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Thermochemical study of the hydroxymethylation reaction

K. Siimer [a], P. Christjanson [a], E. Siimer *,[b]

[a] *Tallinn Technical University, Ehitajate tee 5, EE0026 Tallinn, Estonia*
[b] *Institute of Chemistry of the Estonian Academy of Sciences, Akadeemia tee 5, EE0026 Tallinn, Estonia*

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Abstract

The hydroxymethylation reaction of urea, monomethylolurea, *N,N*-diethylurea, acrylamide, two derivatives of tetrahydro-1,3,5-triazine-2(1*H*)-one and melamine in aqueous solutions (phosphate buffer, pH 8.0) at 30°C has been studied using a Calvet-type microcalorimeter. The values of the heat effects and rate constants for the formation of hydroxymethyl groups have been determined.

Keywords: Hydroxymethyl; Kinetics

1. Introduction

Urea–formaldehyde (UF) resins used for binding wood-based materials must have a guaranteed low formaldehyde (F) emission and, at the same time, must ensure acceptable mechanical properties of the materials. The increasing requirement with respect to F emission has necessitated the search for possibilities of modifying UF resins. Various amides have been proposed for the modification, e.g. acrylamide and its derivatives [1,2]. Triazinone rings can form during the stage of resin synthesis [3], or they can be added at the curing stage [4,5]. The properties of today's UF resins with low F to urea molar ratios have been improved significantly

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* Corresponding author.

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by fortifying them with melamine and/or phenol (see e.g. [6]). The present work originates from these trends in the modification of UF resins.

The first step in the synthesis of UF resins is hydroxymethylation, i.e. the substitution of hydrogen linked to amide (or amine) nitrogen by the methylol (hydroxymethyl) group. The kinetics and thermodynamics of this equilibrium reaction (see Eq. (1)) are preferably studied in weakly basic solution to avoid further condensation reactions.

$$R{-}CO{-}NH_2 + CH_2O \rightleftharpoons R{-}CO{-}NH{-}CH_2OH \qquad (1)$$

Hydroxymethylation is an exothermic reaction involving a change in enthalpy of ≈ 20 kJ mol^{-1} (5 kcal mol^{-1}) [7]. The reaction is a typical second order one. Relatively few data have been published on the rate constants of the hydroxymethylation reaction determined by thermochemical methods. In [8] these values were determined for the reaction of urea with F, and it was shown that during the initial period the main reaction is accompanied by a relatively slow recombination of the molecules of F oligomers, which is an endothermic reaction and must be considered in direct microcalorimetric measurements.

In the case of amides, conditions for the reaction can be chosen to guarantee the formation of dihydroxymethyl derivatives from urea, for example, and monohydroxymethyl compounds from *N*,*N*-dimethylurea [9], i.e. the substitution of only one hydrogen at each amidic nitrogen. In contrast, because of its high reactivity, melamine as a typical primary amine can give different hydroxymethyl compounds up to the formation of hexamethylolmelamine [10].

In this paper the hydroxymethylation of some amides and triazinones (which are also amides) and of melamine as potential modifiers for UF resins has been studied by the direct microcalorimetric method to compare the reactivity of the substrates and to determine the values of the heat effects.

2. Experimental

2.1. Materials, apparatus and methods

Reagent-grade urea, acrylamide and melamine were used without further purification. Aqueous solutions of formaldehyde were obtained by the depolymerization of paraformaldehyde; the derivatives of urea and tetrahydro-1,3,5-triazine-2(1*H*)-one were synthesized according to [11] and [12] and identified by both ^1H and ^{13}C NMR spectrometry [13].

The amides, triazinones and melamine used are characterized in Fig. 1 and Table 1. The acronyms TRMEA and TRMA indicate that these compounds are triazinone derivatives synthesized from ethanolamine and methylamine respectively. All the reactions were carried out in 0.1 M phosphate buffer of pH 8.5. Table 1 shows the maximum number of hydrogen atoms linked to amide nitrogen which can participate in the reaction with F (a) theoretically and (b) under the chosen conditions.

