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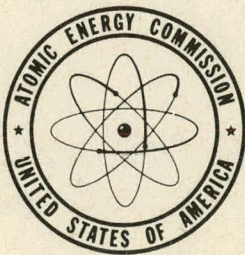
UNITED STATES ATOMIC ENERGY COMMISSION

ANNOTATED BIBLIOGRAPHY OF
 α -FURILDIOXIME

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February 8, 1956

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Charles V. Banks and Joseph P. LaPlante

Introduction

This annotated bibliography of the preparation and use of alpha-furildioxime has been prepared as a reference for analytical research. The authors of this bibliography hope that it will be of service to those engaged in analytical research and that further work on the uses of the vic-dioximes in analytical chemistry may be stimulated by the availability of this reference.

The ^{21 a} references contained herein deal for the most part with the preparation and use of alpha-furildioxime. In addition, the preparations of furoin and furil^u have been included. The references have been listed chronologically and are numbered consecutively.

1880

1. Fisher, E., "Furfuraldehyde," Ber. 13, 1334-1340 (1880) [J. Chem. Soc., 38, 798-799 (1880)].

Furoin, $C_4H_3O \cdot CHO \cdot HCO \cdot C_4H_3O$, was prepared by boiling 40 parts of 2-furfural with 30 of ethanol, 80 of water and 4 parts of potassium cyanide for

three-quarters of an hour. The crystalline mass which deposited on cooling was washed with water, then with ethanol and dried. It was obtained as nearly colorless crystals by precipitating with ethanol from a hot toluene solution. The crystals, m.p. 135° , are soluble in hot water and toluene. It dissolved freely in aqueous or ethanolic solutions of soda, forming a deep red solution. When a rapid current of air was passed through the solution, oxidation took place, the color changed, and crystals of furil, $C_4H_3O \cdot COCO \cdot C_4H_3O$, were deposited. Upon recrystallization from ethanol, furil was obtained in golden needles, m.p. 162° . Furil was soluble in chloroform and hot ethanol.

1882

2. Fischer, E., "Furfural," *Ann.*, 211, 214-232 (1882)
[*J. Chem. Soc.*, 42, 499-500 (1882)].

Furoin was prepared by heating 2-furfural with potassium cyanide in the presence of ethanol. A reddish crystalline mass was obtained, which can be purified by distilling in a carbon dioxide atmosphere and crystallizing from toluene and ethanol. Furoin forms slender crystals, m.p. 135° , which are slightly

soluble in hot water and ether, and soluble in warm ethanol and toluene. It was slightly acidic, dissolving in alkali to form an intensely dark colored solution, having two absorption bands, one between the C and D lines, and the other between the D and E lines.

Furil was obtained by dissolving furoin in the least possible quantity of soda and passing through the solution a rapid stream of air. Furil precipitates in the form of golden-yellow crystals, m.p. 162° , which may be washed with water and recrystallized from ethanol. It was slightly soluble in cold ethanol and ether, and very soluble in water. It can be oxidized by dry air to furillic acid, with the probable composition of $C(OH)(C_4H_3O)_2 \cdot COOH$.

1890

3. Macnair, D. S., "Derivatives of Furoin and Furil," J. Chem. Soc., 58, 1245-1246 (1890).

This paper gives the preparation of deoxy-furoin, $C_4H_3O \cdot CO \cdot CH_2 \cdot C_4H_3O$; furilphenylhydrazone, $C_4H_3O \cdot CO \cdot C(N_2HPh) \cdot C_4H_3O$; furilphenylosazone, $C_4H_3O \cdot C(N_2HPh) \cdot C(N_2HPh) \cdot C_4H_3O$; alpha-furiloxime, $C_{10}H_7NO_4$; and alpha-furildioxime, $C_{10}H_8N_2O_4$.

Alpha-furildioxime can be prepared by treating furil with an excess of hydroxylamine hydrochloride in ethanol at ordinary temperatures. Recrystallization from hot water gave colorless needles containing 1 mole of water. It lost the water of crystallization at 100°, and the anhydrous substance melted at 166-168°. It was very soluble in ethanol and ether, but only slightly soluble in benzene, light petroleum, and water. The beta-furildioxime was obtained when anhydrous alpha-furildioxime was heated with ethanol at 150-160°. It melted at 188-190° with partial decomposition.

1908

4. Tschugaev, L, "A Method for Determining the Configuration of α -Dioximes," Ber., 41, 1678-1684 (1908) [J. Chem. Soc., 94, 554 (1908); C. A., 2, 2385 (1908)].

