temperature; hence the value of 8.9×10^{-10}, which was obtained by the spectrophotometric method, must be reasonably accurate. Comparison of this value with that of 4.9×10^{-10} in 10% ethanol shows that a marked decrease of ionization is apparent in passing from water to 10% ethanol as the solvent.

Since the halogens are negative groups, they should decrease the basicity of quinoline when substituted in various positions. It would be reasonable to predict that the dissociation constant of a haloquinoline would be smaller when the halogen was closer to the nitrogen atom. Table I illustrates that this order is closely followed, 3-fluoroquinoline being the weakest base of these measured and the 6- and 7-isomers being the strongest of the fluoroquinolines. The dissociation constant of 2-fluoroquinoline could not be measured because the compound hydrolyzed in acid solution, but it is believed that, disregarding hydrolysis, the dissociation constant of the 2-isomer would be too small to be measured. The hydrolysis of 2-fluoroquinoline will be discussed in a subsequent paper.

Since the halogens decrease in electronegativity in passing from fluorine through iodine, it might be predicted that a certain fluoroquinoline would be less basic than the corresponding chloroquinoline. This supposition was tested by measuring the dissociation constants of both the 6-fluoro and the 6-chloro derivatives of quinoline. It is evident from Table I that the result is the reverse of what was expected.

TABLE I

DISSOCIATION CONSTANTS OF SOME HALOQUINOLINES AT 25°

Compound	Dissociation constants Spectrophotometric method	Dissociation constants Hydrolysis method
Quinoline in water	$8.9, 8.9, 8.9, 8.7 \times 10^{-10}$	$8.3, 8.6 \times 10^{-10}$
Quinoline[a]	$4.9, 4.9, 4.9, 5.0 \times 10^{-10}$	$4.6, 4.5 \times 10^{-10}$
3-Fluoroquinoline	$2.3, 2.3, 2.3, 2.4 \times 10^{-12}$	$3.0, 3.0 \times 10^{-12}$
5-Fluoroquinoline	$4.8, 4.8, 4.8, 4.8 \times 10^{-11}$	$5.0, 4.9 \times 10^{-11}$
6-Fluoroquinoline	$1.0, 1.0, 1.0, 1.1 \times 10^{-10}$	$9.8, 9.8 \times 10^{-11}$
7-Fluoroquinoline	$1.1, 1.0, 1.1, 1.2 \times 10^{-10}$	No result[b]
8-Fluoroquinoline	$1.2, 1.2, 1.2, 1.2 \times 10^{-11}$	$1.4, 1.4 \times 10^{-11}$
6-Chloroquinoline	$5.4, 5.4, 5.4, 5.3 \times 10^{-11}$	$6.8, 7.0 \times 10^{-11}$

[a] Unless otherwise designated the solvent is 10% ethanol. [b] Not enough 7-fluoroquinoline was available to determine the dissociation constant by hydrolysis measurements.

Experimental

Absorption Measurements.—The same instrument and techniques were used in the absorption measurements as previously described[4]; the solvents were also the same.

Materials.—The bases were obtained and purified as previously described[4]; solutions of hydrochlorides of the bases were prepared by adding a calculated amount of standard hydrochloric acid to a weighed quantity of the base.

***p*H Measurements.**—All *p*H measurements were made with a Beckman Glass Electrode *p*H Meter, Model M, Serial No. 17082, with a saturated calomel electrode as reference electrode. Each solution was placed in a 25° constant temperature bath for at least an hour before measuring its *p*H.

Acknowledgment.—This work is part of a study of the preparation and properties of heterocyclic fluorine compounds being carried out at this Laboratory, and was supported in part by the Office of Naval Research.

Summary

1. The dissociation constants of quinoline, the fluoroquinolines and 6-chloroquinoline in 10% ethanol have been measured spectrophotometrically by the method of Stenström and Goldsmith and compared with values obtained by measurement of the *p*H of the salts of the bases.

