other kind, such as acetylation of any enol of IV, occurred under even these fairly strong conditions.

Any interconversion of diene (I) to ketone IV is highly unlikely since the elements of water would have to be picked up from a strongly dehydrating medium.

Acknowledgment.—The authors wish to express their sincere thanks to E. I. du Pont de Nemours and Company, Wilmington, Delaware, for generous financial assistance in the academic year 1948–1949 which made this study possible.

NEW BRUNSWICK, NEW JERSEY
RECEIVED FEBRUARY 28, 1951

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF LOUISVILLE]

Spectrophotometric Study of 8-Hydroxyquinaldine Chelates. Notes on 8-Quinolinol Chelates

BY J. P. PHILLIPS AND H. P. PRICE

The soluble green complex between ferric iron and 8-hydroxyquinaldine is shown to have the same kind of structure as the corresponding 8-quinolinol complex, but no aluminum complex is formed by 8-hydroxyquinaldine. The solubilities of 8-hydroxyquinaldine and its chelates with zinc and copper were determined and the solubility products of the chelates computed. A comparison with the solubility products of 8-quinolinol chelates and of metal hydroxides demonstrates that the chelates of 8-quinolinols have the same relative stabilities as the metal hydroxides.

8-Hydroxyquinaldine forms chelates like those obtained with the better known 8-quinolinol with the exception that aluminum is not precipitated with 8-hydroxyquinaldine,[1] apparently because of steric hindrance.[2,3] This work is a quantitative study of the properties of several 8-hydroxyquinaldine-metal complexes and a further demonstration that aluminum does not react with this reagent.

Experimental

Ferric Iron Complex.—The formula of the soluble green complex between 8-hydroxyquinaldine and ferric iron was obtained by the method of continuous variations,[4] after running the usual test to determine that only one complex was responsible for the color. Solutions of 0.02 *M* ferric nitrate and 0.02 *M* 8-hydroxyquinaldine in dilute nitric acid were mixed in varying proportions to a total volume of 20.0 ml. The *p*H was adjusted to 2.2 by the addition of dilute sodium hydroxide giving a final volume of 25.00 ml. A Beckman model DU spectrophotometer with 1.00 cm. silica cells was used for all spectrophotometric measurements. The results were calculated at 580 mμ, the point of maximum absorption; the same formula was also indicated at 560 and 600 mμ.

After the complex formula was determined, the intensity of its color as a function of *p*H was determined at 580 mμ by measuring a number of mixtures of 10.0 ml. each of the ferric nitrate and 8-hydroxyquinaldine solutions diluted to 25.00 ml. at various *p*H values. The complex precipitated above a *p*H of about 2.6.

Aluminum.—Solutions of 0.02 *M* aluminum ion and 0.02 *M* 8-hydroxyquinaldine in dilute nitric acid were mixed in varying proportions to a total volume of 20.0 ml. and diluted with a potassium acid phthalate buffer to 25.00 ml. The solutions had a *p*H of 4.0 as measured with a *p*H meter. The spectra of these mixtures from 400–700 mμ showed no maxima, and the plot of extinction against per cent. 8-hydroxyquinaldine indicated that no complex existed at this *p*H. Similar results were obtained at a *p*H of 4.3.

Solubility Measurements.—The solubilities of 8-quinolinol and 8-hydroxyquinaldine were obtained by analyzing samples of solutions saturated with the reagents after three days immersion in a constant temperature bath controlled to ±0.1°. The desired temperatures were approached from both above and below with concordant results. 5.00- or 10.00-ml. portions of the saturated solutions were removed, weighed, and diluted in a volumetric flask to 25.00 ml. with 0.1 *N* hydrochloric acid. The extinctions of these solutions were measured at several wave lengths between 320 and 400 mμ and the concentrations determined by comparison with a calibration curve obtained by dissolving various weighed amounts of 8-quinolinol or 8-hydroxyquinaldine in 0.1 *N* hydrochloric acid and determining the extinction.

