Polarographic Urea–Formaldehyde Kinetic Studies

BY GEORGE A. CROWE, JR.,[1] AND CECIL C. LYNCH

In a previous paper[2] we have shown polarographically the reaction between formaldehyde and urea to be reversible at 25° in 0.05 N lithium hydroxide. It seemed desirable to study the effects of change in temperature and pH on this reaction. Such a study is presented here.

Smythe[3] measured the urea–formaldehyde reaction rate in neutral solution between 30 and 60° and found that the reaction was bimolecular. (Crowe and Lynch[2] showed that the reaction was reversible in 0.05 N lithium hydroxide at 25°, and found that the reverse reaction was monomolecular.) Jahoda,[4,5] Bieber and Trümpler[6,7] and Vesely and Brdicka[7,8] observed that the electroreduction of formaldehyde at the dropping mercury electrode was very low at 25° in neutral solution. As the pH or temperature was increased, the rate of reduction was greatly increased. It was postulated[6,7,8] that formaldehyde was normally hydrated, and that the amount of electroreduction of formaldehyde was a measure of its dehydration rate; maximum dehydration was found to occur above 80°, or at pH 13.14 at 25°.[4,8]

The kinetic study described in this paper indicates that both dehydration of formaldehyde and the assumption of the formation of an anion of urea are necessary to account for the increase of urea–formaldehyde reaction rate with increase of pH. Increase of temperature probably affects the rate of dehydration of formaldehyde without markedly changing the rate of formation of this anion form of urea.

Experimental

The apparatus, chemicals and general technique were as described previously.[2] The supporting electrolytes consisted of 0.05 N lithium hydroxide (pH 12.7), 0.1 M sodium carbonate (pH 11.2), 0.1 M sodium bicarbonate (pH 8.7) and a buffer mixture of 0.05 M boric acid, 0.05 M lithium chloride and 0.045 M lithium hydroxide (pH 10.1). All reagents were C. P. Baker Analyzed except the lithium hydroxide which was Merck and Company lithium hydrate. The solutions were made up to twice the concentrations given above, and diluted with an equal volume of urea, formaldehyde or monomethylolurea solution to be tested.

Reaction rates for the reversible reaction of urea

(1) Present address: Hercules Powder Company, Hercules Experiment Station, Wilmington, Delaware.

(2) Crowe and Lynch, THIS JOURNAL, **70**, 3795 (1948).

(3) Smythe, J. Phys. Colloid Chem., **51**, 369 (1947).

(4) Jahoda, Coll. Czechoslov. Chem. Commun., **7**, 415 (1935).

(5) Kolthoff and Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 353.

(6) Bieber and Trümpler, Helv. Chim. Acta, **30**, 706 (1947).

(7) Wawzonek, Anal. Chem., **21**, 61 (1949).

(8) Vesely and Brdicka, Coll. Czechoslov. Chem. Commun., **12**, 313 (1947).

and formaldehyde to form monomethylolurea are given in Table I. The equilibrium constant appears to be constant within experimental error (±5% of the value determined) for changes of temperature and pH over the ranges tested.

TABLE I

RATES FOR THE REACTION $NH_2CONH_2 + HCHO \rightleftarrows NH_2CONHCH_2OH$, AND AVERAGE POLAROGRAPHIC CURRENT OF FORMALDEHYDE AT VARIOUS pH VALUES AND FOR VARIOUS TEMPERATURES

Temp., °C.	pH	k_f (sec.$^{-1}$)	k_r (sec.$^{-1}$)	K From reaction rates	From equilibrium data	Av. pol. current of 0.00354 M formaldehyde, mma.
25	12.7	2.97×10^{-2}	1.45×10^{-3}	20	26	12.0
25	11.2	3.56×10^{-3}	6.04×10^{-5}	59	35	4.8
25	10.1	6.10×10^{-4}	1.75×10^{-5}	35	55	1.20
25	8.7	2.14×10^{-4}	1.38×10^{-5}	16	60	0.34
15	12.7	1.71×10^{-2}			18	5.97
20	12.7	2.67×10^{-2}			14	8.75
25	12.7	3.36×10^{-2}			30	12.0
25	12.7	2.97×10^{-2}	1.45×10^{-3}	20	26	12.0
30	12.7	9.80×10^{-2}			21	17.8
38	12.7	0.129			20	24.9
40	12.7	0.158			21	26.2

The average polarographic reduction current for formaldehyde with varying temperature and pH is also given in Table I. As can be seen from the table, for a given decrease in polarographic current, lowering the pH from 12.7 slows down the urea–formaldehyde reaction rate more than lowering the temperature. The amount of electroreduction of formaldehyde to methanol occurring at the dropping mercury electrode was about 0.2% of the formaldehyde in solution per hour, and occurred only when −1.65 volts or more was applied to the electrodes. Therefore the amount of reduction of formaldehyde was negligible in comparison to the amount involved in reaction with urea.

