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## 5,8-Dihydroxyquinoline and Its Nickel Derivatives

By HARVEY DIEHL AND FRED H. LOHMAN

Many derivatives of 8-hydroxyquinoline have been prepared and examined, some looking toward increased specificity as precipitating reagents, others toward an increase in the intensity of the color of the metal derivatives. Of the derivatives which have been studied, attention has been centered principally on the alkyl and halogen derivatives on the one hand and on the aromatic azo derivatives on the other. This paper deals with the preparation and properties of an 8-hydroxyquinoline bearing a second hydroxyl group, 5,8-dihydroxyquinoline. In this substance are combined the properties of chelate ring formation with metals and the oxidation-reduction behavior characteristic of the hydroquinones.

### EXPERIMENTAL WORK

**Preparation of 5,8-Dihydroxyquinoline.** The procedure of Matsura and Sone (1) was followed. 8-Hydroxyquinoline was first converted to 5-nitroso-8-hydroxyquinoline by the action of sodium nitrite in hydrochloric acid solution at 0-5°. The nitroso compound was then reduced by iron and hydrochloric acid at 95°.

Seven g. of 5-nitroso-8-hydroxyquinoline hydrochloride was dissolved in 1800 ml. of a solution containing 43.3 ml. concentrated hydrochloric acid. The solution was heated to 95° and 10 g. of iron powder added in small amounts and at frequent intervals over a period of one hour. Stirring was then continued for one hour with the temperature maintained at 95°. The unreacted iron was filtered off and the filtrate concentrated to a small volume at reduced pressure under nitrogen until 5,8-dihydroxyquinoline hydrochloride crystallized. The product was recrystallized from ethanol through which hydrogen chloride had been bubbled; the solvent was removed under reduced pressure as described above. The product was finally recrystallized several times from 10 per cent hydrochloric acid. Found: C 52.7, H 3.8, N 6.9, Cl 17.6; calculated for  $C_9H_8O_2NCl$ : C 54.8, H 4.1, N 7.1, Cl 17.9.

*Potentiometric Oxidation of 5,8-Dihydroxyquinoline.* 5,8-Dihydroxyquinoline was titrated with three standard oxidizing agents, potassium dichromate (in 1 M perchloric acid), cerium (IV)

perchlorate (in 1 M perchloric acid), and potassium ferricyanide (in neutral solution). The titrations were followed with the usual electrode system, platinum vs. saturated calomel electrodes, using a Leeds and Northrup student potentiometer.

*Neutralization of 5,8-Dihydroxyquinoline.* The hydrochloride of 5,8-dihydroxyquinoline was titrated potentiometrically with standard sodium hydroxide using a glass electrode and a Beckman Model G pH meter.

*Metal Derivatives of 5,8-Dihydroxyquinoline.* Solutions of 5,8-dihydroxyquinoline and of various metal ions were brought together and the pH of the resulting solution raised until a precipitate appeared. The metals tested and the pH at which precipitation began were nickel (3.5-4), zinc (6.5), copper (II) (4.0), cobalt (II) (6.0), iron (II) (5.5), magnesium (6.0), and aluminum (hydroxide precipitate).

The precipitation of nickel was studied in some detail. A stock solution containing 1.15 mg. of nickel per ml. as the perchlorate was prepared. A series of precipitations was made in which 5.0 ml. volumes were diluted to 50 ml. with water, and the pH of the various solutions adjusted either with sodium acetate and acetic acid (below pH 6), or with ammonium chloride and ammonium hydroxide (above pH 6). To each solution was added a twenty-five mole per cent excess of reagent in twenty-five ml. of water. The addition was made slowly with constant stirring at room temperature. The precipitates were filtered and washed with water adjusted to the pH at which the precipitation was made. The precipitates were dissolved in 1 M perchloric acid and the solution titrated with standard potassium dichromate. The residual solution was then digested with nitric acid and perchloric acid and analyzed for nickel by precipitation of nickel dimethylglyoxime.

