

for fifteen minutes, giving a clear solution. Most of the alcohol was distilled off and the residual solution, on cooling, deposited white plates of the oxime XIX (500 mg.) melting at 195–196°. Recrystallization from alcohol gave a product melting at 196–197°.

Anal. Calcd. for $C_{22}H_{16}O_2N$: C, 80.20; H, 5.82. Found: C, 80.09; H, 6.21.

Oxidation.—The tetralone XVIII (1 g.) and potassium dichromate (3 g.) were refluxed in acetic acid (30 cc.) for six hours. The green solution was poured into water (100 cc.) and most of the acetic acid was neutralized with sodium carbonate. Some sticky, orange material rose to the top of the solution; this was removed with a spatula. The aqueous solution was extracted with benzene, and the benzene solution then extracted with sodium hydroxide solution (10%). The alkaline extraction was acidified and steam distilled. From the distillate, benzoic acid (200 mg.), m. p. and mixed m. p. 121°, was isolated. The residue in the distilling flask was extracted with ether; from the ether extract, *o*-benzoylbenzoic acid (hydrate) (520 mg.), m. p. and mixed m. p. 88–90°, was isolated. From the sticky orange solid originally found in the oxidation, a very small amount of the red quinone VI, m. p. and mixed m. p. 245°, was isolated by repeated crystallization from alcohol.

Naphthol IV.—The tetralone XVIII (500 mg.), acetic acid (15 cc.) and sulfuric acid (5 drops) were boiled for thirty minutes and then poured into water. The pinkish solid was removed, dissolved in alcohol and the solution decolorized with charcoal. The alcohol was boiled off and replaced by petroleum ether (b. p. 90–100°). On cooling white needles of 3,4-diphenyl- α -naphthol IV (430 mg.) were deposited. These had a melting point and mixed melting point of 142–143° and showed the phenomenon of solidification after melting with remelting at 153–154° (see above under properties of IV). This is the same substance reported by Franssen as having structure XVII.

Acetate IX.—The tetralone XVIII (1 g.), acetic anhydride (7.5 cc.) and sulfuric acid (1 drop) were boiled for fifteen minutes. The cooled solution was poured onto ice and the pinkish solid (m. p. 160–162°) was removed. The solid was dissolved in chloroform and the solution was decolorized with charcoal. Most of the chloroform was removed, alcohol was added and the solution was cooled. White cubes of the acetate IX (950 mg.), m. p. and mixed m. p. 162–162.5°, were obtained. This is the same substance reported by Franssen as having structure XVI.

Summary

1. Diphenylketene and phenylacetylene react by addition to form, in good yield, 3,4-diphenyl- α -naphthol, IV.

2. The structure of the naphthol was proved by degradation and by an independent synthesis from 1,4-naphthoquinone and phenylmagnesium bromide.

3. The work of Franssen on the addition of phenylmagnesium bromide to 1,4-naphthoquinone has been repeated and his structures for the products have been shown to be incorrect. These have been supplanted by the correct structures.

4. The reaction between diphenylketene and acetylenes appears to be quite general, although no solvent, or quite concentrated solutions, must be used in order to bring about a reaction. As yet the mechanism of this reaction is not known, but observations to be reported later indicate that an acetylenic hydrogen atom is not involved because diphenylacetylene also reacts with the ketene.

MINNEAPOLIS, MINNESOTA

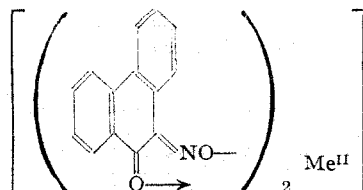
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Ortho-quinone Monoxime Inner Complexes

BY HELMUT M. HAENDLER WITH GEORGE MCP. SMITH

Recently, Ciusa,¹ in work on phenanthrenequinone, observed that the monoxime behaved as do α -isonitroso ketones in reacting even in extremely dilute solutions with salts of cobalt, nickel, and iron. The divalent cobalt and nickel inner complexes obtained were of regular composition, having the structure



(1) Ciusa, *Gazz. chim. Ital.*, **66**, 591 (1936).

In general, cobalt, nickel, and copper form inner complexes more readily than do other metals. To determine, however, the extent to which other inner complexes of this group would form, various metals were tested with phenanthrenequinone monoxime and other oximes possessing the chelating group C, C-NOH, O.²

Inner complexes of cadmium, copper, lead, manganese, and uranyl with phenanthrenequinone monoxime were prepared, and complexes of copper, lead, manganese, nickel, and uranyl with chrysenequinone monoxime also were prepared. In all cases except that of the uranyl compounds

(2) Haendler and Geyer, *THIS JOURNAL*, **60**, 2813 (1938).

