[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Magnetic Susceptibilities of Hydrogenated Pyridine and Quinoline Solutions of Cupric and Nickelous Acetate and Salicylaldehyde

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RECEIVED MAY 10, 1952

The magnetic susceptibilities of hydrogenated pyridine and quinoline solutions of cupric and nickelous acetate and salicylaldehyde were measured before and after reaction with oxygen. The results confirmed other evidence that the cupric salts were reduced to the cuprous valence state. No evidence for a stable univalent nickel compound was obtained. It is suggested that the discrepancy between the magnetic susceptibilities reported here and others previously reported was due to oxygenation by air in the earlier studies.

An exploratory investigation of the homogeneous catalytic hydrogenation of cupric acetate and cupric disalicylaldehyde dissolved in quinoline was reported by Calvin.[1] Subsequent study by Calvin and Wilmarth[2] confirmed the fact that cupric acetate was quantitatively reduced to cuprous acetate, a thermodynamically stable valence state in quinoline solution.

The hydrogenation of cupric disalicylaldehyde was studied in less detail but the color change and general characteristics of the reaction indicated that cuprous salicylaldehyde was the hydrogenation product. A complete account of the mechanism of catalytic hydrogenation and ortho–para-hydrogen conversion by these solutions will be published in the near future. The following experiments are concerned only with the magnetic properties of the hydrogenation products.

An investigation of the magnetic properties of the hydrogenated products of pyridine solutions of cupric and nickelous disalicylaldehyde was made by Tyson and Vivian[3] and Fobes and Tyson.[4] Their measurements of the cupric solutions showed the presence of one unpaired electron both before and after hydrogenation. From this it was concluded that the hydrogenation of the cupric compound in pyridine solution did not involve reduction to a cuprous species but instead involved the reduction of the salicylaldehyde to salicyl alcohol.

A comparison of the similarities of the reactions, such as color change during hydrogenation and chemical nature of the solvent, leads one to believe that the reduction of the copper compounds in quinoline, as reported by Calvin[1] and Wilmarth,[2] and in pyridine, as reported by Tyson and Vivian,[3] probably involves the same mechanism and reaction products. It would appear, then, that either these cuprous compounds must be paramagnetic, a phenomenon which could be achieved by using one *d* electron of each cuprous atom for metal-to-metal bonding in a dimer, or the measurements of Tyson and Vivian[3] must be in error. In order to clarify the above situations a magnetic study of copper and nickel solutions in pyridine and quinoline was undertaken.

Experimental

Solutions of cuprous acetate were prepared in both quinoline and pyridine, with care being taken to exclude oxidants. In addition, solutions of cupric disalicylaldehyde in each of the solvents were hydrogenated and the stoichiometry was determined by following the uptake of the hydrogen manometrically. The magnetic susceptibility of the solutions in the reduced state was measured by the Gouy method; these solutions were then allowed to become oxidized to the cupric species by exposure to air and/or oxygen, and were remeasured.

The hydrogenation of nickel salicylaldehyde was reported[4] to occur under conditions somewhat similar to those reported above, but since this reaction occurred very much more slowly, it was possible that an entirely different process was taking place. These experiments were repeated with the hope of demonstrating the presence of a monovalent species. However, in preliminary attempts the hydrogenation yielded some metallic nickel (highly ferromagnetic) before an appreciable color change had occurred in the bulk of the solution. This situation was remedied by anaerobically filtering off the nickel metal and measuring the remaining solution. An effort was also made to obtain monovalent nickel by reduction of the solutions of nickel disalicylaldehyde with nickel metal under conditions similar to those of the hydrogenation experiments.

Cuprous Acetate Solutions.—A solution of cuprous acetate in quinoline was prepared by introducing a rapidly weighed sample of the analytically pure, dry cuprous acetate into a jacketed all-glass reaction vessel equipped with a magnetic stirrer. The system was evacuated and 15 ml. of purified quinoline, contained in the magnet cell which was sealed to the neck of the reaction vessel, was added to the solid by tilting the apparatus. The solution was hydrogenated (negligible amount of hydrogen absorbed) at 100° to ensure the removal of any trace of cupric salts produced by air oxidation which may have occurred during the introduction of the solid cuprous acetate into the flask. When the solution was clear and of the ruby red color associated with the completely hydrogenated solution, the vessel was immediately cooled and the hydrogen pumped off. The magnet cell in which the magnetic susceptibility of the solution was to be measured (see above) was filled with the solution by properly tilting the apparatus, the cell was sealed off from the reaction vessel while still under vacuum, and the magnetic measurements were made.