## RESULTS AND DISCUSSION

As expected two equivalents of potassium dichromate were required for the titration of 5,8-dihydroxyquinoline in acid solution. This corresponds to the oxidation of the dihydroxy compound to the corresponding quinone (2,3). The standard reduction potential is +0.666v. on the hydrogen scale as determined from the mid-point of the titration, Fig. 1.

The titrations with standard cerate solution showed a very rapid downward drift in potential in the neighborhood of the equivalence-point presumably due to a secondary reaction involving the excess cerate ion and the oxidized form of the 5,8-dihydroxyquinoline.

After the addition of 0.3 milli-equivalents of oxidant per millimole of 5,8-dihydroxyquinoline in excess, the potential becomes stable and approaches the standard potential of the Ce(IV)-Ce(III) system. The standard reduction potential as determined by the cerate titration was found to be +0.648 v.

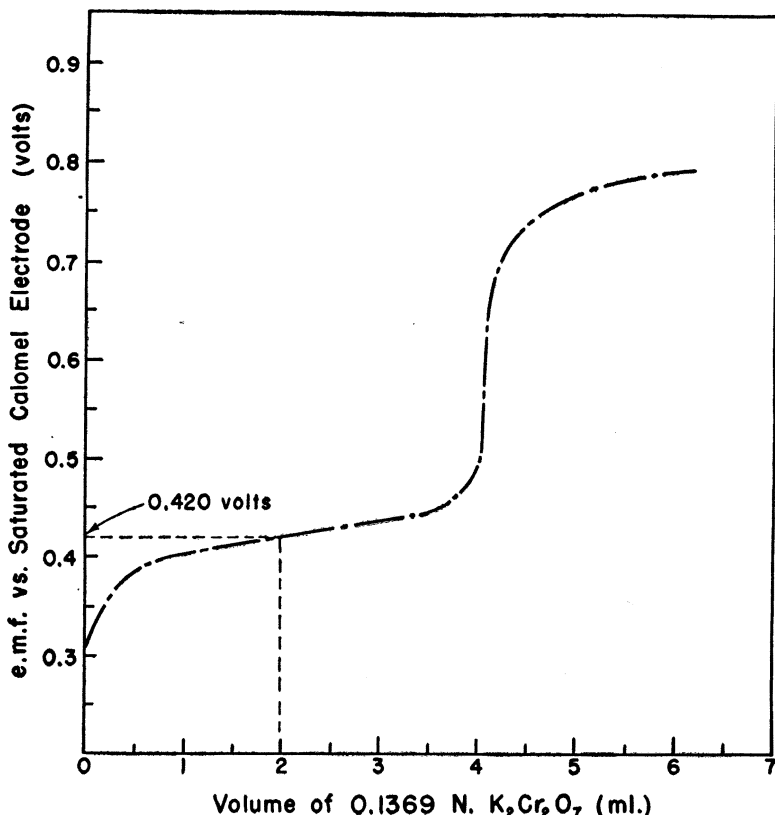


Figure 1. Titration of 55.7 mg (0.282 millimoles) 5,8-dihydroxyquinoline hydrochloride with 0.1369 N potassium dichromate solution in 1 M perchloric acid.

In neutral solution, only one equivalent of oxidizing agent was consumed in the oxidation of 5,8-dihydroxyquinoline. The potassium ferricyanide used is not a sufficiently strong oxidizing agent to oxidize the dihydroxy compound beyond the semiquinone stage.

The curves obtained in titration of 5,8-dihydroxyquinoline with sodium hydroxide are shown in Fig. 2. The first break in the curve corresponds to the neutralization of the hydrochloride salt and the second to the neutralization of one of two phenolic hydrogen atoms. The values for the dissociation constants as determined from the titration curves are  $pK_1=4.5$  and  $pK_2=9.3$ . The third

acidic hydrogen atom appears to be too weak to be titrated in aqueous solution.

