it was originally. This result was obtained experimentally in Sample 4, while in the other cases there could be little doubt that the original concentration would eventually be reached, since the free iodine concentration was still increasing when the experiment was discontinued. It must be pointed out here that sulfurous acid should be left as a product of the reaction. It would seem that when the reaction mixture was shaken with an excess of water the iodine should be reduced by the sulfurous acid. Sulfurous acid, however, is very easily oxidized, so no doubt the ether peroxide or even the oxygen from the air had oxidized this completely to sulfuric acid. This possibility presents another complicating factor in predicting the equilibrium point of the reaction in the presence of atmospheric oxygen.

Summary

1. A study of the reaction between hydrogen sulfide and iodine in ether solution has been carried out.
2. The reaction takes place in two ways, depending upon whether or not water is present in the ether solution. In the presence of water the reaction is incomplete; in the absence of water it is complete.
3. The equilibrium point in the reaction depends upon the relative concentration of the water.
4. Diffused daylight has no appreciable effect on the reaction.
5. Atmospheric oxygen changes the nature of the reaction and suitable precautions must be taken to exclude air.
6. A satisfactory mechanism has been formulated for the reaction and the observations are explained upon this basis.

Madison, Wisconsin

[Contribution from the Laboratory of General Chemistry, University of Wisconsin]

THE INFLUENCE OF WATER ON CERTAIN CHEMICAL REACTIONS. III. THE REACTIONS BETWEEN CERTAIN METALS AND IODINE[1]

By L. B. Parsons

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Although dry zinc and dry iodine do not react to form zinc iodide[2] in the absence of water, the addition of a few drops of water causes an immediate and violent reaction. Several other examples have been recorded in the literature in which the various well-dried halogens failed to react

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[1] The work in this paper is from the thesis presented by L. B. Parsons in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. The subject of this research was suggested by Professor James H. Walton and the investigation was conducted under his direction.

[2] Noyes and Sammet, This Journal, **24,** 498 (1902).

with metals.[3] It was thought of interest to make a study of the behavior of mixtures of various metals and iodine when water and certain organic liquids were added. From the analogies and differences thereby obtained it was hoped that some definite conclusions might be drawn as to the function of water.

Materials Used

C. P. zinc dust was used. The average of three determinations of the hydrogen equivalent gave a metal content of 97.6%. A slight residue of carbon was always left after solution in acid.

A sample of powdered magnesium was available which had a metallic content of 97.7% by the hydrogen equivalent method.

A sample of reduced iron was used which had a metallic iron content of 96.1% as determined by the method of Williams and Anderson.[4]

A sample of powdered antimony labeled C. P. was used without analysis. Finely divided silver was prepared by precipitation of the metal from silver nitrate solution with zinc dust. Samples of the finely divided metals were spread in thin layers on watch glasses and preserved in a desiccator over phosphorus pentoxide to insure dryness. The iodine was resublimed from potassium iodide and preserved in a desiccator over phosphorus pentoxide. The organic liquids used in these experiments were purified by the usual processes and subjected to drying and distillation, the appropriate fraction being preserved until needed in a glass-stoppered bottle in a desiccator over phosphorus pentoxide.

The Effect of Water on Systems of Metals and Iodine

In order to determine whether zinc reacted quantitatively with iodine to form iodide, about 0.1 g. of zinc was mixed with an excess of iodine and 50 cc. of water added. After the violent reaction was over, the liquid was boiled for several minutes to remove the excess of iodine and the iodide titrated with 0.1 *N* silver nitrate solution. Duplicate experiments showed 96.9 and 96.8% of the metal as iodide (compared with 97.6% of the purity of the zinc), indicating that practically all of the metal was converted to iodide.

When magnesium and iodine mixture was treated with water a violent reaction took place with the evolution of hydrogen, as noted by Lerch.[5] The rapidity of the reaction, when a given quantity of water was present, diminished as the amount of the metal-iodine mixture added was increased, until finally a point was reached when the further addition of the mixture caused no reaction, as evinced by the failure to produce heat and by the fact that the iodine could be extracted by a solvent such as carbon disulfide. After the iodide had been dissolved in water, metallic magnesium was found as a residue.

Quantitative experiments similar to those with zinc, in which, however,

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[3] Andrews, *Trans. Roy. Irish Acad.*, **19**, 398 (1842). Wanklyn, *Chem. News*, **20**, 271 (1869). Cowper, *J. Chem. Soc.*, **43**, 153 (1883).

[4] Williams and Anderson, *J. Ind. Eng. Chem.*, **14**, 1067 (1922).

