4.92 and 5.16, respectively, the dashed line in Fig. 3 with slope corresponding to $\mathring{a} = 5.00$ interpolates the data for these salts in the higher range of dielectric constant but overshoots the points for the two systems at $D \approx 7$–8. For two systems at least[4,10] ($Bu_4N{\cdot}BPh_4$ in $MeCN$–CCl_4 and in $PhNO_2$–CCl_4 over the range $36 \geqslant D \geqslant 4.8$), the values of a_K and a_A agree with each other and also with the value a_J derived from the coefficient J of the linear long range term. We therefore prefer to give more weight at present to our data which give agreement with the simple model for which $a_A = a_K = a_J$ and leave to future decision, based on more experimental and theoretical work, the question whether the curvature in Fig. 3 is real or whether it is an artifact introduced by the method of computation.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Kinetic Studies of Urea Derivatives. I. Methylurea

BY WILLIAM H. R. SHAW AND BERNARD GRUSHKIN

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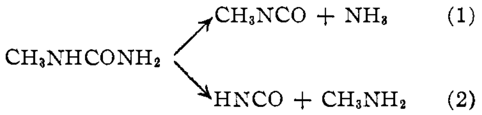
Kinetic data on the dissociation of methylurea in aqueous solutions at elevated temperatures are presented. This compound dissociates by two different processes. Initial products are: (1) methyl isocyanate and ammonia and (2) isocyanic acid and methylamine. These initial products undergo further reaction making it impossible to determine individual rate constants in acid solution. By observing reaction rate as a function of pH this difficulty has been overcome, and first order rate constants for both reactions have been determined. These constants are reported. The effect of temperature and ionic strength also has been studied. The experimental findings are discussed.

Introduction

The kinetic behavior of urea,[1] thiourea[2] and the methylated thioureas[3-5] in aqueous solutions has been examined previously in this Laboratory. Conclusions based on these studies have been reported.[6] From a consideration of this earlier work it became apparent that the collection of comparable data for the methylated ureas would be desirable. Such data, in addition to their intrinsic interest, could be used to evaluate more critically several of the mechanistic interpretations that had been proposed.[6]

Methylthiourea dissociates by two different processes.[3] By analogy with this compound and in accordance with the general mechanism[6] postulated for urea and thiourea derivatives, two parallel reactions would be anticipated for methylurea, *viz.*



$$CH_3NHCONH_2 \begin{cases} \nearrow CH_3NCO + NH_3 & (1) \\ \searrow HNCO + CH_3NH_2 & (2) \end{cases}$$

Consequently four different reaction products would be expected. In acid solution, however, a rapid and quantitative hydrolytic conversion of cyanate ion to ammonium ion occurs.[7,8] Methyl isocyanate is also unstable in media of low pH and, in such solutions, the nitrogen-containing end products of both reactions (eqs. 1 and 2) should be $CH_3NH_3^+$ and NH_4^+. These two products should be formed at equal rates. The rate of production of either might be used to measure the *total* rate of dissociation of methylurea by *both* reaction one (eq. 1) and reaction two (eq. 2), but no information whatever concerning *individual* rates for these reactions could be gleaned from such measurements. In fact without some *a priori* mechanistic reason the very possibility that two distinctly different processes leading to the same reaction products could exist, might go unrecognized. This appears to have been true of the pioneering work of Fawsitt.[9] This investigator was the first and, unless we have overlooked some publications, the only other researcher to present quantitative data on the rate of dissociation of methylurea in aqueous solutions.

Fawsitt concluded that the reaction in acid solution could be represented by

$$CH_3NHCONH_2 + 2H^+ + H_2O \longrightarrow CO_2 + NH_4^+ + CH_3NH_3^+ \quad (3)$$

and calculated first order rate constants based on his experiments in HCl, HBr and H_2SO_4 solutions. Limited data for the reaction in water and in basic media also were reported. The reaction was followed by conventional acid-base titration techniques. Although salts of methylamine and ammonia were identified as reaction products and the evolution of CO_2 noted, the individual rates of formation of these substances were not determined.

