

THE DISSOLUTION OF GOLD
BY SELENIC ACID

by

LOWELL PERRY EDDY

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APPROVED:




Professor of Chemistry


In Charge of Major



Head of Department of Chemistry



Chairman of School Graduate Committee



Dean of Graduate School

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L. P. E.

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THE DISSOLUTION OF GOLD BY SELENIC ACID

I. INTRODUCTION

A. Solvents for Gold

Gold is dissolved by only one single acid—selenic acid. Mercury will physically dissolve gold. A mixture of nitric and hydrochloric acids, aqua regia, converts metallic gold to a solution of auric chloride, which in the presence of excess hydrochloric acid forms chloroauric acid, HAuCl_4 . Aqueous chlorine or bromine solutions chemically dissolve gold. Cyanide solutions with oxygen from the air put gold into solution. This comparative few number of solvents, then, constitutes our manner of converting gold to compound form. Of this group of solvents considerable information is had on dissolving gold in all but selenic acid.

B. Work of Mitscherlich and Lenher on Dissolving Gold in Selenic Acid

The fact that selenic acid dissolved gold was first reported by Mitscherlich (1). Further work on the action of selenic acid on gold was carried out by Lenher (2) in 1902. Lenher stated that with "fairly concentrated acid" gold began dissolving at 230° and proceeded more readily at 300°C . The concentration of the acid was reported only

as "fairly concentrated acid" and it seemed that the reaction should be studied further with regards to concentration of acid and temperature. Furthermore the properties of auric selenate, $\text{Au}_2(\text{SeO}_4)_3$, have only been briefly reported. It was also our interest to investigate the stability of the compound, its oxidizing power and possible uses.

II. SELENIC ACID

A. Preparation of Selenic Acid

Selenic acid was first prepared by Mitscherlich (1). He fused selenium with potassium nitrate and obtained potassium selenate. To a solution of the potassium selenate, he added a solution of a lead salt to produce insoluble lead selenate which was washed with water to remove the soluble potassium salt. The precipitate of lead selenate was suspended in water and hydrogen sulfide gas bubbled into the mixture. Lead sulfide, being more insoluble than the selenate, was produced and there remained a dilute solution of selenic acid. The dilute acid was then concentrated on a water bath.

Lenher's method of preparation of selenic acid (2) was similar to that of Mitscherlich. He was careful to exclude any halogen. Resublimed selenium dioxide was fused with pure potassium nitrate. The resulting selenate was dissolved in water and to a dilute solution, a solution of lead nitrate was added; the resulting lead selenate was washed with water until pure. It was then suspended in water and treated with hydrogen sulfide gas. The dilute acid which resulted was concentrated on the water bath and was used in his work.

Selenic acid can be prepared by the method of Morris (3). The method involves the precipitation of silver selenite and subsequent oxidation of this salt by bromine in aqueous solution. Silver bromide is precipitated, excess bromine boiled off, and any unoxidized selenous acid is removed by precipitation of selenium by hydrogen sulfide.

Pure selenic acid may be prepared by oxidizing silver selenite with bromine or chlorine in the presence of copper carbonate, separating the copper chloride formed from the copper selenate by extraction with acetone and removing copper from the residue by electrolysis (4).

It was desired to have no halogens present in the selenic acid used to dissolve gold. Accordingly an oxidizing agent other than free halogen was necessary to be certain that no halogen was present in the final preparation of selenic acid. Hydrogen peroxide will oxidize selenous acid to selenic acid and be reduced to water. Partial oxidation of selenous acid to selenic acid by thirty per cent hydrogen peroxide has been reported by Meyer and Heider (5) and Huff and McCrosky (6). Complete oxidation of selenous acid to selenic acid by 30% hydrogen peroxide was achieved by Gilbertson and King (7).

