequently refer was in most cases hydrogen peroxide.

Dunstan, Jowett and Goulding[7] found that traces of hydrogen peroxide were formed when mercury was placed under a very dilute solution of sulfuric acid and oxygen bubbled through the liquid for several hours.

The dry reaction between mercury, hydrogen chloride, and oxygen has also been studied, the formation of calomel and oxychlorides of mercury being reported by Berthelot[8] and by Bailey and Fowler.[9]

It has been found in our work that hydrogen peroxide and calomel are formed when samples

(1) Fourcroy, "A General System of Chemical Knowledge," trans. by Wm. Nicholson, Vol. V, 1804, pp. 431–433.

(2) Berthelot, *Ann. chim.*, [5] **23**, 110 (1881).

(3) McCay and Anderson, THIS JOURNAL, **43**, 2372 (1921).

(4) McCay, *Ind. Eng. Chem.*, *Anal. Ed.*, **5**, 1 (1933).

(5) Schönbein, *Ann. physik. Chem.*, **100**, 1 (1857).

(6) Voit, *Ann.*, **104**, 341 (1857).

(7) Dunstan, Jowett and Goulding, *J. Chem. Soc.*, **87**, 1548 (1905).

(8) Berthelot, *Compt. rend.*, **125**, 746 (1897).

(9) Bailey and Fowler, *J. Chem. Soc.*, **53**, 755 (1888).

of mercury, hydrochloric acid, and oxygen are shaken together. The stoichiometry of the reaction has been studied and possible mechanisms have been considered.

Experimental

Materials.—Mercury was purified first by the well-known method of Meyer,[10] then by distillation following the method of Hulett.[11] After use in each experiment, it was washed with distilled water, the method of Meyer again being followed.

Standard solutions of sodium hydroxide and hydrochloric acid were prepared in the usual way. Constant boiling hydrochloric acid was used as primary standard.

Ceric sulfate solutions were prepared from purified ceric oxide and standardized against Bureau of Standards sodium oxalate by potentiometric titration.

As a qualitative test for hydrogen peroxide, the pertitanic acid reaction was used in all cases since it seemed to fit best the requirements of a sensitive and specific test.

Preliminary Experiments.—A typical experiment in which hydrogen peroxide was formed when mercury, hydrochloric acid and oxygen were shaken together was carried out in the following manner. A 50-ml. sample of 2 N hydrochloric acid was placed in a glass-stoppered bottle with 25 ml. of pure mercury, the volume of air above the liquid being displaced by oxygen. This mixture was shaken for fifteen minutes, and the solution was then decanted through a filter to remove the calomel and mercury. This solution gave the following tests:

1. Reduced ceric sulfate solution in the cold, bubbles of gas being liberated.
2. Liberated iodine from potassium iodide solution.
3. Formed a yellow color with titanic sulfate solution.
4. Formed a yellow color with sodium molybdate solution.
5. Gave a fleeting blue color with potassium chromate solution.

Three of the above tests are specific for hydrogen peroxide; the other two are characteristic.

When dilute hydrochloric acid is shaken with mercury in an atmosphere of carbon dioxide, no reaction takes place even after it is shaken for hours. However, when oxygen is used to fill the space above the solution, the reaction proceeds rapidly, as shown by the formation of calomel. Since the oxygen above the liquid must enter the reaction, the air above the solutions in all the experiments was displaced by oxygen unless otherwise stated.

There is some reaction between oxygen, mercury and water, for at first a black scum is formed and after a long period of shaking a greenish deposit forms on the surface of the mercury and mercuric ions may be detected in solution. No hydrogen peroxide can be detected. The greenish powder is evidently a mixture of mercury oxides. The amount of mercury in solution in the mercuric state was relatively large, for it gave heavy precipitates with stannous chloride, hydrogen sulfide and ammonium hydroxide, respectively.

This reaction of mercury and air in the presence of water has been studied by Stock[12] and his collaborators.