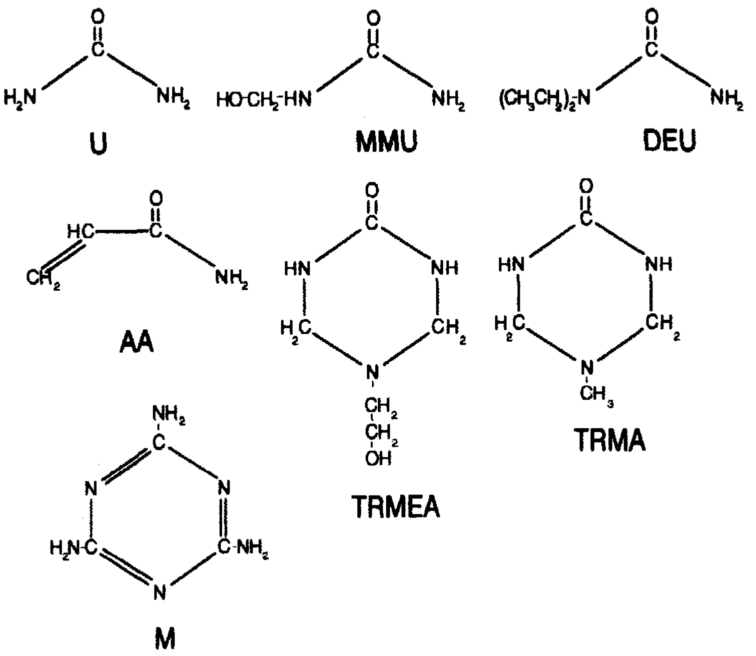

Fig. 1. Structures of the substrates used.

Table 1
Compounds used in the hydroxymethylation reaction

Compound		Number of hydrogens for substitution	
		Maximum (theoretical)	In chosen conditions
Amides			
U	Urea	4	2
MMU	Monomethylolurea	3	1
DEU	*N*,*N*-Diethylurea	2	1
AA	Acrylamide	2	1
Triazinones			
TRMEA	(5-Hydroxyethyl)tetrahydro-1,3,5-triazine-2(1*H*)-one	2	2
TRMA	5-Methyltetrahydro-1,3,5-triazine-2(1*H*)-one	2	2
Amines			
M	Melamine; 2,4,6-triamino-1,3,5-triazine	6	3–4

An LKB 2277 microcalorimeter (“Bioactivity Monitor”) with a glass ampoule measuring cylinder was used at 30.00 ± 0.02°C. The buffered solutions of F and substrate were weighed with an accuracy of 0.2 mg and placed in a 2.8 ml glass ampoule. The reference ampoule contained an equal mass of distilled water. After mixing the components, both ampoules were introduced into the calorimeter and, after 30 min, measurement of the output signal was started using an LKB 2210 potentiometric recorder. The heat flow rate was measured up to the end of the reaction.

The initial concentrations of the components were chosen with low values to give a duration of reaction of $\approx 10-48$ h. In this case the initial period (30 min) of non-registration is relatively small and the curves obtained can be extrapolated to the origin with an error not exceeding 5%.

The obtained curves of heat flow rate vs. time were corrected in respect of thermal inertia using the Tian equation [14]. By integrating the corrected curves the total heat effect of the reaction was calculated.

Evidently the heat flow rate is proportional to the consumption of components in the reaction, and it is therefore also proportional to the rate of reaction. The values of the rate constants were calculated by analysis of the kinetic curve of heat flow vs. time. In most of the reactions a large excess of F was used. In this case the reaction is close to pseudomonomolecular (the kinetic curve is logarithmic) and the value of the effective rate constant can be easily calculated. By dividing this last value by the initial concentration of F, the value of the rate constant of the bimolecular reaction can be found. In fact, the concentration of F in the reaction mixtures decreases continuously, and this fact must be considered even in the case of a large excess of F. Therefore, from the integrated curve of heat effect vs. time, the half-life of the reaction was calculated, and to obtain the value of the rate constant the following well-known equation for bimolecular reactions was used

$$k = \frac{\ln\left(2 - \dfrac{C_{\mathrm{A}_0}}{C_{\mathrm{B}_0}}\right)}{\tau_{1/2} C_{\mathrm{B}_0}\left(1 - \dfrac{C_{\mathrm{A}_0}}{C_{\mathrm{B}_0}}\right)} \qquad C_{\mathrm{B}_0} > C_{\mathrm{A}_0} \tag{2}$$

where C_{A_0} and C_{B_0} are the initial concentrations of the components, substance B being in excess.

The accuracy of the calculated values for the heat effects and rate constants may be estimated as 2% and 10% respectively.

3. Results and discussion

The results of the microcalorimetric experiments are summarized in Table 2. As an example, in Fig. 2, the course of the hydroxymethylation reaction of monomethylolurea is presented.