The fact, that of the various stereoisomerides of an alpha-dioxime, the syn-modification alone yields complex metallic dioxime, was utilized for determining the configuration of dioximes. Stierlin's alpha-anisildioxime, Ber., 22, 376-383 (1889), Hoffmann's alpha-cuminildioxime, Ber., 23, 2064-2066 (1890),

and alpha-furildioxime, m.p. 166-168°, were thus shown to possess the syn-configuration, while Werner and Block's two stereoisomeric 2,2'-dichlorobenzildioxime, Ber., 32, 1975-1985 (1899), which do not form colored complex metallic derivatives, must be amphi and anti-modifications.

An interesting illustration of the method was given by Boeris' stereoisomeric methylanisylglyoxaldioxime, Gazz. chim ital., 23, 11, 165-194 (1894). The modification, m.p. 125°, obtained by Angeli's method of reducing the corresponding peroxide, was probably the amphi-dioxime which does not react with metals to form complexes. By heating, it was transformed into an isomeride, m.p. 200°, which does yield a complex and has the syn-configuration, although Angeli's researches on purely aromatic peroxides show that the amphi-dioximes obtained by reduction are converted into anti-dioximes by heat. An explanation was offered of the abnormal behavior of the preceding aliphatic aromatic dioxime. The nickel and the ferrodipyrindine complexes of alpha-anisildioxime and of alpha-furildioxime were briefly described.

1925

5. Soule, B. A., "Alpha-furildioxime as a Reagent for the Detection and Determination of Nickel," J. Am. Chem. Soc., 47, 981 (1925) [Brit. Chem. Ab., A, 603, (1925); C. A., 19, 1548(1925)].

In the preparation of alpha-furildioxime, furfural was converted into furoin and this in turn into furil by E. Fischer's method. Furil was converted into alpha-furildioxime without purification, by refluxing with hydroxylamine hydrochloride in the presence of methanol. The product was contaminated with a small amount of furiloxime. The product can be recrystallized from ethanol. The colorless crystals appeared to effloresce while drying, leaving a white, powdery residue, which softened and decomposed at 168°. The alpha-furildioxime, when used for analytical purposes, was dissolved in hot water to make a 2% solution or in warm ethanol to make a 10% or 15% solution.

Experiments were made to determine the least amount of nickel that could be detected, the test depending upon the formation of a precipitate. This was found to be one part in 6×10^6 parts of solution.

The method was as follows: To 25 ml. of dilute nickel solution ($1 : 6 \times 10^6$) in a test tube were added 2 ml. of ammonia water ($1 : 4$) and 0.1 ml. of a 10% ethanolic solution of alpha-furildioxime. The tube was stoppered and shaken vigorously for 30 seconds. Immediate filtration left a distinct red precipitate on the filter paper. There was an upper and lower concentration for maximum precipitation.

Sensitivities of Dioximes to Nickel

Reagent	Ratio	Mg. per ml.
Dimethylglyoxime	1:400,000	0.0025
<u>alpha</u> -Benzildioxime	1:2,000,000	0.0005
<u>alpha</u> -Furildioxime	1:6,000,000	0.00017

Qualitative tests were performed by adding a few drops of the reagent to a faintly ammonical solution of the substance to be tested. No precipitate or color change was observed in the case of ammonio-silver, -copper, or -zinc. Ammonio-cobaltous solutions darkened in color. The results with manganese were negative. Iron(III), chromium, or aluminum gave no visible action when tested in ammonical solutions containing

citrate or tartrate. Iron(III) in an ammonical solution containing less than 1 part in 3,000,000 gave a greenish color.

Large amounts of ammonio-cobaltous ion interference were prevented by oxidation of the cobalt with hydrogen peroxide. When large amounts of manganic hydroxide are present, perform the tests in the presence of acetic acid and sodium acetate. This modification also gave good results in the presence of cobalt and zinc.

Chosinsky obtained results corresponding to 11.85% of nickel for the formula, $(C_{20}H_{14}N_4O_6)Ni$, whereas the calculated value is 11.81%. Precipitation was quantitative from solutions containing up to about 65% of ethanol. With higher concentrations the solubility increased and the precipitate formed was crystalline.

A known volume of standard nickel solution, corresponding to about 0.02 g. of nickel was taken for analysis. Each sample was diluted with 100 ml. of water, the desired salt or acid was added, followed by ammonia until a faint odor of ammonia was perceptible.

