With changing pH, both urea and formaldehyde activation equilibria are shifted; whereas with changing temperature, the main change appears to be in the rate of dehydration of the formaldehyde. Thus for a given decrease of formaldehyde reduction current, the urea–formaldehyde reaction rate is affected more by changing the pH than changing the temperature, indicating that the amount of the anion of urea is affected by pH change more than by temperature change.

Summary

The effects of varying pH and temperature on the reversible reaction $HCHO + NH_2CONH_2 \rightleftarrows NH_2CONHCH_2OH$ have been studied, using the polarograph to measure formaldehyde concentration. Equations are presented to relate the urea–formaldehyde reaction rate to the polarographic current of formaldehyde for changes of pH or temperature.

The urea–formaldehyde reaction rate appears to be dependent both upon the rate of dehydration of formaldehyde and rate of anion formation of urea.

A method is given for estimating the fraction of dehydrated formaldehyde at various temperatures and pH values, based on polarographic wave heights of formaldehyde.

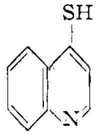
NEWARK, DELAWARE RECEIVED MARCH 18, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN CHEMICAL PHYSICS AND THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY OF MELLON INSTITUTE]

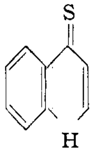
Ultraviolet and Infrared Spectra of Quinoline Derivatives: 2- and 4-Thiols

BY R. B. HANNAN, JR., J. H. LIEBLICH AND ALICE G. RENFREW

This investigation was undertaken in an attempt to determine the type of linkage between the sulfur atom and the quinoline nucleus in the substituted 2- and 4-quinolinethiols. Two structures are possible for these compounds: a thiol structure (A) and a thione structure (B).



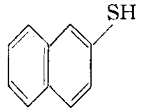
A



B

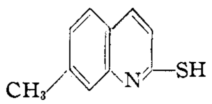
(These may be in tautomeric equilibrium.) Ewing and Steck[1] have attacked the same problem in the hydroxyquinolines by the use of ultraviolet spectra, and it was hoped that their method would be successful with the sulfur analogs. The infrared spectra of these sulfur compounds have also been studied. Unfortunately neither approach has provided an answer to the problem. Since the data may be of some utility, the results will be described briefly.

Ultraviolet and infrared absorption spectra of the following compounds are presented.



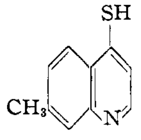
I

2-Naphthalenethiol



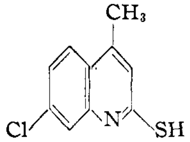
II

7-Methyl-2-quinolinethiol



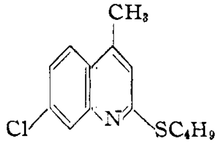
III

7-Methyl-4-quinolinethiol



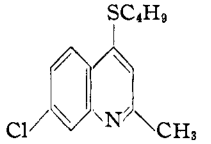
IV

7-Chloro-4-methyl-2-quinolinethiol



V

7-Chloro-4-methyl-2-n-butylthioquinoline



VI

7-Chloro-4-n-butylthio-2-methylquinoline

Few data for comparison are available in the literature. Morton and Stubbs[2] have reported the ultraviolet absorption spectra of 4-methyl-2-quinolinethiol and its ethers in neutral alcoholic solution only. Clinton and Suter[3] give spectrophotometric measurements for two 4-dialkylaminoalkyl sulfides of 7-chloroquinoline. The curve for 7-chloro-4-quinolylmercaptoacetic acid is given by Surrey.[4]

Experimental

The preparation and properties of the quinolinethiols (II, III and IV) have been reported by Renfrew.[5] The preparation of the two thioethers is described below.

7-Chloro-4-methyl-2-n-butylthioquinoline[6](V).—This sulfide was synthesized by the procedure described by

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[1] Ewing and Steck, THIS JOURNAL, **68**, 2181 (1946); Steck, Ewing and Nachod, Abstracts, Washington Meeting, A. C. S., Sept. 1948. page 12L.

