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Melamine formaldehyde compounds. The active species in acid catalyzed reactions

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Abstract

Applying results from previously published kinetic investigations on the hydrolysis and condensation of methylol melamine compounds in acid solution a thorough analysis of the reaction mechanism is given. In the literature it has been discussed whether the acid catalysis takes place by protonation of the triazine ring, if it is a protonation of the methylol side groups or if both types of protonation are active.

In the present paper strong support is given to a kinetic model where the side group activated species are the reactive ones. Ring protonation, on the other side, leads to deactivation. Included are also computer simulations in Matlab of the decomposition of tri- and hexa-methylol melamine in dilute solution, assuming the hydrolysis to take place by series first order reactions. The computer simulations allow us to calculate the relative composition of the reaction mixture as a function of time and to see the effect of changes in the experimental rate constant as the reaction proceeds.

Keywords: Melamine-formaldehyde compounds; Kinetics; Mechanism

1. Introduction

Earlier studies on the kinetics and mechanism of melamine formaldehyde addition, decomposition and condensation have revealed important details of these systems.

The basic capacity of the triazine ring of melamine, which changes with the degree of substitution of the amino nitrogen atoms, leads to facinating kinetics. In some cases the reaction rate passes through maximum points as a function of pH, while in other cases levelling out effects may be seen.

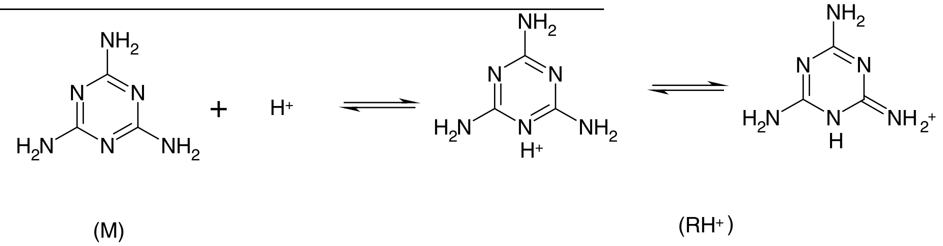
It is the purpose of the present paper to give additional support to a specific reaction mechanism by fine-tuning kinetic data of previously published work both from own laboratory and others.

2. Discussion

2.1. Theory on the decomposition of methylol melamines

The main point in the discussion is the site of attac of acidic catalysts in the decomposition and condensation of methylol melamine model substances and how the basic properties of the triazine ring influences the reaction rate.

As first described by Dixon et al. [1] the basic properties of melamine may be ascribed to the ability to add a proton to a N-atom in the triazine ring.



The acid dissociation constant for a melamine compound protonated by ring addition is defined as:

$$K_{\mathrm{RH}}^{+} = \frac{[\mathrm{M}][\mathrm{H}^{+}]}{[\mathrm{RH}^{+}]} \qquad (1)$$

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$$(1)\quad >\text{N-CH}_2\text{OH} + \text{HA} \rightleftharpoons >\text{NH}^+\text{CH}_2\text{OH} + \text{A}^-$$

$$(2)\quad >\text{NH}^+\text{CH}_2\text{OH} + \text{A}^- \rightleftharpoons >\text{NH} + \text{CH}_2\text{O} + \text{HA}$$

Scheme 1.

where M is a neutral melamine compound (e.g. methylol melamine) and RH^+ is the corresponding ring protonated melamine compound. K_{RH^+} increases with increasing degree of substitution of the six amino hydrogens on the triazine ring.

We have earlier assumed that the acid catalyzed decomposition of methylol melamines proceed by a mechanism similar to that given for methylol ureas [2] (Scheme 1).

The decomposition follows general acid catalysis with step (2) as the rate determining step.

The rate of decomposition of the methylol compound was defined as:

$$r = -\frac{d[F_M]}{dt} = k[F_M] \tag{2}$$

where $[F_M]$ is the total concentration of methylol groups and k is the experimental first order rate constant. In a buffer solution containing the acid HA and its conjugate base A^-, the catalytically active species are H^+, H_2O and HA.

According to the scheme above, the rate of decomposition is given by:

$$-\frac{d[F_M]}{dt} = [>NH^+CH_2OH]\left(k_2'[H_2O] + k_2''[OH^-] + k_2'''[A^-]\right) \tag{3}$$

where k_2', k_2'' and k_2''' are the specific catalytic constants in step *(2)* for the conjugate bases of H^+ (H_2O), H_2O (OH^-) and HA (A^-), respectively.

The activation of a methylol melamine compound is assumed to take place by addition of a proton to a N-atom in a side group to which the methylol group is attached ($>NH^+CH_2OH=SH^+$). Protonation of a N-atom in the triazine ring represents a deactivation which will prevent the formation of SH^+ unless at very high acidities. On the above assumptions we have deduced an expression for the experimental first order rate constant [2].

$$k = \frac{K_{RH^+}}{K_{SH^+}\left(K_{RH^+} + H^+\right)}\left(k_2'[H^+][H_2O] + k_2''K_w + k_2'''K_{HA}[HA]\right) \tag{4}$$

where K_{SH^+} is the acid dissociation constant of SH^+, K_w the ionization product of water and K_{HA} is the dissociation constant of the acid HA.