The present investigation was undertaken in the hope that the existence of the two reactions (eqs. 1 and 2) could be established and corresponding rate constants evaluated. It was felt that this information might be obtained by observing the rate of formation of cyanate, methylamine and ammonia under a variety of experimental conditions.

Experimental

General experimental techniques previously have been described.[1,2,7] The reactions were studied using the method of initial rates and, as before, empirical first order rate constants[2,3] were employed in analyzing the data. The constants k_c, k_a and k_m used in the discussion are based on the rate of production of cyanate, ammonia and methylamine, respectively.

Spectrophotometric analyses were used throughout. Cyanate was determined by the usual procedure.[7] In the

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[1] W. H. R. Shaw and J. J. Bordeaux, THIS JOURNAL, **77**, 4729 (1955).

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

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[6] W. H. R. Shaw and D. G. Walker, *ibid.*, **80**, 5337 (1958).

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[9] C. E. Fawsitt, *J. Chem. Soc.*, **85**, 1581 (1904).

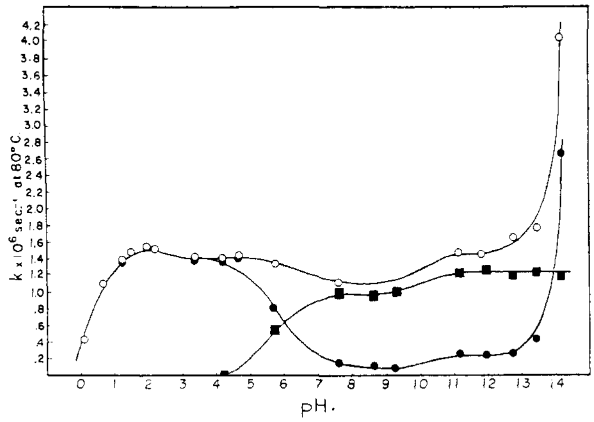

Fig. 1.—Empirical first order rate constants based on methylamine analysis (○), cyanate analysis (■), and ammonia analysis (●) as functions of *p*H.[13] The buffers employed were: potassium biphthalate–HCl, NaOH (*p*H 2.2–6.0); monopotassium phosphate–NaOH (*p*H 6.0–7.5); Borax–HCl (*p*H 8–10). Below *p*H 2 standard HCl was used and the "*p*H" taken as − log (acid concentration).

presence of methylamine, the analytical method of Kruse and Mellon[10] was found to be most convenient for the determination of ammonia. With this method much less interference was encountered than with the Nessler technique.[3] The methylamine analysis is described elsewhere.[11]

Methylurea was prepared by the reaction of methylamine sulfate with potassium cyanate dissolved in a minimum of water.[12] The resultant solution was evaporated to dryness and extracted with hot absolute ethanol. The crude product obtained by evaporation of the ethanol extract then was recrystallized twice from acetone, m.p. 100–101° (lit.[12] 101–102°).

Anal. Calcd. for $C_2H_6N_2O$: C, 32.42; H, 8.16; N, 37.79. Found: C, 33.06; H, 7.99; N, 37.42.

Results

A plot of the empirical first order constants k_a, k_c and k_m *vs.* *p*H is displayed in Fig. 1. These data were collected at 80°. At 60° a product–time curve, Fig. 2, was obtained for *p*H 11.1, and rate constants at five temperatures measured at approximately[13] this same *p*H (11.1 ± 0.2) are presented in Table I. A least squares Arrhenius analysis of these data gave the values for the frequency factor, *A*, and the activation energy, *E*, associated with k_a and k_c. For ammonia production (k_a): $A = 9 \times 10^{13}$ sec.⁻¹, $E = 33.2$ kcal. For cyanate production (k_c): $A = 1 \times 10^{14}$ sec.⁻¹, $E = 32.4$ kcal.