[2] Morton and Stubbs, *J. Chem. Soc.*, 1321 (1939).

[3] Clinton and Suter, THIS JOURNAL, **70**, 491 (1948).

[4] Surrey, *ibid.*, **70**, 2190 (1948).

[5] Renfrew, *ibid.*, **68**, 1433 (1946).

[6] Mrs. Pauline C. Piatt of the Department of Research in Pure Chemistry carried out much of the synthetic work.

Clinton and Suter.[3] *n*-Butylthiol (Eastman Kodak Co.) was dissolved in absolute alcohol containing an equivalent of sodium. The calculated amount of 2,7-dichloro-4-methylquinoline (0.07 mole) was added in portions during ten minutes, and the reaction mixture was refluxed four hours. After removal of alcohol, an ether solution of the sulfide was washed with dilute alkali until no further mercaptan was removed. The crude product was an oil, which crystallized first when supercooled to −30°. Samples were crystallized from methyl alcohol or ligroin (90–100°), using solvent equal to one-half the weight of the sample, and the supernatant liquid was removed by centrifuging in a cold room. Cooling curves indicated a melting point of 22.9°. The sulfide is soluble in ether, acetone, pentane and ligroin, insoluble in water, and tends to form a two-phase system with methanol and ethanol.

Anal. Calcd. for $C_{14}H_{16}NSCl$: N, 5.27; S, 12.06. Found: N, 5.22; S, 11.93.

7-Chloro-4-*n*-butylthio-2-methylquinoline (VI).—Synthesis was carried out as indicated above. Crystallization occurred during concentration of the dry ether solution and was repeated from one-half volume of pentane. Three recrystallizations from two volumes of ligroin (90–100°) gave a white solid, m. p., 53.8–54.5°. It was readily soluble in methyl alcohol and in ether but had a low solubility in hexane.

Anal. Calcd. for $C_{14}H_{16}NSCl$: N, 5.27; S, 12.06; Cl, 13.40. Found: N, 5.45; S, 12.13; Cl, 13.45.

The ultraviolet absorption spectra were obtained with a Cary recording spectrophotometer. The maximum error in the wave length calibration of the instrument was ± 5 Å.

The spectrum of each compound has been obtained in acidic, basic and neutral (alcoholic) solution. These spectra are shown in Fig. 1. Intensities have been presented in terms of absorbance ($\log_{10}I_0/I$) rather than extinction coefficients because the solubilities were so low that concentrations could not be determined. For the aqueous acidic and basic solutions the solubilities were less than 5 mg./l. The solubility in 95% ethanol was higher, and the concentrations of the alcoholic solutions were: (I) 10.3 mg./l.; (II) 6.47 mg./l.; (III) 6.29 mg./l.; (IV) 6.02 mg./l.; (V) 5.36 mg./l.; (VI) 5.19 mg./l.

The infrared absorption spectra were recorded on a Baird spectrophotometer. The wave length accuracy of this instrument is better than ±0.1 micron. All of the spectra shown in Fig. 2 with