Study of the Reaction.—The apparatus used for a more systematic study of the reaction consisted of a 250-ml. narrow-mouthed glass bottle connected by means of a flexible rubber tube to a Hempel gas buret. Water saturated with oxygen was used as confining liquid in the buret, the pressure being maintained equal to that of the atmosphere by means of a leveling bulb. Since the pressure within the system was never very different from that of the atmosphere, the use of tight rubber connections was found to be quite satisfactory. The buret and bottles were filled with oxygen from a cylinder by means of a water displacement arrangement, the gas thus entering the system being saturated with water vapor. The rate of agitation was fairly constant, as the shaking of the bottles was done entirely by machine.

The volume of hydrochloric acid taken for each run was accurately known and immediately after a reaction was stopped the solution was decanted onto a dry filter. The concentration of the acid was not changed in any way other than by the reaction itself, since the first portion of the filtrate was rejected. Samples of the filtered solution were pipetted for analysis. One was titrated with standard sodium hydroxide in order to determine the change in acidity; the other with ceric sulfate (using o-phenanthroline as indicator) to determine the amount of hydrogen peroxide formed. The titration of hydrogen peroxide with ceric sulfate using o-phenanthroline-ferrous complex as indicator has been studied and found satisfactory by Willard and Young.[13]

The following equation was assumed for the reaction

$$2Hg + 2HCl + O_2 = Hg_2Cl_2 + H_2O_2 \qquad (2)$$
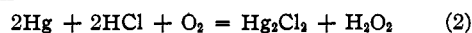
It became evident immediately that the yield of hydrogen peroxide was less than one mole per one mole of oxygen used. This was probably caused by a reaction between the mercury, hydrochloric acid and hydrogen peroxide.

$$2Hg + 2HCl + H_2O_2 = Hg_2Cl_2 + 2H_2O \qquad (3)$$
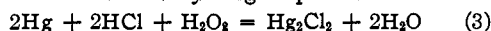
That this reaction is feasible we have proved by shaking mercury with a dilute solution of hydrochloric acid and hydrogen peroxide in an atmosphere of carbon dioxide. As has been stated previously, mercury and hydrochloric acid do not react when oxygen is excluded, and therefore the hydrogen peroxide must take part in the observed formation of calomel.

It is evident from equation (2) that for each mole of oxygen used up, a mole of hydrogen peroxide should be formed. The difference between the number of moles of oxygen used and the number of moles of hydrogen peroxide found at the end of the reaction will give the moles of hydrogen peroxide which have reacted according to

(10) Meyer, Z. anal. Chem., 2, 241 (1863).
(11) Hulett. Phys. Rev., 33, 307 (1911).
(12) Stock, Cucuel, Gerstner, Köhle and Lux, Z. anorg. allgem. Chem., 217, 241 (1934).
(13) Willard and Young, This Journal, 55, 3260 (1933).

equation (3). Both reactions (2) and (3) involve a consumption of hydrochloric acid. The following relation may then be established

$$2[O_2]_{used} + (2[O_2]_{used} - 2[H_2O_2]_{found}) = [HCl]_{used} \quad (4)$$

(The terms in brackets refer to the number of moles of the substance.)

The data in Table I illustrate the results obtained. The theoretical value for the amount of hydrochloric acid used was calculated by substituting in equation (4) the values found experimentally for oxygen used and hydrogen peroxide formed. The experimental value for the acid used is that found by titration of the hydrochloric acid with standard sodium hydroxide before and after carrying out the reaction. The values show good agreement in the case where 1 N hydrochloric acid was used, and fair agreement in the case of 0.1 N acid. The errors in the study with 0.1 N acid are largely experimental, since the apparatus and method used was accurate only to 2–3% for the small changes observed when this dilute acid was used. The values for the oxygen consumed have been corrected for a slight rise in temperature caused by frictional heating during the shaking of the bottles and their contents. The volume change due to this heating was determined experimentally by blank runs with mercury and water under an atmosphere of purified nitrogen. It was also calculated from the temperature differential. The calculated and experimental values were in substantial agreement.

