$$Na_2O_2 + 2SOCl_2 = 2NaCl + SO_2 + SO_2Cl_2.$$

From these experiments the authors conclude that sulfuryl chloride is always one of the products of the action of thionyl chloride on a peroxide, and that a sulfate of the metal is always formed when the reagent is not present in decided excess.

RUTGERS COLLEGE, NEW BRUNSWICK, N. J.

CONTRIBUTION TO THE CHEMISTRY OF GOLD.

BY VICTOR LENHER.

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The general methods by which derivatives of the aurous type of gold may be prepared are limited. Through the work of Krüss,[1] Thomsen,[2] Lengfeld[3] and Diemer, it has been established that when auric chloride is submitted to a temperature of 190°-200° it loses chlorine and the yellow-white aurous salt is formed. Aurous chloride thus prepared is unstable in character, the action of light or elevation of temperature causes it to pass to metallic gold, while the action of water causes hydrolysis with the production of metallic gold along with the trichloride. Aurous bromide is formed by the same general method of procedure as the chloride, and its properties are naturally quite similar. Aurous iodide is formed as a yellow-green precipitate when a soluble iodide is added to a solution of auric chloride, iodine being liberated at the same time. This simultaneous liberation of iodine with the formation of aurous iodide has been made available by Gooch and Moseley[4] as a volumetric method for the determination of gold, the liberated iodine being titrated with sodium thiosulfate.

One of the more general characteristics of the aurous type of derivatives is their instability. Their general tendency is to undergo with ease further reduction to metallic gold.

It has appeared obvious that should auric chloride be capable of losing two atoms of chlorine through the agency of heat and be capable of passing to the aurous state, surely some of the many available reducing agents should be capable of forming a definit aurous chloride. Repeated experiments have been made with gold trichloride and its behavior toward heat, and the best that can be said is that gold monochloride owes its existence to-day to a temperature control which gives a yellow-white solid whose analysis shows approximately the ratio of one atom of chlorine to one of gold and to the characteristic hydrolysis by water into gold and auric chloride.

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[1] *Ann.*, 237, 274 (1887).

[2] *J. prakt. Chem.*, [2] 13, 341 (1876).

[3] *Amer. Chem. J.*, 26, 324 (1901).

[4] *Amer. J. Sci.*, [4] 8, 261 (1899).

The double chlorides which aurous chloride can form are, however, far more stable and through them we can obtain an insight into the chemical character of aurous chloride. A series of systematic studies has been carried out with the view of studying the reducing action of various substances on auric chloride solutions.

Action of Certain Photographic Developers on Auric Chloride Solutions.—The commonly used photographic developers are organic reducing agents whose reducing character may be said to be within the limit of being able to reduce to metallic silver the so-called "latent image" produced in the exposed photographic plate and yet not to reduce the silver halide which has not been submitted to the molecular strain incident to exposure to light.

Aqueous solutions of the developers pyrogallol, hydroquinone, eikonogen, metoquinone, edinol, ortol, glycine, dianol, metol, adurol and amidol, either acidified with hydrochloric acid or made slightly alkalin with sodium hydroxide, when brought in contact with auric chloride solution precipitate gold instantly without apparently producing the intermediate stage of aurous chloride.

Organic Acids.—Certain of the organic acids may be considered to have a reducing character. Formic acid may be cited as one of the organic acids whose reducing character is somewhat pronounced. In presence of formic acid auric chloride in acid solution is not reduced to aurous, nor is metallic gold precipitated until the solution has been allowed to stand a very long time. When, however, such a solution is made alkalin with sodium hydroxide, metallic gold slowly separates out of the solution. Such acids as lactic, acrylic, pyroracemic and phenylacetic, act similarly.

