pyrithiamine is pure pyrithiamine, and that the substance described by Tracy and Elderfield was grossly contaminated with biologically inert material.

Because confusion has arisen in the interpretation of the biological experiments with neopyrithiamine and pyrithiamine, some clarification might result if the name pyrithiamine were retained for the biologically active substance, in view of the facts just described. Possibly a designation such as pyrithiamine (neopyrithiamine) would indicate that the pure substance was employed rather than the old, impure preparation.

THE ROCKEFELLER INSTITUTE
FOR MEDICAL RESEARCH
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The Preparation of New Compounds of Trivalent Nickel[1]

BY LEONARD E. EDELMAN[2]

Introduction

The stabilization of unusual valency states by coördination is a well-known phenomenon in organic chemistry. Numerous examples of this phenomenon exist, such as di- and trivalent silver when coördinated with pyridine, trivalent cobalt in the stable ammines, etc. Illustrations of compounds of metals at stabilized lower states of oxidation are the nickel and manganese complex cyanides. A characteristic of this phenomenon is the specificity of coördinating groups for various metals.

There is some evidence that coördination with the oxime group may be a stabilizing factor for the higher valency states of nickel. Hofmann and Ehrhardt[3] prepared the complex compound, trisodium hexaformoximonickelate(III), and Dubsky and Kuras[4] the red crystalline compound, nickel(III) tribenzamidoxime. Feigl and Kulka[5] considered the red solution formed by nickel salts and dimethylglyoxime in ammoniacal solution in the presence of oxidizing agents such as bromine, nitrates, lead peroxide, etc., to be a solution of a compound of tetravalent nickel, dimethylglyoximonickelic(IV) oxide. They were able to isolate this compound by precipitation upon careful neutralization of its solution.

The present paper contains the description of stable compounds of higher valent nickel derivatives of oximes. The method of formation of the tetravalent oxide prepared by Feigl and Kulka suggested the possibility of forming a salt of higher valent nickel by the interaction of bromine and nickel dimethylglyoxime in an inert solvent.

When bromine is added to the suspension of nickel dimethylglyoxime in carbon tetrachloride, a black solid is formed. When this product is filtered and allowed to dry, it decomposes slowly and reverts to nickel dimethylglyoxime. The black solid dissolves in concentrated ammonium hydroxide to give a deep red solution such as is described by Feigl and Kulka.

A generalization that has been made concerning the stabilization of valance is that if a given coördinating group stabilizes a valence state, than the more negative the group the greater is the stabilization effect. To restate this in different form, certain strongly coördinating groups will displace the oxidation–reduction potential of an ion, and this displacement is greater with more negative groups.

Therefore, the bromine reaction was tried with nickel α-benzildioxime and a trivalent nickel derivative was formed which was stable at room temperature and decomposed slowly at 100°. A stable iodide has also been prepared. The reaction of chlorine with nickel α-benzildioxime in carbon tetrachloride results in the formation of a purple solution which is unstable.

Experimental

α-Benzildioximonickelic(III) Bromide.—Three grams of nickel α-benzildioxime (recrystallized from benzyl alcohol) was placed in 200 ml. of carbon tetrachloride. Five grams of bromine was added with stirring for ten minutes. A dark brown product was formed which was filtered, washed with carbon tetrachloride and air-dried.

The compound is insoluble in water and in all organic liquids such as benzene, alcohols, ethyl ether, acetone and carbon tetrachloride except pyridine. It forms a red-violet solution in pyridine, from which it can be precipitated by the addition of water, or will crystallize upon slow evaporation of the solvent. Concentrated ammonium hydroxide, dilute sodium hydroxide and sodium methylate in alcohol react to form a dark red compound which is insoluble in water but soluble in alkaline media.

The compound slowly decomposes at 100° to revert to the original orange-colored nickel α-benzildioxime. The loss in weight of the compound upon heating to constant weight was 13.58%, which is a measure of the bromine content.

Anal. Calcd. for $NiC_{28}H_{22}N_4O_4Br$: Ni, 9.51; Br, 12.95; C, 54.5; H, 3.59. Found: Ni, 9.34; Br, 13.02; C, 54.6; H, 3.62.

α-Benzildioximonickelic(III) Iodide.—Three grams of recrystallized nickel α-benzildioxime was dissolved in 20 ml. of hot benzyl alcohol, 3 g. of iodine was added and the mixture heated until crystallization started. The reaction mixture was cooled immediately and the product separated as glistening, bronze crystals. The solubility and stability characteristics are the same as the bromide.

Anal. Calcd. for $NiC_{28}H_{22}N_4O_4I$: Ni, 8.85; I, 19.11; C, 50.64; H, 3.34. Found: Ni, 8.98; I, 19.30; C, 51.80; H, 3.48.

Action of Chlorine on Nickel α-Benzildioxime.—Chlorine gas was passed for five minutes through a suspension of 5 g. of recrystallized nickel α-benzildioxime in 200 ml. of carbon tetrachloride. A dark-colored solid and a purple solution formed. The reaction mixture was filtered,

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(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the New York Meeting, September 1947.

(2) Dental Research Associates, Inc., 608 California Avenue, Pittsburgh 2, Penna.

(3) Hofmann and Ehrhardt, *Ber.*, **46**, 1467 (1913); *C. A.*, **7**, 2577 (1913).

(4) Dubsky and Kuras, *Chem. Zentr.*, 102, I 2045 (1931); *C. A.*, **25**, 1708 (1931).

(5) Feigl and Kulka, *Ber.*, **57**, 958 (1924); *C. A.*, **18**, 2663 (1924); A. Okac and M. Polster, *Coll. Czechoslov. Chem. Commun.*, **13**, 561 (1948).