The deduction of Eq. (4) given earlier by Berge et al. [2] may have seemed a little simplified as the total concentration of methylol groups was given as:

$$[F_M] = [M] + [RH^+] + [SH^+] \tag{5}$$

Because [M] and $[RH^+]$ in the definition of K_{RH^+} represent the concentration of neutral and protonated methylol compounds, respectively, Eq. (5) would only be correct for a monomethylol compound. We may, therefore, redefine the expression for $[F_M]$ taking into account the degree of substitution x.

$$[F_M] = x([RH^+] + [M] + [SH^+]) \approx x([RH^+] + [M]), \tag{6}$$

since $[SH^+]$ is very small.

Assuming that the chance of getting a proton added to a side group of a methylol melamine compound is proportional to the number of methylol groups of that compound, we may now define:

$$K_{SH^+} = \frac{x[M][H^+]}{[SH^+]} \tag{7}$$

Combining Eqs. (1), (6) and (7) we then get:

$$[SH^+] = [F_M]\frac{[H^+]K_{RH^+}}{K_{SH^+}\left([H^+] + K_{RH^+}\right)} \tag{8}$$

The expression for $[SH^+]$ is similar to that given in earlier papers, whereas K_{SH^+} has been redefined according to Eq. (7). As will be discussed, the value of K_{SH^+} may be different with primary and secondary methylol groups.

Applying Eq. (4) in a case where the buffer acid HA is the dominating catalytic species the equation for the experimental rate constant reduces to:

$$k_{exp} = \frac{k_2'''K_{HA}[HA]K_{RH^+}}{K_{SH^+}\left([H^+] + K_{RH^+}\right)} \tag{9}$$

Fig. 1 shows the decomposition of tri-methylol melamine, TMM, in acetate buffer at pH 4.6, and in phosphate buffer at pH 6.5 where the buffer acids are the dominating catalytic species. A first order plot is made where η is the degree of conversion of methylol groups. Theoretically, we may consider two cases, assuming that either RH^+ or SH^+ is the reacting species. Then the rate of decomposition may be given as:

$$r = x[RH^+]\sum k_i\left[A_i^-\right] \quad \text{or } r = [SH^+]\sum k_i'\left[A_i^-\right] \tag{10}$$

where x as before is the degree of methylol substitution.

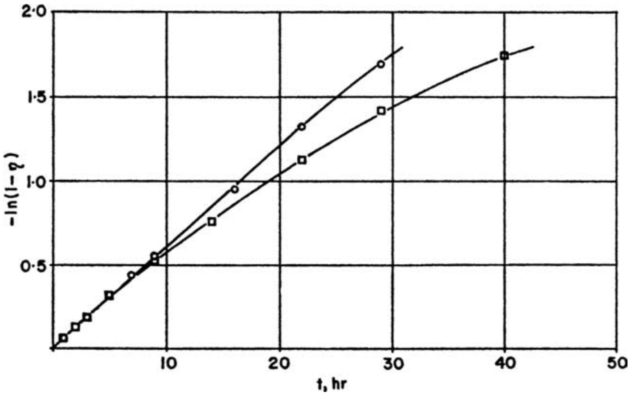


Fig. 1. The decomposition of TMM in buffer solutions. (○) phosphate buffer, $[HPO_4^{2-}] = 0.08$ and $[H_2PO_4^-] = 0.10$ mol/l. (□) acetate buffer, $[AcO^-] = 0.1$ and $[AcOH] = 0.1$ mol l^{-1}. Temperature. 25 °C [Reprinted with permission from Ref. [2] copyright Elsevier].

Also in the case of ring protonation the decomposition is assumed to take place by a mechanism similar to Scheme 1.

Above we have derived an expression for $[SH^+]$ and the corresponding expression for k_{exp}.

Applying Eqs. (1) and (6) we may also calculate an expression for $[RH^+]$:

$$[RH^+] = \frac{[F_M]}{x} \frac{[H^+]}{([H^+] + K_{RH^+})} \qquad \text{giving :}$$

$$k_{exp} = \frac{k_2^{iv} K_{HA}[HA]}{([H^+] + K_{RH^+})} \tag{11}$$

Here, k_2^{iv} is the specific catalytic constant of the conjugate base of the acid HA.

During decomposition of the methylol compound the value of K_{RH^+} will decrease as the amino side groups on the triazine ring become less substituted. Assume an example where K_{RH^+} has changed from $10^{-4.0}$ to $10^{-4.6}$ mol l^{-1} during decomposition of the methylol compound.

Then, in acetate buffer at pH 4.6 with SH^+ as the reactive species, the experimental rate constant k_{exp} will according to Eq. (9) change from:

$$k_{exp} = 0.8k_2''' \frac{K_{HA}[HA]}{K_{SH^+}} \rightarrow k_{exp} = 0.5k_2''' \frac{K_{HA}[HA]}{K_{SH^+}} \tag{12}$$

At the same conditions, assuming RH^+ to be the active species, the change in k_{exp} according to Eq. (11) will be:

$$\begin{aligned} k_{exp} &= 0.8 \times 10^4 k_2^{iv} K_{HA}[HA] \rightarrow \\ k_{exp} &= 2 \times 10^4 k_2^{iv} K_{HA}[HA] \end{aligned} \tag{13}$$

The experimental results shown in Fig. 1 are in accordance with a mechanism where SH^+ is the reactive species. The experimental rate constant will decrease with conversion as predicted by Eq. (12). If RH^+ had been the reactive species one would, according to Eq. (13), expect the experimental rate constant to increase with conversion.

