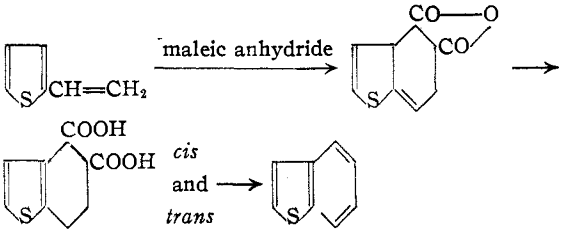

Experimental[6]

2-Thienylethanol.—The Grignard reagent from 130 g. (0.62 mole) of 2-iodothiophene[7] was prepared by the usual procedure and the reagent transferred by nitrogen pressure to a 1-liter, 3-neck, round-bottomed flask, equipped with a mercury-sealed stirrer, dropping funnel and thermometer and immersed in an ice–salt mixture. A solution of 30 g. of ethylene oxide in 100 ml. of dry benzene was added as quickly as possible, while maintaining the temperature at −10°. The reaction was very vigorous and exothermic but was easily controlled by regulating the flow through the dropping funnel and stirring at high speeds. The temperature was allowed to rise to room temperature and the mixture stand for one hour. It was poured into a dilute solution of hydrochloric acid and the ether–benzene layer separated and dried over anhydrous sodium sulfate. The ether and benzene were removed and the product distilled at reduced pressure to obtain 40 g. (50%) of 2-thienylethanol,[8] a water-white liquid, b.p. 99–100° (7 mm.).

2-Vinylthiophene was prepared by the dehydration of 2-thienylethanol,[8] and also by the method of Emerson and Patrick.[9]

Adduct Formation.—2-Vinylthiophene, 60 g. (0.55 mole), and 53.9 g. of maleic anhydride in 150 ml. of dry benzene were gently refluxed for 4 hours on a steam-bath. The hot benzene solution was decanted from the solid residue that had separated during the refluxing; the residue was extracted with 100 ml. of hot benzene. The combined benzene solutions were evaporated at reduced pressure to obtain the adduct.

The adduct was dissolved in 30% potassium hydroxide, solution being effected by gentle warming on the steam-bath. The resultant solution was cooled in an ice-bath and carefully acidified with 6 *N* hydrochloric acid. The precipitated acid was filtered and dried. Recrystallization from methanol gave 45 g. (35%) of 4,5,6,7-tetrahydrothianaphthene-4,5-dicarboxylic acid, m.p. 180–185°; neut. equiv. calcd. 113, found 112.

Anal. Calcd. for $C_{10}H_{10}O_4S$: C, 53.10; H, 4.43. Found: C, 53.14; H, 4.38.

The acid was partially dissolved in 200 ml. of hot ethyl acetate; the volume of the solvent was reduced to 150 ml. On cooling, a white crystalline precipitate separated and was filtered. Evaporation of the filtrate to 75 ml. yielded a second crop of crystals. The total yield was 22 g., which was recrystallized from methanol, m.p. 188–189°.

Anal. Calcd. for $C_{10}H_{10}O_4S$: C, 53.10; H, 4.43. Found: C, 52.92; H, 4.16.

The ethyl acetate-insoluble acid was recrystallized from methanol to obtain 20 g. of white needles, m.p. 194–195°.

Anal. Calcd. for $C_{10}H_{10}O_4S$: C, 53.10; H, 4.43. Found: C, 52.93; H, 4.19.

Isomerization.—Three grams of the acid (m.p. 188–189°) was dissolved in 50 ml. of glacial acetic acid and the solution was saturated with dry hydrogen chloride gas. After the mixture had boiled for 4 hours under a continuous stream of hydrogen chloride, the gas was removed by boiling. The acetic acid solution was concentrated to half its volume after which dilution with water gave the unchanged acid.

One gram of the acid (m.p. 194–195°) was treated with dry hydrogen chloride gas in glacial acetic acid as described above. The isolated product was recrystallized from ethyl acetate, m.p. 186–187.5°. Mixed melting point with the acid (m.p. 188–189°) showed no depression.

