stitutions in the benzene ring. Of further bearing on the latter problem is the observation that halogen atoms in the 2(meta)-position specifically decrease the reaction rate. 2- and 3-*ter.*-butylphenanthrene were synthesized for use in the investigation.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Studies of the Reducing Action of Mercury. III. Hydrogen Peroxide Formation and the Copper-Catalyzed Autoxidation of Quinquivalent Molybdenum and Other Strong Reductants in Acid Solution

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

The first paper[1] of this series dealt with the formation of hydrogen peroxide when mercury and dilute hydrochloric acid are shaken in the presence of air. The second article[2] discussed the use of the mercury reductor in a new method for the determination of molybdenum and mention was made of the catalytic action of copper on the autoxidation of quinquivalent molybdenum.

It will be the object of this work to give data which show more clearly just what takes place in the mercury reductor when heavy metal ions are present and how it is possible to use the mercury reductor as an analytical tool even though the formation of hydrogen peroxide in the reductor is possible. Also, the question of the autoxidation of quinquivalent molybdenum solutions and the copper catalysis of this and of the analogous autoxidations of stannous, titanous and uranous solutions will be discussed more fully.

Hydrogen Peroxide in the Mercury Reductor.—Some of the work on the action of metallic mercury as a reducing agent was done by Schaffhaütl[3] and Carnegie,[4] although neither of these investigators undertook the subject from a quantitative standpoint. Later Borar[5] studied the stoichiometry of the reaction between mercury and potassium permanganate, potassium dichromate, ferric chloride and cupric sulfate.

McCay and Anderson[6] proposed the mercury reductor for use in the quantitative determination of ferric salts, and later they[7] studied the reduction of vanadic acid solutions by mercury. Finally, McCay[8] worked on the reduction of antimonic acid solutions by mercury as a quantitative method for determining antimony.

At present, then, mercury reduction has been proposed as a quantitative and efficient method for the determination of iron, vanadium, antimony and molybdenum. The reduction by mercury of solutions of these elements is always carried out in the presence of hydrochloric acid. It appears rather paradoxical that mercury can be used for the quantitative reduction of the above substances when we recall that mercury and hydrochloric acid will react rapidly with oxygen to form large amounts of hydrogen peroxide. The explanation of this seems to be largely a matter of competing rates, except in the case of antimony.

Solutions of iron, molybdenum, and vanadium salts are known to be good catalysts for the decomposition of hydrogen peroxide. It is then evident that if we shake a mixture of mercury and hydrochloric acid in the presence of oxygen and add small amounts of iron, vanadium or molybdenum salts to the mixture, the hydrogen peroxide should be decomposed catalytically by the heavy metal ions present. There would in such a case be two competing reactions: (a) the formation of hydrogen peroxide in the reaction between mercury, hydrochloric acid, and oxygen; (b) the catalytic decomposition of the hydrogen peroxide by the heavy metal ion. If reaction (a) is faster than reaction (b) we will be able to detect hydrogen peroxide in the mixture, but if step (a) is the slow one, then all the peroxide will be decomposed and will not be evident in the solution. However, the rate of reaction (b) will depend to some extent on the concentration of the heavy metal ion and the rate of its reduction by mercury since the decomposition of hydrogen peroxide by these ions is very probably an alternate oxidation and reduc-

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[1] Furman and Murray, THIS JOURNAL, **58**, 429 (1936).
[2] Furman and Murray, *ibid.*, **58**, 1689 (1936).
[3] Schaffhaütl, *Ann.*, **44**, 25 (1842).
[4] Carnegie, *J. Chem. Soc.*, **53**, 468 (1888).
[5] Borar, *ibid.*, **99**, 1414 (1911).
[6] McCay and Anderson, THIS JOURNAL, **43**, 2372 (1921).
[7] McCay and Anderson, *ibid.*, **44**, 1018 (1922).
[8] McCay, *Ind. Eng. Chem., Anal. Ed.*, **5**, 1 (1933).

tion of the ion as shown in the study of Haber and Weiss.[9]

To test these conclusions in a series of experiments, 25-ml. portions of mercury and 50 ml. of *N* hydrochloric acid were shaken with oxygen supplied from a buret for 150 minutes. The apparatus and technique were the same as in the previous study.[1]

In one pair of experiments 111 ml. of oxygen was consumed without any addition and 118 ml. when 5 mg. of vanadium was added as vanadic acid. A second pair gave 105 ml. without addition and 136 ml. with the addition of 0.5 mg. of iron as ferric chloride, while a third pair used 116 ml. of oxygen without addition and 163 ml. with the addition of 80 mg. of iron as ferric chloride. The effect of vanadium is negligible or very slight, while the iron perceptibly catalyzes the reaction.