[5] Lerch, *J. prakt. Chem.*, **28**, 342 (1883).

the excess of iodine was removed with carbon disulfide, showed that the following percentages of the original metal (97.7% magnesium) were converted to iodide: 78.0, 76.1, 79.5. In these experiments a white, water-insoluble material was obtained that was soluble in dil. sulfuric acid. This was probably magnesium hydroxide or basic iodide. The fact that hydrogen is given off by magnesium in various aqueous salt solutions might account for the low iodide values obtained. Similar experiments with iron (96.1% pure) gave quantities of iron as ferrous iodide varying from 90 to 94% of the metal taken. The solution after extraction of the iodine with carbon disulfide gave no reaction for ferric ion.

Neither antimony nor silver reacted appreciably with iodine in the presence of water.

Effect of Liquids on Mixtures of Metals and Iodine

A number of experiments were carried out with systems of metals and iodine, using various organic liquids instead of water. On account of the nature of the systems, it was not convenient to undertake quantitative analyses of the reaction products. It was found by experience that the reactions were not appreciably affected by such small traces of water as the dry solvents absorb when in contact for a short time with the air of the Laboratory. The method of experimentation finally adopted was to place the metal-iodine mixture in a clean, dry tube (taking care to have a large excess of the metal present) and then to add to this mixture the dry organic liquid. The tubes were stoppered and placed in a desiccator over phosphorus pentoxide and shaken from time to time. Duplicate runs were made in all cases. Where reactions occurred the iodine usually reacted completely with the metal. Whenever a liquid was used which was immiscible with water, the liquid was filtered through a clean, dry Gooch crucible equipped with a freshly ignited asbestos mat. The residue was well washed with the anhydrous solvent to remove the last trace of iodine and then dissolved in an appropriate acid and a test for iodides made. The filtrate was extracted with water, any small amount

TABLE I

MAGNESIUM AND IODINE WITH VARIOUS LIQUIDS

Liquid	Observations	Solubility of magnesium iodide
Ether	Reacted at once forming a dietheride[7]	Soluble[6]
Pyridine	Reacted at once forming a white precipitate which contained zinc iodide and pyridine. Soluble in water	Soluble
Alcohol	Immediate reaction with the evolution of hydrogen	Soluble[6]
Acetone	Slow reaction. Mg ion present in the filtrate. Iodine substituted in acetone	Soluble[6]

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[6] Eichmann, *Jahresber.*, **12**, 69 (1899).

[7] Menschutkin, "Etherides and Other Molecular Complexes of Magnesium Bromide and Iodide," St. Petersburg, **1907**.

of iodine removed from the extract by boiling gently, and tests for the metals and iodide were made by the appropriate methods.

In cases in which the behavior was peculiar or indefinite, the reaction was investigated further.

Magnesium and Iodine.—No reaction was obtained when the mixture was left in contact with carbon tetrachloride, carbon disulfide, benzene, heptane, chloroform, ethyl benzene and quinoline for a period of three days. Magnesium iodide is insoluble in these liquids. The cases in which reaction occurred are listed in Table I.

Zinc and Iodine.—No reaction was observed with carbon tetrachloride, carbon disulfide, benzene, heptane, chloroform and ethyl benzene. Zinc iodide is insoluble in these liquids. The cases in which reaction occurred are listed in Table II.

TABLE II

ZINC AND IODINE WITH VARIOUS LIQUIDS

Liquid	Observations	Solubility of zinc iodide
Ether	Immediate reaction	Soluble[8]
Pyridine	Reacted at once forming addition compound	Soluble
Quinoline	Reacted at once	Soluble[9]
Alcohol	Immediate reaction	Soluble[8]
Acetone	Immediate reaction	Soluble[6]

Iron and Iodine.—No reaction was observed with carbon tetrachloride, carbon disulfide, chloroform, quinoline, pyridine, heptane, ethylbenzene and benzene. Ferrous iodide is insoluble in these liquids. The cases in which reaction occurred are listed in Table III.

TABLE III

IRON AND IODINE WITH VARIOUS LIQUIDS

Liquid	Observations	Solubility of ferrous iodide
Alcohol	Slow reaction, black colloidal material soluble in water obtained. Gave test for ferrous and iodide ions	Peptized
Ether	Similar to alcohol	Slightly soluble;[10] peptized
Acetone	Similar to alcohol	Peptized

Antimony and Iodine.—No reaction was obtained with water, ether, heptane and quinoline after three days' standing. In cases where no reaction occurred antimony tri-iodide was found to be insoluble. The cases in which reaction took place are listed in Table IV.

Silver and Iodine.—No reaction was obtained with water, alcohol, ether, acetone, benzene, ethylbenzene, heptane, quinoline, chloroform, carbon tetrachloride and carbon disulfide, after several days. Potassium iodide solution brings about a reaction with evolution of heat. Silver

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[8] Hampe, *Chem. Ztg.*, **11,** 846; *Jahresber.*, **1,** 398 (1888).