The selenic acid used in the work on this problem was prepared by the method of Gilbertson and King. In

this laboratory the first preparation of selenic acid was not a good one because it was not completely oxidized to selenic acid; it tested 41% H_2SeO_4 and 44% H_2SeO_3 . Methods of analysis of selenous and selenic acids will be described below, and these methods of analysis were of marked importance in the attainment of pure selenic acid. This first preparation did dissolve gold.

A second preparation of selenic acid was made as follows: Black, powdered selenium was oxidized to selenous acid by an excess of concentrated nitric acid (8). Concentrated nitric acid will oxidize sulfur to sulfuric acid but selenium only to selenous acid. The remaining black sediment was removed by filtration through a sintered glass funnel. The clear filtrate was evaporated in an evaporating dish on a water bath until only a cake of selenium dioxide remained. A watch glass, convex side up, was placed over the dish and an inverted funnel over the watch glass. Heat from a small bunsen flame caused selenium dioxide to sublime from the lower side of the cake onto the sides of the evaporating dish and the upper part of the cake. Most of the material was deposited as needle-like crystals on the upper surface of the cake, very little on the sides of the dish and scarcely any on the watch glass. When a reasonable amount of the sublimate had been formed, the dish was allowed to cool and

the sublimed product scraped off; care was taken not to disturb the residual cake. A further crop was obtained by adding a little nitric acid to the residue and repeating the process. Unless the nitric acid is added to the residue before repeating the process, the sublimate becomes pink, indicating some decomposition to elementary selenium. Selenium dioxide vapor (in a sealed tube) is a yellowish green color; there was not any visible during the above-described sublimation, only a white smoke of selenium dioxide.

The sublimated selenium dioxide in amount of 180 grams had added to it 520 milliliters of 30% hydrogen peroxide and the mixture was allowed to stand for 24 hours in one liter flask (7). The mixture was then refluxed in an all-glass apparatus for twelve hours while a slow stream of oxygen was bubbled into the solution. A small portion was withdrawn and on the addition of sulfurous acid, a heavy, red precipitate of selenium quickly formed, indicating the presence of selenous acid. More hydrogen peroxide was added to the boiling flask, oxygen was bubbled in, and refluxing was continued. One-half-milliliter test portions were withdrawn and tested with sulfurous acid. As more thirty per cent hydrogen peroxide was added and refluxing continued with oxygen bubbling into the solution, the precipitate obtained became less heavy and took more time to form. More hydrogen peroxide was added

and oxygen was bubbled into the solution. The oxidation continued for eight days—at that time the test portion plus sulfurous acid was developed only a faint yellow color after two hours standing. Hence the acid was shown to contain only a small trace of selenous acid.

B. Concentrating, Removal of Water

All of the selenium had been oxidized to the plus six oxidation state, and the selenic acid was a dilute solution. The acid was concentrated in three steps. Firstly water was distilled off by heating the dilute acid on the water bath at atmospheric pressure. The second step was to close the system and reduce the pressure to five to ten millimeters of mercury while heating the acid on the water bath and distilling off more water. The final step was to replace the water bath with an oil bath and carefully heat to 150° within a few degree range and with the pressure reduced to five to ten millimeters of mercury boil off the last bit of water. Temperatures above 160° are to be avoided to prevent selenic acid from decomposing.

The liquid remaining in the flask was quickly chilled and frozen in an acetone-dry ice bath. The selenic acid and water crystallized on immersion in the cold bath.

The next morning the contents of the flask were at room temperature; the crystals had some water with them in the flask. Dry air was bubbled through the flask at five to ten milliliters pressure for 19 days to take out some of the water and there resulted a slushy snow-like mass. The crystals were removed from the mass by means of a sintered glass funnel inside a vacuum dessicator. The aspirator was connected to a small suction flask into which was fitted the sintered glass funnel. Dry air was admitted to the dessicator and the dry air passed over the crystals and out through the suction flask. The prepared dry crystalline selenic acid melted at 58°C and was 98% selenic acid. The filtrate liquor contained long, slender needle-like crystals, probably the monohydrate, $\text{H}_2\text{SeO}_4 \cdot \text{H}_2\text{O}$, and tested 87% selenic acid.