The solutions of cuprous acetate in pyridine were handled in exactly the same manner as described above.

Hydrogenation of Cupric Disalicylaldehyde.—A weighed sample of the salt was diluted to the desired volume in a volumetric flask with purified solvent. Five ml. of this solution was introduced into the reaction vessel in the above-described apparatus. Fifteen ml. of this solution was placed in a small flask attached to the apparatus through a ground glass joint and stopcock in such a manner that by turning the flask through 180° its contents would be delivered into the reaction vessel if the stopcock was open. The system was evacuated and the flask and contents were isolated from the remaining apparatus by closing the connecting stopcock. The 5.0-ml. portion was cooled by circulating ice-water through the outer jacket, and was exposed to the vapors of hydrazine for several seconds to reduce a fraction of the cupric disalicylaldehyde to the cuprous state. The vessel was immediately evacuated. This solution was then hydrogenated at 100° until the reduction was completed (as determined by following the rate of absorption of hydrogen at constant pressure). The vessel was then immediately cooled and evacuated. The flask was turned and the 15-ml. portion of the cupric solution was added to the reduced material. The solution was then hydrogenated at 100° with

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[1] M. Calvin, *Trans. Faraday Soc.*, **34**, 1181 (1938).

[2] W. K. Wilmarth, Ph.D. Dissertation, University of California, Berkeley, 1942.

[3] G. N. Tyson, Jr., and R. E. Vivian, THIS JOURNAL, **63**, 1403 (1941).

[4] M. A. Fobes and G. N. Tyson, Jr., *ibid.*, **63**, 3531 (1941).

TABLE I

MAGNETIC DATA ON COPPER COMPOUNDS

	Compound[a]	Molarity of solution	Solvent	Hydrogen absorbed (ml. at S.T.P.) Exptl.	Calcd.	$\chi_m \times 10^6$ (24°)	No. of unpaired electrons
A	Cu(OAc)	0.073	Quinoline	..	..	Diamagnetic	...
B	$Cu(OAc)_2$	.073	Quinoline	..	..	1150	One
C	Cu(OAc)	.054	Pyridine	..	..	Diamagnetic	...
D	$Cu(OAc)_2$	.054	Pyridine	..	..	783[b]	One
E	Hydrog Cu(salicyl.)$_2$	.079	Quinoline	13.7[c]	13.3	Diamagnetic	...
F	Cu(salicyl.)$_2$	.079	Quinoline	..	..	1310	One
G	Hydrog. Cu(salicyl.)$_2$	.080	Pyridine	13.2[d]	13.5	Diamagnetic	...
H	Cu(salicyl.)$_2$	.080	Pyridine	..	..	1279	One

[a] B, D, F and H are results of cuprous solutions exposed to oxygen or air. [b] Precipitation of small amount of solid occurred during the oxygenation so that the susceptibility value has only qualitative significance. [c] The initial solution was 15.0 ml. of 7.9×10^{-2} M Cu(salicyl.)$_2$. [d] The initial solution was 15.0 ml. of 8.0×10^{-2} M Cu(salicyl.)$_2$.

careful observation of the volume and rate of absorption of the hydrogen at approximately one atmosphere until the reduction was complete. The volume of hydrogen absorbed, as measured by a gas buret in the system, agreed well with the calculated amount for reduction of cupric to cuprous species. The vessel and contents were immediately cooled and evacuated. The reduced solution was then transferred under vacuum to the magnetic cell as described above for measurements in the Gouy balance. This procedure was followed for both the pyridine and the quinoline solutions.

Oxidation of the Cuprous Solutions.—In all cases the reduced solutions were exposed to air or to a stream of oxygen and magnetic measurements were repeated. The oxidation, even at room temperature, proceeded as rapidly as the oxygen was able to diffuse into the solutions and the solutions again became paramagnetic, as they were before hydrogenation.

Hydrogenation of Nickel Disalicylaldehyde in Pyridine.—In order to be able to remove the metallic nickel before measuring the magnetic susceptibility of the reduced solution, hydrogenation was accomplished in a flask separated from the magnetic cell by a sintered glass filter. A known amount of solution was placed in the flask, evacuated, and cooled to 0°. Hydrogen gas was admitted at one atmosphere pressure. The system was sealed off and allowed to warm up slowly to 100°. After eight days at this temperature the system was cooled to room temperature and the contents of the flask were filtered into the magnetic cell by appropriately tilting the apparatus and applying the proper temperature differentials to the flask and cell. The magnetic cell and contents were then cooled in a Dry Ice-acetone-bath and were sealed off from the flask and its residue (some solution and metallic nickel). The reduced solution was then measured on a Gouy balance.

