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Thermodynamics of the Hydroxymethylation of Melamine and Urea with Formaldehyde

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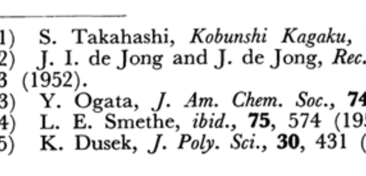
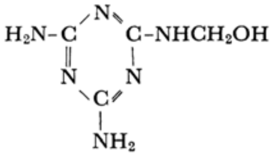
The hydroxymethylation of melamine and urea with formaldehyde in an aqueous solution was studied thermodynamically. The entropy, enthalpy, and free energy of activation for the early stages of the reaction, *i. e.*, the formation of mono-methylol derivatives, and also the changes in the entropy, enthalpy, and molecular heat, *etc.*, were determined in connection with the functionalities. It was confirmed that no marked differences exist between the rate constant of melamine and that of urea, but that the $\Delta S^{\neq}$ and $\Delta H^{\neq}$ values of urea are considerably smaller than the respective values of melamine. Prominent differences do exist between $\Delta S^{\neq}$ and $\Delta H^{\neq}$; the $\Delta S^{\neq}$ and $\Delta H^{\neq}$ terms of melamine amount roughly to 10^5 times and 10^{-5} times those of urea respectively, regardless of the functionalities. These results imply a conspicuous difference between their reaction mechanisms, a difference which is explicable in terms of the characteristics of their amino-group nitrogen. Besides, the solvent effect of dimethylsulfoxide in the hydroxymethylation of melamine was investigated; it will be discussed in connection with the solvation.

Melamine and urea resins, the most prominent members of the amino resins, are produced by the reaction of melamine and urea with formaldehyde; they have commercial importance. The kinetics of the hydroxymethylation of melamine (M) and urea (U) with formaldehyde (F) have been studied previously,[1-5] but there have been no reports on any detailed studies of their thermodynamics.

In view of this, the hydroxymethylation of melamine and urea to obtain the mono-methylol derivatives was investigated thermodynamically in detail at the early stages; from this study, it was found that the entropy and enthalpy of activation show markedly different values in the two cases. This may be a result of the difference in the reaction mechanism. In addition, the solvent effect of dimethylsulfoxide (DMSO) was studied thermodynamically for the early stages of reaction, as it was found by the author that dimethylsulfoxide[*1] is a good solvent for melamine resin.

The stoichiometric equations for the reaction are as follows:





$$H_2NCONH_2 + HCHO \rightleftarrows H_2NCONHCH_2OH.$$

Experimental

Materials. The melamine and urea were commercial products and were used after recrystallization from water and methanol respectively. The formalde hyde was the best-grade formaline (*ca.* 37%); it has been reported[3] that the impurity in the formaldehyde, *e. g.*, the small amount of methanol, does not affect the estimation of the reaction rate.

Kinetic Measurements. First, 500 m*l* of a 0.07 mol/*l* aqueous solution of melamine, 500 m*l* of a 0.07 mol/*l* DMSO-water mixed solution (1 : 4, vol. ratio) of melamine, and 100 m*l* of a 0.50 mol/*l* aqueous solution of urea were prepared. Then, the above melamine and urea solutions were mixed with 100 m*l* of an aqueous formaldehyde solution of a known concentration, so that the F/M(or U) mol ratio became 2.5, with the pH adjusted to 8.0 by the addition of 0.01 N caustic alkali. (The pH value was adjusted by means of a glass electrode pH meter.) Reactions were carried out in a thermostat regulated to the operating temperatures, samples were taken out at appropriate intervals, and the unchanged formaldehyde was analyzed

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[1] S. Takahashi, *Kobunshi Kagaku*, **7**, 169 (1950).
[2] J. I. de Jong and J. de Jong, *Rec. trav. chem.*, **71**, 643 (1952).
[3] Y. Ogata, *J. Am. Chem. Soc.*, **74**, 5728 (1952).
[4] L. E. Smethe, *ibid.*, **75**, 574 (1953).
[5] K. Dusek, *J. Poly. Sci.*, **30**, 431 (1958).

[*1] Melamine is soluble only with difficulty; the only known solvents are liquid ammonia and ethylene glycol, as is well known. (*Cf.* K. Sato, This Bulletin, in preparation).

by the sulfite method.6) As it is known3),*2 that standing for a long time increases the titre of hydrochloric acid in the sulfite method, the sample was run into 40 ml of an ice-cooled *ca.* 1 N sodium sulfite solution and immediately titrated with 0.5 N hydrochloric acid, using thymolphthalein as an indicator.