Qualitatively, it is easy to understand that the relative amount of ring protonated compound becomes larger when the basicity of the melamine compound increases, i.e. K_{RH^+} decreases.

From Fig. 1, we can also see that in phosphate buffer at pH 6.5 the experimental rate constant, taken as the slope of the rate curve, remains constant up to high conversion. This is to be expected according to Eq. (9) when SH^+ is the reactive species and $K_{RH^+} \gg [H^+]$. Assuming RH^+ to be the reactive species, k_{exp} should according to Eq. (11) increase with conversion due to a decrease in the value of K_{RH^+} (the overlap from start of the two decomposition curves in Fig. 1 is a coincidence).

The decomposition of HMM in moderate and strong acid solution is interesting for several reasons. The lack of hydrogen atoms at the nitrogen atoms in the side chains makes this substance considerably less basic than methylol compounds with lower degree of substitution.

Thus, HMM has been estimated to have a value of K_{RH^+} about 10^{-1} mol l^{-1}, which may even be higher [2]. In the case of HMM with all the amino hydrogens substituted a ring protonation will not be in conjugation with a proton in a side group, and it is also for this reason more likely that the activation takes place by addition of a proton directly to a side group on a neutral methylol compound.

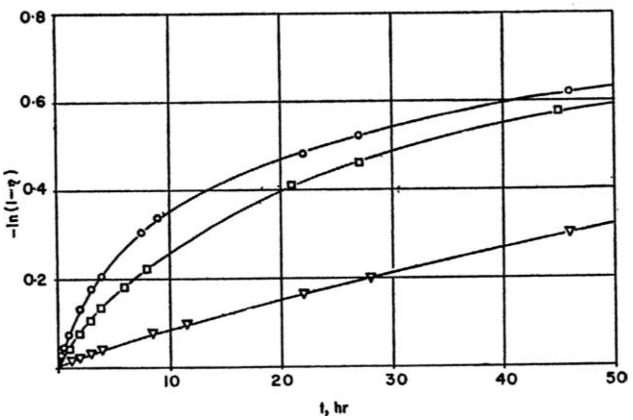


Fig. 2. The decomposition of HMM in moderate acid solutions. (▽) = 10^{-3}, (□) = 5×10^{-3} and (○) = 10^{-2} mol l^{-1} HNO_3 (pH values: 3.1, 2.4 and 2.1, respectively). Ionic strength 0.2 mol l^{-1}. Temperature. 25 °C [Reprinted with permission from Ref. [2], Copyright Elsevier].

The decomposition of HMM in acid solutions is shown in Figs. 2 and 3. It is seen that the initial decomposition rate, until one methylol group has been set free, i.e. $\eta = 1/6$ or $-\ln(1-\eta) = 0.18$, is very much faster than the following decomposition. This is most likely due to the high value of K_{RH^+} for HMM, leading to a low degree of deactivation by ring protonation.

When one methylol group is removed a considerable decrease in the value of K_{RH^+} takes place. The kinetic result is in accordance with the assumption that SH^+ is the reactive species. If RH^+ had been the reactive species an opposite effect would have been expected, that is the lowest rate for the least basic methylol compound. For the sake of order it may be added that in very strong acid solution addition of a proton to the side group of an already ring protonated substance is also a possibility. A more detailed discussion is given by Berge et al. [2].

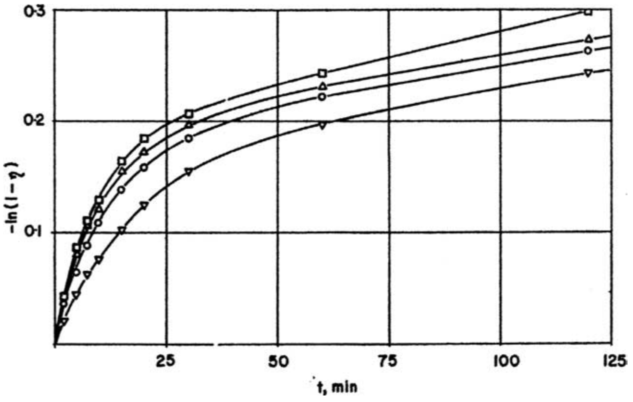


Fig. 3. The initial decomposition of HMM in strong acid solutions. (△) = 0.1, (○) = 0.25, (▽) = 0.5 and (□) = 1.0 mol l^{-1} HNO_3. Ionic strength 2.0 mol l^{-1}. Temperature. 25 °C [Reprinted with permission from Ref. [2], copyright Elsevier].