[9] Beckmann, *Z. anorg. Chem.*, **51,** 239 (1906).

[10] Jackson and Derby, *Am. Chem. J.*, **24,** 15 (1900).

TABLE IV

ANTIMONY AND IODINE WITH VARIOUS LIQUIDS

Liquid	Observations	Solubility of antimony tri-iodide
Alcohol	Immediate reaction	Found soluble by experiment
Acetone	Reacts at once	Soluble by experiment
Benzene	Reacts at once	Soluble
Pyridine	Immediate reaction, white precipitate formed	Soluble by experiment
Chloroform	Slight reaction	Slightly soluble by experiment
Carbon tetrachloride	Reacted slowly to completion on long standing	Very slightly soluble by experiment
Carbon disulfide	Reacted at once; heat evolved	Soluble[11]

iodide precipitates on dilution. Pyridine also brings about a reaction with the formation of a white precipitate. Silver iodide is soluble in potassium iodide solution and in pyridine, while experiments show that silver iodide is insoluble in the other liquids.[12]

Conclusions

The data presented in Tables I, II, III and IV show that the metal and free iodine react, provided the iodide is soluble in the liquid. The logical explanation of this fact seems to be that the metal is covered by a very thin film of the iodide when it is brought into contact with iodine. This thin film serves as a protective coating preventing further reaction. It is not at all improbable that the film of iodide is so thin that it could not be detected by ordinary analytical means. It might be compared to the extremely thin films of aluminum oxide which form over metallic aluminum. When the solvent removes or loosens this film in some manner, a fresh metallic surface is exposed and further reaction takes place. It appears that there are three possible ways in which the solvent may function in removing this film: (1) straight solution, (2) chemical reaction to form well-defined complexes consisting of solvent, metal and iodine, (3) peptization.

The solution of the film is clearly demonstrated by such instances as zinc, iodine and water; antimony, iodine and carbon disulfide; and silver, iodine and potassium iodide solution.

The formation of complexes is well illustrated by magnesium, iodine and ether. It has been shown[7] that these materials react to form a complex (dietheride) that can be crystallized and has a composition corresponding to one molecule of zinc iodide and two molecules of ether. It seems probable that compounds of a similar nature may have been obtained with zinc and magnesium with the various oxygenated solvents which were used.

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[11] Gmelin-Kraut, "Handbuch der anorganischem Chemie," Carl Winter, Heidelburg, **1908**, vol. 3, pt. 2, p. 763.

[12] Seidell, "Solubility Tables," D. Van Nostrand, Co., **1919**, p. 616.

Iron and iodine with alcohol, ether, and acetone present a case in which the removal of the film seems to be due to peptization. A very black, opaque, supernatant liquid was obtained which contained no free iodine. Upon decanting and allowing the liquid to stand for several weeks a fine, black precipitate settled. This was completely soluble in water, and gave a test for ferrous iron and an iodide. It must have existed as colloidal ferrous iodide in the solution. Jackson and Derby[10] claim that pure ferrous iodide is slightly soluble in ether, but no data are available for alcohol and acetone. It seems probable, therefore, that peptization may also be complicated by a true solubility.

In this connection mention should be made of Patten's results.[13] He found that solutions of hydrochloric acid in various solvents seemed to attack metals only when the chloride obtained was soluble in the solvent. He did not attempt to show how far the parallelism went. It is noteworthy that he obtained the most rapid evolution of hydrogen in cases where the chloride was most soluble in the solvent.

That the degree of saturation plays some role in the rapidity of the reaction is shown by the experiment already described in which the violence of the reaction between magnesium and iodine depended upon the quantity of magnesium iodide in the solution. In other experiments the same effect was noted, when the iodide was sparingly soluble. This was most strikingly illustrated in the cases of antimony and iodine in carbon tetrachloride and chloroform.

The widely different behavior of the various systems and the close connection between solubility and reaction in the cases studied justify the above conclusions. The solvent in these cases does not act as a true catalyst; its function is merely to dissolve the thin film of iodide and allow more iodine to come in contact with the metal surface.

Summary

1. A series of experiments has been carried out with mixtures of various metals and iodine to which organic liquids of widely different natures have been added. Qualitative data have been obtained to show whether detectable amounts of the iodide were formed.

2. A close parallelism has been found between the ability of a liquid to bring about the reaction between metal and iodine and the solubility of the metallic iodide in the liquid.

3. It has been demonstrated that water is not peculiar in its ability to produce these reactions and that the logical explanation of the function of water, and the other solvents which produce the reaction, is that it removes the film of solid iodide from the surface of the metal.

Madison, Wisconsin

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[13] Patten, *J. Phys. Chem.*, 7, 151 (1903).