Results and Discussion

Rate Equations and Calculation of Rate Constants for Early Stages of the Reaction. It is known that the reaction rates of the hydroxymethylation of melamine3,7) and of urea8) are both second-order for forward reactions and first-order for reverse reactions; hence, Eq. (1) can be used as the rate equation if the reverse reactions are neglected, while Eq. (2) can be used if the reverse reactions are taken into consideration:

$$\frac{\mathrm{d}y}{\mathrm{d}t} = k(a-y)(b-y) \tag{1}$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} = k(a-y)(b-y) - k'y \tag{2}$$

where k and k' are the forward and reverse rate constants respectively; a, the initial concentration (mol/l) of melamine or urea; b, that of formaldehyde, and y, the concentration (mol/l) of formaldehyde consumed after t minutes. Equations (1) and (2) are transformed into Eqs. (1′) and (2′) respectively:

$$kt = \frac{1}{a-b}\ln\frac{b(a-y)}{a(b-y)} \tag{1'}$$

$$kt = \frac{K}{\sqrt{\beta}}\ln\frac{(2Ky+\alpha-\sqrt{\beta})(\alpha+\sqrt{\beta})}{(2Ky+\alpha+\sqrt{\beta})(\alpha-\sqrt{\beta})} \tag{2'}$$

equilibrium constant,

$$K = \frac{k}{k'} = \frac{y_e}{(a-y_e)(b-y_e)} \tag{3}$$

$$\alpha = -(aK+bK+1),$$

$$\beta = (aK+bK+1)^2 - 4abK^2,$$

where y_e is the y value at the equilibrium state; this value is obtained graphically by plotting the conversion percentage *vs.* the time. In addition, melamine3,7) was previously considered to be mono-, tri- or hexa-functional, and urea1) to be mono- or di-functional; hence, 3a, 6a, and 2a should be used, respectively, in place of "a" in the above equations when melamine is tri- or hexa- and when urea is di-functional. In order to obtain the positive rate constant in Eq. (2′) for the formation of methylol derivatives, $(a-y_e)$, $(2a-y_e)$, $(3a-y_e)$, and $(6a-y_e)$ should have positive values in Eq. (3), corresponding to the functionalities. Therefore, the rate constants were computed for the formation of mono-methylol derivatives ($(a-y_e)>0$) at the above functionalities.

Equation (2′) could be used for the computation of the rate constants when melamine was tri- and hexa- and when urea was di-functional, but it was impossible to use it when they were mono-functional, since it was observed that the $(a-y_e)$ values in Eq. (3) were negative in the majority of the cases under investigation (as the data of Fig. 8 show); hence, we were obliged to use Eq. (1′) when they were monofunctional, assuming that the reverse reaction could be neglected. In order to determine the effect of the reverse reactions, Eq. (1′) was also used when urea was di-functional. These results in an aqueous solution of melamine, in a DMSO-water mixed solution of melamine, and in an aqueous solution of urea are shown in Figs. 1, 2, and 3 respectively, in connection with the functionalities. From these figures, it is kinetically confirmed that the constancy range of the rate constants is, in general, confined within narrower conversion limits with a decrease in the functionalities, even in the range of the formation of mono-methylol derivatives. In particular, the rate constants increase with the reaction time when they are mono-functional and when they approach the constituent of the mono-methylol derivatives; this

TABLE 1. HYDROXYMETHYLATION RATE CONSTANTS ($l\cdot$mol$^{-1}\cdot$min^{-1})

(1) Rate constants of melamine

No.a)	Functionality	Temp., °C 40	50	55	60
1	mono	0.0341	0.1211	0.1612	0.2881
2	tri	0.0114	0.0297	0.0460	0.0741
3	hexa	0.0055	0.0144	0.0212	0.0313
4	mono	0.0262	0.0786	0.1490	0.2831
5	tri	0.0079	0.0199	0.0374	0.0621
6	hexa	0.0039	0.0099	0.0182	0.0306

a) Nos. 1, 2, and 3 denote rate constants in an aqueous solution; Nos. 4, 5, and 6 denote in a DMSO-water solution respectively.

