wave length and at both λ 2654 and 2537 over the temperature range studied, this simple relationship no longer held, indicating that reaction 3, followed by (7), was taking place. The absence of butene among the photolysis products may be interpreted to mean that the free radical cyclization reaction has a substantially lower activation energy than the reaction involving a hydrogen shift to form an olefin. This is to be expected since considerable strain would be present in the transition state required to form butene.

Cyclobutanone.—The large amount of ethylene formed from cyclobutanone indicates that reaction 6, involving the production of ketene, is important. Because ethylene was produced in excess of carbon monoxide at λ 3130, it was suggested originally that ketene further decomposed. To evaluate this hypothesis, water vapor was added in one instance on the assumption that it would react with the ke-

tene vapor to form acetic acid. Experimental difficulties left the test for acetic acid in doubt and it may or may not have been produced. However, it is apparent from the results given in Table I that the water had no important effect on quantum yields and it follows, also, that it did not trap the postulated biradicals. In view of the results later obtained at λ 2654, appreciable ketene decomposition does not appear to have occurred in any event.

The general mechanism postulated above applies to this cycloketone, also. Accepting this mechanism, Φ_{CO} is a measure of ϕ_I and $\Phi_{ethylene}$ is a measure of ϕ_{II}. ϕ_I plus ϕ_{II}, estimated in this way, is about 0.9 at λ 3130 and 1, within experimental errors, at λ 2654; thus, for this compound, photochemical conversion of absorbed energy is high. Polymerization, reaction 7, was important under all conditions in which this ketone was studied.

LOS ANGELES, CAL.

Kinetic Studies of Thiourea Derivatives. III. Trimethylthiourea and Tetramethylthiourea

BY WILLIAM H. R. SHAW AND DAVID G. WALKER

RECEIVED MARCH 20, 1957

Trimethylthiourea has been studied kinetically in aqueous solutions at elevated temperatures. This substance decomposes to form methylamine, dimethylamine and carbon oxysulfide as ultimate products in acid solutions. The decomposition is first-order and is uninfluenced by ionic strength in media of low pH. Rate constants at various temperatures and Arrhenius parameters are reported. Tetramethylthiourea also has been studied under similar conditions. This substance shows little or no tendency to react in neutral solutions. In acidic or basic media, however, hydrolysis is observed. The significance of these findings and their relevance to previous work is discussed.

Introduction

Thiourea,[1] methylthiourea[2] and the dimethylthioureas[3] have been studied previously in this Laboratory. Although some information on the chemistry of trimethylthiourea[4] and tetramethylthiourea[5] is available, no kinetic investigations with these compounds have been reported. The present work was, consequently, undertaken to secure rate data for these substances and to complete, thereby, our kinetic study of the methylated thioureas.

Experimental

Trimethylthiourea (1,1,3-trimethyl-2-thiourea) was prepared by the addition of dimethylamine to methyl isothiocyanate.[6] It was crystallized, m.p. 87° (lit.[4] 87°) twice from water solutions.

Anal. Calcd. for $C_4H_{10}N_2S$: C, 40.68; H, 8.54; N, 23.70. Found: C, 40.77; H, 8.50; N, 23.74.

Tetramethylthiourea (1,1,3,3-tetramethyl-2-thiourea) was prepared by heating bis-(dimethylthiocarbamyl) sulfide under air reflux for several hours,[7] followed by twice crystallizing the resulting mass from water. The product was then distilled at atmospheric pressure, b.p. 243° (lit.[8] 245°).

(1) W. H. R. Shaw and D. G. Walker, THIS JOURNAL, **78**, 5769 (1956).

(2) W. H. R. Shaw and D. G. Walker, *ibid.*, **79**, 2681 (1957).

(3) W. H. R. Shaw and D. G. Walker, *ibid.*, **79**, 3683 (1957).

(4) R. Singh, *J. Indian Chem. Soc.*, **33**, 610 (1956).

(5) M. Schenck, *Z. physiol. Chem. (Hoppe–Seyler's)*, **77**, 370 (1912).

(6) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, New York, N. Y., 1955, pp. 599, 617.

(7) M. Grodski, *Ber.*, **14**, 2754 (1881).

(8) M. Delépine, *Bull. soc. chim. France*, [4] **7**, 988 (1910).

Recrystallization from water gave the final product, m.p. 78° (lit.[8] 78°).

Anal. Calcd. for $C_5H_{12}N_2S$: C, 45.45; H, 9.14; N, 21.1. Found: C, 44.94; H, 8.68; N, 19.6.

