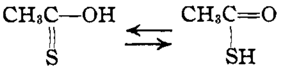
agent.[9] Triethylbismuth and tetraethyllead, however, do not evolve gas with such groups. The small volume of gas evolved from triethylbismuth and 1,3,5-trinitrobenzene is just about the experimental limit of accuracy.

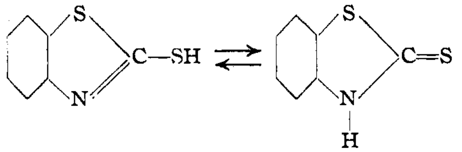
On general grounds triethylbismuth may be preferred to tetraethyllead because it not only gives high values for —SH groups but also is less interfered with by —OH groups. The inflammability and lesser accessibility of triethylbismuth is to be contrasted with the toxicity and accessibility of tetraethyllead.

Some of the results are interesting from the point of view of tautomerism. The replacement of hydrogen by metal noted with thioacetic acid establishes the presence of an —SH group, but throws no light on the equilibrium



$$\mathrm{CH_3\underset{\underset{S}{\|}}{C}{-}OH} \;\leftrightarrows\; \mathrm{CH_3\underset{\underset{SH}{|}}{C}{=}O}$$

Thioenolization is probably affected by the RM compounds used to establish the presence of active hydrogen groups. What may be a pertinent illustration are the results with 1-mercaptobenzothiazole.



Both triethylbismuth and tetraethyllead show the presence of an —SH group. However, tri-*n*-propylboron which reacts with —SH groups but not with the —NH group, gives no reaction with 1-mercaptobenzothiazole. Slight thioenolization is shown by *s*-diphenylthiourea but not by thiourea.

Some solvents may have special enolizing effects.[10]

Summary

Triethylbismuth and tetraethyllead can be used for the detection of the —SH group. These organometallic compounds do not react with the hydrogens in —NH and —C≡CH groups; they do not react with simple —OH groups, although some strong carboxylic acids undergo generally limited reactions; and there is no interference by azo or nitro groups.

The RM compounds may be useful to establish the existence of thioenolization in compounds like thioacetic acid.

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(9) Gilman and Fothergill, THIS JOURNAL, **50**, 867 (1928); Gilman, Fothergill and Towne, *ibid.*, **52**, 405 (1930).

(10) Clutterbuck, Raistrick and Reuter, *Biochem. J.*, **29**, 300 (1926).

AMES, IOWA RECEIVED FEBRUARY 15, 1937

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WASHINGTON]

The Passivity of Iron in Chromic Acid Solutions[1]

BY W. H. CONE AND H. V. TARTAR

In a previous paper[2] the authors described some experiments which showed that iron could be made active in chromic acid solutions if a sufficiently reduced pressure were maintained at the time of placing the iron in the solution. Subsequent experiments have shown that this effect of reduced pressure was associated with the presence of some sulfate ion in the solution. Experiments on iron in chromic acid solutions with and without phosphate or sulfate ion under varying conditions of temperature and pressure are described in this paper. Pertinent data on the adsorption of oxygen by iron are also given.

Materials and Apparatus.—Pure chromium trioxide (CrO_3) was prepared from potassium dichromate and sulfuric acid. The crystals were washed with concentrated nitric acid until free of sulfate and then dried at 80° to remove the nitric acid.

The data reported in this paper were obtained using No. 30 iron wire, for standardizing, Fe 99.84%. Some experiments were made with iron of varying purity without any appreciable effect on the results.

Preliminary tests showed that a reduction of pressure after the iron was placed in the chromic acid solution did not produce activity. Consequently in finding the pressure at which the iron became active, it was necessary to use a fresh piece of the metal each time the pressure was changed. To facilitate changing the sample of iron without changing the pressure, a special apparatus was constructed, Fig. 1. When the pressure in the system had been adjusted to the desired value a sample of iron wire was fed from the spool into the electrode vessel by means of the motor-driven feed rolls. The potential of the wire was determined by connecting to a potentiometer through a saturated calomel half cell. A nearly saturated potassium

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(1) Original manuscript received July 27, 1936.