C. Determining Concentration of the Acid

An easy, quick way to find the concentration was needed. A table relating index of refraction and concentration of selenic acid had been published by Stone (9). A drop of selenic acid was put on the prism of an Abbe refractometer, the prism closed and the water at 20°C was circulated through the instrument. The value obtained for the index of refraction of the 87% acid was $n^{20} = 1.5233$; and that value was beyond 100% on Stone's table.

An indirect method for the titrimetric determination of selenates in the presence of selenites has been described by Soth and Ricci (10). Hydrobromic acid was added to the diluted sample of selenic acid in a boiling flask. The selenic acid was reduced to selenous acid and bromine liberated. This was done in an all-glass apparatus. The bromine was distilled off, and with the accompanying water vapor, condensed and trapped in a potassium iodide solution where the bromine was reduced to bromide ion and iodine liberated. The liberated iodine was then titrated with standard (0.1 N) sodium thiosulfate, standardized against 0.1000 N potassium dichromate solution.

To determine the amount of selenous acid in the selenic acid, total selenium was determined by the method of Stone (9). To the weighed sample of selenic acid, concentrated hydrochloric acid was added, and some water was also added. The selenic acid was reduced to selenous acid. The mixture was heated to boiling and a saturated SO_2 solution was added. The sulfurous acid (SO_2 solution) precipitated all of the selenium from the selenous acid. A temperature of 90°C was maintained until the red precipitate first formed turned black and further additions of SO_2 gave no red color. After digestion at $80\text{--}90^\circ$ for four or five hours, the precipitate was collected on a Gooch filter, washed with cold water until

free from chloride ions, dried at 105-110°C, cooled, and weighed.

This weight of selenium corresponded to the total selenium present—as selenic acid and selenous acid. The per cent selenic acid determined above was equivalent to a definite amount of selenium; any selenium over that amount was equivalent to selenous acid.

For example, the first preparation of selenic acid tested 41.2% selenic acid and 49.7% selenium. The 41.2% selenic acid was equivalent to 22.5% selenium; that left 27.2% selenium equivalent to selenous acid—44.4% selenous acid.

D. Making Dilutions

In order to test the solubility of gold in selenic acid, several concentrations were needed. Various dilutions of selenic acid were made by diluting the 87% acid. A portion of the 87% acid was weighed in a weighing bottle and water was added to make the desired dilution. The strength was then calculated. For example,

wt. of weighing bottle + 87.2% acid	= 15.6904 g.
wt. of bottle empty	= <u>12.0237</u>
wt. of 87.2% acid	= 3.6667
wt. of selenic acid = (3.667)(0.872)	= <u>3.1974</u>
wt. of water in 87.2% acid	= 0.4693

wt. of bottle + 87.2% acid + water	= 16.1616 g.
wt. of bottle, empty	= <u>12.0237</u>
wt. of 87.2% acid + water	= 4.1379

concentration of diluted acid $\frac{3.1974}{4.1379} \times 100 = 77.3\%$

Dilutions of 67, 57, 47, 37, 27 and 17% selenic acid were prepared in like manner.

E. General Properties of Selenic Acid

Concentrated selenic acid, above seventy per cent, is a colorless, oily liquid similar to sulphuric acid. Like sulfuric acid it has a great affinity for water, and it evolves much heat on dilution. Organic matter is charred by concentrated selenic acid. Unlike sulfuric acid, it will oxidize hydrochloric acid to produce chlorine and be reduced to selenous acid. Sulfur dioxide will reduce selenic acid very slowly in the cold but will reduce selenous acid very quickly to produce a red precipitate of selenium—this reaction is a good qualitative test to determine the presence of selenous acid in selenic acid solutions. Selenic acid melts at 58°C. It is a powerful oxidizing agent and a fairly strong acid—its second ionization constant is 1×10^{-2} .