In some cases an excess of the reagent was next slowly added during stirring, in other tests, preliminary heating to various temperatures was tried. An amorphous red precipitate was obtained upon introduction of the reagent. The solution was agitated, filtered and washed with warm water. The paper with contents, was transferred to a beaker and treated with 1:1 nitric acid. The precipitate dissolved and the paper pulp was removed by filtration. The filtrate was evaporated, after the addition of concentrated sulfuric acid. The residue was diluted, made ammoniacal and electrolyzed. It was found that solutions varying from dark red through yellow to violet could be electrolyzed with no apparent difficulty or difference in results. Quantitative separation of nickel from chloride, sulfate, nitrate, and iron(III) in the presence of citrate, tartrate, pyrophosphate, and citric acid was achieved. The use of alpha-furildioxime for the separation of nickel from manganese, zinc or cobalt offered no special advantage over 2,3-butanedionedioxime(dimethylglyoxime).

Determination of nickel in steel: To a solution

of 0.7 g. of steel in 50 ml. of 1:2 nitric acid was added 5 ml. of HCl. The solution was diluted with 200 ml. of water and heated almost to boiling. Then 6 g. of citric acid dissolved in 15 ml. of water was added, followed by 34 ml. of ammonium hydroxide, which brought the total volume up to 300 ml. and gave the proper alkalinity. Alpha-furildioxime was added until precipitation was complete. The precipitate was dried at 120-130°, and weighed. As a check the precipitate was ignited to nickelous oxide. Burning took place quietly between 250-300°. After the oxide had been weighed, it was converted to the sulfate and electrolyzed. When citrate or tartrate was used to prevent the precipitation of iron, there was a danger of contaminating the precipitate with iron(II) alpha-dioxime. This may be prevented by filtering within one-half hour or by use of sodium pyrophosphate.

In quantitative work the precipitate of nickel alpha-furildioxime may be weighed directly, ignited to nickelous oxide, or dissolved and the nickel determined by electrolysis or cyanide titration. Ferrous iron was the only common metal ion that gave

a precipitate with the reagent. The ammonia-cobaltous ion must be oxidized to prevent it from interfering.

1926

6. Ogburn, S. C., "A Qualitative Separation of the Platinum Metals," J. Am. Chem. Soc., 48, 2507 (1926)
[C. A., 20, 3663 (1926)]

This paper gave the procedure for the separation of palladium, platinum, rhodium, ruthenium, iridium and osmium.

The method for the separation of platinum from palladium, rhodium, ruthenium, iridium and osmium is given here. The solution containing the metal ions was treated with a 2% ethanolic solution of alpha-furildioxime and a quantity of ethanol equivalent to 10% of the total volume and boiled for 30 minutes. The mixture was filtered while hot under slight suction. After complete precipitation of the platinum was attained, it was then dried, carefully ignited, first in air, then in hydrogen, cooled and the metallic platinum thus formed was weighed.

7. Nisbet, H. B., "The Reduction of Nitro-Compounds by Aromatic Ketols," J. Chem. Soc., 1928, 3121-3124 [C. A., 23, 2428 (1929)].

In this paper it was stated that benzoin and its homologs in hot ethanolic solution under the influence of a trace of sodium ethoxide reduced nitro-groups to azoxy-groups, no matter what position these groups occupied in the benzene ring. In many cases it was found impossible to isolate the azoxy-compound, but in every case examined it was possible to separate the diketone and thus prove that the nitro-group oxidized the ketol and at the same time suffered reduction. This reaction was utilized in the new preparation of furil by oxidation of the corresponding ketol with nitrobenzene. The azoxybenzene could not be isolated in the reduction of nitrobenzene by means of benzoin, anisoin, or furoin, but by using an excess of the oxidizing agent it was found possible to utilize the reaction as a method of preparing anisil and furil in 80% and 90% yields respectively.

The method for the preparation of furil is; a solution of the ketol (5 g.) and nitrobenzene (4 g.) in 50 ml. of ethanol containing 2 ml. of 6% ethanolic sodium ethoxide was boiled under reflux

for 2-3 minutes and then allowed to cool. The diketone which separated was recrystallized from ethanol. The method gave 4 g. of anisil, m.p. 133°, and 4.7 g. of furil, m.p. 162°.

1929

8. Corson, B. B., and McAllister, "Oxidation of Benzoin to Diketones with Iodine," J. Am. Chem. Soc., 51, 2822-2825 (1929) [C. A., 23, 4944 (1929)].

Benzoin, anisoin, piperoin, and furoin are easily oxidized to the corresponding diketones. The diketones were oxidized with iodine. Gomberg and Bachmann, J. Chem. Soc., 49, 2584 (1927), proposed a mechanism for the reaction which involved the removal of sodium from the dienolic salt. Another mechanism cited was Meisenheimer, Ber., 38, 874 (1905); cf. Garmen, Am. Chem. J., 32, 583 (1904).