(2) Cone and Tartar, THIS JOURNAL, **56**, 48 (1934).

nitrate solution was used as a bridge to connect the calomel cell with the electrode vessel. After measuring the potential of the iron against the chromic acid solution, the wire was cut and the piece removed by closing the circuit activating the electromagnet. The pressure in the system was then changed and the process repeated until a pressure was found at which there was a sudden change in the potential of the iron.

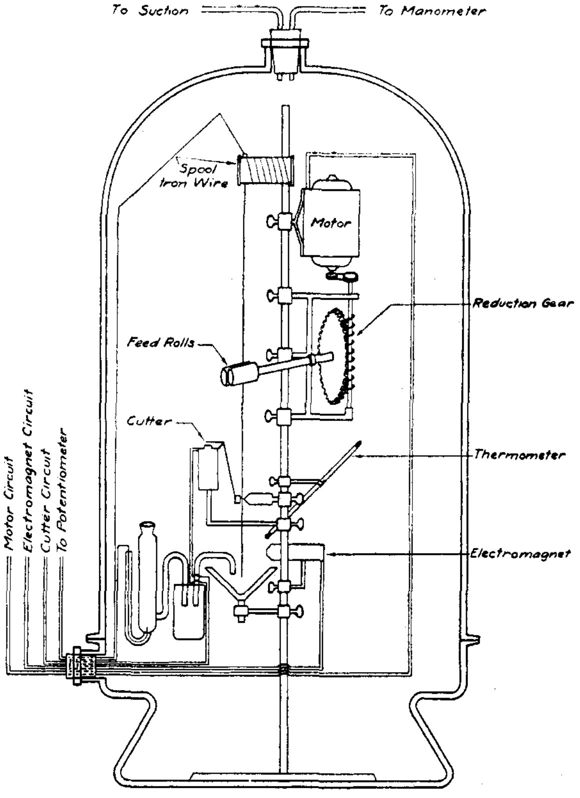

Fig. 1.—Apparatus for studying passivity at reduced pressures.

Experiments with Iron in Chromic Acid Solutions

When iron was placed under reduced pressure and then immersed in a solution of pure chromic acid, of concentrations varying from saturated to quite dilute, it did not become active even when the pressure was reduced to that of the vapor pressure of the solution. Solutions of chromic acid which contained a small amount of sulfuric acid or other activating electrolytes dissolved iron readily if the pressure was sufficiently reduced before placing the iron into the acid. The iron remained passive, however, if introduced into the solution when the pressure was above a given value which is here designated as the transition pressure.

The transition pressures could be determined either by reducing the pressure until the iron was active and then admitting air or oxygen until a sample tested passive or by decreasing the pressure slowly until a sample tested active. The results were the same within 10 mm. Since each test was made on a different piece of the wire, the surface of which varied from test to test, that was about the limit of experimental accuracy although many results did show better agreement.

The transition pressures rose rapidly with rise in temperature. This large temperature coefficient was doubtless due to two factors: changes in the adsorbed layer, and an increased activity of the ions of the activating electrolyte in the chromic acid solution.

Solutions having a high concentration of chromic acid were found to be most suitable. They were less sensitive to changes in the amount of activating electrolyte and the transition pressures occur in a measurable range at ordinary temperatures. The transition pressures were determined for several temperatures using a solution having the composition: CrO_3, 50.5%; H_2SO_4, 6.5%; H_2O, 43.0%. This was designated as solution No. 1. The data obtained with this solution are reported in Table I and Fig. 2.