Reaction of Nickel Metal and Nickel Disalicylaldehyde.—In order to determine whether nickel metal was capable of causing the reduction of the nickel solution, an experiment was performed using the apparatus described above but with slight modifications. The nickel solution and the nickel pellets (in excess) were placed in the flask. The system was evacuated and sealed off under vacuum. The remainder of the procedure, except for the cooling techniques, was followed as described above.

This and the hydrogenation procedure were repeated without the sintered glass filter; in this case the filtration was carried out after the flask was opened.

Oxidation of the "Reduced" Nickel Solutions.—In all cases the solutions were exposed to a small stream of oxygen for several hours and the magnetic measurements were repeated. The results were essentially the same as before oxidation.

Analysis for Nickel.—The dimethylglyoxime precipitation procedure was followed. Five-ml. aliquots of the pyridine solutions were allowed to evaporate to dryness. The residues were digested with a mixture of concentrated nitric and perchloric acids. The resulting solutions were neutralized with a slight excess of ammonium hydroxide and precipitated with an alcoholic solution of dimethylglyoxime. The precipitates were collected on sintered glass filters, washed thoroughly, and finally dried at 110°.

Results and Discussion

The results of the experiments with the cupric and cuprous solutions are summarized in Table I. It is immediately apparent that (1) in all cases the reduced state was clearly diamagnetic, (2) the stoichiometry of hydrogenation corresponded to a change from the cupric to the cuprous valence state, and (3) the oxidation of the reduced state produced solutions which had essentially the same magnetic susceptibility as the cupric state. Therefore it can be concluded that the hydrogenation products were the soluble cuprous compounds. This conclusion is in agreement with the results of Calvin and Wilmarth.[2] In attempting to explain the discrepancy between these results and those of Tyson and Vivian it might be noted that the color changes are much less pronounced in pyridine solution than with the corresponding copper salt in quinoline. The pyridine solutions of the cuprous and cupric salts are still red and green in shade but have a dark background tinge which is usually associated with a broader absorption band in the visible. These cuprous solutions are instantly oxidized when exposed to the air and since Tyson and Vivian report no special precautions in handling

TABLE II

MAGNETIC DATA ON STABILITY OF THE NICKEL SOLUTIONS IN PYRIDINE TO OXYGEN

Solution	Change in weight by magnetic field, g.[a] Before exposure to oxygen	After exposure to oxygen[b]
Hydrog. Ni(salicyl.)$_2$	0.0065	0.0060
Ni(salicyl.)$_2$ after treatment with nickel metal	.0121	.0121

[a] Reported magnetic data in grams because process of anaerobic filtering caused changes in concentration of solutions by partial distillation of solvent. [b] Corrected for solubility of oxygen in pyridine.

TABLE III

MAGNETIC SUSCEPTIBILITY OF NICKEL SOLUTIONS IN PYRIDINE

Solution	Molarity of solution (exptl.)	$\chi_m \times 10^6$ (24°)	No. of unpaired electrons
Ni(salicyl.)$_2$	5.9×10^{-2}	3960	2
Ni(salicyl.)$_2$ after treatment with nickel metal	5.2×10^{-2}	4110	2
Hydrog. Ni(salicyl.)$_2$	3.3×10^{-3}[a]	4140	2

[a] The remainder of the nickel in the hydrogenated solution was present as a nickel mirror and fine nickel metal precipitate.

them it is possible they would not have noticed the oxidation to the cupric state before measurement.

The initial results of the magnetic measurements of the variously treated pyridine solutions of nickel disalicylaldehyde are shown in Table II. Since the above data indicated that the nickel solutions were stable in air, the experiments were repeated without the anaerobic precautions but with chemical analysis of the solutions for nickel content after filtration. The results are shown in Table III.