2. The dissociation constant of a fluoroquinoline is weaker when the halogen is closer to the nitrogen atom.

3. 6-Chloroquinoline is a weaker base than the 6-fluoro derivative.

CHAPEL HILL, NORTH CAROLINA

RECEIVED APRIL 10, 1950

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Hydrolysis of 2-Fluoroquinoline in Acid Solution

BY WILLIAM K. MILLER WITH SAMUEL B. KNIGHT AND ARTHUR ROE

In a previous paper[1] the spectra of 2-fluoroquinoline in both neutral and acid solutions were reported. The spectrum of the compound in 0.01 *M* HCl exhibited two distinct maxima as compared with a single maximum in the spectra of its isomers in acid solution. Roe and Hawkins[2] reported that the 2-fluoro derivatives of both quinoline and pyridine are insoluble in dilute hydrochloric acid, indicating that they do not form hydrochlorides. However, it was assumed that the shift in absorption must be due to salt formation, and an attempt was made to measure the dissociation constant of 2-fluoroquinoline by the method of Stenström and Goldsmith.[3]

A plot of *p*H *vs*. extinction coefficient at two wave lengths resulted in the curves illustrated in Fig. 1. It is readily seen that instead of the usual leveling of extinction, a maximum was reached, and in more acid solutions a decrease in extinction was evident. These results suggested decomposition, and the most logical decomposition was hydrolysis to carbostyril (2-hydroxyquinoline). Comparison of the spec-

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[1] Miller with Knight and Roe, THIS JOURNAL, **72**, 1629 (1950).

[2] Roe and Hawkins, *ibid*., **69**, 2443 (1947); **71**, 1785 (1949).

[3] Stenström and Goldsmith, *J. Phys. Chem*., **30**, 1683 (1926).

trum of 2-fluoroquinoline in 0.01 *M* HCl[1] with that of carbostyril as measured by other investigators[4,5] proved them identical. Hence it was concluded that the shift in absorption of 2-fluoroquinoline in acid solution was due to hydrolysis of the compound and not to salt formation.

The authors' interpretation of the curves in Fig. 1 is as follows. 2-Fluoroquinoline hydrolyzes in acid solution, the rate of hydrolysis increasing with increasing acid concentration. The measurements which led to the plots of *p*H *vs.* extinction in Fig. 1 were made approximately twenty-four hours after the preparation of the solutions. The region of increasing extinction is probably due to the increasing rate of hydrolysis as we pass from higher to lower *p*H values, and at the *p*H of the maximum, hydrolysis is complete after twenty-four hours. Accordingly, it would be predicted that the extinction at any *p*H on the rising portion of either of the curves would approach that of the maximum of that curve if the solution were allowed to stand long enough for hydrolysis to reach completion. If no effect other than hydrolysis were produced by the addition of hydrochloric acid, then a leveling of extinction below a certain *p*H would be expected rather than the maximum as shown in Fig. 1. An explanation for the maximum is found in the weakly basic tendencies of 2-hydroxyquinoline. Ewing and Steck[4] have shown that there is no shift in the spectrum of 2-hydroxyquinoline in passing from neutral to 0.01 *M* HCl solution as the solvent, indicating that there is no appreciable salt formation at that acidity. However, the compound is reported soluble in hydrochloric acid and hence must form salts in higher acid concentrations. Salt formation probably begins at the *p*H of decreasing extinction in Fig. 1, the absorption of the ion apparently being less than that of the molecule at the two wave lengths of the measurements. The extinction coefficient would probably continue to decrease with decreasing *p*H until the acidity of the solution was great enough to prevent hydrolysis of the salt that was formed. This would occur only at a negative *p*H for a base as weak as 2-hydroxyquinoline.