Table I

Passivifying Pressure of Air for Solution No. 1 at Various Temperatures

Temp., °C.	19.9	20.5	21.6	22.6	23.0	23.9
Pres., mm.	51	88	112	115	140	153
Temp., °C.	24.5	25.1	29.1	29.6	34.0	34.3
Pres., mm.	200	200	277	300	368	395

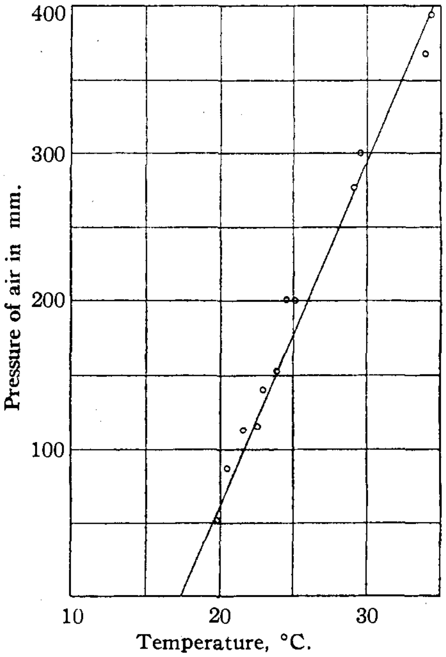

Fig. 2.—Passivifying pressures of air for solution No. 1 at various temperatures.

Similar data were obtained for a solution having the composition: CrO_3, 44.5%, H_2SO_4, 8.3%; HNO_3, 0.2%;

Table II

Passivifying Pressure of Air for Solution No. 2 at Various Temperatures

Temp., °C.	19.1	19.7	19.8	20.4	25.8	30.8	33.0
Pressure, mm.	101	140	140	150	300	565	683

H_2O, 47.0% (solution No. 2) and is shown in Table II and Fig. 3.

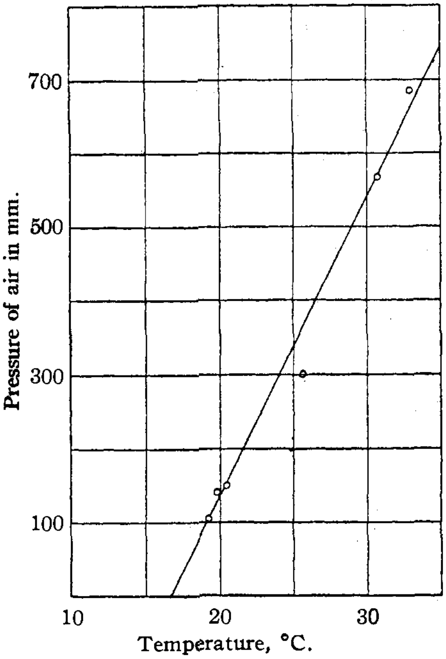

Fig. 3.—Passivifying pressure of air for solution No. 2 at various temperatures.

When oxygen was substituted for air in the apparatus the transitions took place at much lower pressures as shown in Table III and Fig. 4.

TABLE III

PASSIVIFYING PRESSURE OF OXYGEN FOR SOLUTION NO. 1 AT VARIOUS TEMPERATURES

Temp., °C.	23.8	24.5	25.7	25.9	28.5	30.7
Pressure, mm.	40	58	60	63	81	122

When iron was suspended in an atmosphere of hydrogen for a few minutes and then lowered into a chromic acid–electrolyte solution, it was active. To show that this effect was not due to hydrogen dissolved in the chromic acid–electrolyte solution a piece of wire was covered completely with the solution which was then saturated with hydrogen. The iron remained passive. If, however, the iron was raised above the solution into the hydrogen atmosphere and allowed to drain thoroughly it became and remained active when again immersed in the solution. Iron which had been in a hydrogen atmosphere did not become active in solutions of pure chromic acid.

Some experiments were made to determine whether or not a coating of iron oxide would make the iron passive in a suitable chromic acid–electrolyte solution. Iron which was permitted to rust until covered with ferric oxide or heated in air and oxidized to give a bluish color was, after exposure to air, placed in solution No. 1 and also in a 50% solution of pure chromic acid. The oxide readily dissolved in both solutions leaving passive metal with a bright clean surface. When oxidized iron was put under reduced pressure (20 mm.) and then solution No. 1 admitted, the iron oxide dissolved, the metal was active and underwent total dissolution. These results indicate that the cause of passivity of iron in these chromic acid solutions is not an oxide film.