The point of interest is the substances found in the solutions which contained iron and vanadium. In the cases where iron was present in amounts less than 0.005 g., hydrogen peroxide was detected with titanium sulfate, and the iron was found to be largely in the ferric state. In those cases where vanadium was present in amounts less than 0.005 g., the solution was of a deep red color which indicates the presence of pervanadic acid and hydrogen peroxide rather than the reduced vanadyl solution which is blue in color.

No experiments along this line were performed with molybdenum in the mercury reductor, for the quinquivalent molybdenum interferes with most of the color reactions given by hydrogen peroxide. However, it is assumed by analogy that molybdenum would behave quite similarly to iron and vanadium.

The case of antimony is different. McCay[8] found it necessary to carry out the reduction of antimony in an atmosphere of carbon dioxide, and this at once eliminates any interference from the hydrogen peroxide reaction. We have carried out experiments which show that even if very large samples (0.3 g.) of antimonic acid in 2 *N* hydrochloric acid are shaken with mercury in the presence of air, hydrogen peroxide is formed rapidly in large amounts.

Conclusions.—From the foregoing it is to be concluded that large samples (*ca.* 0.1 g.) of iron, vanadium or molybdenum decompose hydrogen peroxide as fast as it is formed in the mercury reductor and the mercury keeps these metal ions in the reduced state. However, when only very small samples (*ca* 0.005 g.) of these substances are taken, the mercury reduction method will not be reliable unless all oxygen is excluded. This means then that the mercury reductor would not be a practical tool for micro-analytical methods unless used in the absence of oxygen. This is in accord with the work of C. F. Fryling and F. V. Tooley,[10] who have found that the silver reductor yields large quantities of hydrogen peroxide when micro-samples of iron are employed.

We determined the molybdenum in the Bureau of Standards Calcium Molybdate, which is certified to contain 35.3% of molybdenum by the accepted Jones reductor method and by gravimetric technique. Using samples varying between 0.4 and 1.0 g. we obtained, by the mercury reduction method, respectively, 34.65, 34.80, 34.43, 33.90 and 33.74%, with an average of 34.3%. Iron and titanium were removed prior to the reduction of the solution by mercury.[11] We detected copper in the solution at this point. Electrolytic and colorimetric estimations of the copper gave 0.05, 0.06, 0.04, 0.06 and 0.07%, average 0.05%. The presence of copper is not mentioned on the certificate of analysis.

We believe that this error in the value for molybdenum is caused by the copper which is in the solution at the time it is reduced by mercury. When the quinquivalent molybdenum solution from the mercury reductor is filtered in the presence of air, the traces of cuprous ion present are oxidized by the air and hydrogen peroxide is formed. The hydrogen peroxide then oxidizes some of the quinquivalent molybdenum, which causes the results to be low.

The formation of the hydrogen peroxide in the reaction between cuprous solutions and molecular oxygen has been studied many times since the original observation of Traube.[12] Our idea is then that we have a cyclic reaction in which hydrogen peroxide oxidizes the quinquivalent molybdenum. It will be shown presently that under certain conditions quinquivalent molybdenum is able to reduce cupric ions to the cuprous state and this makes it possible for the cycle to continue, oxidizing more quinquivalent molybdenum in each step. Such a cycle might be pictured as follows:

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[9] Haber and Weiss, *Proc. Roy. Soc.* (London), **147A**, 332 (1934).

[10] Fryling and Tooley, THIS JOURNAL, **58**, 826 (1936).

[11] The standard procedure of double precipitation by ammonia was used according to Lundell, Hoffman and Bright, "Chemical Analysis of Iron and Steel," John Wiley & Sons, Inc., New York, 1932.