(2) Rate constants of urea

No.b)	Functionality	Temp., °C 40	50	60	70
7	mono	0.0061	0.0122	0.0184	0.0429
8	di	0.0025	0.0052	0.0079	0.0149
9	di	0.0026	0.0057	0.0080	0.0182

b) No. 8 donotes rate constants when reverse reaction is neglected and No. 9 when reverse reaction is taken into consideration.

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6) G. Lemwe, *Chem. Ztg.*, **27**, 896 (1903).

[*2] This fact suggests that the alkali produced by the reaction with sulfite accelerates the decomposition of methylol derivatives into melamine and formaldehyde, or into urea and formaldehyde, respectively.

7) K. Koeda, *Kobunshi Kagaku*, **16**, 62 (1959).

8) G. E. Crowe and C. C. Lynch, *J. Am. Chem. Soc.*, **71**, 3731 (1931).

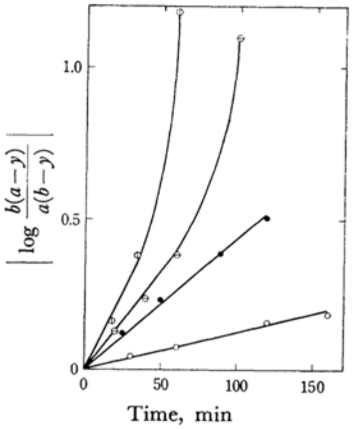


Fig. 1(a).

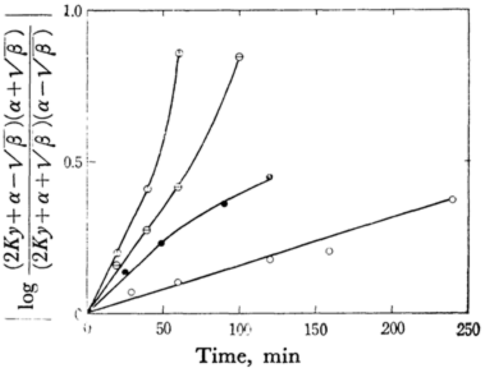


Fig. 1(b).

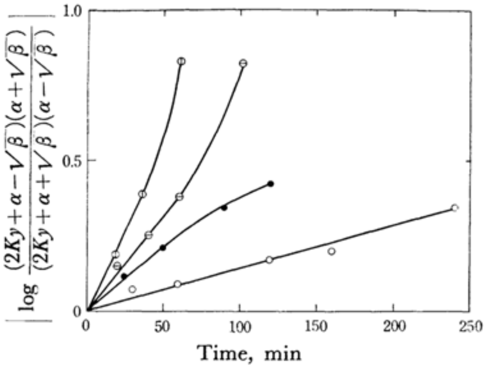


Fig. 1(c).

Fig. 1. Plots of $\log\,[b(a-y)/a(b-y)]$ or $\log\,[(2Ky+\alpha-\sqrt{\beta})\,(\alpha+\sqrt{\beta})/(2Ky+\alpha+\sqrt{\beta})\,(\alpha-\sqrt{\beta})]$ *vs.* time for an aqueous solution of melamine.
(a), (b), (c): Plots when melamine is considered to be mono- ($k'=0$), tri- ($k'\neq 0$), and hexa- ($k'\neq 0$) functional respectively.
—○—: 40°C, —●—: 50°C, —⊖—: 55°C, —⦶—: 60°C
Initial concn.: [melamine] = 0.0583 (mol/l)
[formaldehyde] = 0.1460 (mol/l)

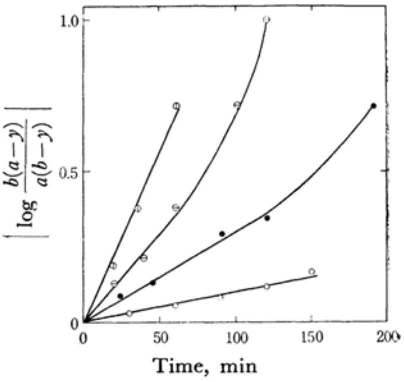


Fig. 2(a).

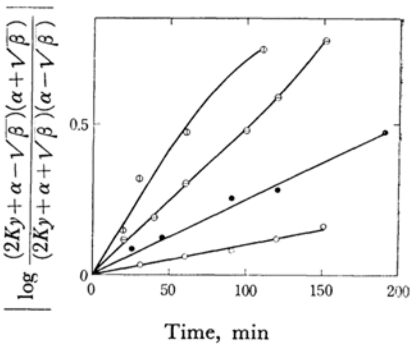


Fig. 2(b).