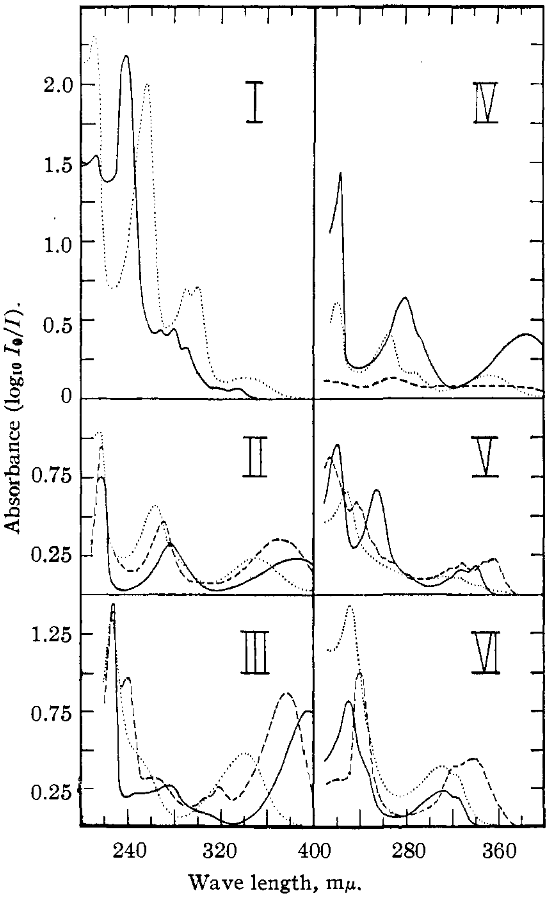


Fig. 1.—Ultraviolet spectra: — 95% ethanol; . . . . . 0.01 *N* sodium hydroxide; - - - - 0.01 *N* hydrochloric acid; I, 2-naphthalenethiol; II, 7-methyl-2-quinolinethiol; III, 7-methyl-4-quinolinethiol; IV, 7-chloro-4-methyl-2-quinolinethiol; V, 7-chloro-4-methyl-2-*n*-butylthioquinoline; VI, 7-chloro-4-*n*-butylthio-2-methylquinoline.

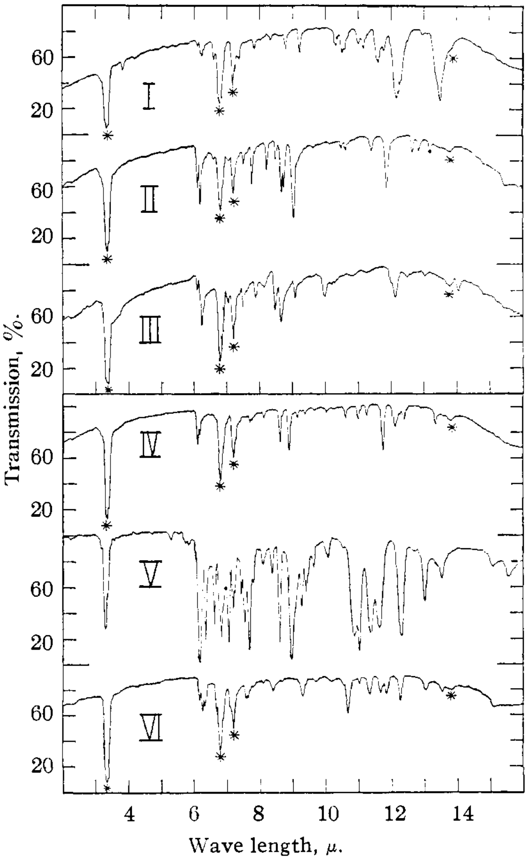


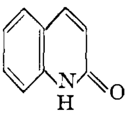
Fig. 2.—Infrared spectra, asterisks denote bands of Nujol: I, 2-naphthalenethiol; II, 7-methyl-2-quinolinethiol; III, 7-methyl-4-quinolinethiol; IV, 7-chloro-4-methyl-2-quinolinethiol; V, 7-chloro-4-methyl-2-*n*-butylthioquinoline; VI, 7-chloro-4-*n*-butylthio-2-methylquinoline.

the exception of V were obtained from suspensions of the solid samples in Nujol. The spectrum of the liquid thioether (V) was obtained from a sample of capillary thickness. The spectra of several of these samples were also obtained as fluorocarbon suspensions and in carbon tetrachloride solution in an attempt to find characteristic absorption bands for S–H or N–H linkages. The spectra of the Nujol suspensions are presented as being most informative.

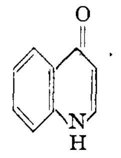
Discussion of Results

A. Ultraviolet Spectra.—Briefly, the conclusions of Ewing and Steck[1] on the hydroxyquinolines were based on the following observations and reasoning. The ultraviolet spectrum of quinoline undergoes a bathochromic shift (displacement of absorption maxima to longer wave lengths) in changing from a neutral to an acidic solvent. Similarly, the spectra of the naphthols undergo a bathochromic shift as the solvent is changed from neutral to basic in character. In either acidic or basic solvents, the spectra of the 3-, 5-, 6-, 7- and 8-quinolinols undergo bathochromic shifts, thus indicating that the oxygen retains its phenolic character and the heterocyclic ring retains its aromatic character in these particular quinolinols.