The solubilities of the metal chelates between 8-hydroxyquinaldine and zinc or copper were measured similarly. Saturated solutions at several different *p*H values were obtained by shaking the pure chelates with water containing varying amounts of dilute hydrochloric acid or sodium hydroxide and allowing equilibrium to be reached in a constant temperature bath. 5.00 or 10.00 ml. portions of the supernatant liquid were then removed and analyzed by comparing the extinction after dilution to 25.00 ml. with 0.1 *N* hydrochloric acid (in which the chelates are completely soluble) with a calibration curve obtained by dissolving weighed amounts of the pure solid chelates in 0.1 *N* acid. At the wave lengths used zinc and copper ions had no appreciable light absorption.

The 8-hydroxyquinaldine used in these experiments was prepared as previously described,[1] vacuum distilled twice and recrystallized twice from dilute ethanol. All other chemicals were reagent grade substances.

Results and Discussion

The method of continuous variations applied to the ferric iron–8-hydroxyquinaldine color (Fig. 1) showed that the green complex in nitric acid solutions has the 1:1 mole ratio to be expected by analogy with 8-quinolinol.[5] The color is not formed below a *p*H of 1.4 and increases in intensity up to the point at which precipitation of an insoluble chelate begins (about *p*H 2.6). In hydrochloric and sulfuric acid solutions the green color was not obtained; in perchloric acid the color formed but faded rapidly. It seems probable that these effects are the result of the reducing action of 8-hydroxyquinaldine on ferric solutions.

When the same method was applied to aluminum and 8-hydroxyquinaldine, a straight line, essentially a Beer's law plot for 8-hydroxyquinaldine, was obtained (Fig. 1). It is evident that under the conditions used no soluble complex formed between aluminum and 8-hydroxyquinaldine; it had already been demonstrated[1,2] that no insoluble complex could be obtained under conditions where one would be expected.

The solubility of 8-hydroxyquinaldine in water was determined at two temperatures and compared

---

[1] Merritt and Walker, *Anal. Chem.*, **16**, 387 (1944).

[2] Irving, Butler and Ring, *J. Chem. Soc.*, 1489 (1949).

[3] Phillips and Merritt, THIS JOURNAL, **71**, 3984 (1949).

[4] Vosburgh and Cooper, *ibid.*, **63**, 437 (1941).

[5] Sandell and Spindler, *ibid.*, **71**, 3806 (1949).

with values obtained similarly for 8-quinolinol (Table I). In view of the very slight structural difference between the two compounds 8-hydroxyquinaldine is less soluble than would be expected. Approximate heats of solution, calculated from the van't Hoff equation, were about 6000 cal./mole for 8-quinolinol and 3000 cal./mole for 8-hydroxyquinaldine.

TABLE I

SOLUBILITIES OF 8-QUINOLINOL AND 8-HYDROXYQUINALDINE IN WATER

Compound	Temp., °C.	Molarity × 10^3	Molality × 10^3
8-Quinolinol	25.2	4.47 ± 0.03	4.51
	30.3	5.38 ± .03	5.42
8-Hydroxyquinaldine	25.2	2.46 ± .05	2.48
	30.3	2.67 ± .05	2.69

The solubilities of the zinc and copper chelates of 8-hydroxyquinaldine were determined in solutions of several different *p*H values (Table II). Solubility products were calculated from the equation

$$S = 4[M^{++}]^3K_a^2/[H^+]^2$$

where $[M^{++}]$ is the concentration of metal ion in the saturated solution and K_a is the acid ionization constant of the reagent.[6,7] Although the solubility products show considerable variation with changing *p*H, the results are about as consistent as would be expected from a calculation neglecting the influence of activity coefficients.

TABLE II

SOLUBILITIES OF METAL-8-HYDROXYQUINALDINE CHELATES AT 25°C.

Metal ion	*p*H	Molarity × 10^4	S × 10^{24}
Cupric	4.45	0.76	3.4
	3.80	2.0	3.1
	3.40	5.7	10.9
	3.31	6.1	8.8
Zinc	6.30	0.079	19
	4.24	1.73	15
	4.06	2.4	18
	3.80	5.35	59
	2.38	22	6.2

Although the above solubilities were determined both at 24.4 and 30.3°, the differences at the two temperatures were not large enough to be detected by the method used.