Looking at Eq. (9) for the experimental rate constant in a buffer system one should be aware of the fact that the conjugate acid of the methylol melamine compound (RH^+) may act as a general acid catalyst in the decomposition reaction. This has been shown by Sato and Maruyama [3] who studied the hydrolysis of di-methylol melamine (DMM) in acid solutions of DMSO/water at 30 °C without added buffers. Catalysis by the conjugate acid of DMM led to a rate profile showing a maximum at a pH value $\sim pK_{RH^+}$. In this case when $[HA]=[RH^+]$ and $K_{HA}=K_{RH^+}$, we may introduce $[RH^+]$ from Eq. (11) into Eq. (9) getting:

$$k_{exp}=\frac{[F_M]}{x}\frac{k_2''''(K_{RH^+})^2[H^+]}{K_{SH^+}\left([H^+]+K_{RH^+}\right)^2} \tag{14}$$

Here the first order rate constant per definition will be dependent upon the concentration of the methylol compound. Eq. (14) shows the following:

$$\text{when } [H^+]\ll K_{RH^+},\quad k_{exp}=\frac{[F_M]}{x}\frac{k_2''''[H^+]}{K_{SH^+}} \tag{15}$$

k_{exp} increases linearly with $[H^+]$

$$\text{when } [H^+]\gg K_{RH^+},\quad k_{exp}=\frac{[F_M]}{x}\frac{k_2''''\left(K_{RH^+}\right)^2}{K_{SH^+}[H^+]} \tag{16}$$

k_{exp} decreases linearly with $[H^+]$

By derivation of Eq. (14) with respect to $[H^+]$ we find that k_{exp} have a maximum value when $[H^+]=K_{RH^+}$.

Our theoretical treatment is in accordance with the experimental results of Sato and Maruyama [3] who give a far more complicated theoretical discussion.

At sufficiently high acidities, pH 1–2, it is observed [2,3] that the experimental rate constant again starts to increase approximately proportionally to $[H^+]$. This increase may be explained assuming that under these conditions even the RH^+ compound could be activated by proton addition to a methylol side group.

The specific catalytic constant for RH^+ in the hydrolysis of DMM at 30 °C in DMSO/water is reported to be $1.2\times 10^{-1}\,l\,mol^{-1}\,min^{-1}$ [3]. This value is in reasonable accordance with the catalytic constant for acetic acid, being $1.1\times 10^{-2}\,l\,mol^{-1}\,min^{-1}$, in the decomposition of TMM at 25 °C in water [2], RH^+ being a stronger acid than acetic acid.

2.2. *Computer simulation of the decomposition of methylol melamines*

The acid hydrolysis of the methylol melamines in dilute solution is assumed to take place by series first-order irreversible reactions, which in the case of TMM may be sketched as (Scheme 2).

$$A_3 \xrightarrow{k_3} A_2+F$$

$$A_2 \xrightarrow{k_2} A_1+F$$

$$A_1 \xrightarrow{k_1} A_0+F$$

Scheme 2.

$$\text{TMM:}\quad \frac{d[F]}{dt}=k[F_{3M}]=k\cdot 3[A_3]=k_3[A_3]\quad \text{giving}\ k_3=3k$$

$$\text{DMM:}\quad \frac{d[F]}{dt}=k[F_{2M}]=k\cdot 2[A_2]=k_2[A_2]\quad \text{giving}\ k_2=2k$$

$$\text{MMM:}\quad \frac{d[F]}{dt}=k[F_{1M}]=k[A_1]=k_1[A_1]\quad \text{giving}\ k_1=k$$

Scheme 3.

Where A_3, A_2, A_1 and A_0 are tri-methylol (TMM), di-methylol (DMM), mono-methylol (MMM) and unsubstituted melamine, respectively, and F is free formaldehyde.

Since, TMM mainly contains primary methylol groups, it is assumed that the degree of substitution does not affect the value of either K_{SH^+} or the rate constant for the decomposition of the activated species.

We may introduce the experimental rate constant k in the various steps: (Scheme 3).

Where $[F_{nM}]$ is the total concentration of methylol groups.

Assuming SH^+ to be the active species in the acid catalyzed decomposition of methylol melamines we may, according to Eqs. (9), when $[H^+]\ll K_{RH^+}$ expect that the experimental rate constant k remains constant to high conversion.

In a concrete case we may apply the experimental rate constant for TMM in phosphate buffer which taken from Fig. 1, is $k\approx 6\times 10^{-2}\,h^{-1}$. The values of k_3, k_2 and k_1 were then calculated and applied in a Matlab computer simulation modelling of Scheme 2. Fig. 4 shows the relative composition of the reaction mixture as a function of time starting with a normalized concentration of TMM = 1. Fig. 5 shows a first order plot giving the experimental rate constant k as the slope of the curve. The rate constant remains constant to high conversion in accordance with the experimental results.

We do not have experimental results with HMM in phosphate buffer at conditions where $[H^+]\ll K_{RH^+}$, but we can see from Fig. 6 in acetate buffer that HMM from start decomposes a little slower than TMM.