The analytical methods for thiocyanate, ammonia, methylamine and dimethylamine have been described.[1-3] Total amine produced was also determined according to the following procedure. Reaction solutions of the thiourea under study were made 10 to 20 mM in standard acid, and the samples were then allowed to react until the total amine concentration was approximately 4 mM. The unreacted acid in the samples was subsequently determined by titration with standard NaOH (approximately 10 mM). During the titration the pH was read at convenient intervals and the end-point taken as the point when the change of pH with a small increment of standard basic solution was a maximum. Titration blanks were always run on aliquots of the unreacted experimental solutions. Results given by this method were compared with those obtained by our usual spectrophotometric techniques. Within the combined experimental uncertainties, the two methods gave identical results.

The procedures used in conducting the kinetic runs and the apparatus employed in this investigation have been described in previous work.[1-3]

Results

Reacted solutions of trimethylthiourea were found to contain methylamine, dimethylamine and carbon oxysulfide. The rates of formation of methylamine and dimethylamine were followed and the corresponding empirical first-order rate constants, k_3 and k_4, were calculated by the rate equation previously presented. Measurements were made with 0.015 M H_2SO_4 and 0.015 M HNO_3 solutions. These solutions also contained tri-

methylthiourea at concentrations ranging from 9.2 to 73.5 mM. In these acid media at 100° the following values were obtained for k_3 and k_4, respectively, 38.2 ± 3.8 × 10^{-7} and 37.2 ± 2.2 × 10^{-7} sec.$^{-1}$. Moreover results in acid solutions containing added sodium nitrate varying in concentration from 0.00 to 1.02 M demonstrated that the rate, under these conditions, was independent of ionic strength. Thus in acid media k_3 and k_4 are, within experimental error, equal and independent of average trimethylthiourea concentration, $\bar{u}$. No thiocyanate ion or ammonia could be detected in the reaction mixtures by our rather sensitive techniques. A first-order reaction producing methylamine and dimethylamine in equimolar amounts is clearly indicated.

The drastic dependence of k_4 on pH (Fig. 1) is quite different from the behavior of the analogous constant obtained with *unsym*-dimethylthiourea, but is very similar to the pH dependence of the k_3's obtained with methylthiourea and *sym*-dimethylthiourea.
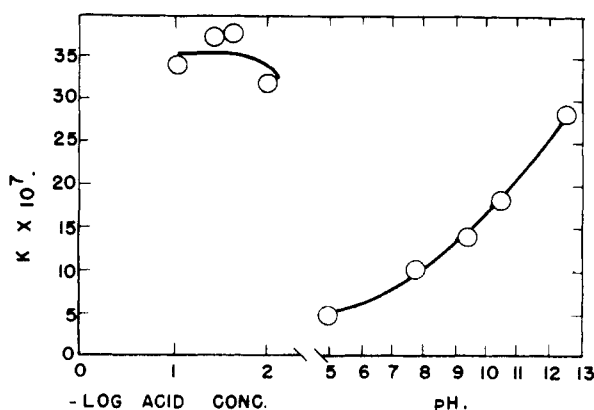

Fig. 1.—Empirical first-order rate constant (k_4) based on dimethylamine production as a function of acid concentration. Runs below pH 8 were made in HNO₃ solutions. Results recorded above pH 8 were obtained with 0.01 M borax buffers. An initial trimethylthiourea concentration of 50 mM was used with reaction times of 3.23 hr. on the basic side and 6.00 hr. in the low pH media.

A least squares analysis of data obtained spectrophotometrically at various temperatures in acid media (Table I) gave a frequency factor of 7.89 × 10^{14} sec.$^{-1}$ and an activation energy of 34.9 kcal. for k_4. A similar analysis applied to the data obtained by total amine analysis yielded a frequency factor of 4.98 × 10^{14} sec.$^{-1}$ and an activation energy of 34.4 kcal. The total amine analysis is somewhat more precise.[9]

Tetramethylthiourea was studied in various media at elevated temperature (Table II). In sharp contrast to the methylated thioureas containing a hydrogen bonded to nitrogen, this compound did not react extensively in neutral solution even at high temperatures and long reaction periods. Significant reaction in acidic and basic media did, however, occur producing dimethylamine and carbon oxysulfide. Ammonia, methyl-

(9) These parameters will reproduce the rate constants in Table I obtained by the titration method with a maximum deviation of 4%.

amine and thiocyanate ion were not detected in the reacted samples. Consequently since the slight reactivity of the compound was most probably due to hydrolysis and not to a simple decomposition no detailed quantitative studies were attempted.