Ten grams of furoin were dissolved in 225 ml. of boiling methanol and to the boiling solution was added a hot, freshly prepared solution of sodium methylate made by dissolving 2.5 g. (105% of the calculated amount, assuming the product to be a disodium derivative of dienol) of sodium in 50 ml. of pure methanol. To the boiling solution was added,

in three portions, 14 g. (106%) of iodine. The final color of the solution was brown. When the heat was removed, furil immediately began to crystallize. The mixture was allowed to cool to room temperature and filtered. A small additional yield was obtained by concentrating the mother solution. The total yield was 8 g., 80%, m.p. 164-165°. The best solvent for recrystallizing furil was benzene. When bromine was substituted for iodine, there was a resultant drop in the yield of 20% to 30%.

The purity of the crude product depends upon the quality of the 2-furfural. The crude furoin (dark brown) was air dried and then allowed to stand for twelve hours in ether. It was filtered and then soaked in fresh ether for a second twelve hour period and again filtered. The ether removed the black tar. The furoin was dissolved in boiling ethanol (150 g. per 500 ml. of ethanol) and precipitated by slowly pouring the hot ethanol solution into 5 volumes of water with rapid stirring. The solid was filtered, dissolved in ethanol and precipitated again with water. The final product was of a light tan color and the supernatant aqueous ethanol from which it separated

was clear and red. Pure furoin has a melting point of 138-139°.

1931

9. Grisollet, H., and Servigne, M., "Principle Organic Reagents used in Inorganic Chemistry," Ann. chim. anal. chim. appl., 12, 321-331 (1930) [C. A., 25, 261 (1931)]/.

The uses of cupferron, benzidine, dicyandiamidine, nitron, dimethylglyoxime, sodium nitroso-2,3,6-naphtholdisulfonate, alpha-benzil dioxime, benzoyl-methylglyoxime, alpha-furyldioxime and ozalene-diuramedoxime are outlined in this installment.

1933

10. Hartmen, W. W., and Dickey, J. B., "The Preparation of Furil," J. Am. Chem. Soc., 55, 1228-1229 (1933) [C. A., 27, 1881 (1933)]/.

The furoin used was prepared in slightly improved yields by a modification of the method of Fischer. In a 22-liter flask fitted with a mechanical stirrer, an S-tube with a dropping funnel and an inverted Liebig condenser, were placed 8 liters of water, 4 kg. (41.65 moles) of freshly distilled furfural, and 3 liters of 95% of ethanol. The re-

action mixture was then heated to boiling and the flame was removed. When the solution had just ceased to boil, a solution containing 200 g. (3.07 moles) of potassium cyanide dissolved in 600 ml. of water was added with stirring as rapidly as the vigor of the reaction would permit. The reaction mixture was boiled for twenty five minutes. The alkaline solution was made acidic to litmus with glacial acetic acid and placed in a cool place to crystallize. The resulting mass of dark-colored tarry crystals was filtered on a large Büchner funnel, washed with cold water, then with cold methanol to remove as much tar as possible. The residue was recrystallized from methanol using 200 g. of Norit. The furil separated as light-brown needles melting at 134-135°. The yield of purified material was 1500 g., 37.5%.

In a 1-liter round-bottomed flask fitted with a mechanical stirrer was placed 158 g. (0.63 mole) of powdered copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), 210 g. of pyridine, b.p. 109-118°, and 90 g. of water. The stirrer was started and the mixture was heated on a water bath until solution was affected. To the

solution was added 57.6 g. (0.3 mole) of furoin, m.p. 134-135°. After a short time the color of the reaction mixture changed from a deep blue color to a deep green with a brownish tinge. Stirring and heating were continued for two hours and the reaction mixture was poured into 1 liter of cold water, filtered on a Büchner funnel, and washed with 500 ml. of cold methanol and recrystallized from methanol using 25 g. of Norit. The yellow crystals obtained melted at 165-166°. The yield of the purified material was 35.9 g., 63%. Furil can be recrystallized satisfactorily from benzene. If desired, the reaction mixture can be cooled and furil removed by filtration. The solution was reactivated by passing oxygen into it.

1937

11. Sircar, A. C., and Guha, S. C., "Condensation of Furil and Furoin," J. Indian Chem. Soc., 13, 704-708 (1936) [Brit. Chem. Ab., A, II, 381, (1937); C. A., 31, 3911 (1937)]/.

Furil condenses with aldehydes in the presence of ammonium hydroxide to form iminazoles, but no oxazoles could be isolated though the condensations were effected at different temperatures and pressures. Condensations of furil and various substances are listed.

1940

12. Diehl, H., "The Applications of the Dioximes to Analytical Chemistry," The G. Frederick Smith Chemical Co. (1940) C. A., 35, 1728 (1941) 7.