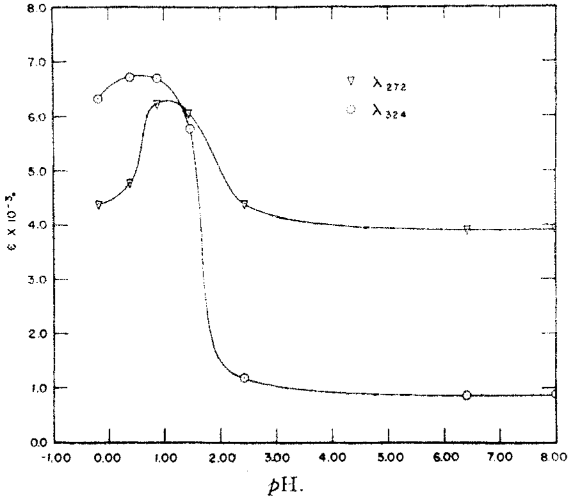

Fig. 1.—*p*H *vs.* extinction coefficient of 2-fluoroquinoline at two wave lengths of 24 hours after mixing the solutions.

In order to test the above suppositions, time curves which showed the variation of extinction with time at the two chosen wave lengths were measured at three different *p*H's, one in the region of the *p*H of the maximum in Fig. 1, and one each at *p*H's on either side of the maximum. It would be expected that a maximum extinction would be reached at any acid *p*H, the time required to reach the maximum decreasing at higher acid concentrations. In addition, the maximum extinction of the time curve should be the same as that of the maximum in Fig. 1 in solutions which are of the same or of less acidity than that of the maximum in Fig. 1, but the extinction of the maximum of the time curves in more acid solutions should be less since salt formation would have begun. A sample plot of extinction *vs.* time at *p*H 0.62 is shown in Fig. 2.

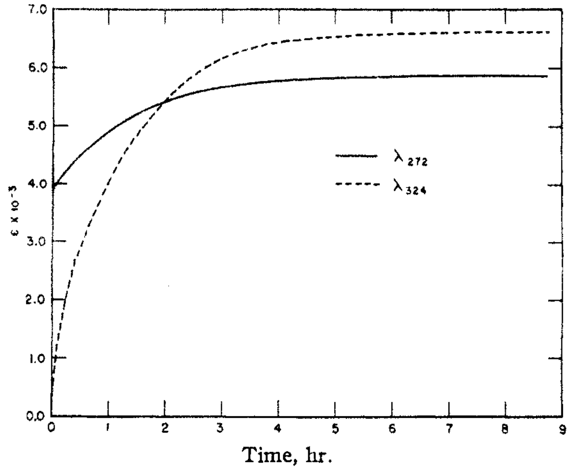

Fig. 2.—Rate of hydrolysis of 2-fluoroquinoline in acid solution.

At this *p*H the maximum was reached in 4–5 hours, and the extinction coefficient was 6.62 × 10^3 at a wave length of 324 mμ. At a *p*H of 1.82 the maximum of the time curve was not reached until about seventy-two hours, but the extinction coefficient was 6.60 × 10^3 or about the same as that at *p*H 0.62, as predicted. However, at a *p*H of approximately 0.0 the maximum was approached so fast that a time curve could not be constructed, and the extinction coefficient had decreased to 6.25 × 10^3. These experiments verify the previous predictions and indicate that salt formation of 2-hydroxyquinoline actually does begin between *p*H 0.5 and 0.0.

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(4) Ewing and Steck, THIS JOURNAL, **68**, 2181 (1946).

(5) Morton and Rogers, *J. Chem. Soc.*, **127**, 2698 (1925).