Aldehydes.—Formaldehyde in alkalin solution is a pronounced reducing agent; when brought in contact with auric chloride in alkalin solution, metallic gold is precipitated at once. In acid solution, formaldehyde is practically without reducing action on gold solutions, indeed auric chloride acidified with hydrochloric acid has been allowed to remain in presence of formaldehyde for months without any appreciable deposition of gold. Neither is reduction to the aurous state occasioned by formaldehyde. The action of a number of other aldehydes has been studied and it may be said that in alkalin solution metallic gold is precipitated more or less rapidly from auric chloride solution, while in acid solution not only is the reduction very greatly impeded and in addition no aurous derivative obtained but an entirely different type of phenomenon presents itself. Such aldehydes as valeric aldehyde, anisic aldehyde, benzaldehyde, salicylic aldehyde and cinnamic aldehyde are immiscible with water and possess the unique property of extracting the auric chloride from the aqueous solution in a manner similar to the extraction of bromine or iodine from water by means of ether or carbon bisulfide.

Ketones.—As might be expected, the ketones deport themselves in a similar manner to that of the aldehydes when brought in contact with gold solutions. In alkalin solution the ketones as a class precipitate metallic gold more or less rapidly from auric chloride without the intermediate production of the aurous state, while in an auric chloride solution acidified with hydrochloric acid, such ketones as are immiscible with water like acetone, methyl-ethyl-ketone, methyl-butyl-ketone, acetyl-acetone, acetyl-methyl-hexyl-ketone, acetophenone and pulegone extract auric chloride from the aqueous layer, the completeness of the extraction being dependent on the solubility of the ketone in water, and of water in the ketone according to the partition law. Furthermore, the ketones in acid solution, like the aldehydes, do not cause formation of aurous types.

Esters.—As a rule the esters, which are immiscible with water, are excellent solvents for auric chloride, removing it as completely from an acidified solution as would be expected from the solubility of the particular ester in water. The esters which have thus proven good solvents for the extraction of auric chloride from solution are ethyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, diethyl oxalate, amyl formate, ethyl malonate, ethyl succinate, ethyl malate and ethyl acetooxalate. It is not possible, however, to say that all esters which are immiscible with water will extract gold chloride from solution inasmuch as with a number of mixed aliphatic-aromatic esters, no extraction takes place; such is the case with methyl benzoate, ethyl benzoate, amyl benzoate, methyl salicylate and ethyl salicylate.

Alcohols.—The alcohols, as a rule, are soluble in water to a considerable degree. Those which are immiscible with water, such as butyl, isobutyl, capryl, amyl, tertiary amyl, benzyl and valeryl alcohols, extract auric chloride from its acidified aqueous solution. In the case of a number of alcohols which are miscible with water in certain proportions, it is possible, by the addition of sodium chloride or magnesium chloride, to cause the alcohol and aqueous solution to separate into two distinct layers in which case the alcohol will extract the gold chloride from the aqueous solution; such is true with propyl, isopropyl, secondary butyl and allyl alcohols. In the aromatic series phenol and paracresol in either acid or alkalin solution quickly precipitate gold from the chloride solution.

Halogen Substitution Products.—The halogen substituted products in general are immiscible with water and cause the formation of two clearly separate layers. Auric chloride is not extracted from its solutions by any of the following: methylene dichloride, methyl iodide, chloroform, bromoform, carbon tetrachloride, amyl bromide, acetylene tetrachloride, acetylene tetrabromide, monobromobenzene, benzoyl chloride, benzal chloride, and, as one would expect, no reduction takes place to either metallic gold or to a lower state of oxidation than the trivalent form.

Sulfides.—Carbon disulfide is entirely without solvent action on gold chloride. It does not extract any of the gold chloride from its solutions. Thiophene, on the other hand, while immiscible with water, gives a distribution of the auric chloride in both layers at first. Later, gradual reduction to metallic gold takes place.

Cyanides.—The cyanides, such as methyl, ethyl, benzyl cyanide and benzonitrile, which are immiscible with water, cause very satisfactory extraction of gold chloride from its aqueous solutions. The cyanides are not reducing in character toward gold solutions.

Amines.—The aliphatic amines, as a rule, are soluble in water and are not of pronounced reducing character toward gold solutions. The aromatic amines, such as aniline, dimethyl aniline, ethyl aniline, *o*-toluidine, *m*-toluidine precipitate gold from either the acid or alkaline solution of gold chloride. Pyridine, piperidine and picoline are soluble in water, but when salt or sodium hydroxide are added two layers are formed with the auric chloride in the organic solvent.