The synthesis of alpha-furildioxime involved three steps, the condensation of furfural to furoin by the benzoin condensation, the oxidation of furoin to furil by air, and the oximation of furil to its dioxime. Commercial furfural can be used as the starting material without preliminary purification.

Reflux a mixture of 1.0 mole of furfural, 1.5 moles of methanol, 6.0 moles of water and 0.12 mole of sodium cyanide for 30 to 40 minutes. Cool, filter and wash the precipitate of furoin which was then used in the next step without further purification. The yield was 25%.

Dissolve the furoin in dilute ethanol containing sufficient sodium hydroxide to effect solution. Cool to 0° and bubble air through the solution. The yield was good.

Reflux a mixture of the crude furil, which should melt above 160°, and hydroxylamine hydrochloride dissolved in methanol for 5 to 6 hours. Filter off the light

brown crystals. The yield was 85%. Recrystallize the product from water and then from ethanol. The product was a colorless crystalline material which effloresced giving a white powder on drying, and which softened and decomposed at 168° .

As little as 1 part of nickel in 6,000,000 parts of water yields a precipitate which may be distinctly seen after filtering the solution on paper. The concentration of ammonium hydroxide was important in this test, there being an upper and a lower limit for maximum precipitation. Silver, copper, and zinc in ammoniacal solutions gave no color with the reagent. Cobalt in ammoniacal solution gave a dark coloration. Iron(III), aluminum, and chromium in ammoniacal solutions containing citrate or tartrate gave no reaction. Small amounts of nickel in the presence of large amounts of cobalt were difficult to detect, but oxidation of the cobalt before carrying out the test eliminates this difficulty.

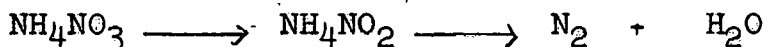
The precipitation of nickel by alpha-furildioxime was complete from weakly ammoniacal solutions of pure nickel salts and from those containing, in addition

to nickel, large amounts of ammonium chloride, ammonium sulfate, ammonium nitrate, ammonium citrate, ammonium tartrate or sodium pyrophosphate. The separation of nickel from zinc, cobalt, manganese, and large amounts of iron are quantitative. The nickel in the precipitate may be determined either by weighing the precipitate itself after drying, by ignition to the oxide, or by the cyanide titration method.

1941

13. Klein, B., "The Oxidation of Acyloins," J. Am. Chem. Soc., 63, 1474-1475 (1941) C. A., 35, 4370 (1941) 7.

It was found in the presence of excess ammonium nitrate, at the temperature of boiling a glacial acetic acid that acyloins in general can be oxidized.



The above equations were substantiated by the following observations. (a), There was a copious evolution of a colorless, odorless, neutral gas insoluble in water, immediately upon mixing the reactants. No gas was evolved when the reactants are heated independently in boiling glacial acetic

acid. (b), Neither lophine nor amarone was produced. Hence, in the course of the reaction no ammonium acetate was formed by metathesis in any appreciable quantity. Ammonium nitrate acts merely in the capacity of a mild oxidizing agent, and can be used to oxidize sensitive alpha-hydroxy ketones to diketones.

In the preparation of furil, 1.1 g. of furoin, m.p. 135°, was dissolved in 10 ml. of boiling acetic acid, 3.2 g. of ammonium nitrate was added in small portions as the reaction was extremely vigorous. When the evolution of gas ceased, the solution was gently refluxed for two hours. The solution was evaporated to dryness under diminished pressure. The dry material was thoroughly extracted with butanol and the solvent evaporated to dryness under diminished pressure. The residue was crystallized from methanol (2 ml.) and then from 80% acetic acid; yield, 0.5 g. of pale yellow needles melting at 160°. The preparations of other diketones were also listed.

1948

14. Reed, S. A., Banks, C. V., and Diehl, H., "The Preparation of Alpha-Furildioxime," J. Org. Chem., 12, 792-793 (1947) [C. A., 42, 1932 (1948)].

A 5-l. flask equipped with a Soxhlet extractor was charged with 3.2 l. of methanol and 208.5 g. of hydroxylamine hydrochloride and the extractor with 190 g. of pure furil. Furil was slowly extracted with methanol into the flask. The methanol was then concentrated to about 500-800 ml. under reduced pressure, not over 35°, and poured into 600 ml. of water at 90°. The mixture was boiled 10-15 minutes with Norit previously extracted with hot hydrochloric acid. On cooling, alpha-furildioxime crystallized. Upon recrystallization a 54-6% yield of pure alpha-furildioxime monohydrate, m.p. 84-50 was obtained. The melting point of anhydrous alpha-furildioxime was 166-168°.