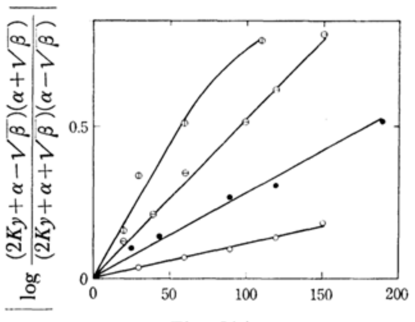


Fig. 2(c).

Fig. 2. Plots of $\log\,[b(a-y)/a(b-y)]$ or $\log\,[(2Ky+\alpha-\sqrt{\beta})\,(\alpha+\sqrt{\beta})/(2Ky+\alpha+\sqrt{\beta})(\alpha-\sqrt{\beta})]$ *vs.* time for a DMSO-water solution of melamine.
(a), (b), (c): Plots when melamine is considered to be mono- ($k'=0$), tri- ($k'\neq 0$), and hexa- ($k'\neq 0$) functional respectively.
—○—: 40°C, —●—: 50°C, —⊖—: 55°C, —⦶—: 60°C
Initial concn.: [melamine] = 0.0583 (mol/l)
[formaldehyde] = 0.1460 (mol/l)

suggests that the hydroxymethylation of mono-methylol derivatives proceeds at a considerable rate in the cases of both melamine and urea, although the $(a-y)$ value becomes very small when they approach the constituent of mono-methylol

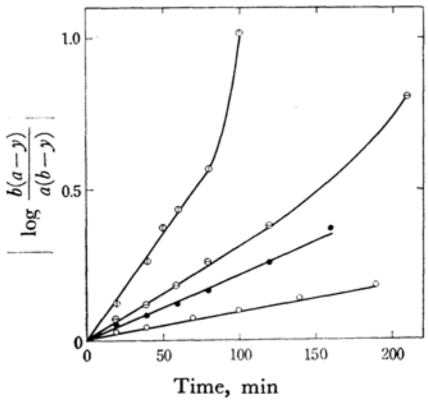


Fig. 3(a).

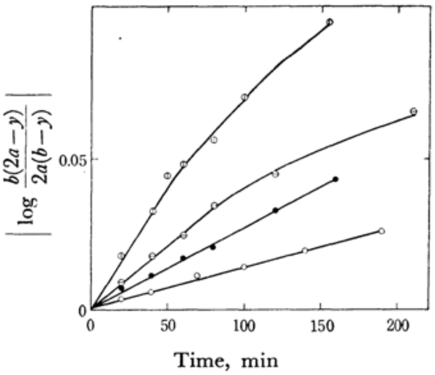


Fig. 3(b).

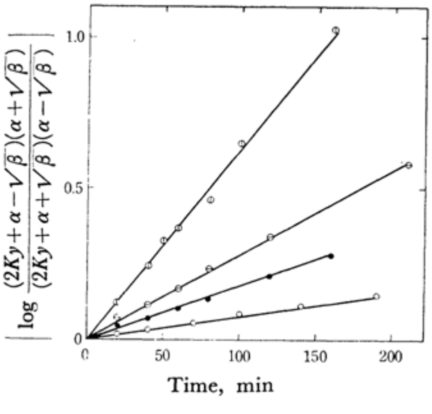


Fig. 3(c).

Fig. 3. Plots of $\log b(a-y)/a(b-y)$, $\log b(2a-y)/2a(b-y)$, and $\log (2Ky+\alpha-\sqrt{\beta})(\alpha+\sqrt{\beta})/(2Ky+\alpha+\sqrt{\beta})(\alpha-\sqrt{\beta})$ *vs.* time for an aqueous solution of urea.

(a), (b), (c): Plots when urea is mono- ($k'=0$), di- ($k'=0$), and di- ($k'\neq 0$) functional respectively.
—○—: 40°C, —●—; 50°C, —⊖—: 60°C, —⦶—: 70°C
Initial concn.: [urea]$=0.250$ (mol/*l*)
[formaldehyde]$=0.625$ (mol/*l*)

derivatives. The rate constants thus obtained are summarized in Table 1.

It can be seen from Table 1 that the rate constants become smaller with an increase in the functionalities; when melamine is tri- and hexa-functional, the rate constants are reduced to, very roughly, 1/3 and 1/6 (respectively) that when it is mono-functional; when urea is di-functional, the rate constant is reduced to, very roughly, 1/2 that when it is mono-functional. Thus, when melamine is tri- or hexa-functional, the rate constants may be considered to indicate those on the amino-group or the amino-group hydrogen of melamine; this is also true in the case of urea.

