for dilute solutions. From these definitions it follows that for any solution, in any solvent

$$pA + pB = pK_W \qquad (30)$$

The scales p_cA and p_cB, defined by (27) and (29), are useful practical scales in many cases. Perhaps the most generally applicable scales are, however, the functions p_sA and p_sB which are defined in terms of the e.m.f. of cells like (3′). For example, from cell (3′)

$$p_sA = (E - E^0_{calomel} - E_L)F/2.303\ RT \qquad (31)$$

where $E^0_{calomel}$ is 0.2455 v. at 25.0°,[47] and E_L is given in Table II. p_sB is calculated from p_sA using equation (30). If a cell other than (3′) is used, an unknown pA may be measured if the cell is first calibrated[20] with a dilute solution of known pA in the same solvent. For the calibration one may use perhaps a dilute solution of hydrogen chloride, or perhaps a buffer solution of a suitable weak acid and its conjugate base. Accurate pK_A values are available for this purpose for a great many weak acids in the system ethanol–water.[8,9]

Acknowledgments.—It is a pleasure to acknowledge helpful discussions with Drs. J. E. Leffler and M. G. Alder of this University, and with Dr. L. P. Hammett of Columbia University. We wish to thank the Research Corporation for a grant-in-aid of this work, and the A.E.C. for the award of a fellowship to B. G.

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[47] H. Riehm, *Z. physik. Chem.*, **A160**, 1 (1932); M. Duboux and G. Pièce, *Helv. Chim. Acta*, **23**, 152 (1940).

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

Urea Formaldehyde Kinetic Studies. III. Polarographic Studies in Dilute Solution

BY LLOYD E. SMYTHE

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The reaction between (a) urea, (b) N-methylurea, (c) N-ethylurea and formaldehyde has been studied in dilute solution at pH 7.15 using the polarographic method for following the concentration of unreacted formaldehyde. This method is given in some detail since it has been found suitable for following the course of industrially used condensations. The diffusion current in the selected buffer, although reduced, was adequate in giving smooth polarographic steps few of which exhibited maxima. Thus the use of maximum suppressors was avoided. The reactions were found to be second order and rate constants and energies of activation have been evaluated. Differences have been observed in the reaction of urea with formaldehyde as compared with the simple N-alkyl ureas and formaldehyde. It is suggested that in the case of alkyl ureas some effective resonance stabilization is lost and the effect becomes more pronounced in dilute solution resulting in increased reactivity. Hydration of both the urea and formaldehyde is appreciable in the region of pH 7; the reactions reaching a certain stage and being unable to proceed further. The effect of acid or alkaline condensing agents in dilute solution would be initially to break down forces of hydration and in the case of alkaline solutions the reaction is reversible. The initial rapid reaction previously observed becomes less important with increasing dilution and the significance of this is discussed.

Part II of this series[1] indicated that dilution of reactants exerted a considerable influence on the nature of the initial reaction between urea and formaldehyde. It was also evident that the analytical method for the estimation of formaldehyde[2] was subject to some errors when working with dilute solutions.

A study of the reaction in dilute solution using urea and N-alkyl ureas was commended. The polarographic method appeared to be the most suitable in this case and Crowe and Lynch[3] had successfully used it employing 0.05 N lithium hydroxide and buffers giving supporting electrolyte pH values from 8.6–12.7. In all cases the reaction was shown to be reversible and equilibrium constants were evaluated. Earlier observations[4] had indicated that while most alkaline condensing agents are effective for the formation of methylol compounds there was evidence of some hydrolysis of the condensation product, equilibrium evidently being attained, particularly at pH values greater then 9.0. In this study it was desirable that the pH of the supporting electrolyte be maintained as closely as possible to 7, so as not to influence materially the forward or reverse reactions. The effect of phosphate buffers on the reaction has been studied[1] and preliminary studies using different supporting electrolytes indicated that Sørensen buffer of seven parts by volume of $M/15$ Na_2HPO_4 and three parts by volume of $M/15$ KH_2PO_4 giving a pH of 7.15 at 25°, provided a suitable supporting electrolyte.

