3-(6-Hydroxynaphthyl-2)-2-cyclohexen-1-one (II).—A solution of 2 g. of I in 20 ml. of xylene was refluxed with 4.0 g. of aluminum chloride for 5 minutes and poured onto ice and dilute hydrochloric acid. The solid was collected on the filter and taken up in acetone–benzene. The organic extract was washed with water and then extracted with 5% sodium hydroxide. The alkaline solution was acidified and the product collected on the filter and purified through its sparingly water-soluble sodium salt; yield 1.2 g. (63.5%) tan plates, m.p. 210–212°. Repeated crystallizations from alcohol gave pale yellow plates, m.p. 215.1–217.4°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.70; H, 5.95.

An oxime was obtained as pale yellow needles from alcohol-hexane, m.p. 234.7–238.4°.

Anal. Calcd. for $C_{16}H_{15}O_2N$: C, 75.87; H, 5.97. Found: C, 75.75; H, 6.12.

3-(6-Methoxynaphthyl-2)-cyclohexanone (III).—A solution of 30 g. (0.12 mole) of 3-(6-methoxynaphthyl-2)-2-cyclohexen-1-one in 160 ml. of purified dioxane[7] was hydrogenated at atmospheric pressure in the presence of 7.0 g. of 5% palladium-on-charcoal catalyst[8] with vigorous stirring[9] at 55°. Reduction ceased upon saturation of the ethylenic double bond. After removal of catalyst and solvent, the product was crystallized from ethanol; yield 18.4 g. (60%) of colorless needles, m.p. 116–119°. Further recrystallizations from ethanol afforded a sample melting at 124–125°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13; OCH_3, 12.20. Found: C, 80.29; H, 7.05; OCH_3, 12.28.

An oxime was obtained as colorless needles from alcohol, m.p. 152.5–154°.

Anal. Calcd. for $C_{17}H_{19}O_2N$: C, 75.80; H, 7.11. Found: C, 75.53; H, 7.12.

3-(6-Methoxynaphthyl-2)-cyclohexanol (V).—A solution of 1 g. of 3-(6-methoxynaphthyl-2)-2-cyclohexen-1-one in 50 ml. of ethanol was hydrogenated in the presence of 150 mg. of platinum catalyst until hydrogen absorption ceased (24 minutes). The product crystallized from alcohol–hexane as colorless needles; yield 0.55 g., m.p. 122–124°. Further recrystallizations from alcohol–water gave colorless plates, m.p. 127.6–129.2°.

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.87. Found: C, 79.72; H, 8.02.

3-(6-Hydroxynaphthyl-2)-cyclohexanone (IV).—A solution of 0.5 g. of 3-(6-hydroxynaphthyl-2)-2-cyclohexen-1-one in 35 ml. of glacial acetic acid was hydrogenated in the presence of 100 mg. of palladium black catalyst until reduction ceased (50 minutes). After removal of catalyst and solvent, the residue was distilled at 0.3 mm. and the distillate crystallized from benzene–hexane; yield 200 mg. of pale yellow needles, m.p. 142.6–145.3°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.89; H, 6.81.

3-(6-Hydroxynaphthyl-2)-cyclohexanol (VI).—A solution of 1 g. of 3-(6-hydroxynaphthyl-2)-2-cyclohexen-1-one in 100 ml. of ethanol was hydrogenated in the presence of 1 g. of WF-7 nickel catalyst[10] at atmospheric pressure until reduction ceased. After removal of catalyst and solvent, the residue was taken up in ether, washed with water and dried. The product was obtained from acetone–petroleum ether as pale yellow plates; yield 250 mg., m.p. 183–194°. Further recrystallizations from alcohol–water afforded colorless needles, m.p. 217.1–218.4°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.45; H, 7.56.

2-Hydroxy-6-(3-hydroxycyclohexyl)-tetralin (VII).—A solution of 2 g. of 3-(6-hydroxynaphthyl-2)-2-cyclohexen-1-one in 50 ml. of alcohol containing 20 mg. of sodium hydroxide was hydrogenated in a bomb in the presence of 600 mg. of Raney nickel catalyst at 130° for 12 hours. The colorless alcoholic solution was filtered and concentrated on the steam-bath. The concentrate was taken up in ether and washed with dilute sodium hydroxide, water and dried over sodium sulfate. The product was obtained by distillation at 0.5 mm. as a colorless glass; yield 1.6 g.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.95; H, 9.14.

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[7] L. F. Fieser, "Experiments in Organic Chemistry," 2nd Edition, D. C. Heath and Company, Boston, Mass., 1941, p. 368.

[8] Baker and Co., Inc., Catalysts, Newark, N. J.

[9] A 3-necked round bottom flask served as the reaction vessel and stirring was accomplished with a stainless steel stirrer made gas tight by means of a stainless steel stuffing box and driven by a 1/2 h.p. drill press at 1750 r.p.m.