1949

15. Feigl, F., and Feigl, H. E., "On the Reactivity of Inner Complex-bonded Palladium. A new Specific Test for Cyanides in Alkaline Solutions," Anal. Chim. Acta, 3, 300-309 (1949) [C. A., 43, 8956 (1949)].

The inner-complex salts of palladium and various dioximes do not enter into oxidation-reduction reactions with carbon monoxide, either in the solid or the molecularly dispersed states. Also a method for the determination of cyanide was given.

16. Weiss, M., and Appel, M., "Catalytic Oxidation of Benzoin to Benzil," J. Am. Chem. Soc., 70, 3666-3669 (1948) [C. A., 43, 1368 (1949)].

In experiments with 636 g. crude benzoin, 300 g. of ammonium nitrate, 6 g. of copper acetate, and 2100 ml. of 80% acetic acid, the yield of benzil was 90%, furoin 91%, and anisoin 97%. Benzoin can be determined in a benzil mixture by the catalytic cleavage of the benzil by sodium cyanide.

17. Bremner, G. M., Jones, D. G., and Imperial Chemical Industries Ltd., "Furil," Brit. Pat. 605,021, (July 14, 1948) [C. A., 43, 690 (1949)].

Furoin in an inert, nonalkaline solvent, was oxidized catalytically with oxygen to furil. Thus, 10 g. of crude furoin, 100 ml. of acetic acid, and 0.1 g. of cobaltous acetate are blown with air 30 minutes at 100°; on cooling, furil precipitated and was filtered off. An additional amount of furil was obtained by adding 200 ml. of water to the filtrate. Total yield of furil was 6.7 g. When 10 g. of recrystallized furoin and 1 g. cobaltous acetate in acetic acid are blown with air 40 minutes at 95°, the yield of furil was 8.0 g. The melting point was 159-160°.

18. Nazarova, L. M., and Syrkin, Y. K., "Dipole Moments of Compounds of the Furan Groups," Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 35-43 (1949) [C. A. 43, 4913 (1949)].

Measurements by the heterodyne method in benzene solution at 25° gave the dipole moment $\mu \times 10^{18}$ for furil 14.2800, 0.7140, 253.1 (48.6), 3.15, and the dipole moments of other furan compounds were also given.

1950

19. Reed, S. A., and Banks, C. V., "Determination of Palladium and Nickel with Alpha-Furildioxime," Proc. Iowa Acad. Sci., 55, 267-275 (1948) [C. A. 44, 973 (1950)]; Brit. Chem. Ab., C., 229 (1950)].

Alpha-furildioxime was found to be more sensitive for nickel or palladium than dimethylglyoxime. Under the optimum conditions 1 mg. of nickel can be easily detected in 6 liters of an aqueous solution and 1 mg. of palladium in 20 liters of an aqueous solution. One can separate palladium from nickel, platinum, iron, cobalt, and many other metals with a single precipitation from strong mineral acid solution. The palladium alpha-furildioxime precipitate can be dried and weighed or it can be ignited to the metal.

Alpha-furildioxime precipitated nickel quantitatively.

Composition of the nickel complex varies with the pH of the solution from which it was precipitated.

1951

20. Rigby, W., "New Reagent for the Oxidation for Acyloins of Diketones," J. Chem. Soc., 172, 793-795 (1951) [C. A., 45, 8977 (1951)].

A yield of 88% of furil was obtained by using 2.4 g. of furoin, 2.4 g. of bismuth trioxide, 8 ml. of acetic acid, and 24 ml. of ethylene glycol mono ethyl ether, when placed on a water bath for 3/4 of an hour. The yield was 88% when 5.1 g. of furoin, 5.1 g. of bismuth trioxide, 30 ml. acetic acid, and 15 ml. of water, were placed on a water bath for 10 minutes. Undiluted acetic acid at 80-5° gave 79% of an inferior product and at 100° the initial product was bronze colored. Various other compounds were listed which do and do not react with bismuth trioxide.

21. Pallaud, R., "Dioxime and Monoximes of the α -Diketones as Analytical Reagents," Chim. anal., 33, 239-244 (1951) [C. A., 45, 8934 (1951)].

The properties and uses of the following oximes were described, dimethylglyoxime, gamma-benzildioxime,

furfuryldioxime, alpha-benzildioxime, benzylmethylglyoxime, benzoylmethylglyoxime, phenylglyoxime, cyclohexanedione, oxalenediamidoxime, oxalenediuramidoxime, diacetylmonoxime, and isatine-beta-oxime.

22. Gahler, A. R., Mitchell, A. M., and Mellon, M. G., "Colorimetric Determination of Nickel with Alpha-Furildioxime," Anal. Chem., 23, 500-503 (1951) [C. A. 45, 5565 (1951)].

