[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Ultraviolet Absorption Spectrum and the Acid Ionization Constant of 8-Hydroxyquinoline

BY K. G. STONE AND LEWIS FRIEDMAN

In connection with some other studies still in progress, it was necessary to have a value for the acid ionization constant of 8-hydroxyquinoline. There was no directly determined value in the literature, although the data of Fox[1] on the hydrolysis of the sodium salt were a good approximation. Two independent methods were used to obtain values for comparison: the solubility method of Davidson[2] and the optical method of Stenstrom and Goldsmith.[3]

Experimental

The 8-hydroxyquinoline (Paragon Testing Laboratories) was recrystallized three times from 50% ethanol and dried over sulfuric acid. The solubility in 0.1 *M* borax–sodium carbonate buffers[4] was obtained by shaking the buffer with excess solid 8-hydroxyquinoline in a constant temperature bath at 25 ± 0.1° for forty-eight hours. Samples were removed with a pipet with a plug of cotton to remove solid particles, acidified with hydrochloric acid, and analyzed by the customary bromination procedure.

The ultraviolet absorption spectrum was measured with a Beckmann model D Quartz Spectrophotometer using 1.0-cm. cells and slit widths from 1.0 to 2.0 mm. as the intensity required. For measurements in 95% alcohol, standard solutions of hydrochloric acid and sodium hydroxide in 95% alcohol were used to control the acidity. The solutions were standardized by diluting 10.0-ml. portions to 175 ml. with water and titrating in the usual manner. The standard 8-hydroxyquinoline solution contained 250 mg. per liter in 95% alcohol. It was found that 20 mg. per liter in the solution measured gave reasonable extinctions, and this concentration was used unless otherwise indicated.

For measurements in aqueous medium, 0.1 *M* hydrochloric acid and sodium hydroxide were prepared and standardized against potassium acid phthalate. Acetate, phosphate and ammonia–ammonium chloride buffers were prepared by dissolving 0.1 mole of acetic acid, potassium dihydrogen phosphate, or ammonium chloride in 600 ml. of water and titrating to the desired *p*H measured against a glass electrode with sodium hydroxide or ammonium hydroxide followed by dilution to 1000 ml. The standard solution of 8-hydroxyquinoline contained 250 mg. per liter in 5% ethanol.

All solutions measured, unless otherwise indicated, contained 20 mg. per liter of 8-hydroxyquinoline and were prepared by mixing suitable volumes of the standard solution and buffer and diluting to 100 ml. The small amount of alcohol in the dilute solutions gave no absorption in the regions measured. All chemicals were C. P. grade or better, and all glassware was calibrated. Solutions containing the same amounts of reagents except 8-hydroxyquinoline were used as blanks in the optical measurements.

Results

The solubility of 8-hydroxyquinoline in borax–sodium carbonate buffers of different *p*H values is summarized in Table I.

TABLE I

SOLUBILITY OF 8-HYDROXYQUINOLINE IN BORAX–SODIUM CARBONATE BUFFERS

*p*H	Moles per liter × 10^3
9.6	6.36
9.8	7.47
10.0	8.43
10.4	11.68

Davidson[2] has shown that the solubility is related to the acid ionization constant by equation (1) where S is the solubility in moles per liter of a

$$S = K_S + (K_S K_A/(H^+)) \qquad (1)$$

substance whose acid ionization constant is K_A, K_S is the "intrinsic solubility" or the moles per liter of acid in the absence of an added base, and (H^+) is the concentration of hydrogen ions in moles per liter. K_S and K_A were found graphically from the data in Table I, and had the values 6.12×10^{-3} and 4.20×10^{-11}.

The effect of *p*H on the ultraviolet absorption is shown in Fig. 1 for alcohol solutions and Fig. 2 for aqueous medium. The extinctions in 0.01 *M* alcoholic hydrochloric acid were not reproducible in the region of 270 mμ or less. After an exposure of ten minutes at 260 mμ the solution was opaque. It is believed that decomposition of the alcohol by a process photo-sensitized by 8-hydroxyquinoline is responsible for the decrease in transmission. No such behavior was observed in the acid aqueous medium. The curves obtained in aqueous acetate and ammonia buffers of *p*H 4 and 10 were identical within experimental error.