[10] H. R. Billica and H. Adkins, *Org. Syntheses*, **29**, 24 (1949).

Studies in Low Concentration Chemistry. V. The Spontaneous Deposition of Silver-111 on Various Metals

BY GEORGE K. SCHWEITZER AND DALE L. WILHELM

RECEIVED JULY 2, 1953

In the past fifty years, numerous publications have indicated an interest in the spontaneous deposition of carrier-free radionuclides from solution onto metal foils. A detailed bibliography of these researches has been compiled by Bonner.[1] Most of the investigators assumed that the process involved was a simple electrochemical displacement. If one makes this assumption, a knowledge of the critical deposition potential of the carrier-free nuclide should allow a prediction to be made as to which solution–metal foil conditions would bring about deposition of the tracer. Such a deposition potential for silver-111 has been measured and a value of −0.77 v. is reported.[2] In most previous experiments, no metal salts of the metal foils were added to the solutions, making it difficult to assign a metal foil potential, and to predict deposition behavior. Erbacher,[3] Joliot[4] and Camarcat, Bouissieres and Haissinsky[5] have helped to clarify the situation by measuring the potentials of various metal foils in solutions to which no corresponding metal salts had been added. However, several depositions have been reported which should not occur according to the relationship of these so-called "anomalous metal potentials" to the deposition potentials of the ions.[1]

This research was undertaken in order to investigate the spontaneous deposition of carrier-free silver-111 onto various metal foils in the absence of ions of the metal.

Experimental

Materials.—The silver-111 isotope was produced by neutron irradiation of palladium foil at the Oak Ridge National Laboratory. Perchloric acid solutions of this radionuclide were prepared by the procedure of Schweitzer and Nehls.[6] Spectrographic analysis of the palladium foil indicated that the silver solutions had a concentration of about 10^{-8} *M*. All inactive chemicals used in these experiments were reagent grade and all solutions were prepared using distilled water. All metal foils were cut square 2.0 cm. on an edge with a short strip 0.3 cm. wide appended by which they could be attached to a support. The foil thicknesses ranged

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[1] A. C. Wahl and N. A. Bonner, "Radioactivity Applied to Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 169–171, 450–459.

[2] L. Rogers, D. Krause, J. Greiss and D. Ehrlinger, *J. Electrochem. Soc.*, **95**, No. 2, 33 (1949).

[3] O. Erbacher, *Z. physik. Chem.*, **156A**, 135 (1931).

[4] F. Joliot, *J. chim. phys.*, **27**, 119 (1930).

[5] M. Camarcat, G. Bouissieres and M. Haissinsky, *ibid.*, **46**, 153 (1949).

[6] G. K. Schweitzer and J. W. Nehls, THIS JOURNAL, **74**, 6186 (1952).

from 0.002 to 0.005 cm. Previous to the potential measurements, the surfaces of all foils, except the platinum ones, were polished with 4/0 flint paper until a completely new surface was exposed. The sheets from which the foils were cut had been secured from the J. T. Baker Company.

Apparatus.—Potential measurements were made with a Fisher Type S Potentiometer with a Rubicon Company galvanometer attached. An Eppley Laboratory standard cell was employed as a reference electromotive force. Leads from the potentiometer circuit were attached to a Beckman fiber type calomel electrode and to the metal foil under investigation, both of these being dipped in the solution. Depositions were carried out in a jacketed 30-ml. beaker. A Model B-1 Eastern centrifugal pump was used to circulate water of the desired temperature through the outer jacket of the beaker. For the 25° measurements, temperature control was provided by a thermostated Sargent heater and circulator in a large bath. For the 3° measurements and the 89° measurements, the reservoirs were a large beaker of ice-water and a large beaker of water just below the boiling point, respectively. A Precision-Scientific Company Mag-mix magnetic stirring apparatus was used to stir the solutions in the 30-ml. beaker.

Radioactivity measurements were made with standard counting apparatus consisting of a Nuclear D-33 end-window counting tube, mounted in a Tracerlab SC-10 sample holder, attached to a Tracerlab P-4 preamplifier and a Tracerlab SC-2A scaler. All measurements of *p*H were made with a Beckman Model G *p*H Meter.

Sampling.—Silver ion concentration changes in the solutions were determined by the removal of 0.100-ml. samples at regular time intervals. The number of samples taken in each run was adjusted so that the error incurred by the removal of the silver from the bulk of the solution was less than the error inherent in the radioactivity measurements. The samples were evaporated to dryness on metal planchets in preparation for counting.