TABLE I

INNER COMPLEXES OF PHENANTHREQUINONE MONOXIME (PqxH) AND CHRYSENEQUINONE MONOXIME (CxH)							
Inorg. salt	Solvent for inorg. salt	Color	M. & P. No.	Formula	% yield	Metal analyses, %	
						Calcd.	Found
Cd(OAc) ₂	Alcohol	Brownish orange	5-D-12	[Cd = (Pqx) ₂] ^a	80	Cd, 20.2	20.1
Cu(OAc) ₂	Water	Chocolate-brown	7-E-11	[Cu = (Pqx) ₂]	80	Cu, 12.5	12.5
Pb(OAc) ₂	Water	Light brown	7-C-12	[Pb = (Pqx) ₂]	85	Pb, 31.8	31.5
Mn(OAc) ₂	Water	Yellowish brown	15-J-8	[Mn = (Pqx) ₂]	80	Mn, 11.0	11.3
UO ₂ (OAc) ₂	Alcohol	Bright yellow	9-L-8	[UO ₂ = (Pqx) ₂ ·2C ₂ H ₅ OH]	95	<i>b</i>	
UO ₂ (OAc) ₂ ^c	Alcohol	Brick red	5-J-11	[UO ₂ = (Pqx) ₂]	90	U, 33.3	33.0
Cu(OAc) ₂	Water	Red-brown	8-J-5	[Cu = (Cx) ₂]	80	Cu, 10.4	10.4
Pb(OAc) ₂	Alcohol	Red-brown	8-J-7	[Pb = (Cx) ₂]	70	Pb, 27.6	27.7
Mn(OAc) ₂	Alcohol	Olive green	15-L-7	[Mn = (Cx) ₂]	95	Mn, 9.2	9.4
NiCl ₂	Alcohol	Green-brown	16-A-12	[Ni = (Cx) ₂]	75	Ni, 9.7	9.8
UO ₂ (OAc) ₂	Alcohol	Yellow-orange	9-L-10	[UO ₂ = (Cx) ₂ ·2C ₂ H ₅ OH]	80	<i>d</i>	
UO ₂ (OAc) ₂ ^e	Alcohol	Orange-brown	5-H-12	[UO ₂ = (Cx) ₂]	75	U, 29.2	28.8

^a Forms unstable greenish black addition compound with pyridine. ^b Ratio of [UO₂ = (Pqx)₂] : C₂H₅OH determined. Calcd. 1:2. Found 1:1.95, 1:2.10. ^c Made by heating the alcohol addition compound to 100°. ^d Ratio of [UO₂ = (Cx)₂] : C₂H₅OH determined. Calcd. 1:2. Found 1:1.96. ^e Made by heating the alcohol addition compound to 100°.

the simple inner complex formed. In the case of the uranyl complex, a compound containing two moles of ethyl alcohol, probably coordinated directly to the uranyl, first precipitated and then decomposed on heating to the normal inner complex.

In addition to the complexes described, tests³ on these two oximes indicate that chromium, mercury (I), palladium, rhodium, and zinc also form complexes.

Retenequinone monoxime exhibits the same reactive tendencies as the two oximes used; the colors shown, however, are somewhat duller than those of the phenanthrenequinone monoxime complexes but not as dark as those of the chrysenequinone monoxime compounds. 2-Nitrophenanthrenequinone monoxime gives colors duller than the phenanthrenequinone monoxime complexes but also somewhat duller than those from the 4-nitro isomer. Whether these indications will be supported by observations on other types of complexes remains to be seen.

It originally was intended to measure the absorption spectra of these complexes, but due to their insolubility this plan was, of necessity, abandoned. We hope, however, to carry out this phase of the problem with certain complexes which seem to show greater promise from the standpoint of solubility.

The description of color is so vague that it was felt a more tangible reference would be useful. All the complexes prepared have been classified according to the color charts of Maerz and Paul,⁴

(3) Haendler, *J. Chem. Education*, **16**, 66 (1939).

(4) Maerz and Paul, "Dictionary of Color," McGraw-Hill Book Co., Inc., New York, N. Y.

by assigning them what we have termed the M. and P. No., being the actual color plate reference of the compound.

Experimental

Phenanthrenequinone Monoxime.—Phenanthrene, purified by the method of Bachmann,⁵ was oxidized to the quinone as described by Jakubowitsch and Worobjowa,⁶ purified by the method of Moore and Huntress,⁷ and converted to the monoxime by Goldschmidt's procedure⁸; m. p. 158–159°.

Chrysenequinone Monoxime.—Purified chrysene⁹ was oxidized and converted to the oxime according to Graebe and Hönlgsberger¹⁰; m. p. 162–163°.

Inner Complexes.—The complexes of phenanthrenequinone monoxime (C₁₄H₉NO₂ = PqxH) and chrysenequinone monoxime (C₁₈H₁₁NO₂ = CxH) were prepared by treating a hot alcohol solution of a slight excess of the oxime with either an alcohol or water solution of the metallic salt and adjusting the pH of the mixture with ammonium hydroxide or acetic acid until coagulation of the precipitate occurred. The compounds, after filtration, were purified by extraction of the excess organic compound with alcohol. The complexes are extremely stable, insoluble in practically all organic solvents commonly available, soluble with decomposition in warm glacial acetic acid, and are only slightly attacked by mineral acids in most cases. For the sake of simplicity the preparational data are presented in tabular form.