Structure Proof of Adduct.—The acid (m.p. 188–189°) and 1.5 g. of sulfur were placed in a 50-ml. claisen flask, fitted with a gas trap, containing silver nitrate solution. The flask was immersed in an oil-bath and heated to 200°, where the mixture turned dark brown and began to effervesce, with the evolution of hydrogen sulfide gas. The gas was evolved rapidly at 205°; heating was continued until the evolution stopped, as evidenced by the formation of silver sulfide.

To the aromatized anhydride was added 15 g. of barium hydroxide and the mixture distilled to yield a yellow oil, which was steam distilled from a solution of potassium hydroxide. The yellow oil was identified as thianaphthene through the picrate, m.p. 145–147°. Mixed melting point with an authentic sample of thianaphthene picrate showed no depression.

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[6] All melting points were determined using a conventional melting point block. Analyses are by A. A. Sirotenko formerly of this department.

[7] W. Minnis, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 357.

[8] J. W. Schick and H. D. Hartough, This Journal, **70**, 1646 (1948).

[9] W. S. Emerson and T. M. Patrick, *J. Org. Chem.*, **13**, 730 (1948).

Low Concentration Chemistry. VI. Some Properties of Tracer Gold in Solution

By George K. Schweitzer and William N. Bishop

Received July 16, 1953

The purpose of these experiments was to investigate the radiocolloidal behavior, solvent extraction properties and adsorption characteristics of gold in very low concentration solutions using gold-199 as a tracer.

Experimental

Preparation of Gold Solutions.—Gold-199 was obtained from the Oak Ridge National Laboratory in irradiated platinum foil. The nuclide has a half-life of 3.3 days,[1] decaying with the emission of 0.45-, 0.29- and 0.24-mev. β-particles and 0.21-, 0.16- and 0.05-mev. γ-rays.[2] A modification of the method of Gile, Garrison and Hamilton[3] was used to separate the gold and then hydrochloric acid solutions of the gold were prepared. Spectrographic analysis of a piece of the platinum foil and the microchemical test of Hahn[4] indicated that the gold solutions were more dilute than 10^{-8} M.

Adjustments of *p*H.—The various solutions were adjusted to desired *p*H values by adding either sodium hydroxide or hydrochloric acid solution. Measurements of *p*H were made on a Beckman Model G-2 Glass Electrode *p*H Meter using microelectrodes.

Sample Preparation.—Samples were taken with a 0.100-ml. micropipet and syringe. These samples were placed on copper planchets or glass cups and evaporated to dryness under a heat lamp.

Radioactivity Apparatus.—Radioactivity measurements were made with a 3.5 mg./cm.^{2} end-windows, halogen-quenched G–M tube attached to a Tracerlab SC-2A Scaler. All samples were counted for a sufficiently long time to give a standard deviation equal to or less than 1%.

Filtration.—Five-ml. portions of the radiogold solution originally 0.01 *N* in hydrochloric acid were adjusted to desired *p*H values and were filtered through Whatman No. 50 filter paper. Samples were taken before and after filtration, the differences in radioactivities being used to determine the percentage removal.

Centrifugation.—Portions of the radiogold solution originally 0.01 *N* in hydrochloric acid were adjusted to desired *p*H values, placed in centrifuge tubes holding about 0.7 ml., and allowed to stand until adsorption equilibrium had been reached. This latter process required a time of about an

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[1] L. A. Beach, C. L. Peacock and R. G. Wilkinson, *Phys. Rev.*, **76**, 1385 (1949).

[2] O. Haber, F. Humbel, H. Schneider and A. DeShalit, *Helv. Phys. Acta*, **24**, 629 (1951).

[3] J. D. Gile, W. M. Garrison and J. G. Hamilton, *J. Chem. Phys.*, **20**, 339 (1952).

[4] F. L. Hahn, *Microchemie ver. Microchim. Acta*, **38**, 136 (1951).

hour. Then the solutions were sampled, centrifuged for 30 min. in a Misco Microcentrifuge at about 25,000 times gravity, and finally resampled. The differences in radioactivities were again employed as a measure of the amount of gold removed.