The constancy of the magnetic susceptibility when calculated on the basis of the analytically determined nickelous concentrations indicates that either no univalent nickel was formed or that, if formed, it must have had the same susceptibility as the original divalent nickel and, in addition, did not react at an appreciable rate with oxygen of the air. However, it seems unlikely that the univalent state is thermodynamically stable under these conditions, as the attempted reduction with nickel metal produced no observable change even after ten days at 100°. While Fobes and Tyson[4] also concluded that the nickelous ion was not reduced to the univalent state, they apparently did not observe the unmistakable presence of nickel metal as a hydrogenation product, although their description of a green to yellow color change during the hydrogenation is consistent with our observations. One might reconcile the two studies by assuming that nickel was produced in Fobes and Vivian's reaction but that it was so finely divided that it remained unobserved in a colloidal suspension during the hydrogenation and was reoxidized by air upon exposing the products to air. In our studies the metal was formed as a nickel mirror and in such massive form that its ferromagnetic properties could readily be demonstrated through the glass walls of the container. These reactions were not more thoroughly explored since the authors of this paper were primarily interested in the cuprous solutions.

Acknowledgments.—The major portion of this work has been carried out under Contract N6onr-238-TO-IV between the Office of Naval Research and the University of Southern California.

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Thermodynamic Properties of the Liquid Ternary System Bismuth-Cadmium-Tin

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RECEIVED MARCH 13, 1952

The activity of cadmium in liquid Bi-Cd-Sn alloys has been determined with the aid of e.m.f. measurements. From these values the integral molar excess free energy and the partial molar excess free energies of all components have been calculated.

Elliott and Chipman[2] have recently published a thermodynamic analysis of the liquid ternary alloys Bi-Pb-Cd, Pb-Cd-Sb and Sn-Cd-Pb. In the following a similar analysis is presented for the system Bi-Cd-Sn. The partial free energy of mixing of cadmium has been determined from the e.m.f. of galvanic cells involving these alloys, pure cadmium, and a salt melt consisting of KCl, LiCl and $CdCl_2$. Therefrom, (1) the excess integral molar free energy and (2) the excess partial molar free energy of each of the three components have been calculated.

Experimental

The experimental procedure was essentially the same as that described in a previous paper by Elliott and Chipman.[3] In particular, the same type of cell with four legs, one for pure cadmium and three for alloys, was used.

To minimize changes in the alloy composition due to eventual side reactions, each leg of the cell contained as much as 8 to 10 g. of alloy or pure cadmium. The connection with the measuring circuit was made by tungsten leads sealed in Pyrex capillaries. The tips of the tungsten leads were cleaned by cathodic treatment in a NaOH solution.

The electrolyte was a mixture of 45.0 g. of KCl, 35.5 g. of LiCl and 4.3 g. of $CdCl_2$. The salts were dehydrated separately at 230 to 250° within about one day. To prevent hydrolysis during this procedure, ammonium chloride was added which decomposed to HCl and NH_3. The salt mixture was melted in an argon atmosphere and heated slowly to 600°. The melt was always clear without filtration and remained clear when kept under purified argon.

The cell was floating in a stirred bath of 10 kg. of liquid lead in an electrical furnace. The temperature of the lead-bath was kept constant within 0.2° by means of a thermocouple and a Leeds-Northrup Micromax controller. In addition, the temperature of the electrolyte in the cell was determined with the aid of a thermocouple protected by a Pyrex tube and a potentiometer. The temperature difference between the two thermocouples was always less than 0.3°, in general less than 0.1°.

The potential difference between legs containing alloys and the leg containing pure cadmium was determined consecutively at about 410, 450, 560, 530 and 475°. Within half an hour at constant temperature, no changes of the e.m.f. greater than 0.01 mv. were observed.

After each run the cell was destroyed. The weight of each alloy sample was determined and compared to its original weight. The difference was in no case greater than 10 mg. Some loss was due to small amounts of alloy sticking to the glass. No indication of side reactions was found.

The observed potentials were plotted *versus* temperature. In all cases, practically straight lines were obtained. Potentials interpolated for 500° and temperature coefficients are compiled in Table I. For some alloys independent runs were reported. In general, the agreement is very satisfactory, but in some cases there are minor deviations. For the binary alloys, Bi-Cd and Cd-Sn, only a few compositions were investigated, since values obtained by previous investigators can be used for the following evaluation.

Calculations

Deviations from ideality are in general expressed in terms of activity coefficients, designated by γ_i for component i. For the present objective, it

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[1] Research Laboratory, National Lead Company, South Amboy, N. J.

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[3] J. F. Elliott and J. Chipman, *Trans. Faraday Soc.*, **47**, 138 (1951).