III. GOLD DISSOLUTION IN SELENIC ACID

A. Description of Gold Used

The gold used in the present work was pure gold wire, 0.490 millimeters in diameter, flattened to a thickness of 0.035 millimeters. A piece of the flattened wire, about 1.5 mm. by 3 mm. weighed about three or four milligrams.

B. Using Various Dilutions of Acid

1. Rapid Heating

Three milligrams of the flattened gold wire dissolved rapidly in one gram of 98% selenic acid, the action started at 180° and proceeded very rapidly at 240°C. The gold and acid were heated in a tube over a microburner and the temperature went up very rapidly. The solution was a dark yellow color, and on cooling the solution became a lighter yellow, but no crystals of gold selenate separated. The formed gold selenate was soluble in the excess of selenic acid.

By heating more slowly with the microburner, another sample, 17 mg. of the wire, was treated with one gram of 98% selenic acid. The dissolution started at 150° and progressed rapidly at 250°; the heat had been applied for

twenty minutes. Two hundred milligrams more of gold wire were dissolved in the same solution to produce a reddish-amber solution of gold selenate. Yellow microcrystals separated on cooling.

In this series of experiments the gold and selenic acid were contained in a tube which was joined to an air condenser by means of a ground glass joint. The tube and the condenser were inside a glass chimney; heat was applied at the bottom of the chimney by means of a microburner. Heat from the burner heated the tube containing the gold and selenic acid and also heated the air condenser. As a result the acid in the tube became more concentrated as the heat was applied—the water vaporized and rose in the air condenser.

The following table summarizes the results of this series:

Acid	Action Started	Action Completed	Time
98%	150°C	250°C	8 min.
87	170	230	8
77	205	250	7
67	210	242	7

2. Slow Heating

In order to minimize the effect of the acid becoming more concentrated as it was heated, the apparatus was modified. The air condenser was replaced by a water-cooled condenser, the outside chimney was removed, and the micro-burner was replaced by some nichrome resistance wire connected to a varitran. The heating element allowed slower, more reproducible heating.

In this series of experiments one-half milliliter of selenic acid was used on 2.8 mg. of flattened gold wire, 0.025 mm. thick and having a surface area of about 7.5 square mm. With the slow heating there was less vapor lock in the new apparatus.

Acid	Action Started	Action Completed	Time
98%	135°C	190°C	10 min.
87	160	230	12
77	185	245	6
67	205	245	3
57	185	245	5
47	115	245	10
37	180	245	5
27	105	215	100

The temperature at which the action started was the temperature at which the solution became a faint yellow color; the action was said to be completed when the gold was all dissolved. The time noted in the above tables was the minutes between time of first pale yellow color and complete solution.

3. Constant-Temperature Heating

a. Open System. Another series of experiments was performed to determine at how low a temperature the gold would dissolve, with very slow heating. One-half milliliter of selenic acid and 3.8 mg. of gold (12 sq. mm. area) were used in each case.

With one-half ml. of 98% selenic acid on 3.8 mg. of gold a light yellow solution was apparent at 94°C, after being warmed gently for eight minutes; and after five hours heating, the temperature never becoming more than 140°, the gold had all dissolved.

With the 87% acid, after fourteen minutes gentle heating the temperature was at 120°, at which the action started, and after sixty hours, the temperature not higher than 134°, the gold had all dissolved.

The 77% acid started acting on the gold after two hours, action starting at 130°; the temperature was never above 137°, and the gold dissolved in 120 hours.

With the 67% acid, it took 24 hours for the action to start at 130°, the temperature during heating varied from 115 to 130°, and the gold dissolved in 17 days.

b. Closed system. In order to eliminate the effect of the acid becoming more concentrated during the heating process, the gold and acid were put into a thick-walled pyrex test tube, and the tube was sealed. A constant-temperature bath was obtained by boiling chlorobenzene in a reflux apparatus; the chlorobenzene boiled at 130°C.