Centrifugation of solutions to which carrier gold(III) chloride had been added were also performed. Solutions originally 0.1 *N* in hydrochloric acid and others originally 1.5 *N* in hydrochloric acid were adjusted to a *p*H value of 5.0, sampled and centrifuged as before.

Extraction.—Five-ml. portions of radiogold solution of the desired normalities in hydrochloric acid were stirred with an equal volume of diethyl ether. The layers were separated and samples were taken from each. Extractions from solutions containing carrier gold(III) chloride and 1.5 *N* in hydrochloric acid were carried out in a similar manner.

Adsorption.—Five-ml. portions of the radiogold solution originally 0.01 *N* in hydrochloric acid were adjusted to various *p*H values, placed in 12-ml. weighing bottles with two 5-mm. soft-glass beads, and shaken for one hour. Exploratory experiments had shown that maximum adsorption is reached in this time. The solutions were sampled before and after shaking, the differences in radioactivities being ascribed to adsorption onto the container and the glass beads.

Similar experiments were performed, each sample being shaken with 100 mg. of 20-mesh silica. Then a series in which each sample was shaken with 10 mg. of Norit A decolorizing carbon was run.

Results

All the following values with the exception of those for the adsorption on glass are the averages of at least three separate determinations. These average values listed in the tables are given with the standard deviations attached; those on graphs have the standard deviations indicated by vertical lines unless the standard deviation is less than 2.0 percentage points.

Filtration and centrifugation of the tracer (less than 10^{-8} *M*) solutions of gold gave indications that gold shows radiocolloidal behavior under certain solution conditions, as do many other elements.[5] The results of the centrifugation and filtration studies are shown in Fig. 1. The marked decrease in removal of gold in the acid region might be ascribed to the formation of chloroaurate complexes. Likewise the formation of hydroxoaurate complexes could produce the effect observed in the basic region. The large removal in the more neutral region is characteristic of radiocolloids. However, the possibility that minute amounts of impurities might be acting as reducing agents for the gold(III) cannot be entirely ruled out. Table I contains the results of centrifugations of carrier gold solutions, group A being the solutions originally 0.1 *N* in hydrochloric acid and group B being those originally 1.5 *N* in the same acid. Because of the variation in the literature values given for the solubility of gold(III) hydroxide[6] and the lack of data concerning the form of the gold(III) ion in solution, it is not possible to ascertain whether the solubility product of the hydroxide was exceeded in the solutions or not. As the concentration of electrolyte in the solutions is increased, the amount of radiocolloidal gold decreases, as previous observations on other elements have indicated.[5] As the gold concentration is increased, the percentage of gold removable as aggregates decreases, this observation also being in accord with previous researches.[5] The decrease in per cent. of coagulated gold with an increase in concentration is consistent with an assumption that the coagulation process becomes more effective under similar conditions of *p*H and salt concentration when fewer ions of gold are present in solution, such an assumption being contrary to the ordinary principles of analytical chemistry.[7]

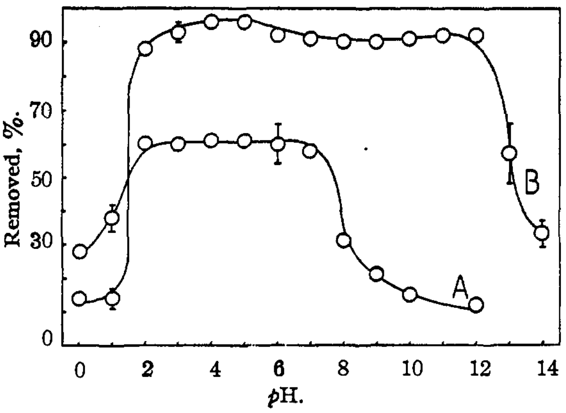

Fig. 1.—Percentage of gold removed by filtration (A) and centrifugation (B) from tracer gold solutions originally 0.01 *N* in hydrochloric acid as a function of *p*H.

TABLE I

CENTRIFUGATION OF GOLD SOLUTIONS AT *p*H 5.0

Group	Gold concn., *M*	Centrifuged, %
A[a]	Tracer	96 ± 2
	10^{-7}	77 ± 2
	10^{-4}	11 ± 2
	10^{-1}	3 ± 2
B[b]	Tracer	47 ± 3
	10^{-7}	16 ± 2
	10^{-4}	2 ± 2

[a] Solutions originally 0.1 *N* in hydrochloric acid. [b] Solutions originally 1.5 *N* in hydrochloric acid.