Results

Potential Measurements.—The potential existing between metal and solution was measured for various metal foils in distilled water made up to a *p*H of 3.0. These measurements were made at 25.0°. The trends in potential with respect to time and the magnitudes of these values referred to the standard hydrogen electrode are indicated in Fig. 1. At least two duplicate runs were made on all metals. The greatest disagreement in values of successive runs occurred with aluminum, for which the standard deviation of the plotted values is 0.04 v. This standard deviation is based on three runs.

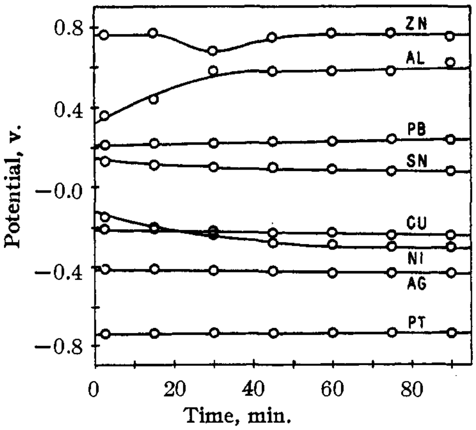

Fig. 1.—Metal foil potentials measured in 0.001 *N* perchloric acid solution plotted as a function of time; temp., 25°.

Deposition.—Deposition of tracer radiosilver was attempted on all metals for which metal foil potentials had been measured, except silver. The depositions were carried out under the same solution conditions which existed in the potential measurements. All metals which were investigated removed tracer radiosilver from solution. In each case, after approximately 120 min. immersion in the solution, the percentage removed had reached a maximum value. All plots of the percentage deposited as a function of time resembled the ones shown in Fig. 2. Table I represents values of percentage removal at the maximum for various metal foils and also a measure of the rate of deposition, expressed as the time required for one-half the maximum percentage deposited to be removed from solution.

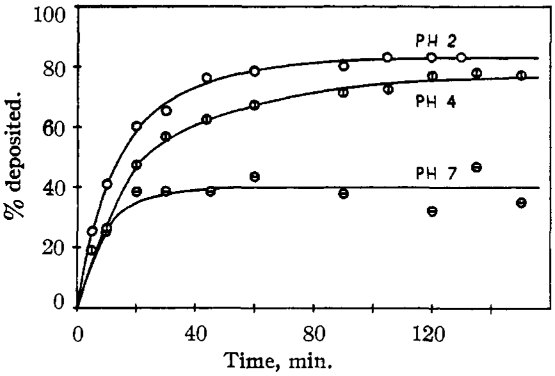

Fig. 2.—Per cent. radiosilver deposited on platinum as a function of time for several *p*H values; temp., 25°.

Surface Effects.—Additional depositions were made on copper foils which had been polished with the flint paper. No general reproducibility could be attained. Foils were then prepared by electroplating copper foils in an acidic copper sulfate bath using copper foil anodes. Then copper foils were prepared by anodic etching in a similar bath using a current of 1.5 amp. for five min. Neither of these methods produced reproducibility in the data. It was found that runs reproducible within 5% could be obtained if a single platinum foil were used. The deposited radiosilver could not be removed from the foil by allowing the foil to stand in the solution, but it was found that hot concentrated nitric acid effected a satisfactory removal.

***p*H and Temperature Effects.**—The rates of deposition of radiosilver onto platinum from perchloric acid solutions with *p*H values of 2.0, 4.0 and 7.0 at 25° were observed and the results are shown in Fig. 2. The data for plotting these curves were the averages of two or more runs at each *p*H value, the data being duplicated within 5% at *p*H values of 2.0 and 4.0. The values determined in successive runs at a *p*H value of 7.0 varied widely, disagreeing as much as 15%. Then the rates of deposition onto platinum from perchloric acid solutions at a *p*H value of 2.0 were observed at 3° and at 89°. The results of the temperature experiments are shown in Fig. 3. These curves were plotted from averaged values of the data from two or more runs, all runs agreeing within 5%.

Effect of Added Ions.—Depositions of tracer radiosilver onto copper foils from solutions 0.1 and 0.5 *M* in copper(II) perchlorate made up

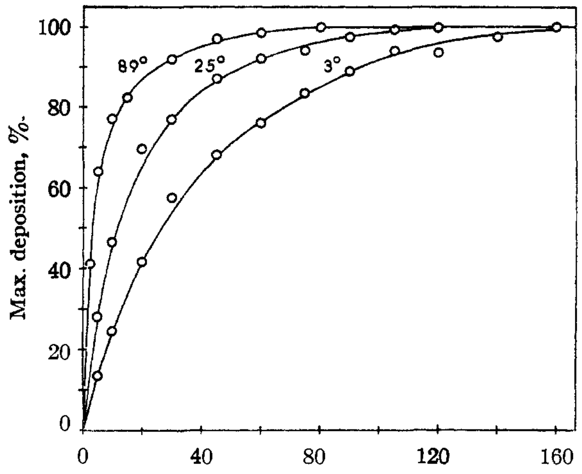

Fig. 3.—Per cent. of maximum deposition of radiosilver on platinum as a function of time at several temperatures.

to a *p*H value of 2.0 with perchloric acid could not be reproduced. However, all curves were of the type as shown in Figs. 2 and 3.