Conversely, the spectra of the 2- and 4-quinolinols do not undergo a shift in either acidic or basic media. This is explained by postulating the existence of these compounds in their respective keto forms.



2-Quinolone



4-Quinolone

In these compounds, the oxygen has lost its phenolic character and the spectrum does not undergo the bathochromic shift exhibited by the naphthols. Similarly, the heterocyclic ring has lost its aromatic character and the spectrum does not undergo the shift exhibited by quinoline.

It was hoped that the same reasoning could be applied to the sulfur analogs. The ultraviolet spectrum of 2-naphthalenethiol (I) was obtained and was found to undergo a bathochromic shift on going from neutral to basic medium (see Fig. 1). It would then be anticipated from the reasoning cited above that the spectra of the quinolinethiols would exhibit bathochromic shifts in acidic or basic media while the spectra of the quinolinethiones would remain unchanged in neutral, acid and basic media.

The spectra of 7-methyl-2-quinolinethiol (II), 7-methyl-4-quinolinethiol (III) and 7-chloro-4-methyl-2-quinolinethiol (IV) were obtained in neutral, acidic and basic media (see Fig. 1). Contrary to the anticipated results, the spectra of these three quinolinethiols exhibited hypsochromic shifts (displacements of absorption maxima to shorter wave lengths). These results cannot be explained by the reasoning applied to the bathochromic shifts observed for the quinolinols. A similar hypsochromic shift was encountered by Specker[7] and confirmed by Ewing and Steck[1] with solutions of 4-pyridone.

The spectrum of 7-chloro-4-*n*-butylthio-2-methylquinoline (VI) undergoes a bathochromic shift in an acidic medium but is not shifted in a basic medium. This is consistent with the sulfide structure in which the sulfur has lost its thiol character while the heterocyclic ring has retained its aromatic character.

7-Chloro-4-methyl-2-*n*-butylthioquinoline (V) dissolved very slowly in the aqueous solvents and it appears probable that the anomalous changes in the spectra are due to decomposition of the sulfide.

B. Infrared Spectra.—In a further attempt to confirm the structure of the mercaptoquinolines as thiols or thiones, their infrared spectra were recorded (see Fig. 2). It was hoped that the thiols would exhibit the characteristic absorption band associated with the S–H stretching vibration at 2400–2600 cm.$^{-1}$ (3.85–4.17μ). However, only the 2-naphthalenethiol spectrum showed this absorption band. The thiones would be expected to show an absorption band at about 3400 cm.$^{-1}$ (2.94μ), characteristic of the N–H stretching vibration. None of these compounds showed any absorption bands in this region. The thiones would also be expected to show a band characteristic of the $C{=}S$ group in the 1400–1500 cm.$^{-1}$ region (6.67–7.13μ). However, the inherent weakness of this band and the complexity of the thioether spectra in this region indicate that this criterion will not provide any help. Therefore the infrared spectra do not offer a solution to the problem.

Summary

The ultraviolet absorption spectra of 2-naphthalenethiol, 7-methyl-2-quinolinethiol, 7-methyl-4-quinolinethiol, 7-chloro-4-methyl-2-quinolinethiol, 7-chloro-4-methyl-2-*n*-butylthioquinoline and 7-chloro-4-*n*-butylthio-2-methylquinoline were obtained in neutral, acidic and basic solvents. The observed wave length shifts are anomalous with respect to the reasoning used in establishing the structure of quinolinols and quinolones.

The infrared absorption spectra of these compounds have also been obtained but do not provide any further indication of their structure.

PITTSBURGH 13, PENNSYLVANIA RECEIVED JULY 5, 1949

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[7] Specker and Gawrosch, *Ber.*, **75**, 1338 (1942).