gas, each with a potential barrier, and not those corresponding to bending and stretching of bonds. This can only be true if the oxygen layer is mobile.

Differential heats of adsorption usually fall with increasing surface coverage. Attempts have been made to correlate this variation of the differential heats of adsorption with physical properties of the surface. However, due to lack of sufficient experimental data on the same system, this problem still remains unsolved. The presence of oxygen as a surface contaminant will cause a large heat effect for the initial adsorption of hydrogen on some metals. Upon this effect will be superimposed the effect due to the intrinsic surface heterogeneity. Incomplete elimination of hydrogen after a reduction of a sample will also produce high initial heats for an adsorption of oxygen on a metal. Thus the extremely high initial heats of chemisorption of hydrogen and oxygen on metal systems which have been reported may be attributed in part to the presence of incompletely removed hydrogen and oxygen.

Also, the different properties of powders and films may be attributed to incomplete elimination of the surface contamination of the powder. Using nickel, Roberts observed that a thoroughly reduced powder surface showed adsorption characteristic almost identical with those associated with nickel films.[10]

It is of great importance to obtain a well defined, reproducible, clean surface in studies of surface phenomena. Our method serves as a means for preparing such a surface for platinum black samples in the study of the hydrogen, oxygen, platinum system. This method for preparing a surface through a thermally indicated titration with hydrogen and oxygen may be extended to other metal powders. In the study of the chemisorption of different gases, other reactions may be used for a thermal titration provided that the reaction takes place on the metal being investigated and at least one of the reactants is mobile on the surface of this metal at the temperature being used. The products of the reaction also should be easily removable. The use of a thermally indicated titration also provides an excellent method for determining surface areas of samples. The surface monolayer volume of 1.10 l. STP for hydrogen obtained from our hydrogen titration, while removing oxygen, agrees well with the value of 1.10 l. STP hydrogen calculated from the BET nitrogen determination.

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[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

The Absorption of Oxygen by Nickel Dimethylglyoximate in Strong Alkaline Solutions[1]

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Nickel dimethylglyoximate dissolved in strong alkaline solutions appears to absorb oxygen in a reversible manner. Deoxygenation of the solutions may be accomplished by heating, by bubbling an inert gas through the solution or by reducing the pressure above the solution. Spectral measurements of deoxygenated solutions proved them to be identical to a solution prepared in the absence of oxygen. The oxygenated solutions are diamagnetic. Careful neutralization of the basic solutions yielded a weakly paramagnetic red complex believed to contain some of the nickel (III) complex with the formula $Ni(DH)_2OH$ (DH^- is the dimethylglyoximate anion). This is the first report of an oxygen-carrying nickel chelate. Palladium dimethylglyoximate does not show this behavior.

Introduction

Although there have been numerous studies on the oxidation of nickel dimethylglyoximate in alkaline solutions, there is little agreement to be found in the literature. Various nickel(IV) species have been postulated having nickel to dimethylglyoxime ratios of 1:2, 1:3 and/or 1:4.[3] Likewise there are reports of Ni(III) species with the nickel to ligand ratios of 1:1, 1:2, 1:3 and/or 1:4.[4] From a survey of this literature on the alkaline oxidation of $Ni(DH)_2$,[5] it is obvious that the products formed depend upon these several variables: the *p*H, the oxidant, the presence of excess DH_2 and whether ammonia or alkali hydroxide is used to obtain the basic conditions.

When oxygen was bubbled through a strongly alkaline solution of $Ni(DH)_2$, the orange-red color deepened considerably. Further investigation of the effect of oxygen on these alkaline solutions proved that the oxygen was being absorbed in a reversible manner, the soluble nickel chelate apparently acting in the capacity of a reversible oxygen carrier. Slow neutralization of the alkaline solution yielded a red compound believed to be a mixture of $Ni(DH)_2$ and the trivalent nickel com-

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(1) This article is based upon part of a dissertation submitted in partial fulfillment of the requirements for the M.S. degree at the Louisiana State University, 1959.

(2) Celanese Corporation Fellow in Chemistry, 1958–1959.

(3) F. Feigl, *Ber.*, **57B**, 759 (1924); M. Hooreman, *Anal. Chim. Acta*, **3**, 635 (1949); A. Okac and M. Simek, *Chem. Listy*, **52**, 1903 (1958); K. Yamasaki and C. Matsumoto, *Nippon Kagaku Zesshi.*, **77**, 1111 (1956).

(4) E. Booth and J. D. H. Strickland, THIS JOURNAL, **75**, 3017 (1953); K. B. Yatsimirsku and F. M. Grafova, *Zhur. Obshchei Khim.*, **22**, 1726 (1952); L. S. Nedezhiua and P. M. Kovalenko, *ibid.*, **24**, 1734 (1954); V. M. Peshkova and N. V. Mel'chakova, *Metody Analyza Redkikhi Tsvet. Metal. Sbornik*, 53 (1956).

(5) In this article DH_2 is used to designate the dimethylglyoxime molecule, DH^- to represent the univalent ion with one hydrogen ion removed, and $D^=$ to represent the bivalent ion with two hydrogen ions removed.

plex $Ni(DH)_2OH$. It now appears significant that none of the previous workers has excluded oxygen from the reactions and we show that oxygen alone plays a very important role in these alkaline solutions.