The change of the polarographic wave height of formaldehyde with temperature is shown for pH 8.7 and pH 12.7 in Fig. 1. The log of formaldehyde wave height is plotted $vs.$ the reciprocal of the absolute temperature, as in an equation derived from the Arrhenius equation

$$\text{Log} \frac{i_2}{i_1} = \frac{\Delta E_{aa}}{2.303 \times 1.987} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (1)$$

where i_1 and i_2 are the formaldehyde wave heights for absolute temperatures T_1 and T_2, and ΔE_{aa} is the apparent energy of activation for the reduction of formaldehyde at the dropping mercury electrode. The lower, steeper slopes are limited by the rate of dehydration of formaldehyde; the upper, less steep slope is dependent only on the change of viscosity of the solution and the change of mercury mass and drop time with temperature.

The sum of the effects of change of viscosity, mercury mass and drop time would give an apparent activation energy of about 4000 cal. per mole, as compared to the upper slope of 3560 cal. per mole. This indicates that only free formaldehyde is present above 55° at pH 12.7, and above 81° at pH 8.7. This latter value is in agreement with the value of 80° found by Yahoda.[4]
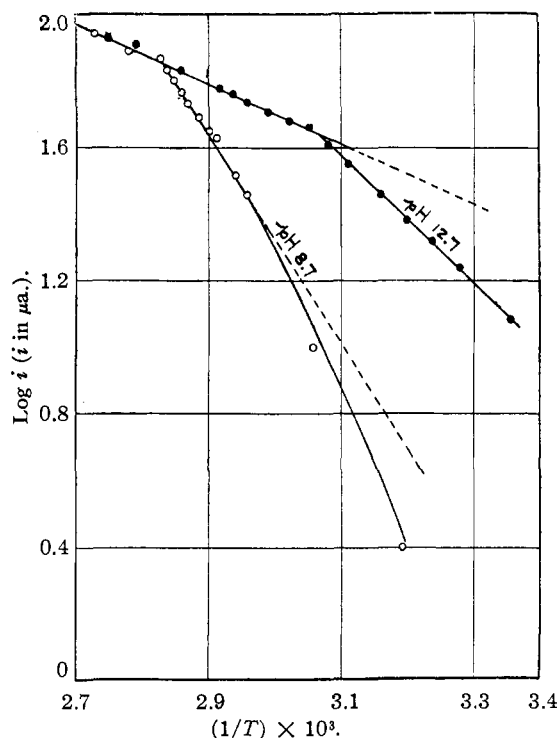

Fig. 1.—Formaldehyde dehydration with temperature.

The extent of dehydration of formaldehyde was estimated as the ratio of the actual formaldehyde wave height to the total dehydrated wave height from Fig. 1. At 25° the formaldehyde was found to be about 41% dehydrated at pH 12.7, and about 1.2% dehydrated at pH 8.7.

The forward urea–formaldehyde reaction rates were calculated with corrected formaldehyde values, and the same reaction rates were obtained as before, within experimental error. Since the extent of the reaction was small in evaluation of initial slopes, the values of the reaction rate constants obtained and the equilibrium constant should not differ significantly from the values given previously.[2] The results showed this to be true. It appeared impossible to calculate the observed effect of change in reaction rate with pH from the data included here, since not only does the concentration of formaldehyde in the reaction vary with pH, but also the concentration of the anion of urea appears to vary with pH.

For the change of urea–formaldehyde reaction rate with temperature in neutral solution, Smythe[3] found the energy of activation to be 14,700 cal./

mole. Calculated by the Arrhenius equation from Table I, the effective energy of activation (ΔE_a) at pH 12.7 was 15,900 cal./mole, which is in agreement with Smythe within the limits of experimental error.

Equations were developed to relate the urea–formaldehyde reaction rate and the polarographic wave height of formaldehyde for changes of pH and temperature.