Solutions of chromic acid containing phosphoric acid or sodium sulfate show the same behavior as those containing sulfuric acid. For example, a solution containing 50.7% CrO_3, 8.6% Na_2SO_4, 40.7% H_2O had a transition pressure in air of 70 mm. at 28.7° while a solution containing CrO_3, 50.5%; H_3PO_4, 6.5%; H_2O, 43.0% gave under similar conditions a transition pressure of 150 mm. at 26°.

That this phenomenon of activation by reduced pressure extends over a wide range of concentration of chromic acid is illustrated by a solution having the composition CrO_3, 24.0%; H_2SO_4, 8.0%; H_2O, 68%. The transition pressure in air was 460 mm. at 22°.

To make sure that the results were not influenced by the electromagnetic fields in the apparatus a few points were checked in an apparatus free from all electrical circuits. The method was slow and laborious but sufficient data were obtained to show that the electric and magnetic fields produced no noticeable effect.

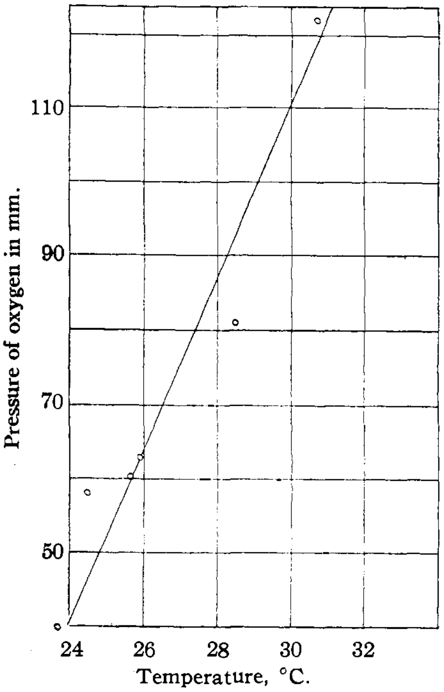

Fig. 4.—Passivifying pressures of oxygen for solution No. 1 at various temperatures.

Adsorption of Oxygen by Iron

Since the experiments described above show that oxygen plays a dominant role in the production of passivity in the chromic acid-electrolyte solutions, it was deemed advisable to determine the extent and reversibility of the adsorption of oxygen on an iron surface of the type under consideration. The apparatus was patterned after that used by Benton and White.[3] Provision was made for the collection and measurement of the gas as it came from a Töpler pump.

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(3) Benton and White, THIS JOURNAL, 52, 2325 (1930).

The oxygen was prepared by decomposing potassium chlorate. The gas was washed thoroughly and dried before it was admitted to the adsorption chamber.

Nitrogen of excellent commercial grade, which had been passed over copper at 400° to remove traces of oxygen, was used to determine the free space in the apparatus.

The iron sample was prepared by cutting 50 g. of the No. 30 iron wire into very short lengths. This was cleaned thoroughly and then heated *in vacuo* for seventy-two hours under a reduced pressure of 10^{-2} mm. No provision was made for the reduction of any invisible oxide that may have been formed by the brief contact with air because the desire was to have a surface similar to that which had been used in the previously described experiments. It is also somewhat doubtful whether the iron was completely outgassed under these conditions. The complete removal of oxygen was hardly necessitated, however, because the object was the determination of measurable adsorption in the region of transition pressures. The results of a typical run are shown in Table IV.

TABLE IV

ADSORPTION OF OXYGEN BY 50 GRAMS OF IRON AT 25°

Pressure, mm.	Cc. adsorbed (standard conditions)	Pressure, mm.	Cc. adsorbed (standard conditions)
4.0	0.07	313.5	0.21
11.0	.13	411.7	.23
51.5	.17	515.0	.29
107.3	.18	639.0	.42
195.1	.15	682.0	.49
252.3	.17		

No high degree of accuracy is claimed in the low pressure region, but above 200 mm. very concordant results were obtained. The adsorption was found to be reversible. All of the oxygen entering the apparatus could be recovered at the end of a run within the limits of the reading of the buret. There were no visible signs of oxide formation even after repeated runs on the same sample of iron. Calculations made indicated that the adsorbed layer might be several molecules deep.