Experimental

The polarographic measurements were made with a Tinsley ink recording polarograph (V722/1) employing d.c. amplification of the current passing through the solution in the polarographic cell. The recorder unit was a moving coil d.c. pen type milliameter, the standard speed being 1 inch per minute corresponding to a voltage change of 0.5 v. The "capillary constant" K was 23.82 using 0.1 M CH_2O in Sørensen buffer containing dissolved air; applied voltage −1.65 v., head of mercury 501 mm., drop time 2.52 sec., temperature 25°. The radius of the capillary orifice[5] ρ determined in 0.2 M KCl at 25° using an open circuit was 25 microns.

With Sørensen buffer supporting electrolyte containing dissolved air, the half-wave potentials were −1.65 and −1.73 v. *vs.* the mercury pool electrode and *vs.* the saturated calomel electrode, respectively. Concentration of formaldehyde within the range 0.01–0.10 M exhibited this half-wave potential but concentrations of 0.10–0.50 M resulted in a shift to a slightly more negative potential. Figure 1 shows the relation between the diffusion current in microamperes and concentration expressed as molarity. Sensitivities corresponding to full scale deflection on the recording chart were selected to give the largest possible step. Ac-

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[1] L. E. Smythe, THIS JOURNAL, **74**, 2713 (1952).

[2] L. E. Smythe, *J. Phys. Colloid Chem.*, **51**, 396 (1947).

[3] G. A. Crowe and C. C. Lynch, THIS JOURNAL, **70**, 3795 (1948); **71**, 3731 (1949); **72**, 3622 (1950).

[4] L. E. Smythe, unpublished work.

[5] O. H. Müller, "The Polarographic Method of Analysis," J. Chem. Education, Easton, Pa., pp. 182–190, 1951.

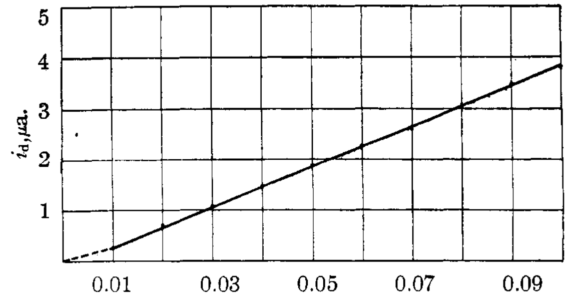

Fig. 1.—Molar concentration formaldehyde *vs.* diffusion current (microamperes).

curacy of measurement was ±0.05 μÅ. over the range 0.01–0.10 M CH_2O. Slight maxima were exhibited with formaldehyde alone in the buffer and it was not found necessary to eliminate these as step heights were reliably determined by drawing a line representing the limiting current as shown in polarogram A, Fig. 2. In this case other means for estimating the diffusion current did not prove as reliable as the method employed. It is interesting to note that in the studies of the reaction mixture of urea and formaldehyde, the urea in each case acted as a maximum suppressor giving a well defined step shown in polarogram B, Fig. 2.

Some studies carried out with 0.10–0.50 M formaldehyde solutions revealed that the maxima exhibited offered some difficulty in measurement of diffusion current. Although these maxima were also effectively suppressed in the presence of urea and substituted ureas, the accuracy was only of the order ±0.2 μÅ. The maxima in all cases appeared to be 2.5 μÅ. greater than the line drawn through the step and used for measuring the diffusion current.

As dissolved oxygen was not removed from any of the solutions, zero suppression was used in the range 0.01–0.10 M CH_2O, the recorder zero adjustment being used to depress the oxygen step. Zero suppression was not found necessary in the range 0.10–0.50 M CH_2O, using lower sensitivities. The polarograph cell was a modification of the simple Heyrovsky cell, holding 4 ml. of solution. Temperature control was by means of a thermostat bath to within ±0.05°. The height of mercury above the capillary orifice was maintained constant by a leveling device.