TABLE I

EXPERIMENTAL RESULTS ON THE STOICHIOMETRY OF THE REACTION

Normality of HCl	Time, hours	(1) O₂ used	(2) H₂O₂ found	(3) HCl used	(4) HCl calcd.	Diff., % (3) – (4)
			—Millimoles—			
1.044	3.50	5.136	4.056	12.54	12.43	+0.6
1.011	4.00	6.434	4.758	16.20	16.22	−0.1
1.011	4.75	8.308	4.943	23.77	23.35	+1.8
1.011	2.00	2.870	2.435	6.526	6.61	−1.2
0.09798	2.00	1.59	1.50	3.53	3.36	+6
.09798	2.50	1.77	1.57	4.22	3.94	+7
.09798	1.00	0.92	0.96	2.00	1.84	+8
.09798	2.00	1.69	1.63	3.65	3.50	+5

Total volume of hydrochloric acid taken in each case was 100 ml. Volume of mercury used in each case was 25 ml. Capacity of bottle used was 250 ml.

The data in this table show that the reaction between mercury, hydrochloric acid and oxygen takes place in accord with equations (2) and (3), the actual mechanism of these reactions being neglected for the moment. Any radically different reaction should cause the molar ratios to

differ by whole number factors, and the data show maximum deviation factors of 0.05–0.07. If both reactions (2) and (3) went to completion, the stoichiometric relations would then be as given in equation (1), as will readily be seen if the sum of equations (2) and (3) be divided by two.

In many of the experiments, readings of the oxygen buret were taken at intervals of fifteen minutes in order to get some idea of the rate of the reaction. The data in Table II are typical readings. The increase in rate during the early part of the reaction was found to be due to the state of division of the mercury. In all our work fresh samples of pure dry mercury were taken for each experiment. The data in columns four and five of Table II were taken on the same sample of mercury: immediately after the last reading in column four was taken, the solution was decanted from the mercury, which was then washed by decantation until it was free from hydrogen peroxide. A fresh sample of acid was introduced and the data shown in column five taken. At the time of change of solution, the mercury was found to be completely broken into tiny droplets which were coated with a layer of calomel. This fine state of division is evidently necessary for the fast reaction rate. The slow decline in rate during the latter part of the reaction is to be attributed to the increasing effect of reaction (3).

TABLE II

DATA ON THE RATE OF THE REACTION

Time, min.	(1)	Total ml. of O₂ used (uncorr.) (2)	(3)	(4)	(5)
15	4.20	3.20	4.20	5.00	14.60
30	9.10	7.20	7.90	10.30	33.20
45	15.10	12.40	11.80	16.30	52.90
60	20.85	17.60	15.70	24.00	72.20
75	27.95	23.95	...	30.30	
90	35.35	31.00	...	38.30	
105	42.00	37.20	29.40	48.80	
120	49.65	44.75	33.90	64.40	
135	57.50	54.10	38.60	83.30	
150	69.50	69.80	43.00		
165	88.20	85.60			
180	102.30	97.80			
195	120.50	114.40			
210	137.70	130.80			
225	153.55	146.20			
240	168.30	161.80			
255	181.90				
270	196.30				
285	209.45				

Nos. (1), (2), (4) and (5) were run with 1.011 N HCl. No. (3) was run with 0.09798 N HCl. Nos. (4) and (5) were run with the same sample of mercury.

A time interval between the beginning of shaking and the first appearance of calomel was observed frequently during the foregoing experiments. Mention of this fact has been made by McCay.[4] Further study of this led to the conclusion that a maximum time lag between the beginning of shaking and the first appearance of calomel occurs at a concentration of hydrochloric acid of about 3 N, the actual time elapsed being of the order of five minutes. In the cases of dilute (0.01–0.1 N) and concentrated (10–12 N) hydrochloric acid, the time interval is only a few seconds. By using air rather than oxygen in the bottles above the solution, the first appearance of calomel is further delayed.

Mixtures of mercury, 3 N hydrochloric acid, and air were shaken for four minutes (at which time no calomel was visible) and subsequently analyzed. The solutions were found to contain equimolecular quantities of hydrogen peroxide and mercuric chloride.[13a] The amount present approximated 0.03 millimole of each.