Thermodynamic Quantities between an Initial System and an Activated Complex. Arrehenius plots of the rate constants in the above cases are shown in Figs. 4, 5, and 6, from which it is obvious that these plots are linear. The entropy ($\Delta S^{\neq}$), enthalpy ($\Delta H^{\neq}$), and free energy ($\Delta F^{\neq}$) of activation, as well as the equilibrium constant ($K^{\neq}$), were computed from the energy of activation and the frequency factor obtained from Figs. 4, 5, and 6. The results are given in Table 2, where the increase in the functionalities results in a decrease of $\Delta S^{\neq}$ and an increase of $\Delta F^{\neq}$, while $\Delta H^{\neq}$ remains constant; however, these influences are much smaller than those of the increase in the functionalities upon the rate constants.

Also, it may be remarked that both the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values of urea are obviously smaller than those of melamine, regardless of the functionalities. For instance, with regard to $\Delta S^{\neq}$, the lowest value of melamine (*ca.* -16 eu) is much smaller than the highest value of urea (*ca.* -38 eu). Besides, the rate constants obtained from Eq. (1′) and Eq. (2′) show slightly different values in the case of urea (*cf.* Table 1, Nos. 8 and 9), but there is almost

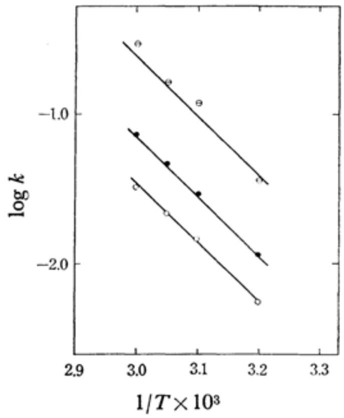


Fig. 4. Arrhenius plots for an aqueous solution of melamine.
—⊖—, —●—, —○—: Plots when melamine is considered to be mono-, tri- and hexa-functional respectively. (*cf.* Table 1, Nos. 1—3)

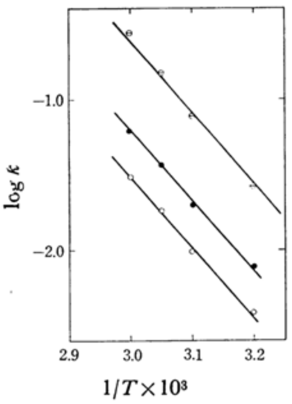


Fig. 5. Arrhenius plots for a DMSO-water solution of melamine.
—⊖—, —●—, —○—: Plots when melamine is considered to be mono-, tri-, and hexa-functional respectively. (*Cf.* Table 1, Nos. 4—6)

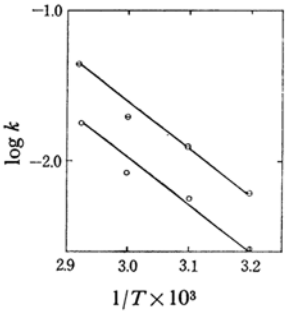


Fig. 6. Arrhenius plots for an aqueous solution of urea.
—⊖—, —○—: Plots when urea is considered to be mono- and di-functional respectively (*Cf.* Table 1, Nos. 7 and 9)

no difference between the thermodynamic quantities in this case. As the formation of methylol derivatives is small during the early stages of the reaction, the difference in the rate constants obtained from Eq. (1′) and from Eq. (2′) may be small. Therefore, the thermodynamic quantities are omitted in Table 2, in which urea is considered to be di-functional and in which the reverse reaction is neglected; this was also the case when melamine was tri-functional, though the data are here omitted. While the rate constants were calculated neglecting the reverse reaction in the mono-functional case, as has been stated above, the thermodynamic quantities may, analogously, not be affected by the reverse reaction.