TABLE I

DEPOSITION ON VARIOUS METALS AT 27°

	1st run		2nd run	
Metal	Max. removed,[a] %	Half-time, min.[b]	Max. removed,[a] %	Half-time, min.[b]
Zn	75	25	..	..
Al	65	20	..	..
Pb	45	15	60	10
Sn	15	15	25	30
Cu	85	15	75	30
Ni	85	15	35	25
Pt	75	10	70	15

[a] Given to the nearest 5%. [b] Given to the nearest 5 min.

Discussion

The anomalous metal foil potentials measured in perchloric acid at a *p*H value of 3.0 are in reasonable agreement with those measured in 0.1 *M* hydrochloric acid,[3] in 0.125 *M* nitric acid,[4] and in dilute hydrofluoric acid,[5] except for silver. A value of −0.42 v. has been obtained in this investigation as compared to previously measured values of −0.29 v. in 0.1 *M* hydrochloric acid and −0.26 v. in 0.125 *M* nitric acid. It is interesting to note that none of the anomalous silver foil potentials are even close to the deposition potential of tracer radio-silver, which is reported as −0.77 v.[2]

Table I indicates that it is difficult to draw any conclusion relating either high rates of deposition or large percentages deposited to electropositive character in the metals. It seems that the lack of reproducibility in the various runs might be assigned to differences in the surfaces of the individual metal foils. Since determinations of anomalous metal potentials can be duplicated using different foils that have undergone pretreatment with flint paper, while deposition determinations cannot be reproduced using similarly prepared foils, one questions whether there is any direct relation between the anomalous potentials and the deposition behavior. Camarcat, Bouissieres and Haissinsky,[6] from their data on the spontaneous deposition of protactinium, conclude that there is more of a relation between deposition behavior and the standard electrode potentials of the metals than between the deposition behavior and the anomalous potentials. This investigation shows no apparent relation to either potential.

The results of the surface effect studies seem to indicate that the surface plays an important role in the deposition behavior. Just exactly what this role is cannot be concluded from the present work. Perhaps differences in adsorption of silver ions or atoms onto the surfaces may be involved. Numerous authors[7] have treated this possibility from a theoretical viewpoint, and conclude that this is a likely explanation.

The data from the deposition on the platinum foil indicate that the maximum amount deposited decreased as the *p*H value went from 2.0 to 7.0. This effect may be due to the tendency of tracer silver to form radiocolloids as the *p*H of the solution is increased.[6] With increases in temperature, the rate of deposition onto platinum increased. The fact that hot concentrated nitric acid was necessary to remove the radiosilver from the platinum indicates that the silver has been deposited as an atom and probably does not exist in the form of an adsorbed ion.

Some investigators have hypothesized that the lack of reproducibility in spontaneous deposition behavior was due to the absence of any intentionally added ions corresponding to the metal foil under consideration. To test this hypothesis in the case of silver, depositions onto copper from solutions containing macro amounts of copper(II) ion were run. The results could not be duplicated, thus lending no support to the hypothesis.

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[7] M. Haissinsky, "Electrochimie des substances radioactives et des solutions extremement diluées," Herman and Cie, Paris, 1946, pp. 27-34; J. Byrne, L. Rogers and J. Greiss, *J. Electrochem. Soc.*, **98**, 447, 452, 457 (1952); M. Haissinsky, *Experientia*, [4] **8**, 125 (1952).

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Acylhydrazones of *o*-Oxy- and *o*-Aminoaldehydes and Ketones as Tridentate Complexing Agents

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In the course of previous works on chemical reactions of complexes[1] a number of acylhydrazones of salicylaldehyde, 5-bromosalicylaldehyde, *o*-oxynaphthaldehyde, *o*-oxyacetophenone and *o*-aminobenzaldehyde were prepared. These products are able to react as tridentate groups and to yield, with nickel, bicyclic and polynucleate complexes.

The data obtained for a series of acylhydrazones are given in Table I.

Experimental

Preparation of the Acylhydrazones.—The solution of aldehyde or ketone and acylhydrazines (1 mole:1 mole) in alcohol was heated under reflux on steam-bath for about one hour and cooled. Water was often added in order to obtain a larger yield of crystalline precipitate. The products were purified by recrystallization from 95% or dilute alcohol.

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[1] L. Sacconi, THIS JOURNAL, **74**, 4503 (1952); *Z. anorg. allgem. Chem.*, **277**, 176 (1953); *Gazz. chim. ital.*, in course of being printed.