Solubility products were computed for 8-quinolinol chelates from the data on their solubility in 1 *N* acetic acid available in the literature,[8] using the acid ionization constant for 8-quinolinol previously determined.[7] The order of magnitude of the solubilities is about the same as for 8-hydroxyquinaldine chelates (Table III).

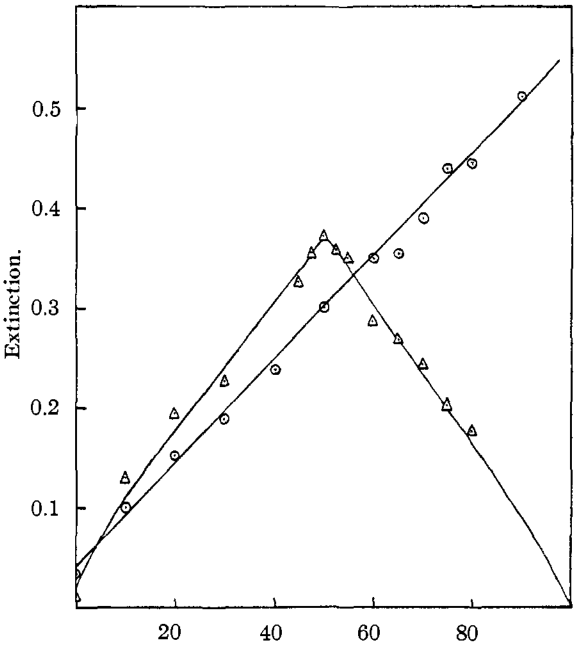

Fig. 1.—Formulas of 8-hydroxyquinaldine complexes by continuous variations method: △, ferric complex at 580 mμ (*p*H 2.2); ⊙, aluminum at 425 mμ (*p*H 4.0).

Application of the stability measurement technique of Calvin and Wilson[9] to 8-quinolinol chelates[10] gave approximately the same relative solubilities as those calculated here, assuming that increasing stability is accompanied by decreasing solubility. According to Flagg's method[11] the higher the *p*H at which a metal begins to precipitate with 8-quinolinol, the more soluble the resulting precipitate will be; these data also give the same relative solubilities.

TABLE III

SOLUBILITY PRODUCTS OF METAL SALTS OF 8-QUINOLINOL AND METAL HYDROXIDES

Metal ion	Solubility products	
	Hydroxides[a]	Chelates
Cu^{+2}	6 × 10^{-20}	1.57 × 10^{-24}
Ni^{+2}	8.7 × 10^{-19}	9.0 × 10^{-23}
Co^{+2}	1.6 × 10^{-18}	1.24 × 10^{-22}
Zn^{+2}	1.8 × 10^{-14}	5.8 × 10^{-22}
Mn^{+2}	4 × 10^{-14}	4.75 × 10^{-20}
Pb^{+2}	2.5 × 10^{-16}	4.5 × 10^{-19}
Mg^{+2}	1.2 × 10^{-11}	1.04 × 10^{-16}[b]

[a] Values obtained from Lange's "Handbook." [b] Value calculated from data of Stone and Furman, *Anal. Chem.*, **16**, 596 (1944).

A comparison of these solubility products with those for the corresponding metal hydroxides (Table III) indicates that the order of increasing solubility of the hydroxides and 8-hydroxyquinolates is the same.

Acknowledgment.—This work was supported by a grant from the Cottrell Research Corporation.

LOUISVILLE, KENTUCKY RECEIVED FEBRUARY 10, 1951

---

[6] Flagg, "Organic Reagents," Interscience Publishers, Inc., New York, N. Y., 1948, p. 71.

[7] Phillips and Merritt, THIS JOURNAL, **70**, 410 (1948).

[8] Treadwell and Ammann, *Helv. Chim. Acta*, **21**, 1249 (1938).

[9] Calvin and Wilson, THIS JOURNAL, **67**, 2003 (1945).

[10] Mellor and Maley, *Nature*, **159**, 370 (1947).

[11] Ref. 5, p. 55.