On the Reaction between Urea and Formaldehyde in Neutral and Alkaline Solutions

VI. Experimental Studies of the Activation Energy and the Heat of Reaction

NILS LANDQVIST

Rydboholms A.B., Rydboholm, Sweden

The activation energies of the formation and hydrolysis of mono- and dimethylol urea were determined. The activation energies of the reactions between urea — formaldehyde and monomethylol urea — formaldehyde were found to be 15.4 kcal/mole, and the activation energies of the corresponding hydrolysis reactions 20.4 kcal/mole. The heat of reaction of the formation reactions was found to be the same in both cases: 4.9 kcal/mole.

The activation energy of the reaction between urea and formaldehyde at equal concentrations was determined by *e.g.*: (1) Smythe¹; the amount of unreacted formaldehyde of the 4 M unbuffered reaction solutions was determined by means of the hydroxylamine titration method. The activation energy obtained was 14.7 kcal/mole; (2) Smythe²; the reactions in dilute, unbuffered solutions (0.1 M) were studied by means of polarography. Activation energy obtained: 15.3 kcal/mole; (3) Crowe and Lynch³; polarographic determinations in 0.05 M LiOH at low concentrations of the reactants. Activation energy: 15.9 kcal/mole.

The activation energy of the reaction between monomethylol urea and formaldehyde was determined by Květoň and Králová⁴. ~2 M reaction solutions and the amount of unreacted formaldehyde determined by means of the hydroxylamine method. Activation energy: 12.2 kcal/mole.

The activation energy of dimethylol urea hydrolysis was also studied by Květoň and Králová⁴. Hydroxylamine method used, activation energy: 16.9 kcal/mole.

As regards the moderate accuracy of the hydroxylamine titration method, reference is given to Landqvist⁵.

The purpose of the following paper is to describe experimental studies of the activation energies of mono- and dimethylol urea formation and hydrolysis. The heat of reaction of the forward reactions is given.

Table 1. The activation energy of mono- and dimethylol formation and hydrolysis reactions.

Reaction solution	Buffer	C_{buffer}	pH	Temperature °C	Rate constant $\times 10^5$	E kcal/mole
4.0 M urea + 0.4 M formaldehyde	KH_2PO_4	0.025	6.70	20	6.5	16.0
				30	16.1	14.9
				40	35	14.9
		0.050		20	10.2	14.8
				30	23.1	16.2
				40	54	16.2
		0.100		20	16.0	15.4
				30	38	15.1
				40	84	15.1
	borax	0.050	9.20	20	6.0	15.1
				30	14.0	15.7
				40	32	15.7
	Na_2CO_3	0.050	10.00	20	12.2	Av. 15.4
				30	30.0	16.2
				40	73	16.8
1.0 M monomethylol urea + 1.0 M formaldehyde	KH_2PO_4	0.025	6.70	20	2.40	15.6
				30	5.8	15.3
				40	13.1	15.3
		0.050		20	3.8	15.1
				30	8.9	15.4
				40	20.2	15.4
		0.100		20	6.9	14.9
				30	16.0	15.9
				40	37	15.9
	borax	0.050	9.20	20	2.60	14.9
				30	6.0	16.1
				40	13.9	16.1
	Na_2CO_3	0.050	10.00	20	12.2	Av. 15.4
				30	30.2	16.8
				40	71	16.4
1.0 M monomethylol urea	KH_2PO_4	0.025	6.70	20	0.221	20.5
				30	0.70	19.9
				40	2.01	19.9
		0.050		20	0.35	20.3
				30	1.10	20.3
				40	3.20	20.3
		0.100		20	0.60	20.4
				30	1.88	20.8
				40	5.7	20.8
	borax	0.050	9.20	20	0.233	20.7
				30	0.74	20.4
				40	2.23	20.4
	Na_2CO_3	0.050	10.00	20	0.46	Av. 20.4
				30	1.52	21.0
				40	4.6	21.3

0.5 M dimethylol urea	KH ₂ PO ₄	0.025	6.70	20	0.33	19.7
				30	1.03	
				40	2.99	20.8
		0.050		20	0.53	20.7
				30	1.70	
				40	5.02	20.4
		0.100		20	0.98	20.4
				30	3.11	
				40	9.0	20.1
	borax	0.050	9.20	20	0.302	20.8
				30	0.97	
				40	2.79	20.1
	Na ₂ CO ₃	0.050	10.00	20	1.08	Av. 20.4
				30	3.7	21.6
				40	11.9	22.3

* In all cases such an amount of a chloride of the buffer cation was added that a cationic strength corresponding to 0.200 M solutions was maintained.