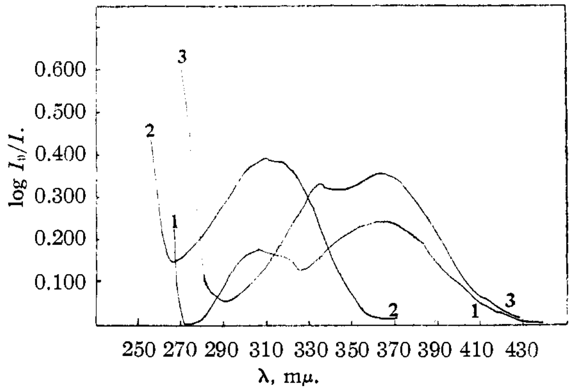

Fig. 1.—8-Hydroxyquinoline in 95% ethanol: 1—0.01 *M* HCl; 2—neutral alcohol; 3—0.01 *M* NaOH.

The Effect of *p*H

In both Figs. 1 and 2 there are two isobestic points, *e. g.*, Fig. 2, 320 and 340 mμ. Thiel[5] has

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(1) J. J. Fox, *J. Chem. Soc.*, **97**, 1119 (1910).

(2) D. Davidson, *J. Chem. Ed.*, **19**, 221–226 (1942).

(3) W. Stenstrom and N. Goldsmith, *J. Phys. Chem.*, **30**, 1683 (1926).

(4) I. M. Kolthoff and J. J. Vleeschhouwer, *Biochem. Z.*, **189**, 191 (1927).

(5) A. Thiel, *Fortschr. Chem. Physik, physik. Chem.*, **18**, 38 (1924).

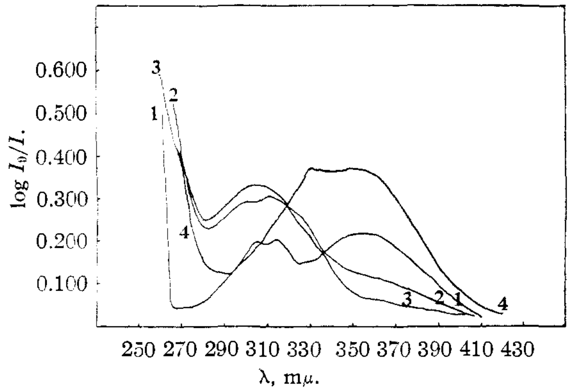
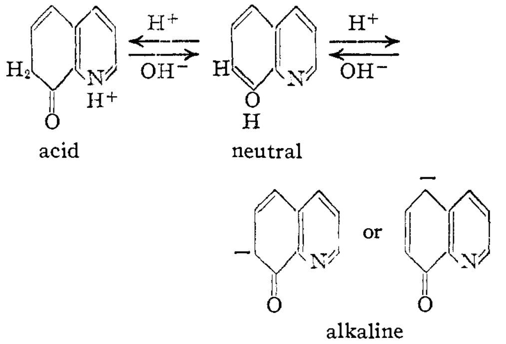


Fig. 2.—8-Hydroxyquinoline in aqueous buffers: 1—0.01 M HCl, pH 2; 2—0.01 M acetate, pH 4 and ammonia, pH 10; 3—0.01 M phosphate, pH 7; 4—0.01 M NaOH, pH 12.

shown that an isobestic point is indicative of a change in structure of the molecule with a change in pH, and so the question arises as to the nature of the acid and base species. Stone and Furman[6] have come to the conclusion from polarographic data that above pH 10 there is a carbonyl group in the molecule. By comparison with the data published by Morton and collaborators[7] it seems apparent that in alkaline medium (4, Fig. 2) the peak may be assigned to a mixture of 7,8 and 5,8 keto tautomers. In neutral medium (3, Fig. 2) the peak at 305 mμ may be assigned to the pyridine nucleus and the intensity is increased by the hydroxyl group on the carbon alpha to the heterocycle atom. In acid medium (1, Fig. 2) the peak at 355 mμ appears to be a carbonyl peak and the one at 305–315 mμ the pyridine nucleus peak. It is noteworthy that the spectra in buffers of pH 4 and 10 in aqueous medium are very similar, and thus nearly the same species must be present in both solutions.