Hydrocarbons.—A large number of saturated hydrocarbons have been brought in contact with gold chloride solution, and so far as reducing or extractive powers are concerned the results have all been negative.

Miscellaneous Organic Liquids.—Certain of the substituted esters such as ethyl cyanoacetic ester extract auric chloride from its aqueous solution, while ethyl dichloroacetate, ethyl trichloroacetone, and ethyl chlorocarbonate are without extractive power. Epichlorhydrin, acetic anhydride, paraldehyde, citral, guaiacol, acetone cyanhydrin and amyl nitrite extract auric chloride from its solutions; amyl nitrate and nitrobenzene give partial extraction, while nitromethane, ethyl nitrate, nitrotoluene, allyl mustard oil, phenetol and anethol, are without extractive action. Tributyrin causes a distribution of the auric chloride in both layers. Pyrrhol, anisidine, phenetidine, β-benzaldoxime and phloroglucinol reduce auric chloride solutions more or less rapidly to metallic gold. Vanillin, methylvanillin and coumarin quickly give metallic gold from alkaline solution, but in acid solution the reactions are quite different. With vanillin, auric chloride gives a characteristic red-brown precipitate insoluble in water and in dilute acid, while with coumarin or with methylvanillin no precipitate forms, a fact of more or less interest in connection with the analysis of commercial flavoring extracts.

By the contact of various types of organic compounds with auric chloride solution a number of kinds of reactions may be expected:

1. In acid solution such substances as the photographic developers precipitate metallic gold.

2. In alkalin solution most of the readily reactive compounds precipitate gold, while many of the same compounds give metal in acid solution, yet gold in alkalin solution is far more susceptible to even the mildest of reducing agents; indeed, light alone will slowly cause most of the known alkalin solutions of gold to deposit metal.

3. A large number of the organic liquids are excellent solvents for auric chloride, extracting it as completely from aqueous solution as the mutual solubilities of the solvent and water toward each other will permit. The more immiscible the liquid and water the better the extraction of the auric chloride. Further, by means of the insolubility of various metallic chlorides in a given solvent, it has been possible to make many separations of gold from other metals, and with many of the solvents the differential solubility of the gold chloride enables the concentration and purification of gold. The best extracting agents studied are to be found in the aldehydes, ketones, aliphatic esters and cyanides.

None of the organic substances worked with cause the reduction of the auric type to the aurous.

Action of Certain Inorganic Reducing Agents on Auric Chloride. Metals.—From the position of gold in the electrochemical series, it is obvious that the metals for the most part will replace the gold from its solution as chloride and in turn will cause it to be deposited. However, this, while true, does not necessarily indicate that the contact of metal with auric chloride solution will not give aurous chloride before the further reduction to the metallic state takes place. Actual experiment shows that the more active metals such as zinc, iron, aluminum and magnesium, cause the immediate precipitation of gold when gold chloride is in excess, while under the same conditions the more inactive metals such as lead, mercury, bismuth, cadmium, antimony and copper, deposit the gold more slowly.

Metallic arsenic, when introduced into an auric chloride solution, gradually bleaches the yellow auric to the colorless aurous. This is in line with the observation that arsenious solutions reduce auric chloride to aurous.

Various inorganic reducing agents, such as hydroxylamine, hydrazine, the alkaline nitrites, phosphorous acid, hypophosphorous acid, stannous chloride, hydrogen sulfide, ferrous sulfate and ferrous bicarbonate, have been carefully studied in their action toward auric solutions but in no case has it been possible to observe the production of the aurous state intermediate to the precipitation of metallic gold.

Action of Sulfurous Acid and the Sulfites.—von Haase[1] has studied the

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[1] *Z. Chem.*, 1869, 535.

action of the alkaline sulfites on an auric solution and describes several double aurous sulfites. In neutral or acid solution auric chloride when treated with a solution of sulfurous acid quickly deposits metallic gold, but, as has been shown by Diemer in this laboratory, when the gold chloride solution contains a considerable quantity of such chlorides as those of sodium, potassium, calcium, magnesium, zinc and cadmium, the auric solution is much more stable to the action of sulfurous acid.