As shown in Fig. 2, the extraction studies on tracer amounts of gold show very little variation from those reported for macroconcentrations.[8] While there was but ten percentage points difference in the amount extracted for these two concentrations, solutions 1.5 *N* in hydrochloric acid showed a progressive increase in the amount of gold extracted as the gold concentration increased. These results are shown in Table II. The larger amounts extracted as the concentration of the gold increases might be explained by a self-salting action.[9]

TABLE II

EXTRACTION OF GOLD FROM WATER INTO DIETHYL ETHER[a]

Gold concn., *M*	Tracer	10^{-7}	10^{-4}	10^{-1}
Extracted, %	88 ± 2	91 ± 2	94 ± 2	98 ± 2

[a] Solutions 1.5 *N* in hydrochloric acid.

The adsorption of the very low concentration gold on glass and silica indicated that this seems to

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(5) G. K. Schweitzer and W. M. Jackson, *J. Chem. Educ.*, **29**, 513 (1952).

(6) F. Jirsa and H. Jelinek, *Z. Elektrochem.*, **30**, 534 (1924); H. L. Johnston and H. L. Leland, THIS JOURNAL, **60**, 1439 (1938).

(7) J. D. Kurbatov and M. N. Kurbatov, *J. Phys. Chem.*, **46**, 441 (1942).

(8) F. Mylius and C. Heuttner, *Ber.*, **44**, 1313 (1911); F. Mylius, *Z. anorg. Chem.*, **70**, 211 (1911); W. A. E. McBryde and J. H. Yoe, *Anal. Chem.*, **20**, 1094 (1948).

(9) N. H. Nachtrieb and R. E. Fryxell, THIS JOURNAL, **70**, 3547, 3552 (1948).

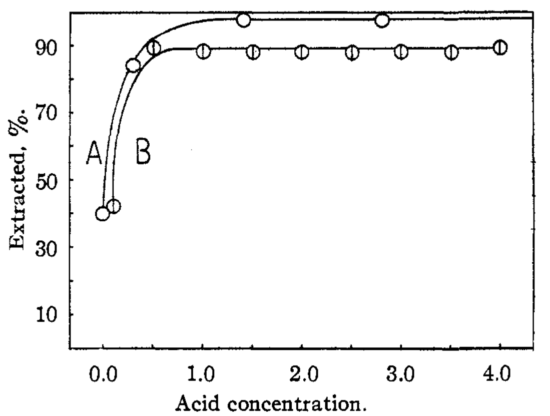

Fig. 2.—Percentage of gold extracted into diethyl ether as a function of hydrochloric acid concentration: curve A, literature values for 2 × 10^{-2} *M* gold; curve B, tracer gold.

be an effect dependent upon the total surface area. Increasing the available surface by the addition of silica increased the amount of adsorption but had no appreciable effect upon the shape of the adsorption curve as shown in Fig. 3. The peak in the adsorption curve at a *p*H value of about 2 might be explained by a consideration of the adsorbing species and the charge on the silica. In acid solutions the charge on the silica is probably positive due to adsorption of hydrogen ions and the adsorbing species could be the tetrachloroaurate(III) ion. At *p*H values lower than 2, the dissociation of tetrachloroauric(III) acid is less, and at *p*H values higher than 2, the silica has less of a positive charge, probably even becoming negative in the basic region. Also it should be recognized that the tetrachloroaurate(III) ion would tend to change into various chlorohydroxoaurate(III) ions as the solution becomes basic, but this would not alter the negative charge of the complex ion. The adsorption on Norit A carbon was found to be almost independent of the *p*H; however, it should be noted that the carbon tended to buffer solutions originally between a *p*H of 4.0 and 9.0 to a final *p*H of 7.5. The results of these experiments are given in Table III. It seems possible to explain the adsorption on carbon by the reduction of the gold(III) to the metallic form by the carbon, as has been reported for macroconcentrations of gold.[10]