TABLE I

RATE CONSTANTS[a] FOR THE DISSOCIATION OF METHYLUREA

Temp., °C. ± 0.1	$k_m \times 10^6$	$k_c \times 10^6$	$k_a \times 10^6$
50	0.0195 ± 0.0005	0.0152 ± 0.0002	0.0033 ± 0.0006
60	.0799 ± .002	.0685 ± .0008	.0123 ± .0011
70	.400 ± .012	.284 ± .008	.075 ± .004
80	1.48 ± .15	1.24 ± .06	.253 ± .013
90	4.74 ± .14	3.72 ± .10	.897 ± .054

[a] The rate constants k_m, k_c and k_a are first order empirical constants based on the rate of methylamine, cyanate and ammonia production respectively. The *p*H measured at room temperature was 11.1 ± 0.2 for all runs. Rate constants are expressed in reciprocal seconds.

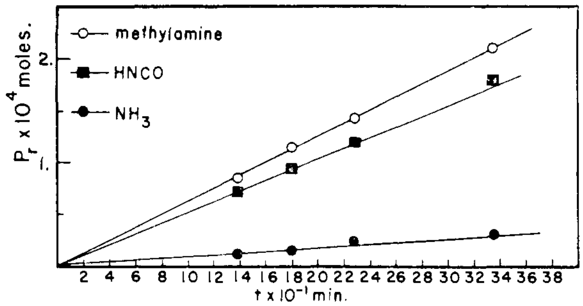

Fig. 2.—Product concentration, P_r, as a function of reaction time, *t*, for the dissociation of methylurea at 60° and *p*H 11.1.[13] The initial reactant concentration was 129.86 m*M*.

At *p*H 4.6, ionic strength was varied from 0.02 *M* to 1.00 *M*. No change in the rate of methylamine production was observed.

Discussion

The general features of the rate–*p*H curves (Fig. 1) merit detailed consideration. It should first be noted that cyanate is not detected in reaction mixtures of *p*H < 4. With increasing *p*H, however, the rate of cyanate production increases initially and then becomes constant in solutions studied of *p*H > 11. These results are in accord with and provide strong evidence for the reaction represented by eq. 2. The absence of cyanate in acid is, of course, attributable to its conversion to ammonia[6–8]

$$NCO^- + 2H^+ + H_2O \longrightarrow NH_4^+ + CO_2\uparrow \qquad (4)$$

If this interpretation of the data is accepted then the true first order rate constant associated with eq. 2 can be assigned unambiguously. In basic media, this constant, k_2, must be equal to the empirical first order constant based on cyanate production, k_c.

The rate of ammonia production is equal to the rate of methylamine production in media of low *p*H. This observation is in accord with Fawsitt's conclusion (eq. 3). Below *p*H 2 both rates decrease with decreasing *p*H. This behavior can be interpreted in terms of the increased concentration of inactive protonated methylurea cation in equilibrium with methylurea. Analogous results have been obtained with other urea derivatives.[1–5] Above *p*H 5 a new sequence of effects is observed. The empirical constant k_a at first falls, passes through a region of *p*H independence (approx. 11–13), then abruptly rises again. These results are in general agreement with eq. 1 and eq. 4. The abrupt rise in ammonia production above *p*H 13 can be attributed to the onset of a base-catalyzed parallel reaction that does not produce cyanate. An analogous effect is observed with methylthiourea.[3] Despite these complications it seems quite reasonable to identify k_a with the true k_1 (for eq. 1) in the narrow *p*H region of 11–13.

Between *p*H 2 and *p*H 13, the rate of methylamine production shows little dependence on acid concentration. Above *p*H 13 the sharp upswing in k_m

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[11] F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," Vol. IV, 3rd Ed., D. Van Nostrand Co., Inc., New York, N. Y., 1954, p. 31 (1,2-naphthoquinone-4-sulfonate).

[12] W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans–Green, Inc., New York, N. Y., 1957, p. 266.

[13] The *p*H values used in Fig. 1 and others mentioned in this work were measured at room temperature.

shows that methylamine like ammonia is also produced by the base-catalyzed parallel reaction noted above.