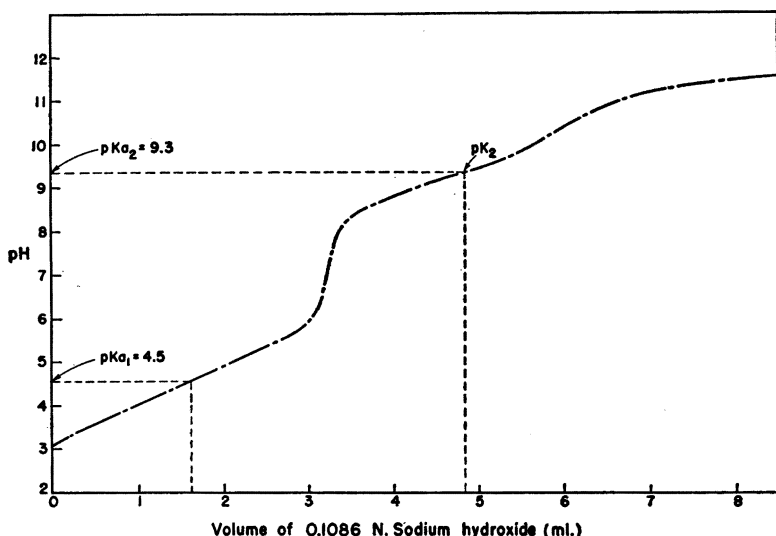


Figure 2. Titration of 60.5 mg (0.331 millimoles) 5,8-dihydroxyquinoline hydrochloride with 0.1086 N sodium hydroxide solution.

The data obtained in the precipitation of the nickel derivative are shown in Table I. The ratio of equivalents of oxidizing agent consumed to the weight of nickel present indicates that two distinctly different compounds are formed depending on the PH at which the precipitation is carried out. Below pH 6 the derivative contains four moles of 5,8-dihydroxyquinoline per mole of nickel; above pH 6 the derivative contains two moles of 5,8-hydroxyquinoline per mole of nickel.

**Table I.**  
pH—Precipitation—Composition Data for Nickel  
5, 8-Dihydroxyquinolates

	4 <sup>a</sup>	5 <sup>b</sup>	pH 6 <sup>b</sup>	7 <sup>b</sup>	8 <sup>b</sup>
Nickel Taken (mg)	5.86	5.86	5.86	5.86	5.86
Nickel Precipitated (mg)	1.90	5.16	4.23	4.73	4.68
Nickel Filtrate (mg)	3.86	0.32	1.38	0.81	0.77
Nickel Recovered	5.76	5.48	5.61	5.54	5.45
Per Cent Precipitation	32.8	88.2	72.0	85.5	81.0
Meq. of Oxidant	.189	.713	.304	.315	.310
Meg. of Oxidant per Millimole of Nickel	5.85	8.11	4.21	3.91	3.89
Moles of H <sub>2</sub> Q <sub>2</sub> per Mole of Nickel	2.92	4.05	2.10	1.93	1.94

<sup>a</sup> 50 mg. of 5,8-dihydroxyquinoline hydrochloride reagent added; <sup>b</sup> 75 mg of reagent added.

As shown in Table I nickel is not completely precipitated by 5,8-dihydroxyquinoline, even at pH 8. This indicates an appreciable solubility for both of the nickel compounds.

The nickel precipitate when dried to constant weight showed sufficient variation in composition as to be of little use in the gravimetric determination of nickel.

#### SUMMARY

5,8-Dihydroxyquinoline, a compound which exhibits the combined properties of chelate ring formation and hydroquinon-equinone oxidation, has been examined and its standard reduction potential and acid dissociation constants measured. It forms two nickel derivatives in which the ratios of organic compound to metal are four to one (precipitated below pH 6) and two to one (precipitated above pH 6). The nickel derivatives are somewhat too soluble to be useful for the gravimetric separation of nickel.

#### References

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