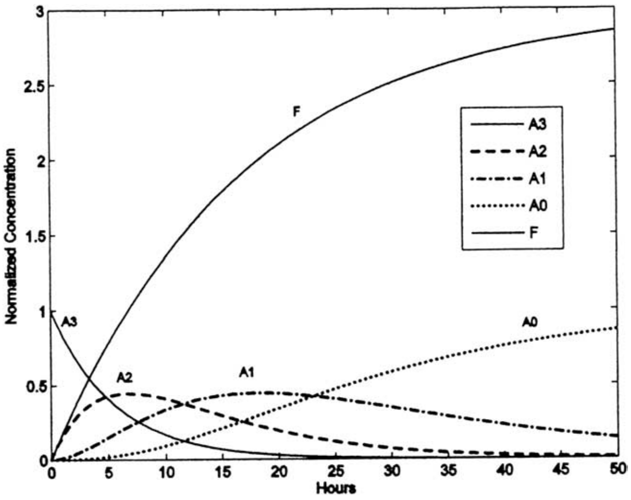


Fig. 4. Matlab simulation of the decomposition of TMM showing the relative composition of the reaction mixture as a function of time (case taken from phosphate buffer run in Fig. 1. where $[H^+]\ll K_{RH^+}$).

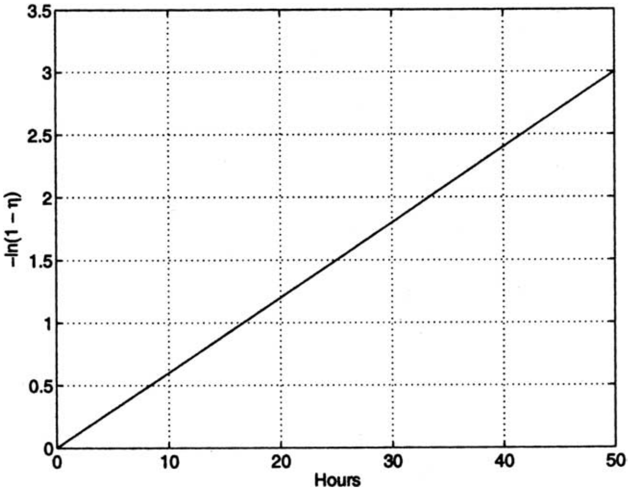


Fig. 5. Matlab simulation of the decomposition of TMM showing a first order plot where η is the degree of conversion of methylol groups (case taken from phosphate buffer run in Fig. 1 where $[H^+] \ll K_{RH^+}$).

Comparing initial decomposition rates in acetate buffer, we find experimental rate constants of 6×10^{-2} and $4\times10^{-2}\ h^{-1}$ for, respectively, TMM and HMM. The difference in initial decomposition rate, indicating the difference in reactivity between primary and secondary methylol groups, may even be a little higher as TMM is somewhat deactivated by ring protonation already from start, while initially, this is not the case for HMM. From Eq. (9) we may calculate that with TMM the deactivation at start reduces k with a factor of 0.8. Correcting for this, the decomposition rate of primary methylol groups is likely to be approximately twice as high as that of secondary groups, and we stipulate the initial rate constant for decomposition of HMM in phosphate buffer to be $3\times10^{-2}\ h^{-1}$. The reason for the difference between TMM and HMM may be due to internal hydrogen bonding between a protonated methylol group and a neighbouring secondary methylol group. It is not unlikely that both K^{+}_{SH} as well as the rate constant for decomposition of the activated species have changed by going from primary to secondary methylol groups. Possibly, the formation of SH^+ species may be somewhat more favourable in the case of secondary methylol groups while their reactivity become a little decreased.

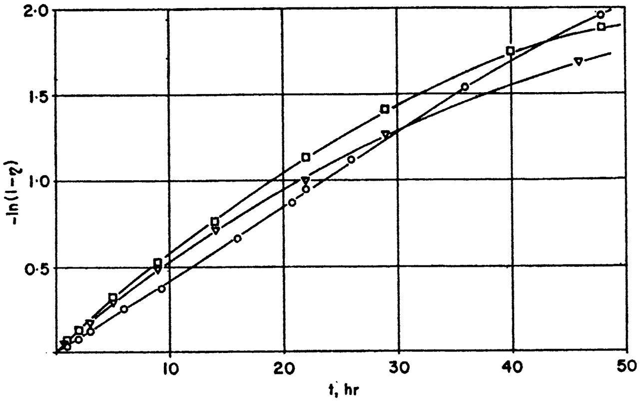
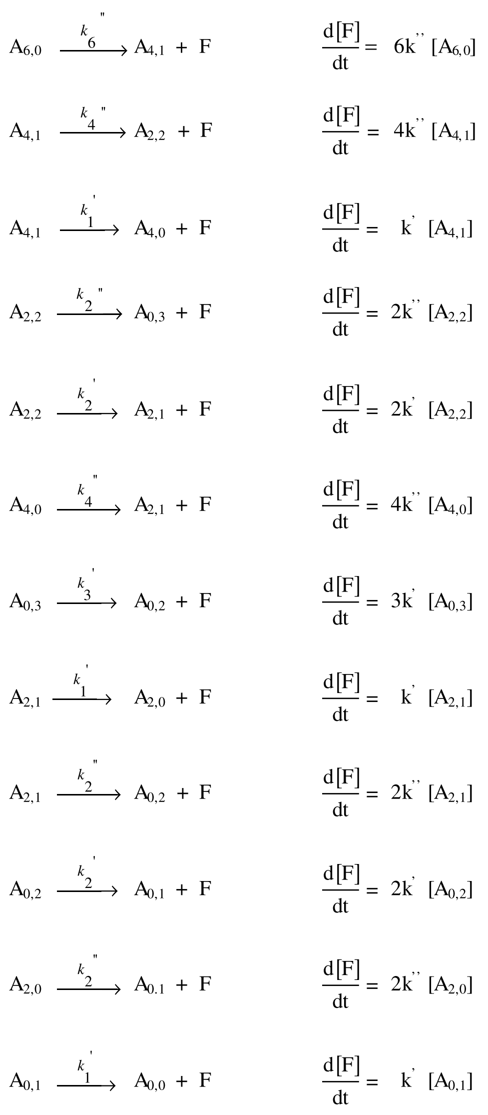