Nickel was determined colorimetrically by forming the nickel alpha-furildioxime complex, which was extracted with 1,2-dichlorobenzene. The transmittance of the extracted yellow-colored complex was measured at 438 m μ . After solution of sample, a suitable aliquot (20-75 ml.) was taken. Then 5-10 ml. of 10% solution of potassium tartrate, 5-10 ml. of 3 M acetic acid solution and sufficient 20% sodium hydroxide solution were added to adjust the pH to 8.0. In a separatory funnel, 10-15 ml. of an 0.1% ethanolic solution of alpha-furildioxime was added, and the nickel complex was extracted with 5 ml. portions of acid-free 1,2-dichlorobenzene. Copper in small amounts was removed by shaking the extraction with 5-10 ml. of dilute ammonium hydroxide (1:50). The transmittance was measured and the amount of nickel

was determined from a calibration curve.

The ions that do not interfere with the extraction are acetate, arsenate, arsenite, barium, benzoate, bromide, cadmium, calcium, chloride, chlorate, dichromate, fluoride, formate, H sulfite, iodate, iodide, lactate, lithium, magnesium, molybdate, nitrate, oxalate, orthoborate, orthophosphate, persulfate, potassium, pyroborate, salicylate, selenate, sodium, strontium, sulfate, sulfite, tartrate, thiocyanate, thiosulfate, tungstate, and vanadate.

Lead and uranyl ions do not interfere although they form very slight precipitates. Unless complexed these ions interfere, aluminum, antimony, beryllium, bismuth, cerium, chlorostannate, chlorostannite, chromate, cobalt, copper, iron(II), iron(III), manganese, mercury, thorium, titanium, zinc, and zirconium. Gold, platinum, and palladium form yellow solutions with the reagents. Perchlorate, pyrophosphate, cyanide, periodate, sulfide, and citrate prevent extraction of nickel. Silicate in concentrations greater than 100 mg. interferes. Chloroform can be used in place of 1,2-dichlorobenzene for extraction.

23. Tsumaki, T., and Yamaguchi, M., "Pyrolysis of Inner Complex Salts," J. Chem. Soc. Japan, 70, 10-12 (1949) [C. A., 45, 4657 (1951)].

Pyrolysis of various nickel complexes was studied in an atmosphere of nitrogen. Nickel furildioxime decomposed at 270° yielding ammonia, 2-cyanofuran, and difurylfurazan, $C_4H_3O \overline{C:NON:CO} C_4H_3$, long prisms, m.p. 62° , insoluble in water, and soluble in ethanol, ether, benzene, petroleum ether. It was stable against hot alkali and acid. It can easily be steam-distilled and sublimed.

24. Holden, B., and Rigby, W., "Bismuth-Catalyzed Air-Oxidation of Acyloins," J. Chem. Soc., 1951, 1924-1925 [C. A., 46, 936 (1952)].

The oxidation of acyloins in various solvents was cited. The solvents were ethylene glycol mono ethyl ether in acetic acid, acetic acid, 25% of ethylene glycol mono ethyl ether in acetic acid, and 25% of water in acetic acid. It was found that air was superior to oxygen, the latter led to discoloration and by-products. Oxygen did not increase the rate of oxidation. The yields were lower than those for the corresponding bismuth acetate oxidation.

1953

25. Shinra, K., and Ishikawa, K., "Organic Analytical Reagent, I. Alpha-Furildioxime," J. Chem. Soc. Japan, 74, 271-273 (1953) [C. A., 47, 9848 (1953)]/.

Alpha-furildioxime was synthesized from furoin through furil. The product contains the anti-form and another isomer in the ratio of 1:1.

26. Shinra, K., and Ishikawa K., "Organic Analytical Reagents," J. Chem. Soc. Japan, 74, 353-355 (1953) [C. A., 47, I0398 (1953)]/.

Synthesized furildioxime consisted of equal amounts of alpha-(anti)- and gamma-(amphi)- isomers. The anti-form reacts only with nickel to form an insoluble precipitate. The newly isolated beta-form has a m.p. of 184-5°. The absorption spectra of the three forms are identical.

27. Peshkova, V. M., and Gallai, Z. A., "Amperometric Titration of Nickel with Dioximes," Zhur. Anal. Khim., 7, 152-157 (1952) [C. A., 47, 1536 (1953)]/.

Various dioximes including alpha-furildioxime were tested in the amperometric titration of nickel. Alpha-furildioxime was undesirable because the precipitate it formed was slow to coagulate at room temperature.