The deviation or "sag" between 7.5 and 11 can be interpreted in terms of complicating reactions involving the products. Reactions that can occur in addition to the primary dissociations (eqs. 1 and 2) include

$$CH_3NCO + NH_3 \longrightarrow CH_3NHCONH_2 \tag{5}$$

$$CH_3NCO + CH_3NH_2 \longrightarrow CH_3NHCONHCH_3 \tag{6}$$

$$HNCO + CH_3NH_2 \longrightarrow CH_3NHCONH_2 \tag{7}$$

$$HNCO + NH_3 \longrightarrow H_2NCONH_2 \tag{8}$$

These complications can be minimized by reducing the amount of reactant decomposed. By this technique the concentration of products can be lowered sufficiently to make the rates of these complicating reactions negligible compared to the rates of the primary dissociations (eqs. 1 and 2). Product–time plots at *p*H 11.1 are shown in Fig. 2. The linearity of these plots shows that, at this *p*H, conflicting back reactions have been eliminated. An examination of this figure also reveals that the methylamine line can be generated by summing the ordinates of the ammonia line and the cyanate line. This observation coupled with the data in Table I makes it possible to conclude that

$$k_{12} = k_1 + k_2 \tag{9}$$

where k_{12} is a composite constant experimentally equal to k_m. Thus by these data the existence of both primary dissociation reactions (eqs. 1 and 2) is firmly established. As noted earlier (Introduction) Fawsitt measured an over-all rate constant (for eq. 3). On the basis of the arguments presented above this rate constant is equivalent to k_{12}. At 99.2° Fawsitt reports a value of 48.5×10^{-5} min.$^{-1}$ for his first order rate constant calculated on the basis of logarithms to the base ten. Recalculation gives a value of 1.9×10^{-5} sec.$^{-1}$ for k_{12} based on his data. Using our Arrhenius parameters for k_1 and k_2 the value anticipated for k_{12} at 100° was calculated to be 1.6×10^{-5} sec.$^{-1}$. Thus, within combined experimental uncertainties, the results are in essential agreement.

Both primary dissociation reactions proceed more slowly than the decomposition of urea, but of even greater interest is the conclusion that cyanate production (eq. 2) in the absence of base catalysis proceeds from 4–6 times faster (Table I) than ammonia production (eq. 1). For analogous reactions with methylthiourea just the opposite is true. A more detailed discussion of these and other findings will be presented in the last paper of this series.

Acknowledgments.—The authors gratefully acknowledge the generous grant from Research Corporation of New York that made this study possible. It is also a pleasure to express our thanks to The University of Texas Research Institute for the leave granted to W. H. R. S. that provided time for research and the preparation of this and other papers.

AUSTIN, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Electrolytic Oxidation in Liquid Ammonia. I. Carbonic Acid Amides[1]

BY A. F. CLIFFORD AND M. GIMÉNEZ-HUGUET

RECEIVED AUGUST 7, 1959

Amides such as ammonium carbamate and urea have been oxidized electrolytically in liquid ammonia. The product, which appears to be azodicarbonamide, or a condensation (deammonation) polymer of it is isolated as potassium azodicarbonate. Since the electrolysis of hydrazodicarbonamide gives the same product, it is postulated that the oxidation proceeds through a hydrazine derivative. Absorption spectra are reported for the region 200–400 mμ.

Introduction

When concentrated aqueous solutions of sulfates,[2] phosphates,[3] carbonates[4] or borates[5] are electrolyzed with shiny platinum anodes at high current densities, especially in the presence of a non-polarizable anion such as fluoride ion,[6] peroxydisulfates, etc., result.

The process is assumed to consist of the anodic abstraction of an electron from the sulfate ion (for example) to form the sulfate free radical ion, SO_4^-, two of which combine to give the peroxy anion.[7] The peroxide mechanism of anodic oxidation due to Glasstone and Hickling[8] has been ably refuted by Haïssinsky[9] and by Frumkin, *et al.*[10]

Similar processes are known involving other elements besides oxygen, *e.g.*, thiosulfate yielding tetrathionate[11] and sulfite yielding dithionate.[12] Thus it seemed reasonable to believe that similar catenation compounds of nitrogen could be formed under suitable conditions by anodic oxidation of amides of the elements S, P, C, B and possibly others. The fact that small amounts of azoben-

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[1] This work was supported by the Office of Ordnance Research under Contract No. DA-33-008-ORD-1233 with Purdue University.

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