The first 30 min of reaction, which is not measurable using an LKB microcalorimeter, does not influence the calculation of values in prolonged experiments. In contrast, the secondary heat effects, such as the heats of mixing and of the recombination of F oligomers, are automatically excluded. Furthermore, the end of the latter endothermic reaction is mentioned in some experiments.

Table 2
Heat effects and rate constants of the hydroxymethylation reaction

Amide	Molarity, M		Molar ratio F/amide	Heat effect			Rate constant, M^{-1} min^{-1} mol^{-1} of $-CH_2OH$
	Amide	F		Total in J	in kJ mol^{-1} of		
					amide	$-CH_2OH$	
U	0.03795	0.5376	14.2	4.64	48.47	24.2	0.0080
	0.1531	0.6849	4.47	13.78	42.31	21.2	0.0164
	0.4052	0.2220	0.548	15.73	–	22.6	0.0177
MMU	0.1585	0.3693	2.33	7.95	18.33	18.3	0.0110
DEU	0.4715	3.4010	7.21	30.77	25.17	25.2	0.0049
	0.2352	1.6646	7.08	15.16	25.72	25.7	0.0051
AA	0.7790	3.4094	4.38	50.66	25.17	25.2	0.0013
TRMEA	0.1253	2.5478	20.33	13.55	42.06	21.0	0.0032
	0.04205	0.5061	12.04	4.66	43.08	21.5	0.0088
	0.03555	0.2033	5.72	2.64	29.02	14.5	0.0052
TRMA	0.1207	2.5143	20.83	14.36	46.35	23.2	0.0040
M	0.01721	0.2182	12.68	2.41	53.10	17.7[a]	0.0083[a]
	0.04359	0.0262	0.601	0.899	–	13.3	0.0155

[a] Calculated assuming the substitution of three hydrogens in melamine.

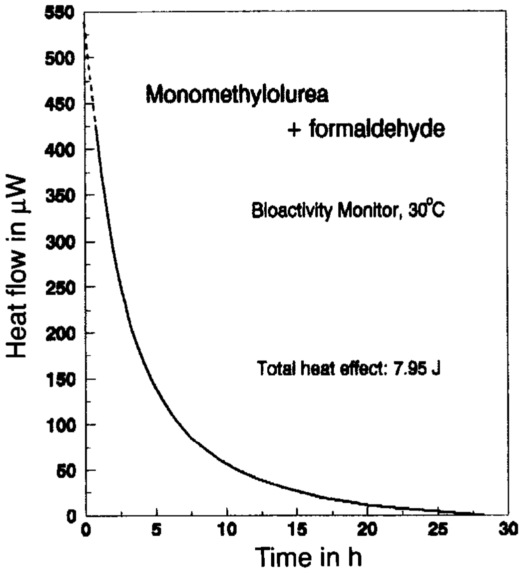

Fig. 2. Heat flow vs. time in the hydroxymethylation reaction of monomethylolurea at 30°C.

Titrimetric experiments using the hydroxylamine method for determination of F were carried out in addition to the calorimetric ones to verify the number of hydrogens substituted in the hydroxymethylation reaction. This study showed that, under the chosen conditions, up to 2.3 hydrogens may be substituted in urea during very long reactions, but usually this number is close to 2. In melamine, 3–4 hydrogens are substituted, depending on the concentrations and molar ratio of the components.

The total heat effect in the experiments was equal to 1–50 J.

As seen in Table 2, the heat effect of the reaction calculated per 1 mol of hydroxymethylol group formed at amidic nitrogen depends to some extent on the structure of the amide and the initial concentration of the components, and is on average equal to 22 kJ mol^{-1} (5.3 kcal mol^{-1}). For melamine this value is somewhat lower ($\approx$ 16 kJ mol^{-1}).

The compounds used have different reaction abilities. The double bond in acrylamide (AA) causes the low mobility of the amidic hydrogen, and the rate constant is equal to 0.0013 M^{-1} min^{-1}. DEU and the studied triazinone compounds have the same rate constant value, $\approx$0.005 M^{-1} min^{-1}. In the case of triazinones as substrates, the mechanism of the hydroxymethylation reaction is evidently more complicated (with a negative heat effect in the initial period) and needs elucidation by using other physico-chemical methods. The most reactive compound is urea, which rapidly forms the hydroxymethylated compounds MMU and *N,N'*-dimethylolurea. The rate of the reaction diminishes if a large excess of F is used. The experiments prove indirectly that the first hydrogen atom is substituted faster than subsequent ones.

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