Fifty milligrams of flattened gold wire was used in each tube. Three tubes were prepared, one with some 98% selenic acid, one with one-half milliliter of 87% selenic acid, and one with one-half milliliter of 67% acid.

The sealed tubes were put into the flask containing the boiling chlorobenzene, and they were suspended in the vapors. Action started in the tube containing the gold and 98% acid after ten minutes in the flask, and solution of the gold was complete in three days.

In the tube with the 87% acid and gold, some action was apparent after eight and one-half hours. Action was complete in twenty-six days. There was only a very slight action in the tube containing the 67% acid and gold after twenty-six days.

It was desirable to know the action at a temperature above 130° ; so bromobenzene, which boiled at 154°C , was put into the reflux apparatus. Some 98% selenic acid and 20.8 mg. of gold, one-half milliliter of 87% acid and 20.8 mg. of gold, and one-half milliliter of 63% acid and 22 mg. of gold were placed in heavy-walled pyrex test tubes, and the tubes were sealed.

With the 98% acid the gold was in solution after thirteen hours in the 154° bath. It took thirteen days for the 87% acid to dissolve the gold at 154°C . The 63% selenic acid did not have any action on the gold in thirteen days at 154°C .

In the sealed tubes the acids of 87% strength and stronger in a reasonable time dissolved the gold at a temperature as low as 130°C . The more dilute acid, 67%, would eventually dissolve the gold at 130° . At the higher temperature, 154° , the concentrated selenic acid (87% and stronger) dissolved gold in a shorter time.

These data showed that in the open tubes the more dilute acids, below 67%, dissolved gold when the heat supplied concentrated them to strengths above 67%.

IV. GOLD SELENATE, PROPERTIES

A. General

Gold selenate was obtained as very small golden yellow crystals. It was soluble in hot concentrated selenic acid; much salt dissolved in a small amount of acid formed a reddish-amber solution—the crystals separated on cooling. It was insoluble in water; gold selenate was precipitated from a selenic acid solution by dilution. It was insoluble in nitric acid and sulfuric acid. Hydrochloric acid decomposed the salt and evolved chlorine. It was decomposed by heat to give metallic gold. Gold selenate seemed to be light sensitive—the golden yellow salt darkened on exposure to light and air. When the salt was covered with concentrated selenic acid in a test tube, light did not decompose it. When the salt was taken out of the selenic acid solution and put on a slide, decomposition occurred. Perhaps the decomposition on the slide was due to the oxidizing action of the salt on dust particles from the air.

B. Oxidizing Agent

Gold selenate is a powerful oxidizing agent. The higher valence of gold and the higher valence of selenium

makes the salt sensitive to reduction. As was pointed out in the analytical work, selenic acid oxidizes hydrochloric acid; and gold selenate likewise oxidizes hydrochloric acid. It was desired to further test the oxidizing power of the salt on some organic liquids.

About 5 milligrams of gold selenate was placed in a three-inch test tube, and one milliliter of the liquid was placed on the salt. After careful agitation the tube was stoppered and allowed to stand. In most cases the salt turned black in a matter of hours, and after several days a deposit of selenium or gold was observed.

The following table summarizes the results:

Organic solvent	Appearance of salt	Appearance of solvent	Oxidation
Chloroform . . .	black, Se and Au deposited	clear .	positive
Carbon tetra-chloride . .	yellowish, no change .	clear .	negative
Ethyl alcohol .	black, faint gold mirror, faint red of selenium	clear .	positive
Ethylene glycol .	black, faint red of Se.	clear .	positive
Diethyl ether .	black, faint deposit of gold	clear .	positive
Ethyl acetate .	black, faint deposit of gold and selenium	clear .	positive
Acetone	black, Se and Au deposited	clear .	positive
Benzene	black	amber .	positive
Toluene	black, gold deposited .	amber .	positive
Xylene	black, gold mirror formed	clear .	positive

C. Crystals

The crystals obtained from separating gold selenate from selenic acid solutions by dilution with water were very small—too small to tell much about their crystalline structure under high magnification by a microscope.