The behavior of 2-fluoroquinoline in acid solution suggested that the other 2-halo derivatives might react similarly. However, identical spectra of 2-chloroquinoline were obtained in neutral and 0.01 M HCl solutions. These results led to the measurement of the spectrum of the compound in 6 M HCl in an effort to obtain evidence of hydrolysis in a strongly acid solution. A marked shift of the spectrum was evident, but it bore no resemblance to that of carbostyril. However, since the solution was so strongly acid, the curve could represent the absorption of the hydrochloride of either 2-chloroquinoline or carbostyril. To distinguish between the two, the solution was neutralized with calcium carbonate; the excess calcium carbonate was filtered off and washed, the washings being added to the filtrate. The solution was then diluted to twice its original volume, after having added enough hydrochloric acid to make the final concentration of the solution 0.01 M with acid. The spectrum of this solution was measured, and a curve which was almost identical with that of 2-chloroquinoline in neutral and 0.01 M HCl solutions was obtained. Consequently, it is concluded that 2-chloroquinoline is not hydrolyzed in acid solution at normal temperatures as is 2-fluoroquinoline, but that the former compound will form a hydrochloride if made strongly acid.

Experimental

Absorption Spectra.—The spectra were measured and plotted using the same technique as previously described[1]; the haloquinolines and the solvents were also the same.

***p*H Measurements.**—The *p*H measurements were made with a Beckman Glass Electrode *p*H Meter, Model M, Serial No. 17082, with a saturated calomel electrode as reference electrode. The *p*H meter was standardized at *p*H 3.57 with a saturated solution of potassium hydrogen tartrate.[6]

Acknowledgment.—This work is part of a study of the preparation and properties of heterocyclic fluorine compounds being carried out at this Laboratory, and was supported in part by the Office of Naval Research.

Summary

1. Spectrophotometric evidence has indicated that 2-fluoroquinoline is hydrolyzed to 2-hydroxyquinoline in acid solution, the rate of hydrolysis increasing with increasing acid concentration; the spectrum undergoes further change in very strongly acid solution, probably caused by the formation of the salt of 2-hydroxyquinoline.

2. Spectral measurements have indicated that 2-chloroquinoline is not hydrolyzed in acid solution at normal temperatures but will form a hydrochloride if made strongly acid.

[6] Lingane, *Anal. Chem.*, **19**, 810 (1947).

CHAPEL HILL, N. C. RECEIVED APRIL 26, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

The Effect of Temperature on the Thermodynamic Properties and Interfacial Tension of Water with Some Alkyl Esters of Monochloroacetic Acid[1]

BY JOSEPH J. JASPER AND WILLIAM J. MAYER

The interfacial tensions of many organic liquids against water have been determined and reported in the literature. Such data, however, are not available, especially for ranges of temperature. Neither is there appreciable evidence of systematic study and correlation of interfacial tension data with properties of the two molecular species involved in the formation of the interface, regardless of its numerous applications in theoretical and industrial chemistry. The purpose of this investigation was to obtain the interfacial tensions of a series of esters of monochloroacetic acid with water over an appreciable temperature range, and to formulate empirical equations relating these variables. With these data it was possible to calculate the entropy, latent heat and total energy attending the formation of the interfacial surface. This is the first of a series of such studies which will subsequently include the same esters of different monohalogen acetic acids—compounds which possess groups of variable electronegativity at the ends of the molecules.

Experimental

Preparation and Purification of the Esters.—The methyl, ethyl, *n*-propyl and *n*-butyl esters of monochloroacetic acid were used in this investigation. Eastman Kodak Company white label grades of the methyl and ethyl esters were obtained, while the *n*-propyl and *n*-butyl esters were prepared by the method of Fieser.[2] For final purification of the esters, the vacuum fractionation methods described by Morton[3] were employed. A 15-inch column was used, which was packed with single-turn glass helices and fitted with a total reflux variable take-off head. The middle third, the fraction which boiled at constant temperature, was collected for use.

To test the purity of the esters, time–temperature cooling curves were constructed according to the method described by Morton.[4] Purity was judged by the flatness of the temperature horizontal since the weight per cent. purity can be determined only if the nature of the impurity

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Detroit meeting of the American Chemical Society, April, 1950.

[2] L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, 1944, p. 133.

[3] A. A. Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, Chapters IV and V.

[4] A. A. Morton, *ibid.*, p. 40.