THE ACTIVATION ENERGIES

The activation energy investigations were carried out as previous studies at 20° C; Landqvist⁵. The temperature interval was 20—40° C. The pH values of the reaction solutions refer to 20° C.

Since the pK of the buffers are dependent on the temperature, and the OH⁻ catalysis of the reactions is comparatively small, it seems to be most important to keep the concentration of the buffer acid and base as constant as possible (Landqvist⁵⁻⁶).

The compositions of the reaction solutions and the reaction rate constants obtained can be found in Table 1. The activation energy, *E*, from experimental data are included in the table. Examples of the Arrhenius equation relationship are given in Fig. 1.

Fig. 1. The relationship between the logarithm of the reaction rate constant and the inverse of the temperature. 4.0 M CO(NH₂)₂ + 0.40 M HCHO; C_{KH₂PO₄} = 0.025 (x), 0.050 (O) and 0.100 (●). pH 6.70.

Fig. 2. The relationship between the reaction rate constant and the concentration of the KH₂PO₄ buffer at pH 6.70. The temperatures were: 20° C (x), 30° C (O) and 40° C (●).

At all temperatures and reactions acid — base catalysis as previously reported (Landqvist⁵⁻⁸) occurred. An example of the reaction rate constant-buffer concentration (constant cationic strength) relationship is given in Fig. 2. If the curves corresponding to the different temperatures are extrapolated to a reaction rate constant equal to zero, the same (negative) abscissa value was found. These observations support the assumption that the changes in pH due to the change in temperature can be neglected, as regards their influence on the catalysis. The change in the buffer activity is unknown. The activation energies of KH_2PO_4 and borax buffered solutions support an assumption that the influence from this is moderate. In the case of Na_2CO_3 buffers slightly different figures are obtained. The differences between the formation and hydrolysis activation energies are all of the same order, why the carbonate behaviour is probably due to changes in the catalytic properties.

From Table 1 we find reasons to accept the activation energy value 15.4 kcal/mole of the formation reactions; the corresponding hydrolysis figure is 20.4 kcal/mole.

HEAT OF REACTION

The heats of reaction of mono- and dimethylol urea formation were determined calorimetrically. In order to reduce the influence from side reactions; *i. e.* formation of dimethylol urea from urea and formaldehyde and mono- and dimethylol urea hydrolysis, and in order to obtain as complete reactions as possible, the study was made on solutions containing an excess of urea or formaldehyde respectively. In the latter case no formation of tri- and tetramethylol urea is likely to occur, as could be concluded from the consumption of formaldehyde. The catalytic properties were selected to give proper reaction rates. The experiments were carried out as follows.

Monomethylol urea formation. An amount of 500 ml of a 4.0 M urea solution, 0.025 M with respect to Na_2CO_3 , pH 11.50, was poured into a Dewar vessel. Through holes in the cork stopper of the vessel a stirrer and a Beckman thermometer were immersed in the urea solution. Through another hole in the stopper a "test tube" was immersed. The tube was made of a polyethylene sheet, and contained 50 ml of a 4 M formaldehyde solution, pH 11.50. When a constant temperature was obtained, 20° C, the tube was torn and the two reactants quickly mixed. Heat transfer through the vessel was corrected for by extrapolation of the time — temperature curve. Corrections for the heats of dilution of the reactants were obtained by replacing the formaldehyde respective urea by distilled water with the same buffers dissolved. The specific heat of the reaction solution was determined by immersing a polyethylene "test tube" containing a known amount of ice. The heat absorption by the calorimeter was determined by the same technique and with distilled water in the vessel.

Dimethylol urea formation. The same technique was used in this case as well. The solution was 500 ml 1.0 M formaldehyde, 0.050 M Na_2CO_3 , pH 11.50. The tube contained 4.5 g dry monomethylol urea. Solid monomethylol urea was used in order to prevent influence from hydrolysis reactions. The substance was brought into solution rapidly, and disturbances from this step of the experiment were negligible.

The chemicals used were of A. R. quality, except for the formaldehyde, which was a Merck product containing only traces of methyl alcohol and formic acid ($<4 \cdot 10^{-4}$ M in solutions containing 380 g/l). The monomethylol urea was prepared in accordance with Walter and Gewing⁹; cryoscopic molecular weight: 90 ± 2 .

The heat of reaction was found to be the same for both mono- and dimethylol urea formation, namely 4.9 kcal/mole.

It may be of some interest to compare the activation energy differences ΔE , and the heat of reaction, Q . For processes in solutions we have: $\Delta E \cong Q$. The average difference between the formation and hydrolysis activation energies are 5.0 kcal/mole (Table 1). This figure, as compared with the heat of reaction 4.9 kcal/mole, shows that a good agreement is present.

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