The polarographic procedure outlined above has been used to follow the progress of urea—formaldehyde condensations on the industrial scale. When the sample is diluted with buffer the reaction rate is effectively retarded and formaldehyde already combined is not eliminated. This may be the case with other supporting electrolytes. The progress of a typical condensation employing 500 parts by weight of 40%, w./v. formalin, 185 parts by weight of urea, one part by weight of $Na_2HPO_4 \cdot 2H_2O$ was followed by withdrawing 1-ml. samples and adding to 110 ml. of buffer solution at 25°. The polarogram was taken using 4 ml. of this solution, the concentration of free formaldehyde being estimated from Fig. 1.

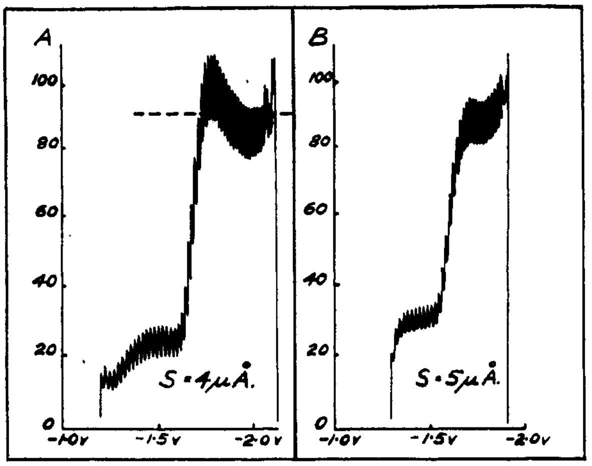

Fig. 2.—A, wave form of 0.07 M CH_2O in buffer; B, wave form of 0.063 M CH_2O in buffer with urea and monomethylolurea (S = sensitivity).

Chemicals used were of analytical reagent grade or specially purified in the case of urea.[6] N-Methyl- and N-ethylureas were prepared by the method of Davis and Blanchard.[7]

TABLE I

DATA FOR THE REACTION BETWEEN EQUIMOLAR (0.1 M) AMOUNTS OF FORMALDEHYDE AND UREAS

Temp., °C. ±0.05°	No. of experiments	Urea	$k \times 10^4$ l. mole^{-1} sec.$^{-1\,a}$	CH_2O used 1st. 300 sec., %	End of reaction M conn. CH_2O	ΔE_a (approx.)^b
25	7	NH_2CONH_2	1.7 (14,000)	1.0	0.035	15,300
35	5	NH_2CONH_2	3.8 (12,000)	1.0	.032	
25	8	$MeNHCONH_2$	8.3 (8,000)	7.5	.050	14,100
35	6	$MeNHCONH_2$	18.0 (6,000)	8.0	.047	
25	6	$EtNHCONH_2$	7.0 (10,000)	7.0	.054	14,000
35	4	$EtNHCONH_2$	15.5 (9,600)	7.4	.051	

[a] ***k*** equals average for number of seconds in parentheses minus 300. [b] In calories. Evaluated for two temperatures only owing to loss of CH_2O at temperatures greater than 35°.

The reactions were second order. Important effects were:

Effect of Dilution. For urea and formaldehyde in equimolar proportions at 25°, previous results[1,2,6] together with those given in Table I show that for *p*H values close to 7, rate constants increase with increasing dilution of reactants attaining maximum values with 0.5 M solutions and falling off as dilution increases further. Anion formation of urea may increase with dilution attaining limiting values in the region of 0.5 M solutions. Thereafter competition for the nucleophilic nitrogen of urea involves increasingly stronger forces of hydration of the urea molecule. Formaldehyde would be fully hydrated[2] under these conditions of *p*H and dilution and depolymerization would not be involved. For 0.1 M solutions the percentage of formaldehyde reacted in the first 300 seconds now reduces to less than 1% as compared with much higher percentages for stronger solutions.[2] The reaction is now of the slow bimolecular variety from zero time. Crowe and Lynch[3] have shown that increasing hydroxyl ion concentration results in higher rate constants. This would increase dehydration of both the methylene glycol and urea thus resulting in relatively higher rates as compared with those in Table I. In the same table it is shown that the reaction does not go to completion under the conditions stated. At *p*H 7 the reaction is not reversible but is second order from zero time until 65% of the formaldehyde has been used up, thereafter no reaction takes place since forces of hydration cannot be overcome. This has been confirmed by allowing the reaction mixture to stand for several days after 65% stage had been attained; no further reaction took place. In addition monomethylolurea, methylenebisurea, methylenebismethylurea and monomethylolmethylenebisethylurea showed no signs of hydrolysis[8] in the buffer over periods of up to three weeks at 25°. At *p*H greater than 8.6 Crowe and Lynch[3] have shown the reaction to be reversible and thus while increased hydroxyl ion concentration increases the reaction rate in dilute solution it also promotes hydrolysis of the reaction product possibly preceded by dehydration.