28. Peshkova, V. M., and Gromova, M. I., "Colorimetric Determination of Rhenium with the use of Dioximes," Vestnik Moskov., Univ., 7, No. 10, Ser. Fiz. Mat. i Estestven. Nauk No. 7, 85-97 (1952) [C. A., 47, 5301 (1953)]

Rhenium formed colored compounds with alpha-furildioxime in the presence of stannous chloride in strongly acid solutions. Alpha-furildioxime formed yellow-orange, orange, raspberry-red solutions, depending on the quality of the reagents. The red compound was extracted with organic solvents (chloroform). The resulting solutions obeyed Beer's law and were applicable for the colorimetric determination for rhenium. Tests can be made in the presence of molybdenum. The maximum absorption was at 533 m μ . Alpha-furildioxime has the greatest maximum absorption, the extinction coefficient was 24,000. With test solutions containing molybdenum, it was necessary to add a similar amount of molybdenum salts to standards or the results will be low.

1954

29. Cramer, F., "Occlusion Compounds. Basic Catalysis by Intramolecular Hollow Spaces," Chem. Ber., 86, 1576-1581 (1953) [C. A., 48, 8005 (1948)]

The hollow space of an occlusion compound (OC)

was a space of high electron density and behaved in many respects like an electron donor. Furoin was readily oxidized in alkaline solution, but in neutral or acid media oxygen was consumed very slowly. When cyclodextrin was added to a solution of furoin, pH = 10, enediol form increases, absorption maximum shifts from 280 to 308 m μ and the oxidation velocity was increased. The reaction velocity increases 2.1 times when the pH was increased from 9 to 10.25 in the presence of cyclodextrin and at pH 12 the reaction was very rapid. Cyclodextrin can form (OC) in solutions.

1955

30. Peshkova, V. M., "Effect of the Structure of the Oxime Molecule on the Properties of its Compounds with Metals," J. Anal. Chem. USSR, 10, 77-83 (1955).

Alpha-furildioxime, with conjugated bonds and oxygen in the heterocycle, gave a compound with nickel in the pH range of 6.4-10.5. The values for the molar extinction and distribution coefficient are 10,000 and 47, respectively. The unsymmetrical dioximes, and alpha-furildioximes are, therefore, of great interest for colorimetry. The compound formed between

alpha-furildioxime and bismuth has a considerably more intense color than the other dioximes of bismuth. Lead alpha-furildioxime has a yellowish color. Alpha-furildioxime is related to the unsaturated compounds for which absorption in the longer wave bands is characteristic, nickel and copper derivatives absorb in the visible spectrum.

31. Menis, O., and Rains, T. C., "Colorimetric Determination of Palladium with Alpha-furildioxime," Anal. Chem., 27, 1932 (1955).

A spectrophotometric method for the determination of microgram quantities of palladium with alpha-furildioxime was developed. Palladium forms with the reagent in a 0.1 to 1.4 N hydrochloric acid medium, a yellow-colored complex which obeys Beer's law at 420 m μ . The colored complex was readily extractable into chloroform, in which medium it adhered to Beer's law at the 380 m μ wavelength. In the aqueous phase, in the presence of 10% ethanol up to 5 γ of palladium per ml. of final volume, the colored complex was stable for 20 minutes, after which time the absorbance decreased slowly. In the organic phase the colored complex was stable for at least 24 hours. This reagent was highly specific for palladium. Platinum

group metals and gold do not interfere. In the presence of highly colored ions, extraction with chloroform eliminates all interference, except interference of cyanide ions, which prevent the formation of the palladium alpha-furildioxime complex. The method was very sensitive. Concentrations as low as 0.1 p.p.m. of palladium can be determined in 5-cm. cells. The precision at the optimum spectrophotometric range was within 1%.

The yellow complex of palladium alpha-furildioxime was formed by transferring 59.0 γ of palladium (as palladium chloride) to a 25 ml. volumetric flask, and adding successively 1 ml. of reagent solution of alpha-furildioxime, followed by dilution with water to the calibrated volume. The complex exhibits an absorption peak at 420 m μ , when measured against a reagent blank solution.

The yellow complex of palladium alpha-furildioxime was formed by transferring 74.0 γ of palladium (as palladium chloride) to a 30-ml. separatory funnel, and adding successively 1 ml. of concentrated hydrochloric acid and the requisite amount of alpha-

furildioxime. A 10-ml. portion of chloroform was sufficient to remove the palladium complex from the aqueous solution after a 20-second shaking period. The organic layer was removed and collected in a 25-ml. volumetric flask. Approximately 0.5 gram of anhydrous sodium sulfate was added and the extract was diluted to volume with chloroform. The complex exhibits an absorption peak at 380 m μ when measured against chloroform, the reagent blank solution.

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