From the Arrhenius equation and equation (1), a relationship was found between urea–formaldehyde forward reaction rates (k_1 and k_2) at two temperatures and polarographic wave heights of formaldehyde (i_1 and i_2) at the same two temperatures, and at a constant pH.

$$\log \frac{k_2}{k_1} = \frac{\Delta E_a}{\Delta E_{aa}} \log \frac{i_2}{i_1} \qquad (2)$$

where ΔE_a was 15,900 cal./mole and ΔE_{aa} was 10,000 cal./mole for pH 12.7 over the range of 15 to 40°. Using these values, k_f was calculated from formaldehyde wave height, and at pH 12.7.

t, °C.	k_f (pH 12.7)	
	Calcd.	Found
15	0.015	0.017
20	.028	.027
25	.045	.034
30	.085	.098
38	.14	.13
40	.16	.16

For changes of pH at a given temperature, the urea–formaldehyde forward reaction rate was calculated from the polarographic wave height of formaldehyde by the equation

$$k_t = iB/A(A - i) \qquad (3)$$

where k_t was the forward reaction rate, i the formaldehyde wave height, and A and B constants. Equation (3) was deduced from analogy to the second-order equation $kt = x/a(a - x)$ and consideration of the relative amount of formaldehyde available for either electroreduction or reaction with urea. From the values in Table I, at 25° with $A = 15$ and $B = 0.12$

pH	k_t	
	Calcd.	Found
12.7	0.032	0.030
11.2	.0038	.0036
10.1	.00070	.00061
8.7	.00019	.00021

Reverse reaction rates k_r can be calculated from the forward reaction rate k_t and the equilibrium constant K, where $K = k_t/k_r$.

The mechanism and reaction rate of the urea–formaldehyde reaction to form monomethylolurea appears to involve the dehydration of formaldehyde (the hydrated form, $H_2C(OH)_2$, does not react) and also the formation of an anion of urea. This anion is assumed to be a resonance structure

$$NH_2\overset{\displaystyle O}{\overset{\|}{C}}-NH^- \longleftrightarrow NH_2-\overset{\displaystyle O^-}{\underset{}{C}}=NH$$
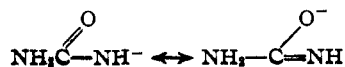
With changing pH, both urea and formaldehyde activation equilibria are shifted; whereas with changing temperature, the main change appears to be in the rate of dehydration of the formaldehyde. Thus for a given decrease of formaldehyde reduction current, the urea–formaldehyde reaction rate is affected 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 $HCHO + NH_2 CONH_2 \rightleftarrows$ $NH_2CONHCH_2OH$ 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.
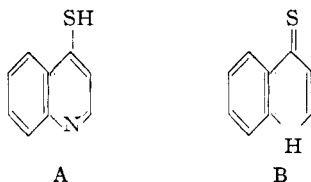

# Ultraviolet and Infrared Spectra of Quinoline Derivatives: 2- and 4-Thiols

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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).
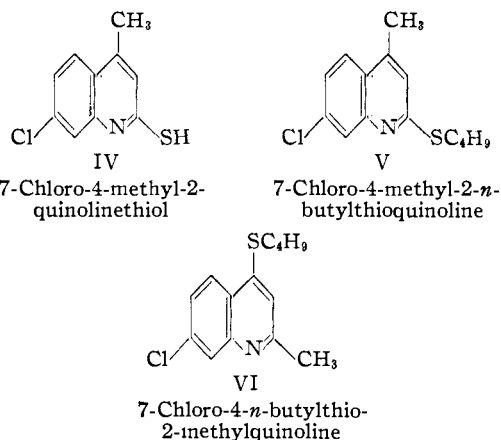

A   B

(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	II	III
2-Naphtha-lenethiol	7-Methyl-2-quino-linethiol	7-Methyl-4-quinolinethiol
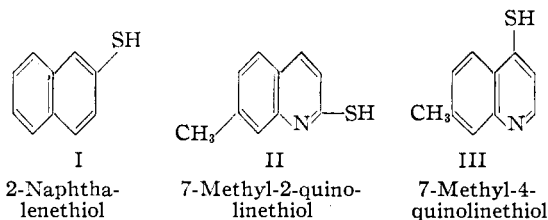
(1) Ewing and Steck, THIS JOURNAL, **68**, 2181 (1946); Steck, Ewing and Nachod, Abstracts, Washington Meeting, A. C. S., Sept. 1948. page 12L.

IV	V
7-Chloro-4-methyl-2-quinolinethiol	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-dialkyl-aminoalkyl 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

(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.