For N-methylurea the rate constant relationship between urea and N-methylurea which was approximately 6 to 1 in the case of 8 M solutions becomes reversed and the reaction with N-methylurea is now five times more rapid. This feature of the reaction which also holds for N-ethylurea is discussed under the heading reaction mechanism.

Column 5, Table I shows that a higher percentage of formaldehyde is utilized in the first 300 seconds in the case of both N-methylurea and N-ethylurea, as compared with urea. This fits in with the fact that the alkyl ureas lose resonance stabilization as compared with urea and the rate

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(6) L. E. Smythe, THIS JOURNAL, **73**, 2735 (1951).

(7) T. L. Davis and K. C. Blanchard, *ibid.*, **51**, 1790 (1929).

(8) For details see Part IV this series, not yet published.

of anion formation is increased. The effect becomes more pronounced with increasing dilution since both urea and the alkyl ureas are very weak bases. The relative effect in the case of the alkyl ureas is greater even though anion formation may reach limiting values in the region of 0.5 *M* solutions. In the case of the alkyl ureas examined, only approximately 50% of the formaldehyde combines and it is thought that two effects are important in this case. Methylenebisureas may be the principal reaction products, involving the utilization of all the urea and half of the formaldehyde. When formed, no further reaction of the methylenebisureas with the formaldehyde takes place owing to both hydration and the greater difficulty of the reaction between formaldehyde and the nitrogen with the attached alkyl group. The reaction is not reversible and will not proceed further even after periods of days.

It will be appreciated that the above considerations apply to mono- and disubstituted ureas and the fact that dimethylureas will not give dimethylol derivatives and triethylurea will not react with formaldehyde at all[9] is additional evidence that structure of urea plays an important part in determining the reactivity of these derivatives.

For N-ethylurea the rate constant for 8 *M* solutions and not recorded in Part II, was found to be 1.6×10^{-5} l.mole^{-1} sec.$^{-1}$ (30°), with 42% of the formaldehyde utilized in the first 300 seconds and ΔE_a 15,900 calories. This may be compared with data for urea and N-methylurea given in Table I and previously.[1,2,7]

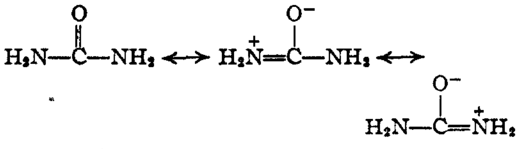
Effect of Buffer.—It has been shown previously that the addition of an acid phosphate buffer increases the reaction rate. However, since the relative increase is known and results are compared using the one medium in the case of dilute solutions, the presence of the buffer should not materially affect the conclusions to be drawn.

Energy of Activation.—ΔE_a appears to be of the same order as previous determinations.[1–3,6] Even though the energies of activation are only accurate to approx. ±1000 cal. per mole it is interesting to note that the values are somewhat lower for the alkyl ureas.

Reaction Mechanism and Substitution in the Urea Molecule

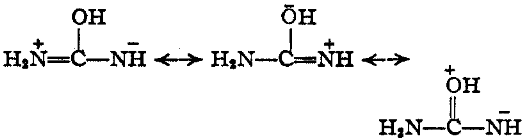
The nucleophilic nitrogen of urea must attack the electrophilic carbon center of formaldehyde to yield N-methylolureas, methylenebisureas, etc.[1–3,6] Tautomeric and/or mesomeric forms enhancing the nucleophilic nature of the reactive nitrogen are more likely to be involved in the reaction than others. A similar attack by nucleophilic oxygen is less important since this would lead to the formation of unstable compounds and an equilibrium strongly displaced in favor of the original reactants.