Experimental

Materials.—All reagents employed were of reagent grade quality. The nickel dimethylglyoximate was prepared in the usual manner as given in standard quantitative analysis texts. The samples were washed well with hot water and dried at 110°. Solutions of $Ni(DH)_2$ in strong alkali could be prepared in either of two ways. The solid complex could be dissolved, very slowly and with vigorous stirring, in a strong alkaline solution (10–15% NaOH); or a solution containing an equivalent amount of nickel salt, such as $NiSO_4$, could be added to a strongly alkaline solution containing an equivalent amount of dimethylglyoxime. In either case the final solutions were identical (as shown by spectral measurements), and since the latter procedure was easier and much more rapid to carry out, it was employed for most of the experiments. Water solutions were deoxygenated by bubbling an inert gas (usually argon) through the solutions.

2. **Spectral Measurements.**—Visible and ultraviolet spectra were obtained using a Beckman model DK recording spectrophotometer employing one centimeter quartz cells.

3. **Analytical Results.**—Chemical analysis of two different samples of the red compound (dried in a vacuum desiccator overnight) obtained by careful neutralization of oxygenated strongly alkaline solutions of $Ni(DH)_2$ gave the results:

	% C	% H	% Ni	C/Ni	H/Ni
Calcd. for $Ni(C_8H_{14}N_4O_4)$	33.29	4.85	20.32	8	14
Calcd. for $Ni(C_8H_{14}N_4O_4)OH$	31.08	4.92	19.19	8	15
Found	32.72	5.29	19.9	8.04	15.5
	32.58	5.19	20.0	7.96	15.1

Results and Discussion

Nickel dimethylglyoximate dissolves in strongly alkaline solutions producing an intense red color. The color appears more intense if an excess of dimethylglyoxime is present in the solution. However, if the $Ni(DH)_2$ is dissolved in a strongly alkaline solution which previously has been deoxygenated, the color produced is red-orange. The color deepens slowly to an intense red upon exposure of the solution to the atmosphere and rapidly upon treatment with pure oxygen. The visible and near ultraviolet spectrum for the deoxygenated solutions, with or without excess dimethylglyoxime, shows two absorption bands with maxima occurring at 390 and 325 $m\mu$. The spectrum for a solution as normally prepared in the presence of atmospheric oxygen or for an intentionally oxygenated solution, again with or without excess dimethylglyoxime present, shows three absorption bands with maxima at 442, 390 and 320 $m\mu$. The new band arising in the visible region appears as a strong shoulder to the 390 $m\mu$ band.

The oxygen which is taken up by the originally deoxygenated orange solution may be removed by at least three different methods, each of which produces the original orange-colored solution again:

(1) Heating at about 70° for 30 minutes.

(2) Exposure to reduced pressure in a vacuum desiccator at room temperature for several hours.

(3) Bubbling argon gas through the solution at room temperature for several hours.

Oxygenation and deoxygenation were repeated several times and presumably could have been repeated many, many times.

The presence of extra DH_2 in the solution increases the rate of formation of the red color upon oxygenation, but the spectral data do not indicate that the excess DH_2 has any effect on the *major* product present in the oxygen-containing solutions. It has not yet been determined what the ratio is of absorbed oxygen to nickel complex. We hope to be able to report this at a later time.

Rough magnetic measurements indicate that the oxygenated solution is diamagnetic while the deoxygenated solution may exhibit a slight paramagnetism. It should be realized, however, that the solutions were primarily 10–15% NaOH and were measured in glass vessels, both of which contribute heavily toward making the samples very "dilute magnetically." The oxygenated solutions showed definite but variable oxidizing capacity toward potassium iodide. The oxidizing capacity depended upon how rapidly the alkaline solutions were neutralized, the slower the neutralization, the greater the oxidizing capacity.

Careful neutralization of the strongly alkaline solutions yielded a dark red solid which proved to be weakly paramagnetic and weakly oxidizing toward potassium iodide. This material lost its paramagnetism when dried at 100° for several hours. The chemical analysis of this product after drying in a vacuum desiccator indicates that it is a mixture rather than a single compound. The analysis, the magnetic behavior and the oxidizing capacity suggest that the mixture consists of diamagnetic $Ni(DH)_2$ and the proposed new compound $Ni(DH)_2OH$, which contains the paramagnetic and oxidizing Ni(III). A separation of these two insoluble inner complexes has not yet been achieved so that the definite formulation of the paramagnetic species must be considered speculative at this time.

This appears to be the first report of an oxygen-carrying nickel chelate compound. Similar experiments involving the analogous palladium dimethylglyoximate have not revealed any unusual behavior of this complex toward oxygen in strongly alkaline solutions. Work is in progress now to determine the actual oxygen uptake by $Ni(DH)_2$ solutions and by dimethylglyoximates of other metal ions such as Cu(II), Fe(II) and Co(II).

NOTE ADDED IN PROOF.—A. Okáč and M. Šimek (*Coll. Czech. Chem. Comm.*, **24**, 2699 (1959)) in a study of the reaction of $Ni(DH)_2$ with several oxidizing agents in alkaline solutions found that the reaction with oxygen is very complicated. They report that up to 16 moles of O_2 per mole of $Ni(DH)_2$ is taken up by the complex in 1.5 *N* KOH over a period of about 40 days and that the chelating agent itself in alkaline medium absorbs oxygen in a one to one mole ratio.

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