Fig. 6. The decomposition of TMM and HMM in acetic acid/acetate buffer with $AcO^- = AcOH = 0.1\ mol\ l^{-1}$. (○) HMM and (▽) TMM with 10% DMSO. (□) TMM without addition of DMSO. Temperature. 25 °C [Reprinted with permission from Ref. [2], Copyright Elsevier].

In order to make a model simulation of HMM in a similar way as that given for TMM, we have to take into consideration that primary methylol groups decompose twice as fast as secondary methylol groups. The various steps included are shown in Scheme 4 below.

In the scheme $A_{s,p}$ symbolize the type of melamine compound, where s is the number of secondary methylol groups and p is the number of primary methylol groups. Thus, $A_{6,0}$ means HMM, $A_{0,1}$ means MMM, $A_{0,0}$ means unsubstituted melamine and so on.

The experimental rate constants for the decomposition of primary and secondary methylol groups are, respectively, k' and k''. Referring to a concrete case in phosphate buffer at pH 6.5 the rate constants as estimated above are $k' = 6\times10^{-2}\ h^{-1}$ and $k'' = 3\times10^{-2}\ h^{-1}$ (Scheme 4).



$$A_{6,0} \xrightarrow{k''_6} A_{4,1} + F \qquad \frac{d[F]}{dt} = 6k''[A_{6,0}]$$

$$A_{4,1} \xrightarrow{k''_4} A_{2,2} + F \qquad \frac{d[F]}{dt} = 4k''[A_{4,1}]$$

$$A_{4,1} \xrightarrow{k'_1} A_{4,0} + F \qquad \frac{d[F]}{dt} = k'[A_{4,1}]$$

$$A_{2,2} \xrightarrow{k''_2} A_{0,3} + F \qquad \frac{d[F]}{dt} = 2k''[A_{2,2}]$$

$$A_{2,2} \xrightarrow{k'_2} A_{2,1} + F \qquad \frac{d[F]}{dt} = 2k'[A_{2,2}]$$

$$A_{4,0} \xrightarrow{k''_4} A_{2,1} + F \qquad \frac{d[F]}{dt} = 4k''[A_{4,0}]$$

$$A_{0,3} \xrightarrow{k'_3} A_{0,2} + F \qquad \frac{d[F]}{dt} = 3k'[A_{0,3}]$$

$$A_{2,1} \xrightarrow{k'_1} A_{2,0} + F \qquad \frac{d[F]}{dt} = k'[A_{2,1}]$$

$$A_{2,1} \xrightarrow{k''_2} A_{0,2} + F \qquad \frac{d[F]}{dt} = 2k''[A_{2,1}]$$

$$A_{0,2} \xrightarrow{k'_2} A_{0,1} + F \qquad \frac{d[F]}{dt} = 2k'[A_{0,2}]$$

$$A_{2,0} \xrightarrow{k''_2} A_{0.1} + F \qquad \frac{d[F]}{dt} = 2k''[A_{2,0}]$$

$$A_{0,1} \xrightarrow{k'_1} A_{0,0} + F \qquad \frac{d[F]}{dt} = k'[A_{0,1}]$$

Scheme 4.

The results of the Matlab computer simulations of the decomposition of HMM, applying Scheme 4, are shown in Figs. 7(a) and (b) and 8.

Fig. 7(a) and (b), shows the relative composition of the reaction mixture as a function of time starting with a normalized concentration of HMM = 1. The computed curves are presented in two separate figures (a) and (b) in order to make it easier to read.

Fig. 8 shows a first order plot giving the experimental rate constant *k* as the slope to the curve. The rate constant steadily increases with time and approaches the value for the decomposition of primary methylol groups at high conversion.

Looking at the results with HMM in acetate buffer, shown in Fig. 6, we can see that a plot of $-\ln(1-\eta)$ gives a straight line up to high conversion. Here two counteracting effects are operating which may outweigh each other. The decreasing value of K_{RH^+} during decomposition is expected to give a decrease in the experimental rate constant *k*, but this may be compensated by an increase in *k* due to a change from secondary to primary methylol groups.