The purple-colored filtrate decomposed and deposited a dark solid which was insouble in the carbon tetrachloride. The residue could be extracted with chloroform to yield more purple solution, which also decomposed in a few minutes.

It was found possible to add sufficient chlorine to a sample of nickel α-benzildioxime to dissolve it completely, but this solution was also unstable.

Hydrolysis of α-Benzildioximonickelic(III) Bromide.—Approximately 1 g. of α-benzildioximonickelic(III) bromide was stirred in 50 ml. of cold concentrated ammonium hydroxide. A maroon-colored compound formed which was somewhat soluble in the ammonia solution. The product was filtered, washed with distilled water, and dried in a desiccator.

The product decomposes slowly to give nickel α-benzildioxime. It is slightly soluble in dioxane but insoluble in water and in organic liquids such as benzene, carbon tetrachloride, diethyl ether, ethanol and acetone.

Action of Bromine on Other Nickel-oximes.—Besides α-benzildioxime and dimethylglyoxime, other nickel-oxime derivatives were treated with bromine in carbon tetrachloride solution. These include α-furildioxime, cyclohexanedionedioxime, glyoxalglyoxime, diacetylmonoöxime monophenylhydrazide and ethylenediamine-bis-diacetyldioxime. The last of these gave a stable bromide and the glyoxalglyoxime gave an unstable derivative. The other compounds were decomposed by the bromine.

MELLON INSTITUTE
PITTSBURGH, PENNA.

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The *p*-Phenylphenacyl Ester of Phenylacetic Acid

BY EDWIN ERICKSON AND I. MOYER HUNSBERGER

Drake and Sweeney[1] reported 63° (dec.) as the melting point of the *p*-phenylphenacyl ester of phenylacetic acid. In the course of undergraduate instruction we recently had occasion to prepare this ester and found it to melt at 88.2–88.8° (cor.). Five preparations[2] showed the same melting point.

Experimental

***p*-Phenylphenacyl Phenylacetate.**—This compound was prepared by the standard method.[3] The light tan crude product was recrystallized three times from ethanol (once with charcoal). The pure white analytical sample melted 88.2–88.8° (cor.) to a completely colorless melt.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.43; H, 5.60.

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(1) N. L. Drake and J. P. Sweeney, THIS JOURNAL, **54**, 2059 (1932).

(2) Two of these were performed by Mitzi Wheeler and Donald Granger.

(3) S. M. McElvain, "The Characterization of Organic Compounds," The Macmilian Co., New York, N. Y., 1947, p. 185.

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The Dissociation Constant of Hypobromous Acid

BY LADISLAS FARKAS AND MENACHEM LEWIN[1]

In studying the decomposition of hypohalite solutions, it is necessary to know the composition of these solutions which depend on the dissociation constants of the acids. Since there is some controversy over this constant in the literature, we have redetermined this constant for hypobromous acid. Shilow and Gladchikova[2] found by electrometric titration that K_{HOBr} at 20° $= 2.06 \times 10^{-9}$ and according to the same method, K_{HOCl} at 20° $= 3.16 \times 10^{-8}$. While the latter value is in good agreement with the results of other investigators[3,4] and is also close to the figure obtained by Skrabal and Berger[5] from the kinetics of the hypochlorite decomposition (*viz.*, 5.6×10^{-8} at 25°), the correctness of the above value of K_{HOBr} was questioned by Skrabal.[6] He calculated from data on the rate of decomposition of hypobromite depending upon the *p*H, the much lower value of 2×10^{-11} at 25°.

The following method was used for the determination of the dissociation constant of the hypobromous acid: To a hypochlorite solution, kept at a *p*H approximately equal to its *pK*, the equivalent amount of bromide was quickly added and the change of the *p*H was accurately measured by means of a glass electrode. Since, upon the addition of the bromide, all the hypochlorite was converted to hypobromite,[7] the observed Δ*p*H according to the Henderson–Hasselbach formula was in good approximation, equal to the Δ*pK* of hypochlorous and hypobromous acid.

In Table I, the results of a series of experiments are given. In these experiments, the solutions used were prepared by a method previously described.[8] The bromide was added to the hypochlorite solution while the electrodes were immersed in that solution. The final *p*H was established within a few seconds after the addition of the bromide[7,9] and remained constant for more than 15 minutes. The solutions were analyzed for hypochlorite before, and for hypobromite immediately after, the addition of the bromide according to the method already described[8]; no change in the oxidation capacity was found, the hypochlorite being quantitatively converted to hypobromite.

TABLE I

Expt. no	Total hypohalite moles/liter	Init. *p*H	Final *p*H	Δ*p*H
9	0.00344	7.21	8.46	1.25
12	.00344	7.46	8.72	1.26
1	.0172	7.54	8.80	1.26
5	.00344	7.57	8.83	1.26
6	.00344	7.73	9.00	1.27
2	.0172	8.09	9.32	1.23

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(1) Research Council of Israel, Hakirya, Israel.

(2) Shilow and Gladchikova, THIS JOURNAL, **60**, 490 (1938).

(3) J. W. Ingham and J. Morrison, *J. Chem. Soc.*, 1200 (1933).

(4) Hagisawa, *Bull. Inst. Phys. Chem. Research* (*Tokyo*), **19**, 1220 (1940).

(5) A. Skrabal and A. Berger, *Monatsh.*, **70**, 163 (1937).

(6) A. Skrabal, *Z. Elektrochem.*, **48**, 314 (1942).

(7) L. Farkas, M. Lewin and R. Bloch, THIS JOURNAL, **71**, 1988 (1949).

(8) L. Farkas and M. Lewin, *Anal. Chem.*, **19**, 662 (1947).

(9) In case the initial *p*H of the hypochlorite solution is below 7 or above 8.2, the observed Δ*p*H is smaller than the above figure.