Reaction Mechanism. Since the values of both $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ in urea have been confirmed to be considerably smaller than those of melamine

TABLE 2. THERMODYNAMIC QUANTITIES IN THE ACTIVATED STATE FOR THE HYDROXYMETHYLATION OF MELAMINE AND UREA AT 50°C

No.	Compound	Functionality	$\Delta S^{\ddagger}$ eu/mol	$\Delta H^{\ddagger}$ cal/mol	$\Delta F^{\ddagger}$ cal/mol	log PZ l/mol·sec	$K^{\ddagger}\times 10^{16}$ l/mol
1	Urea	mono	−38.6	11100	23600	4.4	0.3
2		di	−41.3	11100	24600	3.9	0.1
3	Melamine	mono	−11.9	18600	22400	10.2	2.4
4		tri	−14.4	18600	23200	9.7	0.7
5		hexa	−16.1	18600	23800	9.3	0.3
6	Melamine[a)]	mono	−9.5	19500	22500	10.8	1.9
7		tri	−12.3	19500	23400	10.2	0.5
8		hexa	−13.8	19500	23900	9.8	0.2

a) DMSO-water solution

TABLE 3. RATIO OF THE ENTROPY AND ENTHALPY OF ACTIVATION TERMS AT 50°C

No.[a)]	Functionality		$\exp\left(\frac{\Delta\Delta S^{\ddagger}_{\mathrm{I-II}}{}^{\mathrm{b)}}}{\boldsymbol{R}}\right)$	$\exp\left(\frac{\Delta\Delta H^{\ddagger}_{\mathrm{II-I}}{}^{\mathrm{c)}}}{\boldsymbol{R}T}\right)$
	Melamine	Urea		
1	mono	mono	6.3×10^{5}	0.9×10^{-5}
2	tri	di	7.2×10^{5}	0.9×10^{-5}
3	mono	—	3.0×10^{-1}	4.2
4	tri	—	3.1×10^{-1}	4.2
5	hexa	—	3.2×10^{-1}	4.2

a) Nos. 1 and 2 exhibit the comparison between an aqueous solution of melamine (I) and an aqueous solution of urea (II); Nos. 3, 4, and 5 exhibit the comparison between an aqueous solution of melamine (I) and a DMSO-water solution of melamine (II).

b) $\Delta\Delta S^{\ddagger}_{\mathrm{I-II}} = \Delta S^{\ddagger}_{\mathrm{I}} - \Delta S^{\ddagger}_{\mathrm{II}}$

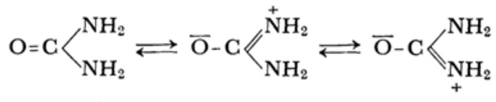
c) $\Delta\Delta H^{\ddagger}_{\mathrm{II-I}} = \Delta H^{\ddagger}_{\mathrm{II}} - \Delta H^{\ddagger}_{\mathrm{I}}$

regardless of the functionalities, a difference in mechanisms is suggested. The small value of $\Delta S^{\neq}$ in urea (*ca.* -40 eu) is particularly interesting, as such small values are rare; the frequency factor is *ca.* 10^{10}—10^{12} (l/mol·sec) in an ordinary second-order reaction, corresponding to a $\Delta S^{\neq}$ value of -13.0—-3.6 eu at 50°C.

According to Eyring,[9)] the rate constant may be represented as $k=\kappa \boldsymbol{RT}/\boldsymbol{Nh}\exp(\Delta S^{\neq}/R)\exp(-\Delta H^{\neq}/\boldsymbol{RT})$; hence, its ratio can be divided into the entropy and enthalpy of activation terms as $k_1/k_2=\kappa_1/\kappa_2 \exp(\Delta\Delta S^{\neq}{}_{\mathrm{I-II}}/\boldsymbol{R})\exp(\Delta\Delta H^{\neq}{}_{\mathrm{II-I}}/\boldsymbol{R}T)$, where κ, $\boldsymbol{h}$, $\boldsymbol{N}$, and $\boldsymbol{R}$ represent the transmission coefficient, Planck's constant, Avogadro's number, and the gas constant respectively. In order to study quantitatively the influence of the substrate and the solvent effect upon the rate constants' ratio, the $\Delta\Delta S^{\neq}$ and $\Delta\Delta H^{\neq}$ terms in the above equation may be used, using those in an aqueous solution of melamine as a standard. The results are given, in connection with the functionalities, in Table 3, where symbols with the I subscript refer to an aqueous solution of melamine, and those with the II subscript, to an aqueous solution of urea and a DMSO-water mixed solution of melamine. It was confirmed that no marked differences exist between the rate constant of melamine and that of urea (see Table 1), but that the $\Delta S^{\neq}$ and $\Delta H^{\neq}$ of urea are considerably smaller than the respective values of melamine. That is, when the rate constant is divided into $\Delta S^{\neq}$ and $\Delta H^{\neq}$ terms, prominent differences do exist between them; the $\Delta S^{\neq}$ and $\Delta H^{\neq}$ terms of melamine amount roughly to 10^5 times and 10^{-5} times those of urea respectively, regardless of the functionalities, as is shown in Table 3. From this table, a marked difference in the reaction mechanisms is clear; that is, the $\Delta S^{\neq}$ term of melamine becomes 6.3×10^5 times that of urea when both of the rate constants are computed as mono-functional, and 7.2×10^5 times, when melamine is tri- and urea is di-functional. These functionalities correspond to their number of amino-groups. On the contrary, the $\Delta H^{\neq}$ term of melamine becomes 0.9×10^{-5} times that of urea regardless of the functionalities.