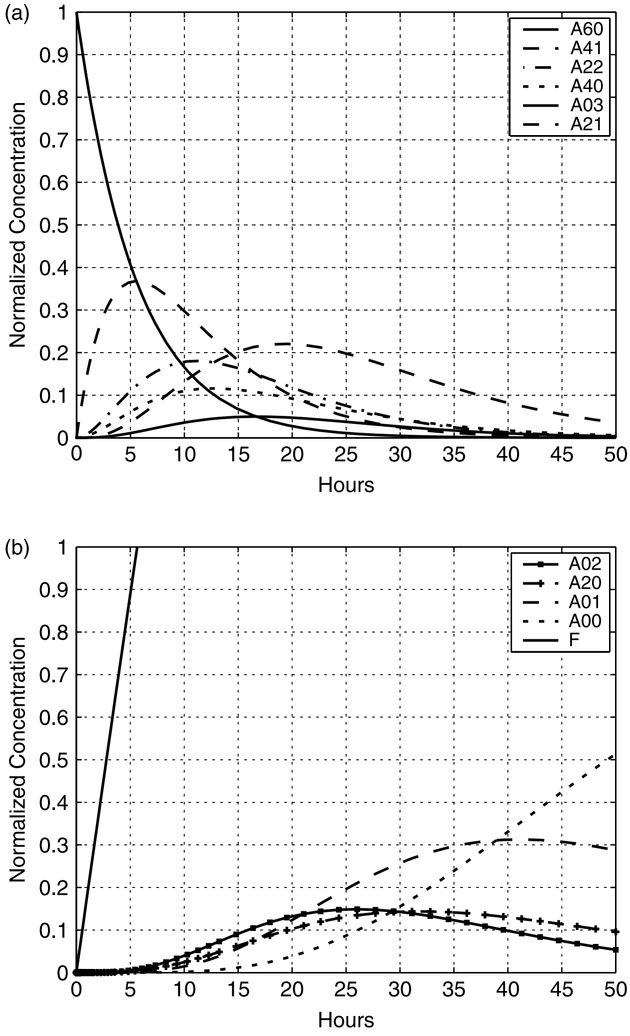


Fig. 7. (a) and (b) Matlab simulation of the decomposition of HMM showing the relative composition of the reaction mixture as a function of time (conditions adjusted to the case with TMM in phosphate buffer, Figs. 4 and 5).

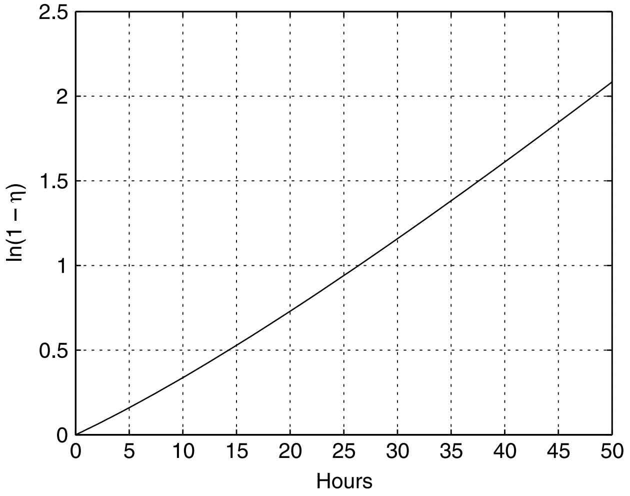


Fig. 8. Matlab simulation of the decomposition of HMM showing a first order plot where η is the degree of conversion of methylol groups (conditions adjusted to the case with phosphate buffer applied in Figs. 4 and 5).

2.3. Theory on the condensation of methylol melamines

The condensation of methylol melamines in acid solution with the formation of methylene bonds has been a subject of great interest and many investigations have been presented in the literature [4–8]. Related studies include the application of melamine compounds as crosslinkers in the curing of coating compositions [9,10].

It is generally accepted that the methylene bond formation implies specific acid catalysis although it has been claimed that the bimolecular condensation and also the curing of functional alkydes with melamine-formaldehyde compounds takes place by a conventional S_N2 mechanism [11]. This suggestion, which may be a question of semantics, seems rather unlikely and is contradicted by the general and fundamental knowledge on the subject acid–base catalysis described in the literature [12–14]. In catalysis by bases, however, there may often be an ambiguity between general base catalysis and nucleophilic catalysis [14]. Beyond question the self condensation of melamine formaldehyde compounds and also their curing with alkydes take place by a bimolecular reaction in the rate determining step, while the hydrolysis of methylol- and methoxymetyl melamines in dilute solution show first order kinetics.

We have clearly shown that the reaction between TMM and excess melamine leading to methylene bond formation takes place by a specific acid catalyzed bimolecular reaction [15]. The initial second order rate constant passes through a maximum as a function of $[H^+]$. The position of the maximum may be calculated from our model assuming that the activation starts with proton addition to methylol group on neutral melamine rings. It is, therefore, surprising to see that our previous presentations have been erroneously interpreted in the way that we should have given a S_N1 mechanism for the condensation of methylol melamines [11,16].