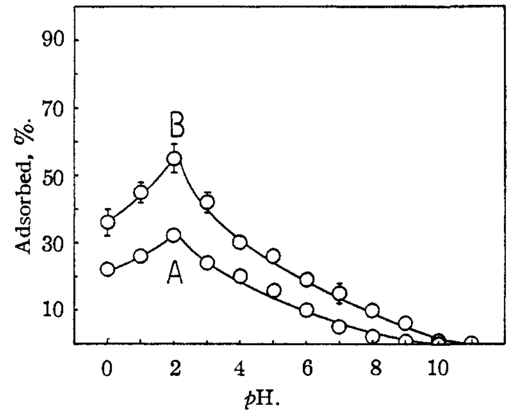

Fig. 3.—Percentage of gold adsorbed onto glass and silica from tracer gold solutions originally 0.01 *N* in hydrochloric acid as a function of *p*H: curve A, adsorption on container and two glass beads; curve B, adsorption on container, two glass beads, and 100 mg. of silica.

TABLE III

ADSORPTION OF TRACER GOLD ONTO NORIT A CARBON[a]

*p*H Original	*p*H Final	Adsorbed, %	*p*H Original	*p*H Final	Adsorbed, %
0.0	0.0	97 ± 2	6.0	7.5	94 ± 2
1.0	1.0	97 ± 2	7.0	7.5	94 ± 2
2.0	2.0	96 ± 2	8.0	7.5	94 ± 2
3.0	3.0	95 + 3	9.0	7.5	93 ± 2
4.0	7.5	94 ± 2	10.0	10.0	93 ± 4
5.0	7.5	94 ± 2	11.0	11.0	93 ± 2

[a] Solutions originally 0.01 *N* in hydrochloric acid.

Acknowledgment.—The authors wish to express their gratitude to the United States Atomic Energy Commission for the grant which supported this research.

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[10] O. Ruff, F. Ebert and F. Luft, *Z. anorg. allgem. Chem.*, **170**, 49 (1929); H. Wohling, *Z. angew. Chem.*, **45**, 720 (1932); V. E. Heymann, K. Solomon and H. Kieffer, *Z. anorg. allgem. Chem.*, **187**, 97 (1930).

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A Derivative of a New Sulfur Heterocycle[1]

BY GEORGE P. SCOTT

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Recent research on azulenes, tropolones and cyclooötatetraene has indicated wide-spread interest in large ring compounds containing aromatic or pseudo-aromatic structures. This report describes the preparation of a compound which very probably contains a sulfur atom in a seven-membered ring involving a system of double bonds formally analogous to the thiophene system.

The diethyl ester of thiodiacetic acid was condensed with *o*-phthalaldehyde using a sodium methoxide catalyst as in the Hinsberg thiophene synthesis.[2,3] Upon acidification of the precipitated sodium salt, an impure, orange, crystalline acid was obtained. Although very unstable in solution, it was found possible to recrystallize it rapidly from hot, 80% ethanol containing a little hydrochloric acid. The analysis and neutral equivalent of the resulting product corresponded to 3-benzothiepin-2,4-dicarboxylic acid[4](I).

Because of the instability of this compound, attempts to prepare simple acid derivatives and reduction products have failed. Refluxing in 15% ethanol produced a white, crystalline, sulfur-free acid in high yield (95%). This was identified as 2,3-naphthalenedicarboxylic acid (II) by analysis and mixed melting point of its anhydride.

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[1] This work was aided by a grant from the Research Corporation.

[2] D. E. Wolf and K. Folkers, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 435.

[3] For comparable carbon ring syntheses see D. S. Tarbell, G. P. Scott and A. D. Kemp, THIS JOURNAL, **72**, 379 (1950); L. F. Fieser and M. M. Pechet, *ibid.*, **68**, 2577 (1946); J. Thiele and E. Weitz, *Ann.*, **377**, 1 (1910).

[4] Nomenclature and numbering is based upon the *Chemical Abstracts* system, A. M. Patterson, L. T. Capell and M. A. Magill, *C. A.*, **39**, 5889 (1945).