TABLE I

RATE CONSTANTS OBTAINED AT VARIOUS TEMPERATURES IN ACID SOLUTIONS

Temp. ± 0.1°	$\bar{u}^a$	t^b	First-order rate constant,[c] sec.$^{-1}$ × 10^7 k_4
71.2	49.7	43.7	0.64
79.5	20.1	12.6	2.45^d
80.0	49.5	21.4	2.38
90.0	49.0	11.0	8.10
90.0	99.9	6.15	9.83^d
100.0	48.3	3.57	37.2
100.0	29.4	5.97	37.1^d
109.6	8.91	5.85	120^d
110.3	48.1	3.86	129
119.9	4.01	3.78	366^d

^{a} $\bar{u}$ is the average concentration of trimethylthiourea (mmoles/l.). ^{b} t is reaction time in hours. ^{c} The constant is based on the rate of dimethylamine production measured spectrophotometrically except values marked with superscript d. ^{d} These values were obtained by the titration method described in the Experimental section.
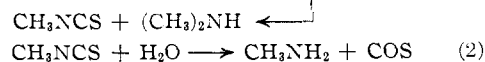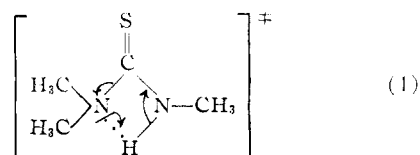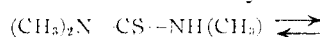
TABLE II

THE HYDROLYSIS OF TETRAMETHYLTHIOUREA

| Medium	Time, hr.	Temp., °C.	Initial tetramethylthiourea, mM	Me₂NH[a] formed, mM
Water	123	110 ± 2	98.5	0.334
Water	18.5	150 ± 5	200	4.5
0.5 M HNO₃	25.5	110 ± 2	98.5	55.2
0.5 M NaOH	70	110 ± 2	98.5	137

^{a} No NH₃, MeNH₂ or NCS⁻ could be detected in the reaction mixtures.

Discussion

All of the data obtained with trimethylthiourea can be rationalized by the reaction scheme

$(CH_3)_2N-CS-NH(CH_3) \rightleftharpoons$

$$\left[\begin{array}{c} S \\ \| \\ C \\ H_3C \diagdown \diagup \diagup \uparrow \\ N \quad N-CH_3 \\ H_3C \diagup \diagdown \diagdown \diagup \\ H \end{array} \right]^{+} \qquad (1)$$

$CH_3NCS + (CH_3)_2NH \longleftarrow$

$CH_3NCS + H_2O \longrightarrow CH_3NH_2 + COS \qquad (2)$

Since reaction 2 is fast in acid solution, methylamine and dimethylamine should be produced in equimolar amounts. The stoichiometry (Results) is in accord with this reasoning since $k_3 = k_4$. As before the behavior of the empirical rate constant k_4 with increasing pH can be attributed to the occurrence of complicating reactions. With increasing pH the amines are no longer predominantly in the protonated form. Since the reverse of reaction 1 must take place through the unionized amine the reverse reaction will be more important at high pH. The other possible reaction

$$CH_3NCS + CH_3NH_2 \longrightarrow (CH_3NH)_2CS \quad (3)$$
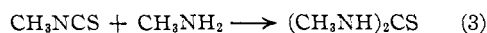
is also most probably involved.

The finding that tetramethylthiourea does not decompose establishes that a hydrogen atom bonded to nitrogen is necessary for decomposition to take place. It also provides additional strong support for the conclusion previously presented[3] that methyl groups do not migrate and that decomposition takes place by intramolecular hydrogen transfer and dissociation of the activated complex.

A more detailed theoretical interpretation of this and other data will be presented in the last paper of this series.

The Polarography of Quinoxaline[1]

BY MURRAY P. STRIER AND J. C. CAVAGNOL[2]

The reductions of quinoxaline at the dropping mercury electrode, conducted in buffered media in the pH range of 1 to 10, show well-defined, pH dependent waves. The influence of variations in buffer components, concentration and ionic strength on the nature of the waves have been investigated. The course of the reduction at all pH levels is not affected by changes in buffer components, buffer concentration or ionic strength. However, certain variations in half-wave potentials and diffusion current constants occur. Reduction to 1,4-dihydroquinoxaline is postulated for the whole pH range. From pH 1 to pH 2 reduction may proceed by a bimolecular, one-electron process that is not completely reversible. Reduction may also proceed by this process at pH 3 but this is apparently not true as the concentration of buffer components is increased. Over the pH range of 4 to 10 the simultaneous addition of two protons and two electrons is presumed to occur in an essentially reversible manner. Catalytic hydrogen waves are manifested following the formation of dihydroquinoxaline at pH's < 7 but are absent at higher pH's. At pH 7 the catalytic wave appears only at high buffer concentration.