Summary

1. Several new inner complexes of phenanthrenequinone monoxime and chrysenequinone monoxime have been prepared.

(5) Bachmann, *THIS JOURNAL*, **57**, 557 (1935).

(6) Jakubowitsch and Worobjowa, *J. prakt. Chem.* **143**, 281 (1935).

(7) Moore and Huntress, *THIS JOURNAL*, **49**, 1328 (1927).

(8) Goldschmidt, *Ber.*, **16**, 2178 (1883).

(9) Liebermann, *Ann.*, **158**, 306 (1871).

(10) Graebe and Hönlgsberger, *Ann.*, **311**, 262 (1900).

2. Tests have shown the existence of other inner complexes of these and also other quinone oximes.

3. An increase in the complexity of the sub-

stituent groups on the organic compounds tested appears to cause a darkening in the color of the metal complexes.

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The Entropy of Hydrogen Cyanide. Heat Capacity, Heat of Vaporization and Vapor Pressure. Hydrogen Bond Polymerization of the Gas in Chains of Indefinite Length

BY W. F. GLAUQUE AND R. A. RUEHRWEIN

This paper reports the results of low temperature calorimetric measurements on solid and liquid hydrogen cyanide. The data have been used to calculate the entropy of hydrogen cyanide gas and the experimental result has been compared with the value calculated from available band spectrum data.

It has been shown by Sinosaki and Hara¹ and by Felsing and Drake² that hydrogen cyanide gas is partially polymerized, and it is therefore necessary to apply a correction in obtaining the entropy of HCN from the entropy of the actual gas.

The measurements were made in a calorimeter with the laboratory designation Gold Calorimeter III which has been described previously.³ The standard thermocouple which had been compared with a helium gas thermometer³ was compared with oxygen and hydrogen vapor pressures during the course of this work. Agreement was found to within 0.05° at all temperatures measured. The resistance thermometer was calibrated directly in terms of the vapor pressure of hydrogen for temperatures below 20°K.

Preparation and Purity of Hydrogen Cyanide.—Hydrogen cyanide was prepared by a method described by Perry and Porter.⁴ 18 Normal sulfuric acid was dropped on sodium cyanide until enough gas had been generated to make 300 cc. of liquid hydrogen cyanide. The gas from the generator was passed through 2 tubes of anhydrous calcium chloride and 3 tubes of phosphorus pentoxide. All of the tubes were 30 cm. long and 3 cm. in diameter. A considerable amount of a dark brown product was left in the reaction vessel.

The collected liquid was distilled three times, a portion being discarded at the beginning and end of each distillation. A purified portion of 135 cc. remained. This was distilled in a vacuum-jacketed column, for a reason

to be discussed later. The whole system could be subjected to a high vacuum and between each distillation the hydrogen cyanide was solidified by means of liquid air and pumped with a mercury diffusion pump.

The material was a clear colorless liquid and it remained so even after a portion had been allowed to stand at room temperature for about one year.

From the slight rise in heat capacity below the melting point, due to premelting, the liquid-soluble solid-insoluble impurity was estimated to be of the order of one mole in one hundred thousand moles of hydrogen cyanide.

An interesting phenomenon was observed when the solidified hydrogen cyanide was warmed from or cooled to liquid air temperatures in a glass bulb. Intense flashes of bluish-white light were emitted in the temperature range 100 to 200°K. both on warming or cooling. The static discharge probably was due to strains set up in the solid by an unequal rate of temperature change. The discharge was accompanied by a cracking sound characteristic of crystals breaking under strain. The temperature range of the effect was obtained roughly by sealing a well into the glass bulb so that a thermocouple could be introduced.

The above effect is an interesting demonstration of the necessity of providing glass bulbs with a protective sheath to prevent contact of such materials with liquid air in case of breakage. It appears that solid hydrogen cyanide cooling in contact with liquid air would be practically certain to explode although we did not try it. Electrostatic effects in some degree are to be expected when such materials are fractured.

The Melting Point and Vapor Pressure of Hydrogen Cyanide.—A summary of the melting point investigation is given in Table I.

The values of the vapor pressure are given in Table II. The measurements were made by means of a Société Générale cathetometer with a precision of 0.002 cm., used as a comparison instrument with a standard meter. The standard acceleration of gravity was taken as 980.665 cm. sec.⁻² and the acceleration at this location as 979.973 cm. sec.⁻². The meniscus height corrections were taken from the work of Cawood and Patterson⁵ and the corrections to international

(1) Sinosaki and Hara, *Tech. Repts. Tohoku Univ.*, **8**, 297 (1929).

(2) Felsing and Drake, *This Journal*, **58**, 1714 (1936).

(3) Glauque and Egan, *J. Chem. Phys.*, **5**, 45 (1937).

(4) Perry and Porter, *This Journal*, **48**, 299 (1926).

(5) Cawood and Patterson, *Trans. Faraday Soc.*, **29**, 514 (1933).