Solutions of 3 N hydrochloric acid containing small amounts of mercuric chloride were shaken with mercury and air, and the time elapsed before the first appearance of calomel was measured. The amount of mercuric chloride in these solutions was varied from a mere trace up to 0.03 millimole per 50 ml. of solution. It was found that the time interval before the appearance of calomel was dependent on the amount of mercuric chloride in the solution at the start, the larger the original content of mercuric chloride, the shorter the time interval. This fact leads immediately to the conclusion that in 3 N hydrochloric acid a certain minimum concentration of mercuric chloride is necessary before calomel appears by the reaction

$$HgCl_2 + Hg = Hg_2Cl_2 \qquad (5)$$

**Discussion of the Mechanism of the Reaction.** —This reaction falls in the category of a group of important studies in the field of "autoxidation." A short review of the many mechanisms proposed for such reactions is to be found in a recent paper by Raikow.[14] These involve the oxidation of water by active oxygen, the formation of electromeric forms of hydrogen peroxide, etc. None of them has proved completely satisfactory in the past, nor does any of them fit all the facts of this

interaction of mercury, oxygen and hydrochloric acid.

The data at hand do not allow one to fix the mechanism of the reaction, but we do wish to postulate a probable sequence of reactions which involve the intermediate formation of the HO_2 molecule in solution, evidence for which has been given in the studies of Haber and Weiss[15] and Weiss.[16] The first step in such a mechanism could be either of the reactions

$$Hg + H^+ = Hg^+ - H \text{ (on surface)} \qquad (a)$$
$$Hg + O_2 = Hg^+ - O_2^- \text{ (on surface)} \qquad (b)$$
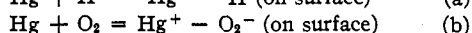
or both might occur at neighboring points on the surface. Either of these initial steps could be followed by the probable reactions

$$Hg^+ - H + O_2 = Hg^+ + HO_2 \qquad (c)$$
$$Hg^+ - O_2^- + H^+ = Hg^+ + HO_2 \qquad (d)$$
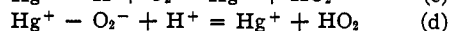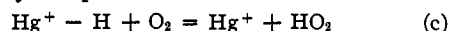
The formation of hydrogen peroxide would then take place by either

$$2HO_2 = H_2O_2 + O_2 \qquad (e)$$

or

$$HO_2 + Hg^+ - H = Hg^+ + H_2O_2 \qquad (f)$$
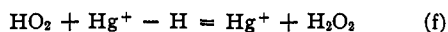
Such a mechanism assumes the reduction of either hydrogen ion or oxygen on the surface of the mercury as indicated in (a) and (b).

This mechanism is substantiated by the work of Traube[17] and Fischer and Priess[18] in which hydrogen peroxide was produced by bubbling oxygen around an electrode which was serving as cathode in an acid electrolysis. The latter investigators found an amalgamated gold cathode to give the best yields, the mercury coating in this instance serving to prevent the recombination of the hydrogen atoms liberated. Since concentrated hydriodic acid attacks mercury with a brisk evolution of hydrogen, it may be said by analogy that hydrochloric acid should be able to form a potential layer of hydrogen on the surface of the mercury even though it is not liberated in the form of hydrogen gas.

Smith[19] made a study of the conditions under which mercury causes the evolution of hydrogen from acids and was experimentally able to obtain hydrogen gas from mercury and hydrochloric acid. However, the method used seems to have inherent in it the possibility of creating internal potential differences which would result in an electrolysis rather than a direct displacement.

(13a) The mechanism by which mercuric ions are formed in the solution will be considered under the discussion of the reaction mechanism.

(14) Raikow, *Z. anorg. allgem. Chem.*, **189**, 36 (1930).

(15) Haber and Weiss, *Proc. Roy. Soc.* (London), **A147**, 332 (1934).

(16) Weiss, *Trans. Faraday Soc.*, **31**, 668 (1935).

(17) Traube, *Ber.*, **15**, 2434 (1882).

(18) Fischer and Priess, *ibid.*, **46**, 698 (1913).

(19) Smith, *Phil. Mag.*, [6] **17**, 833 (1909).

It is possible that the vigorous agitation used in our experiments might cause an electrification of the mercury in some way.