A few experiments were made to determine the effect of reduced pressure on iron in nitric acid. If the pressure in a small vessel containing a piece of iron wire was reduced to about 2 mm. and then concentrated nitric acid (sp. gr. 1.42) allowed to flow in around the wire, the iron became active and dissolved completely provided the capacity of the pump was great enough to pump off the gases as fast as they were formed.

These results agree with the work of Freundlich, Patscheke and Zocher[4] in which they found that slow filling of evacuated vessels, containing iron mirrors, with nitric acid caused greater activity than when they were filled rapidly.

The differences which they observed between the "vacuum mirrors" and the "air mirrors" were probably due to the oxygen remaining on the iron which can only be removed by heating to about 300° under pressures of 10^{-2} mm.

Discussion of Results

These experiments show that iron is passive in solutions of chromic acid at all concentrations. No evidence was found of periodic passivity which occurs in certain concentrations of nitric acid. If the chromic acid contains a sufficient concentration of activating ions the concentration of the oxygen surrounding the iron is the factor which determines whether it will be active or passive when placed in solution. That this effect of oxygen is due to adsorption is indicated by the adsorption data. It should be noted, however, that while the adsorption apparatus was as dry as it was possible to make it, water vapor was necessarily present in the other apparatus. To what extent this water vapor affects the adsorption of oxygen is not known.

From this and the previous work the writers have gradually come to the belief that the primary condition for the passivification of iron is the formation on the surface of an adsorbed layer of oxygen or of a "two dimensional compound" of oxygen and iron.[5] Definite oxides may be formed subsequently, particularly in the case of anodic passivation. Such oxides are readily soluble, however, in the acidic solutions used by the authors. Evans[6] has succeeded in isolating these films of oxide from iron which had been treated with various passivifying agents but his experiments fail to prove that these films were the primary cause of passivity. The fact that an oxide-covered iron wire may be made active or passive in chromic acid–electrolyte solutions by merely changing the pressure on the iron before immersion in the liquid makes it appear doubtful whether the oxide layer is an essential factor for passivification in these media.

Summary

1. Iron under reduced pressure becomes active when placed in solutions of chromic acid containing sulfuric acid or other activating electrolytes. In pure chromic acid solutions iron does not become activated by reduction of pressure.

2. The pressure of air or oxygen required to produce passivity increases rapidly with rise in temperature.

3. An atmosphere of hydrogen causes iron to be active in a chromic acid–electrolyte solution.

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[4] Freundlich, Patscheke and Zocher, *Z. physik. Chem.*, **128**, 321 (1927); *ibid.*, **130**, 289 (1927).

[5] See Fredenhagen, *ibid.*, **43**, 1 (1903); **63**, 1 (1908); Evans, *Trans. Faraday Soc.*, **18**, 6 (1922).

[6] Evans, *J. Chem. Soc.*, 1020 (1927); 2651 (1929).

4. Data on the adsorption of oxygen by iron have been given.

5. Oxides of iron were found to be soluble in chromic acid solutions and oxide-covered wires could be made active by a reduction of pressure.

6. An adsorbed film of oxygen as a primary cause of passivity has been discussed.

SEATTLE, WASH. RECEIVED MARCH 31, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE CITY COLLEGE OF NEW YORK]

Organic Reagents[1] in Qualitative Analysis. III. The Analysis of the Common Metals of the Alkaline Earth Group and Magnesium Using 8-Hydroxyquinoline

BY LEO LEHRMAN, M. MANES AND J. KRAMER

In the field of qualitative analysis the detection of the alkaline earth metals, especially in small amounts, is one of the most difficult of all. Though a number of organic reagents have been suggested for this purpose, most of them have certain disadvantages which prevent their use in a scheme of analysis. Either they are not specific, or the presence of some other normally occurring metal interferes or else the reagent cannot be employed for separations. However, one organic substance, 8-hydroxyquinoline (oxin, 8-quinolinol), which has already been used as a precipitant for metals,[2] was found to be excellent reagent in the analysis of the group.