To account for the effect of pH it is necessary to have a change in structure. We suggest the following reaction, equation (2), as a possible explanation



(2)

The species in alkaline medium (eq. 2) has been suggested by Pirrone[8] as the reacting structure in the reaction of 8-hydroxyquinoline, benzaldehyde and ammonia. This tautomeric shift is also in agreement with the results of Stone and Furman,[6] and with the work of Stimson and Reuter[9] on cytosine and isocytosine.

The acid ionization constant of 8-hydroxyquinoline may be evaluated from the spectroscopic data by the method of Stenstrom and Goldsmith.[2] The extinctions at 350 mμ for pH 7, 10 and 12 were used for the neutral molecule, the partially ionized molecule, and the completely ionized molecule. The results of the solubility and spectroscopic methods are listed in Table II with the hydrolysis value of Fox[1] for comparison. It is seen that the agreement is good for such a small value of this ionization constant. A consideration of ionic strengths of the solutions used would affect the values to some extent.

Table II

K_A for 8-Hydroxyquinoline

Method	$K_A \times 10^{11}$
Solubility	4.20
Spectroscopic	4.28
Hydrolysis	3.68

Nature of Oxine Salts

There has been some discussion as to the nature of the soluble form of the so-called insoluble metallic oxinates. Magnesium oxinate was prepared and some of the ammonia–ammonium chloride buffer was saturated with the fresh moist material. The spectrum of the resulting solution is shown in Fig. 3 with a spectrum of 8-hydroxyquinoline at a concentration of 2 mg. per liter in the same buffer. Since the two curves show marked differences, the logical conclusion is that the soluble magnesium oxinate is present in the form of a complex and not as free magnesium

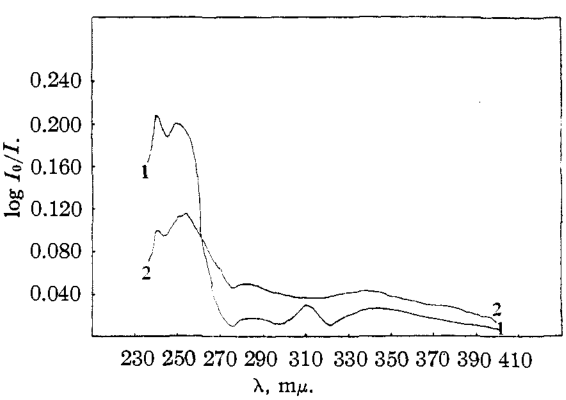


Fig. 3.—1—8-Hydroxyquinoline, 2 p. p. m. in pH 10 buffer; 2—pH 10 buffer saturated with magnesium oxinate.

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(6) K. G. Stone and N. H. Furman, unpublished work.

(7) R. A. Morton, A. Hassan and T. C. Calloway, *J. Chem. Soc.*, 883 (1934); R. A. Morton and W. T. Earlam, *ibid.*, 159 (1941); R. A. Morton and A. S. de Gouveia, *ibid.*, 916 (1934); R. A. Morton and E. Rogers, *ibid.*, **127**, 2698 (1925).

(8) F. Pirrone, *Gazz. chim. ital.*, **66**, 518 (1936).

(9) M. M. Stimson and M. A. Reuter, This Journal, **67**, 2191 (1945).

ion and 8-hydroxyquinoline. Further measurements of this kind on other metallo-organic compounds should permit a generalization concerning the state of the soluble material.

The Solubility of Magnesium Oxinate

Since the concentration of magnesium oxinate in the *p*H 10 buffer is so low (Fig. 3), it is necessary to measure the absorption in the region of 250 mμ in order to estimate the solubility. It was found that Beer's law was obeyed up to 9 mg. of 8-hydroxyquinoline per liter of buffer at 250 *m*. As is evident from Fig. 3, at 250 mμ a correction is necessary when using Beer's law on the metallo-organic solution. This factor was estimated to be 3, and the resulting solubility was calculated to be 1×10^{-5} mole of magnesium oxinate per liter of buffer. This value is in fair agreement with the value 1.9×10^{-6} found by Stone and Furman[10] using the polarographic method, and probably has an undeterminable error due to the estimated factor.