[12] Traube, *Ber.*, **15**, 659 (1882).

$$Cu^2 + Mo^5 = Cu^1 + Mo^6 \qquad (1)$$
$$2H^+ + 2Cu^1 + O_2 = 2Cu^2 + H_2O_2 \qquad (2)$$
$$2H^+ + 2Mo^5 + H_2O_2 = 2Mo^6 + 2H_2O \qquad (3)$$

With such a cyclic mechanism in mind, we have studied many conditions under which the autoxidation of the molybdenum solutions is apparently catalyzed by copper and all of the results of these experiments seem to verify the mechanism which we have postulated.

Experimental Studies on the Copper-Catalyzed Autoxidation of Quinquivalent Molybdenum Solutions.—First, in order to show that it is actually copper which causes the error in the determination of molybdenum by mercury reduction, we studied the effect of traces of copper sulfate on the determination of molybdenum in a standard ammonium molybdate solution. The ammonium molybdate solution was standardized by the silver molybdate method.[13] Copper was added in the form of a very dilute cupric sulfate solution. Total volume of solution at time of shaking was 30 ml. Hydrochloric acid concentration at time of shaking was 3 *N*.

TABLE I

EFFECT OF COPPER ON THE DETERMINATION OF MOLYBDENUM IN A STANDARD MOLYBDATE SOLUTION BY THE MERCURY REDUCTION METHOD

Copper added, mg.	0	0	0.1	0.4	0.7	1.1
Error, mg.	−0.2	+0.1	− .7	−1.1	−1.4	−1.7

If the mechanism for the autoxidation of the quinquivalent molybdenum is as indicated in equations (1), (2) and (3) the oxidation by air must take place while the solution is being filtered. This being the case, the volume of solution which passes through the funnel should have some effect on the amount of molybdenum oxidized. This was studied by taking equal samples of the ammonium molybdate solution and adding the same amount of cupric sulfate to each, then diluting the samples with 3 *N* hydrochloric acid to varying volumes before shaking with mercury. The results of this volume effect on the amount of molybdenum oxidized are shown in Table II.

TABLE II

DEPENDENCE OF COPPER AUTOXIDATION EFFECT ON VOLUME OF THE SOLUTION AT THE TIME OF FILTRATION

Copper added, g.	Total volume at time of filtering, ml.	Molybdenum Found, g.	Molybdenum Taken, g.	Error, mg.
....	30	0.2495	0.2494	+0.1
0.0005	30	.2483	.2494	−1.1
....	80	.2496	.2494	+0.2
.0005	80	.2463	.2494	−3.1
....	140	.2492	.2494	−0.2
.0005	140	.2450	.2494	−4.4

In all the experiments of Table II the copper was present at the time of reduction of the molybdenum with mercury. In order to study more fully the actual effect of the copper, we prepared a large quantity of quinquivalent molybdenum by reducing a concentrated molybdic acid solution with mercury. This reduced solution was then diluted with water and acid to yield a solution which was 0.1 *M* in molybdenum content and 2 *N* in hydrochloric acid. The solution was stored in a closed buret system under carbon dioxide and its normality with respect to the Mo^5—Mo^6 change was checked each day. Samples of this quinquivalent molybdenum solution were run into flasks, varying amounts of cuprous or cupric solutions added, then air bubbled through the mixture for a given length of time. In this way it was possible to change the copper and acid concentrations readily and also vary the time of contact of the solution with air.

The data of Table III were taken from a series of experiments run in this way, the rate of air bubbling being relatively constant throughout. These experiments prove definitely that copper is acting as a catalyst for the autoxidation of the quinquivalent molybdenum for here we are only bubbling air through a mixture of quinquivalent molybdenum and traces of copper. The HCl concentration was 1 *N* in all cases, total volume of solution being 150 ml.

TABLE III

EFFECT OF CUPRIC AND CUPROUS IONS UPON THE OXIDATION OF QUINQUIVALENT MOLYBDENUM SOLUTIONS BY AIR

Time of air bubbling, min.	Copper added, mg.	Error, mg.
15	...	+0.1
15	0.5 Cu^{++}	−1.1
15	1.0 Cu^{++}	−2.6
15	2.5 Cu^{++}	−3.2
30	...	±0.0
60	...	−0.4
30	1.0 Cu^{++}	−3.1
60	1.0 Cu^{++}	−3.4
15	0.5 Cu^{+}	−2.3
15	1.0 Cu^{+}	−2.5
30	1.0 Cu^{+}	−2.8