To account for this thermodynamical evidence, the probable mechanism may be considered to be as follows:

Urea is regarded as a resonance hybrid, as is shown below[10)]:



$$O{=}C{<}^{NH_2}_{NH_2} \rightleftarrows \overline{O}{-}C{\ll}^{\overset{+}{N}H_2}_{NH_2} \rightleftarrows \overline{O}{-}C{\ll}^{NH_2}_{\underset{+}{N}H_2}$$

(I) (II) (III)

The electrophilic carbon center of formaldehyde must attack the nucleophilic nitrogen of urea to yield methylol urea, but the amino-group nitrogen must be positive in charge because of the resonance structures of II and III; this may be responsible for the markedly low value of the entropy of activation, since $\Delta S^{\neq}$ is the measurement of the randomness of a system and is a measure of the freedom from restraint of motion among the reactants,[*3] and since also the active centers of urea and formaldehyde are both positive, thus greatly reducing the degree of freedom during the formation of an activated complex. According to the collision theory, $\Delta S^{\neq}$ represents the effective collision number of molecules; hence, the repulsive force acting between the same charges may reduce the chance of collision. From the above considerations, the observed low value of entropy of activation may be accounted for.

The infrared spectra of urea are shown in Fig. 7, where it may be seen that $\nu_{C=O}$ appears at 1680 cm^{-1} and, hence, shifts toward a longer wavelength side than in the ordinary $\nu_{C=O}$,[11)] suggesting a diminution of its bond order by the resonance structures of II and III, and also suggesting an easy breakage of the N–H bond to form a nucleophilic conjugate base (see IV). From the above consideration, it may readily be guessed why the hydroxymethylation of urea shows a relatively low value of enthalpy of activation (*ca.* 11 kcal), even though it involves the breakage of the relatively strong N–H bond. Therefore, hydroxymethylation may occur for the most part

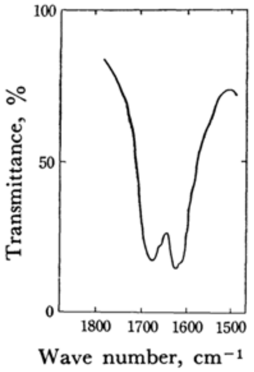
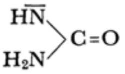


Fig. 7. Infrared spectra of urea (KBr disk method).



$$\begin{matrix}H\overline{N}\\ H_2N\end{matrix}{>}C{=}O$$

(IV)

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9) S. Glasstene and H. Eyring, "The Theory of Rate Process," McGraw-Hill Book Company, Inc., New York (1941), p. 199.

10) W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 1944 (1942).

11) N. J. Leonard, F. H. Owens, *ibid.*, **80**, 6039 (1958), *etc.*

[*3] For reactions in a solution, the entropy effects also include changes in the randomness of the solvent molecules, as new species requiring differing degrees of solvation are formed from the reactants.

with an electrophilic attack of formaldehyde on the conjugate base of urea (IV), because of the nucleophilic nature of nitrogen.

On the other hand, melamine, unlike urea, has sufficient basicity.[12-14] As its amino-group nitrogen is nucleophilic enough to suppress the breakage of the N–H bond, *i. e.,* to suppress the conjugate base formation, it seems probable that the values of $\Delta S^{\neq}$ and $\Delta H^{\neq}$ of melamine are, together, larger than those of urea. Hence, the reaction must proceed with an electrophilic attack of formaldehyde on nucleophilic melamine molecules. The most important point is that, even though melamine and urea are both amino resins, from the thermodynamic study it seems that the mechanisms of their formation may be different as a result of the different characteristics of their amino-group nitrogen.