The more active metals, such as zinc, which are capable of liberating hydrogen from water, react readily with water and oxygen to form hydrogen peroxide. Amalgams also react with oxygen in the presence of acids to yield large quantities of hydrogen peroxide. For example, Müller and Barchmann[20] obtained a 3.77% solution of hydrogen peroxide using cadmium amalgam.

The appearance of mercuric ions in solution during the early stages of the reaction is readily accounted for in the light of the work of Richards and Archibald,[21] who found that hydrochloric acid will dissolve a small amount of calomel. The calomel undergoes a type of auto-oxidation-reduction

$$Hg_2Cl_2 + 2Cl^- = Hg + HgCl_4^- \qquad (6)$$
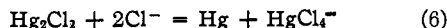
We have repeated these observations of Richards and Archibald in a qualitative manner and found that the solution obtained by dissolving calomel in 3 N hydrochloric acid gives the same reactions as the solution obtained when mercury, 3 N hydrochloric acid, and air are shaken together for three minutes. Both solutions give characteristic tests for the mercuric ion with both stannous chloride and hydrogen sulfide.

It is to be concluded then that the appearance of mercuric ion during the early stages of our reaction is caused by the interaction of the first-formed calomel with hydrochloric acid according to equation (6) and not to a direct oxidation of the mercury in the reaction which yields hydrogen peroxide.

The fact that mercury when shaken with pure water and oxygen gives no peroxide, but does give oxides of mercury and a soluble mercuric compound, points to the necessity of hydrogen ions and perhaps to active hydrogen as essential to the mechanism of forming hydrogen peroxide.

Conclusions

It is at once evident that this reaction has a wide-spread and diversified importance. Throughout chemical literature scattered references are to be found in which workers encountered unexplained difficulties when mercury and acid solutions were employed in the presence of air, the usual changes in procedure in such cases

being to use a vacuum or inert atmosphere technique. Some of these troubles may well have been due to the formation of varying amounts of hydrogen peroxide.[22]

It is obvious that hydrogen peroxide formation is possible in many electrode equilibria unless air and oxygen have been rigorously excluded.

This reaction is of great importance in connection with methods involving the use of mercury with acid solutions as reducing agent in analytical processes. Preliminary experiments along this line have already been carried out and further study is in progress.

The reaction is not limited to mercury, for most noble metals and amalgamated active metals undergo a similar reaction with formation of hydrogen peroxide. This may account for a few of the difficulties which have arisen in the use of the silver reductor. This point is also being followed up in conjunction with the studies on the mercury reductor.

Summary

1. It has been shown that mercury, dilute hydrochloric acid and oxygen interact to form hydrogen peroxide and calomel. The stoichiometry of the formation and decomposition may be represented by

$$2Hg + 2HCl + O_2 = Hg_2Cl_2 + H_2O_2$$
$$2Hg + 2HCl + H_2O_2 = Hg_2Cl_2 + 2H_2O$$
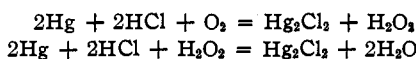
2. The consumption of oxygen is approximately constant in any given unit of time after a sufficient dispersion of the mercury has been produced by shaking, provided a sufficient concentration of acid is maintained.

3. In the initial stages of the reaction, hydrogen peroxide and mercuric salt appear in the solution in equivalent quantities.

4. We regard an active layer of hydrogen at the mercury surface and the formation of the substance HO_2 as probable intermediates in the process. Many other mechanisms may be adduced to explain the stoichiometry.

(20) Müller and Barchmann, Z. Elektrochem., 40, 188 (1934).
(21) Richards and Archibald. Z. physik. Chem., 40, 385 (1902).

(22) Since this paper was first submitted to the Editor. a publication by Weiss [Trans. Faraday Soc., 31, 1547 (1935)] has appeared on the catalytic decomposition of hydrogen peroxide on metal surfaces. The present paper should have a direct bearing on this work of Weiss, especially in relation to his conclusion that the hydrogen peroxide observed in the autoxidation of metals is a stationary state concentration due to the formation and decomposition reactions. He finds that mercury does not catalytically decompose hydrogen peroxide in acid solution.