For un-ionized urea one may write the canonic forms



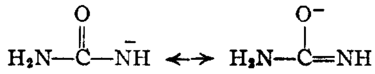
$$H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \longleftrightarrow H_2\overset{+}{N}=\overset{\overset{\displaystyle O^-}{|}}{C}-NH_2 \longleftrightarrow H_2N-\overset{\overset{\displaystyle O^-}{|}}{C}=\overset{+}{N}H_2 \quad \text{(i)}$$

derived from the amide form or

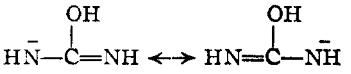


$$H_2\overset{+}{N}=\overset{\overset{\displaystyle OH}{|}}{C}-\overset{-}{N}H \longleftrightarrow H_2N-\overset{\overset{\displaystyle \overset{-}{O}H}{|}}{C}=\overset{+}{N}H \longleftrightarrow H_2N-\overset{\overset{\displaystyle \overset{+}{O}H}{\|}}{C}-\overset{-}{N}H \quad \text{(ii)}$$

from the imidol form. The amide structure is seen to be more important partly owing to the possibility of equivalent canonic forms, partly owing to a more probable type of charge distribution. In this form, however, the nitrogen is deactivated as a nucleophilic center. For anionic urea the canonic forms may be written

From (i) or (ii) 

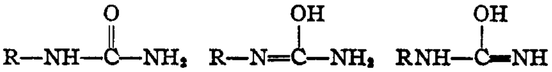
$$H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{-}{N}H \longleftrightarrow H_2N-\overset{\overset{\displaystyle O^-}{|}}{C}=NH \quad \text{(iii)}$$

From (ii) 

$$H\overset{-}{N}-\overset{\overset{\displaystyle OH}{|}}{C}=NH \longleftrightarrow HN=\overset{\overset{\displaystyle OH}{|}}{C}-\overset{-}{N}H \quad \text{(iv)}$$

(iv) has more resonance stabilization than (iii) owing to equivalent canonic forms; it also appears to have nitrogen activated for nucleophilic reactions. On these considerations (i) is predominating over (ii) under static, *i.e.*, non-reacting conditions. The anionic forms necessary for the initial condensation are evidently obtained mainly through the ionization of (ii). In other words, (ii) is a stronger acid than (i), since the former gains resonance energy on ionization to the anionic forms (iii) and (iv), mainly to (iv). Under acidic conditions, therefore, the distinction between (i) and (ii) disappears and the N-methylol type of condensation is no longer favored.

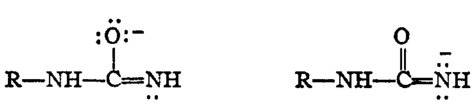
The tautomeric forms of a simple alkyl urea such as N-methylurea may be written



$$R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 \qquad R-N=\overset{\overset{\displaystyle OH}{|}}{C}-NH_2 \qquad RNH-\overset{\overset{\displaystyle OH}{|}}{C}=NH$$

v vi vii

With R = Me or Et, the inductive effect is toward the adjacent nitrogen and (vii) is less likely than (vi). The principal anionic forms are



$$R-NH-\overset{\overset{\displaystyle :\ddot{O}:^-}{|}}{C}=\ddot{N}H \qquad R-NH-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{-}{\ddot{N}}H$$

It is seen that both the un-ionized and ionized forms of the alkyl ureas lose resonance stabilization in comparison with corresponding forms of urea and this may be responsible for the increased reactivity since there is less resonance energy to lose on combining with formaldehyde. In this case the alkyl ureas would show increased values of k and decreased values for ΔE_a against urea. The results tend to confirm this view.

It would be expected that substitution of Et for Me would increase this effect so that N-ethylurea should show slightly higher values for k than N-methylurea. Table I, however, does not indicate any significant difference between the behavior of N-methyl- and N-ethylurea. An examination of the behavior of a larger series of alkyl ureas might illustrate this trend more clearly.

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[9] A. Einhorn, *Ann.*, **361**, 113 (1908).