Summary

The effect of *p*H on the ultraviolet absorption of aqueous and alcoholic solutions of 8-hydroxyquinoline has been investigated. The acid ionization constant has been determined by solubility and spectroscopic methods and found to be 4.2×10^{-11}. The nature of the soluble magnesium oxinate has been investigated through the ultraviolet absorption and the solubility has been measured in ammonia buffers of *p*H 10.

[10] K. G. Stone and N. H. Furman, *Ind. Eng. Chem., Anal. Ed.*, **16**, 596 (1944).

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The Heats of Combustion of Cyclopentane, Cyclohexane, Cycloheptane and Cyclooctane

BY RALPH SPITZER[1] AND HUGH M. HUFFMAN[2]

Introduction

Information about the structure and energy of cyclic hydrocarbons is of considerable interest in connection with the problem of restricted rotation about the carbon–carbon single bond. According to the classic strain theory, both cyclopentane in the planar configuration and cyclohexane in either the chair or the boat form should be essentially strain-free because the bond angles are almost or exactly tetrahedral.

With the discovery of a force hindering rotation about carbon–carbon single bonds in open chain paraffins[3] it gradually became apparent[4] that the same force should operate in cycloparaffins with the result that either cyclopentane or cyclohexane should be destabilized depending on whether the restricting force is repulsive or attractive. In fact, one of the most useful theoretical results of this research is to help make the decision in favor of repulsion.

At the time this work was undertaken (1939–1940) there were no reliable heats of combustion on cycloparaffins and it was impossible to interpret the accurate work of Kistiakowsky and coworkers[4] on heats of hydrogenation of cycloölefins. Recently, however, making use of the unpublished results of this work and other data, Pitzer[5] has correlated the energy data on cyclic hydrocarbons on the basis of the concept of a non-planar cyclopentane molecule, first suggested by Aston,[6] *et al.*

Experimental

The Calorimeter.—The method and calorimetric system, which is of the non-adiabatic type, have been previously described.[7] The essential differences in the present technique were that a Parr double valve bomb was used, instead of the single valve bomb, to minimize gas leakage and the amount of reaction was determined both from the mass of the sample and, in some experiments, from measurement of carbon dioxide evolved in the combustion.

The mass of the sample was determined as the difference of two masses, the initial mass of filled ampoule plus platinum crucible and the final mass of glass residue plus platinum crucible. In the earlier experiments (with cyclopentane) it was observed that the final mass depended on the treatment of the glass residue. The mass determined after heating the crucible and contents on a hot plate was greater by as much as 0.4 mg. than found after igniting. This may have been due to some of the sample or products of combustion having been occluded in the glass residue. Because of the uncertainty in regard to the mass of the sample the results of the combustions of cyclopentane and cyclohexane based on the mass determination were given no weight in arriving at the final value, which is based solely on the carbon dioxide determination.

In later experiments on cycloheptane and cyclooctane, in which we used a 20- or 30-g. crucible in place of the 3-g. crucible used earlier, the weighings were quite reproducible and so analyses were run only occasionally.

The combustible impurities in the oxygen were removed by slow passage through a furnace containing vanadium pentoxide catalyst at 400° and then through Ascarite and Dehydrite absorbers to remove water and carbon dioxide.

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[1] Present address: Department of Chemistry, Oregon State College, Corvallis, Ore.

[2] Present address: Bureau of Mines, Petr. Expt. Sta., Bartlesville, Okla.

[3] Kemp and Pitzer, *J. Chem. Phys.*, **4**, 749 (1936).

[4] Conn, Kistiakowsky and Smith, THIS JOURNAL, **61**, 1868 (1939). This possibility was first suggested to them by Schomaker.

[5] Pitzer, *Science*, **101**, 672 (1945).

[6] Aston, Schumann, Fink and Doty, THIS JOURNAL, **63**, 2029 (1941).

[7] Huffman and Ellis, *ibid.*, **51**, 41 (1935).