If the cyclic mechanism which we have postulated for the copper-catalyzed autoxidation of quinquivalent molybdenum is to be feasible, it must be shown that the first step as indicated by

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(13) McCay, THIS JOURNAL, **56**, 2548 (1934).

equation (1) is possible. This step involves the formation of cuprous ions from the reaction between cupric ions and quinquivalent molybdenum and is the starting point of the cycle. The graph of Fig. 1 shows the potentials of the two systems Mo^6/Mo^5 and Cu^2/Cu^1 plotted against acidity. The data for the copper system were taken from the work of Carter and Lea[14] and the data for the molybdenum system from the work of Foerster, Fricke and Hausswald.[15] These curves are for the equivalent mixtures of Mo^6/Mo^5 and Cu^2/Cu^1. If we consider the potentials of pure cupric solutions and pure quinquivalent molybdenum solutions, we must take into account the logarithmic concentration term in the equation

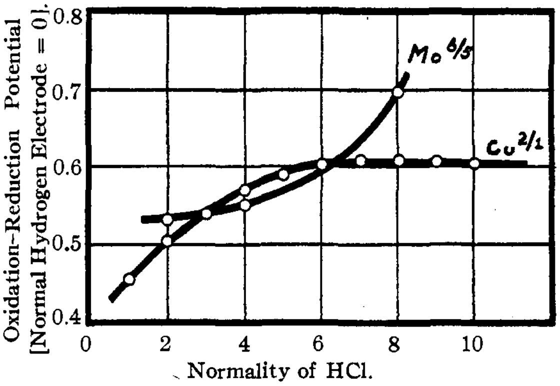

Fig 1.—Graphs of oxidation-reduction potentials of $Mo^{6/5}$ (25°) and $Cu\ ^{2/1}$ (18°) systems as functions of acidity.

$$E = E_0 + \frac{0.059}{n} \log \frac{(\mathrm{Ox})}{(\mathrm{Red})} \tag{4}$$

If we consider the ratio of (Ox)/(Red) as being of the order of $^1/_{1000}$ in the case of quinquivalent molybdenum and $^{1000}/_1$ in the case of cupric solution, then the concentration term will lower the molybdenum potential by 0.17 volt and raise the copper potential by 0.17 volt. This will then place the molybdenum potential more than 0.2 volt below that of the copper system. Under these conditions, quinquivalent molybdenum would readily reduce cupric ions in 1 *N* hydrochloric acid. However, this could not proceed for very long, for the molybdenum potential is rising and the copper potential dropping as the reaction proceeds.

A portion of a freshly prepared quinquivalent molybdenum solution was mixed with a solution of cupric sulfate and the mixture adjusted to 1 *N* concentration of hydrochloric acid. A few ml. of potassium thiocyanate solution was then added. The mixture turned dark red in color due to the formation of the complex between the thiocyanate ion and quinquivalent molybdenum, but a heavy white precipitate was formed at the same time. This precipitate was filtered off and proved to be cuprous thiocyanate. This is therefore experimental proof that quinquivalent molybdenum can reduce cupric ions to the cuprous state in 1 *N* hydrochloric acid.

It is further evident from Fig. 1 that at an acid concentration of about 5 *N* the potential of the equilibrium mixture of Mo^6/Mo^5 is always below that of the Cu^2/Cu^1 system. This would suggest that in 5 *N* hydrochloric acid quinquivalent molybdenum should be rapidly and continuously autoxidized in the presence of traces of copper, since at this acidity the molybdenum will keep more of the copper reduced. The results of such an experiment are given in Table IV.

TABLE IV

EFFECT OF 1 MG. OF CUPRIC ION ON THE OXIDATION OF SOLUTIONS CONTAINING 0.2525 G. OF Mo^V IN 5 *N* HCl

Time of air bubbling, min.	30	15	30	30
Copper added, mg.	...	1.0	1.0	1.0
Error, mg.	±0.0	−23.2	−20.5	−20.5

Conclusions.—The data presented seem to verify our ideas of a cyclic autoxidation mechanism for quinquivalent molybdenum in which cuprous ions play the important role of first reacting with atmospheric oxygen to yield hydrogen peroxide. Such a reaction accounts for the difficulties in the determination of molybdenum by the mercury reduction method when small amounts of copper are present. Although it was not easily possible to detect hydrogen peroxide as an intermediate in this case, several instances are discussed in the next section which are quite analogous to this and in which hydrogen peroxide is readily detected.