Introduction

The polarography of quinoxaline (I) was undertaken in order to determine whether 1,2,3,4-tetrahydroquinoxaline (II) could be obtained by electrochemical methods. The over-all reduction is represented by

$$+ 4e + 4H^+ \longrightarrow \qquad (1)$$
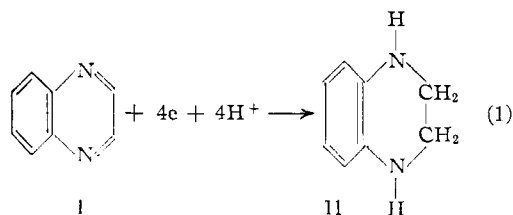
The literature on polarography involving reduction at the dropping mercury electrode contains only two references to simple quinoxalines. Winkel and Proske[3] obtained a polarographic wave for 2,3-dimethylquinoxaline in 0.1 M ammonium chloride solution, but no analysis is given. Sartori and Furlani[4] studied the polarographic reduction of quinoxaline, its methiodide and its di-N-oxide. They found that quinoxaline gives a nearly reversible, 2-electron wave having an $E_{0.5}$ of -0.267 v. S.C.E. at pH 0 and 25°. Both prewaves and kinetic waves were found, in agreement with the present work. The formation of dihydroquinoxaline and the absence of the tetrahydro form were postulated.

The roles of ionic strength and buffer composition were minimized, in contrast to the present paper.

Equation 1 demonstrates that pH is a critical factor in governing the reduction process. The need for employing buffered solutions having adequate ionic strength as supporting electrolytes has been stressed elsewhere.[5] Quinoxaline was studied systematically by varying buffer components, ionic strength, buffer concentration, pH and reductant concentration.

Experimental

Materials.—Quinoxaline was prepared by the method of Cavagnol and Wiselogle.[6] The product, resublimed prior to use was colorless and melted at 31.0–31.5°. It was used in the form of a 0.010 M stock solution stored under nitrogen in the dark. All supporting electrolyte components were C.P. grade and the suitability for polarographic work was established by blank runs.

Stock solutions of 0.110 N sodium hydroxide and 0.205 N hydrochloric acid were prepared and stored under nitrogen.

Apparatus.—A manual instrument of the type described by Kolthoff and Lingane[7] was used. Both the applied potential and the resulting current (as the potential across a 10,000-ohm precision resistor) were measured with a Leeds and Northrup student-type potentiometer. With this apparatus, solutions of 5.8×10^{-4} M cadmium sulfate in 0.100 M potassium chloride gave an $E_{0.5}$ value of -0.597 ± 0.001 v. vs. S.C.E. and an $I_d/Cm^{2/3}t^{1/6}$ value of 3.38 ± 0.02 at 25°.

All measurements were performed in a 100-ml. Berzelius

(1) Abstracted from a dissertation submitted to the Graduate School by Murray P. Strier in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Jan. 1952.

(2) Research Center, General Foods Corp., Tarrytown. N. Y.

(3) A. Winkel and G. Proske, *Ber.*, **69**, 1917 (1936).

(4) G. Sartori and C. Furlani, *Ann. chim. (Rome)*, **45**, 251 (1955), *C. A.*, **49**, 15557b.

(5) J. J. Lingane, THIS JOURNAL, **61**, 2099 (1939); N. H. Furman and K. G. Stone. *ibid.*, **70**, 3055 (1948); P. J. Elving and C. Teitelbaum, *ibid.*, **71**, 3916 (1949); P. J. Elving and C. S. Tang, *ibid.*, **72**, 3918 (1950); P. E. Stewart and W. A. Bonner, *Anal. Chem.*, **22**, 793 (1950); P. J. Elving. K. C. Komyathy. R. E. Van Atta, C. S. Tang and I. Rosenthal, *ibid.*, **23**, 1218 (1951).

(6) J. C. Cavagnol and F. Y. Wiselogle, THIS JOURNAL, **69**, 795 (1947).

(7) I. M. Kolthoff and J. J. Lingane, "Polarography." Interscience Publishers, Inc., New York, N. Y., 1946, Chapter XIV.