When sulfurous acid solution is slowly added from a buret to an auric chloride solution containing any of the above-mentioned chlorides, the pronounced yellow color of the auric solution gradually fades until the solution finally becomes colorless. The appearance of this colorless stage represents the production of aurous chloride. In order to establish the reduction ratio of sulfurous acid to auric chloride, solutions of sulfur dioxide in water were prepared of such strength that the buret readings would correspond to less than the last significant figure given in terms of oxygen. These sulfurous acid solutions were standardized on resublimed iodine and on the iodine liberated from pure potassium iodide by means of permanganate which had been standardized on ferrous ammonium sulfate, oxalic acid, and electrolytic iron.

The first stage in the reduction of auric solutions by the addition of sulfurous acid may be indicated:

$$AuCl_3xM^{II}Cl_2 + SO_2 + 2H_2O = AuClxM^{II}Cl_2 + H_2SO_4 + 2HCl.$$

The production of the colorless solution corresponds exactly to the above ratio and gives an end point which is so sharp that it can be used as the basis of a volumetric determination of gold.

Action of Arsenite Solutions.—When a dilute solution of sodium arsenite is added to auric chloride solutions containing sodium chloride, magnesium chloride, etc., decoloration of the auric solution takes place and the aurous form of gold results. The reduction ratio may be expressed:

$$AuCl_3xM^{II}Cl_2 + Na_2HAsO_3 + H_2O = AuClxM^{II}Cl_2 + 2NaCl + H_3AsO_4.$$

In the case of sodium arsenite, it may be said that the reduction equivalent has been studied as carefully as has been the case with sulfurous acid, and while the end point of the reduction from the yellow colored or auric state to the colorless aurous condition is by no means as clear cut with arsenious solutions as is the case with sulfurous, by continued slow addition of the arsenious solution to the auric the exact point where the solution is completely bleached corresponds to the production of the aurous state.

Conclusions.

1. In alkalin solution a large number of the active organic substances precipitate gold at once.
2. In acid solution only a few types of organic compounds reduce gold

chloride to metal instantaneously. Many of the organic liquids which are immiscible with water, extract auric chloride from its aqueous solution.

3. It has not been possible to produce the aurous type of compounds by the use of an organic reducing agent.

4. Of the inorganic reducing substances sulfurous acid and arsenious oxide are the only ones studied which are capable of reducing auric to aurous gold, all others throw out metallic gold. Of these two, sulfurous acid is by far the more satisfactory reagent for reducing auric compounds to the aurous form. Its use is with the double auric chlorides, for in the absence of another salt, sulfurous acid reduces auric chloride directly to metallic gold, without apparent indication of production of the aurous state.

UNIVERSITY OF WISCONSIN, MADISON, WIS.

AUROUS CHLORIDE.

BY MELVIN E. DIEMER.

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Although univalence is one of the factors which places gold in the first group of the periodic system, the derivatives of the valence of one have not received as much attention along certain lines as is desirable.

The most satisfactory work of recent times on aurous chloride has been conducted by Lengfeld[1] who heated auric chloride for some time at a temperature of 185°. He states that at this temperature it slowly dissociates into gold and chlorine.

A few years later experiments were made in the laboratory of Professor Lenher in which auric chloride was heated to 100° and the substance weighed at definit intervals of time, thereby determining the loss of chlorine. These results plotted graphically gave a continuous curve, which showed no break or indication of change from auric chloride to pure metallic gold, and at the time apparently indicated a questionable existence of aurous chloride.

The auric chloride used in the above experiments was prepared by dissolving metallic gold in aqua regia, and removing the excess of acid by evaporation. This was in reality $HAuCl_4$ with, beyond doubt, a considerable quantity of water.

This work was repeated by the author, using material prepared in a like manner, and the same results obtained. Furthermore, when the substance thus prepared was heated in an atmosphere of hydrochloric acid gas, there was no intermediate step apparent between auric chloride and metallic gold.

Further experiments along this line were undertaken and it was found that if the auric chloride was prepared in another manner, the result of

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[1] *Am. Chem. J.*, 26, 324 (1901).