Copper-Catalyzed Autoxidation of Reducing Substances in Acid Solution.—The autoxidation of cuprous ions in hydrochloric acid solution has been studied by Wieland and Franke,[16] Filson and Walton,[17] and others. Hydrogen peroxide is formed in this reaction in large amounts and no salt has been found so far which speeds up the autoxidation of the cuprous ion. Wieland

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[14] Carter and Lea, *J. Chem. Soc.*, 499 (1925).

[15] Foerster, Fricke and Hausswald, *Z. physik. Chem.*, **146**, 81 (1929).

[16] Wieland and Franke, *Ann.*, **473**, 289 (1929).

[17] Filson and Walton, *J. Phys. Chem.*, **36**, 740 (1932).

and Franke point out the fact that it is only in acid solution that hydrogen peroxide is formed during the autoxidation of the cuprous ion.

With these facts in view, we think that it may be said that the copper-catalyzed autoxidation of reducing substances in acid solutions possibly proceeds in most cases by a cyclic mechanism similar to that which we have postulated for the autoxidation of quinquivalent molybdenum.

Filson and Walton[17] and Haring and Walton[18] found copper salts to be excellent catalysts in the autoxidation of stannous chloride solutions and even detected hydrogen peroxide in the non-catalyzed reaction. The equations which they gave for the catalyzed reaction were

$$2CuCl_2 + SnCl_2 = 2CuCl + SnCl_4 \qquad (4)$$

$$4CuCl + 4HCl + O_2 = 4CuCl_2 + 2H_2O \qquad (5)$$

It is possible that equation (5) involves hydrogen peroxide as an intermediate according to our reasoning.

The copper-catalyzed autoxidation of ascorbic acid has been studied by Barron, De Meio and Klemperer[19] who found that in acid solution the reaction is dependent both on *p*H and copper concentration. They write a mechanism which is analogous to that postulated here and which includes hydrogen peroxide as an intermediate.

Luther and Michie[20] found that the rate of autoxidation of quadrivalent uranium solutions containing small amounts of sulfuric acid was increased markedly by the addition of traces of copper. This reaction was not thoroughly studied but it appears to be another case in which the cyclic mechanism involving hydrogen peroxide would apply.

We have studied qualitatively the effect of small amounts of copper on the rate of autoxidation of titanous chloride solutions which contained hydrochloric acid. The rate was increased greatly by the addition of cupric sulfate and when the red color of the titanous salt had disappeared, the solution rapidly became yellow, which was indicative of the presence of hydrogen peroxide.

Conclusions.—In all the cases cited a reducing agent capable of reducing cupric ions to the cuprous state has been employed. In this way a system is set up in which cuprous ions are available for autoxidation and with an excess of oxygen the cycle may proceed until either all the reducing agent has been oxidized or its potential has been raised so high that it can no longer furnish cuprous ions. From these facts and the instances in which hydrogen peroxide has been actually detected in such reactions, we think it probable that in general a cyclic reaction such as indicated in equations (1), (2) and (3) is the mechanism. This is not to be confused with the frequently studied chain reactions such as the sulfite oxidation which take place in nearly neutral or alkaline solution.

Summary

1. The mercury reductor gives satisfactory results when used for the determination of iron, vanadium and molybdenum on a macro scale, for these ions catalytically decompose any hydrogen peroxide formed. It could be used for microdeterminations only when oxygen was rigorously excluded. In the macro-determination of antimony, oxygen must be excluded because the hydrogen peroxide that is formed is not decomposed catalytically by the antimonite.

2. Quinquivalent molybdenum is rapidly autoxidized when small amounts of copper are present as catalyst. A mechanism for this reaction has been postulated which involves hydrogen peroxide as intermediate.

3. It is believed that the cyclic mechanism postulated will apply to most copper-catalyzed autoxidations which take place in acid solution as, for example, those of titanous, stannous and uranous ions.

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[18] Haring and Walton, *J. Phys. Chem.*, **37**, 133 (1933).

[19] Barron, De Meio and Klemperer, *J. Biol. Chem.*, **112**, 625 (1936).

[20] Luther and Michie, *Z. Elektrochem.*, **14**, 826 (1908).