Some of the crystals were digested with 87% selenic acid on them at 100°C for eight days. On microscopic examination, there were seen many six-sided plates which were isotropic (dark under polarized light); some crystals were not hexagonal—those were anisotropic (under polarized light they blacked out every ninety degrees). The crystals were still quite small even after the period of digestion. They probably belong to the hexagonal system.

A larger amount of gold selenate was sealed in a tube with some 87% selenic acid. The tube and contents were heated at 175°C for five days; all of the salt was not in solution, and the solution was a reddish-amber color. The temperature was gradually lowered over a period of a month. The tube was opened and some crystals were taken out for examination. There were crystals that were much larger than had been obtained before, but still not large enough for crystallographic analysis. The habit of the crystals was platy.

D. Possible Uses of Gold Selenate

Both gold and selenium are used separately to make ruby glass. With both gold and selenium together as gold selenate perhaps the salt will find use in the glass industry to make ruby glass.

In order to test its coloring properties, some glass was made. A soda glass with approximate composition $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$ was made by taking two grams anhydrous sodium carbonate, one gram calcium carbonate, and three and six-tenths grams silicon dioxide. About one milligram of gold selenate was added to the dry mixture, and the constituents were thoroughly mixed. The batch was heated in a small porcelain crucible by means of a gas-oxygen torch. The glass was allowed to cool, and then it was reheated. A lovely pink-violet glass was the result.

Some gold selenate on a glass slide was heated in the flame of the gas-oxygen torch; the part of the slide covered by the salt was a golden color by reflected light and a blue color by transmitted light.

Another use of gold selenate would be as an oxidizing agent, but probably not an important use because of its cost, insolubility, difficulty of preparation, and difficulty of preservation.

V. SUMMARY

Selenic acid is the only single, simple oxygen acid that will dissolve gold.

Pure selenic acid can be prepared by oxidizing sublimed selenium dioxide with 30% hydrogen peroxide. The dilute acid thus prepared can be concentrated on a water bath and then on an oil bath, and crystalline selenic acid can be obtained from the concentrate. The crystalline acid melted at 58°C; it was very hygroscopic. The acid was a very powerful oxidizing agent. Concentrated selenic acid is similar to concentrated sulfuric acid.

Pure gold wire, 0.5 millimeters in diameter, was flattened to 0.035 millimeters in thickness and was used in the dissolution experiments. Various dilutions of acid were used on the gold; selenic acid, 27% to 98%, dissolved the gold when heated in an open system, temperatures varying from 105°C when the action started, to 245°C when the action was rapid. The dilute acids became more concentrated during the heating of the acid and gold; water boiled out of the tube.

With the gold and selenic acid sealed in a tube and heated, there was no water lost, and only selenic acid 87% and stronger dissolved the gold at an appreciable rate. At 130°C, 98% selenic acid dissolved 50 milligrams

of gold in three days; while at 154°C 98% selenic acid dissolved 21 milligrams of gold in thirteen hours. The 87% acid took considerably longer.

Gold selenate, $\text{Au}_2(\text{SeO}_4)_3$, is a yellow, micro-crystalline salt, insoluble in water; it can be separated from selenic acid by dilution with water. It is a very powerful oxidizing agent on inorganic substances and many difficultly-oxidizable organic solvents are oxidized by it. Crystals were grown that were larger than those obtained by precipitation of the salt from a selenic acid solution by dilution, but they were still too small for crystallographic work. Some microscopic evidence indicated that the crystals probably belong to the hexagonal system. Gold selenate may find use as a coloring agent in preparing ruby glass and as a new oxidizing agent.

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