In this work a method of analysis of the alkaline earth metals and magnesium, using 8-hydroxyquinoline, has been developed which makes it possible to detect small amounts. In brief Ca^{++} and Mg^{++} are precipitated by the organic reagent in an ammoniacal solution containing ammonium salts. The Ca^{++} is then separated from Mg^{++} in acetic acid as the oxalate and the Mg^{++} reprecipitated as the 8-hydroxyquinoline salt by making the solution alkaline with ammonia. A distinct advantage of the use of 8-hydroxyquinoline is that any excess in the filtrate can be removed easily by evaporation, as it is apparently volatile with steam. The solution is then analyzed for Ba^{++} and Sr^{++} by one of the usual methods.

Together with the scheme of analysis a test has been worked out using tannic acid in an alkaline solution,[3] which gives a preliminary indication of the alkaline earth metals.

Experimental

1. Reaction of Alkaline Earth and Alkali Metals with Tannic Acid in Alkaline Solution.—To varying amounts from 1–500 mg. of the metals, separately, 1 ml. of 2% tannic acid solution was added and then made alkaline with 6 *M* sodium hydroxide solution. Ba^{++}, Sr^{++} and Ca^{++} gave blue-green solutions or precipitates while the others were tan colored; 1 mg. of Ba^{++}, Sr^{++} or Ca^{++} in the presence of 500 mg. of the others, except NH_4^+ gave the same result. When ammonium salts are present the solution is made distinctly alkaline with sodium hydroxide, carefully warmed until all the ammonia is volatilized and then the test is carried out. Thus 1 mg. of Ba^{++}, Sr^{++} and Ca^{++} in the presence of 500 mg. NH_4^+ gave a positive result.

2. Reaction of Ba^{++}, Sr^{++}, Ca^{++} and Mg^{++} with 8-Hydroxyquinoline.—Varying amounts from 1–500 mg. of each of the above, separately, were mixed with 5–30 ml. of saturated ammonium chloride solution, made alkaline with ammonia and 15% solution of 8-hydroxyquinoline in 6 *M* acetic acid[4] added, keeping the solution alkaline with concentrated ammonia, until no further precipitation took place. This is indicated by a yellow supernatant liquid. In order to distinguish a precipitate of a metal 8-hydroxyquinoline compound from that of the reagent itself, at first the solution was kept above the melting point, 73–74°, of the 8-hydroxyquinoline. However, it was found that the calcium salt is appreciably soluble in the hot solution. So, instead, a preliminary test was made using a saturated solution of the reagent in concentrated ammonia. The results of these experiments showed that Ca^{++} and Mg^{++} are completely precipitated while Ba^{++} and Sr^{++} are not precipitated at all.

Using the same procedure and various combinations of the metals, it was found that 1 mg. or more of Ca^{++} and Mg^{++} could be separated completely from 500 mg. of Ba^{++} or Sr^{++} or any combination of both. Similar results were obtained using Na^+ and K^+ instead of Ba^{++} and Sr^{++}.

However, when large amounts of Ca^{++} and Mg^{++} were precipitated in the presence of large amounts of Ba^{++} and Sr^{++}, as much as 5 mg. of Ba^{++} and Sr^{++} was adsorbed by the precipitate. Furthermore, in the presence of 500

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[1] Most of the organic reagents are made by the Eastman Kodak Co., Rochester, N. Y.

[2] "Organic Reagents for Metals," Hopkin & Williams, Ltd., London, Eng., p. 51.

[3] L. Rosenthaler, *Mikrochemie*, **14**, 363–368 (1934); G. Ammer and H. Schmitz, *Wasser*, **8**, II, 161–168 (1934).

[4] This solution was chosen in preference to alcohol and diluted acetic acid solutions as a result of experiments showing less volume of the precipitant would be necessary.