The solvent effect of DMSO upon the hydroxymethylation of melamine is shown below. It is clear from Table 1 that the rate constants in an aqueous solution decrease as small amount of DMSO are added, but that this decrease becomes smaller with a rise in the temperature. As is shown in Table 3, Nos. 3—5, the decrease in rate is associated with an increase in the value of $\Delta H^{\neq}$, but is somewhat slightly opposed by an increase in the value of $\Delta S^{\neq}$ regardless of the functionalities. Though the details of the solvent effects are still unknown, some discussion is possible. DMSO is a polar solvent and dissolves a certain amount of melamine, suggesting a facility of solvation between these substances and, analogously, one between DMSO and formaldehyde. Such solvation also hinders the effective collision between the active centers of the reactants, decreases as the temperature is raised, and causes the orientation[15] of the reactants, from which effects the observed decrease in the rate, increase in the value of $\Delta H^{\neq}$, and increase in the value of $\Delta S^{\neq}$ are, respectively, accounted for. According to Cox *et al.,*[15,16] the greatest entropy decrease in the formation of the activated complex is observed for the least polar solvent; this can be explained by the solvation mechanism, which coincides with the present results. Recently the solvent effects of DMSO and other dipolar aprotic solvents on a certain substitution have been studied thermodynamically[17-19]; it has thus been confirmed that $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are notably affected by the addition of a small amount of DMSO. This fact causes us to attach more importance to the solvation than to other factors, *e. g.,* the dielectric constant[*4]; our results correspond almost exactly with those shown in the above literature.

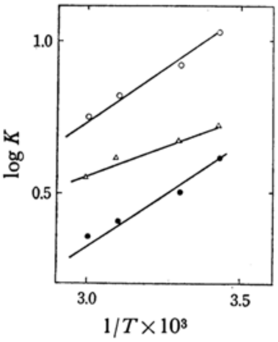

Fig. 8. Plots of $\log K$ *vs.* $1/T$.

—○—, —●—: Plots when melamine[a)] is considered to be tri- and hexa-functional respectively.

—△—: Plots when urea[b)] is considered to be di-functional.

a) Initial concn.: [melamine]=0.0583 (mol/*l*), [formaldehyde]=0.1460 (mol/*l*)
Here, y_e at 20°C, 40°C, 50°C, and 60°C are obtained as 0.086, 0.074, 0.062, 0.051 (mol/*l*) respectively.

b) Initial concn.: [urea]=0.250 (mol/*l*), [formaldehyde]=0.625 (mol/*l*)
Here, y_e at 20°C, 40°C, 50°C, and 60°C are obtained as 0.319, 0.305, 0.291, and 0.280 (mol/*l*) respectively.

TABLE 4. THERMODYNAMIC QUANTITIES IN THE EQUILIBRIUM STATE FOR THE HYDROXYMETHYLATION OF MELAMINE AND UREA AT 20°C

Compound	Functionality	ΔS, eu/mol	$-\Delta H$, cal/mol	ΔC_p, cal/mol·°K
Melamine	tri	−5.1	3200[a)]	−7.1
	hexa	−8.1	3200[a)]	−8.5
Urea	di	−3.7	2100[a)]	−13.1

a) Exothermic

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[*4] The solvent-polarity effect has been formulated by Ingold.[20] The theory is probably good for similar solvents, *i. e.,* DMSO and sulfolane, but not for dissimilar solvents, *i. e.,* water and DMSO.

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Thermodynamic Quantities between Initial and Final Systems. When melamine or urea is considered to be multi-functional and has a positive equilibrium constant, K, Eq. (3) can be used.[3,7,21] As the data in Fig. 8 show, the value of $(a-y_e)$ is slightly negative in the majority of cases, indicating that di-methylol derivatives could be formed in small quantities; hence, the equilibrium constant may be computed from Eq. (3), as it is considered to be multi-functional. (Melamine is tri- or hexa- and urea is di-.) If melamine and urea are considered to be tri- and di-functional respectively, and if these functionalities correspond to their number of amino-groups, the former shows a larger equilibrium constant than the latter (Fig. 8); this result, analogous to that of an activated complex, may be explained mainly in terms of the difference in the characteristics of the amino-group nitrogen. (Amino-group nitrogen in melamine is more negative than that in urea.) In these cases, we tested to see whether Ulich's first approximate equation[22] is applicable. The relation between log K and $1/T$ is shown in Fig. 8, from which the first equation may be said to be valid; next, from Ulich's second approximate equation,[22] the mean values of the changes of enthalpy (ΔH), entropy (ΔS), and molecular heat (ΔC_p) were computed. They are given in Table 4; in this case the influences of the functionalities are analogous to those of an activated complex.

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