The most comprehensive investigations on the acid catalyzed condensation of methylol melamine compounds

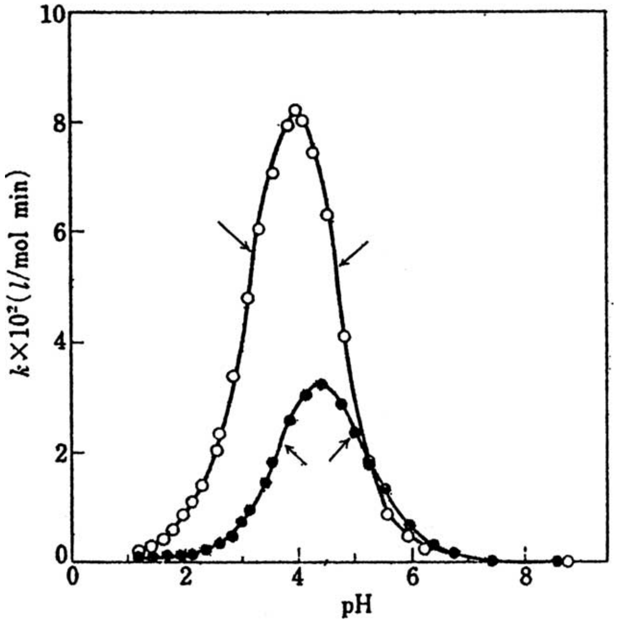


Fig. 9. Observed curve (k vs. pH) at 35 °C: (→), inflection points; (●), for M1.97Fo; for M2.95F [Reprinted with permission from Ref. [7], copyright Japan Chemical Society].

have been done by Sato and co-workers [5–7]. Studying the self condensation of trimethylol melamine (M2.95F) and dimethylol melamine (1.95F) they obtained the profiles shown in Fig. 9 of the initial overall rate constant k vs pH, defined by $R_0 = k[\mathrm{M}_n\mathrm{F}]^2$, where R_0 is the initial rate of formation of methylene linkages, and $[\mathrm{M}_n\mathrm{F}]$ is the concentration of the methylol compound. Assuming several different theoretical possibilities for the condensation reaction it was concluded that in the pH range 2–7 the experimental results were best fitted to a rate expression based on:

$$\begin{aligned} R_0 &= k_2[\mathrm{MCH_2OH}][\mathrm{HM^+CH_2OH}] \\ &\quad + k_3[\mathrm{MCH_2OH}]\left[\mathrm{MCH_2^+}\right] \\ &= k_2'[\mathrm{MCH_2OH}][\mathrm{HM^+CH_2OH}] \end{aligned} \tag{17}$$

where $k_2' = k_2 + k_3(K_2/K_1)$, K_1 and K_2 being equilibrium constants defined by: Scheme 5, i.e. the methylol melamine molecule $\mathrm{MCH_2OH}$ is in equilibrium with the conjugate acid $\mathrm{HM^+CH_2OH}$ (ring protonation) and the carbonium ion $\mathrm{MCH_2^+}$ (side group activation). Note the direction of the equilibrium constants K_1 and K_2.

By a mass balance and application of the equilibrium constants K_1 and K_2 the second order experimental rate constant would become:

$$k = \frac{k_2' K_1[\mathrm{H^+}]}{(1 + K_1[\mathrm{H^+}])^2} \tag{18}$$

$$\mathrm{MCH_2OH} + \mathrm{H^+} \xrightleftharpoons{K_1} \mathrm{HM^+CH_2OH}$$

$$\mathrm{MCH_2OH} + \mathrm{H^+} \xrightleftharpoons{K_2} \mathrm{MCH_2^+} + \mathrm{H_2O}$$

Scheme 5.

Eq. (18) has a maximum value when $[\mathrm{H^+}] = K_1^{-1}$. If we assume the value of k_2' to be the same for (M1.95F) and (M2.95F) $k_{\max}$ would be $(1/4)k_2'$ in any case.

Experimentally, it was found that the rate constant k for the self condensation of TMM is about three times higher than that of DMM at their respective maximum points as shown in Fig. 9. This might be explained by a difference in the value of k_2', but this is rather unlikely.

It seems more probable that one by introduction of k_2' has lost some important details of the condensation reaction. If it is assumed that the ring protonation leads to unreactive species while side group protonation gives the reactive species, the rate in the pH range 2–7 would be given by:

$$R_0 = k[\mathrm{M}_n\mathrm{F}]^2 = k_3[\mathrm{MCH_2OH}][\mathrm{MCH_2^+}] \tag{19}$$

Here, the initial concentrations are:

$$[\mathrm{MCH_2OH}] = \frac{[\mathrm{M}_n\mathrm{F}]_0}{1 + (K_1 + K_2)[\mathrm{H^+}]} = \frac{[\mathrm{M}_n\mathrm{F}]_0}{1 + K_1[\mathrm{H^+}]} \tag{20}$$

$(K_1 \gg K_2)$

$$\left[\mathrm{MCH_2^+}\right] = \frac{[\mathrm{M}_n\mathrm{F}]_0 K_2[\mathrm{H^+}]}{1 + (K_1 + K_2)[\mathrm{H^+}]} = \frac{[\mathrm{M}_n\mathrm{F}]_0 K_2[\mathrm{H^+}]}{1 + K_1[\mathrm{H^+}]} \tag{21}$$

Insertion of Eqs. (20) and (21) in the rate expression (19) gives:

$$k = \frac{k_3 K_2[\mathrm{H^+}]}{(1 + K_1[\mathrm{H^+}])^2} \tag{22}$$

Applying Eq. (22) we may now calculate the rate constant k at the maximum points for DMM and TMM. K_1 values may be taken from the position of the maximum points on the pH scale where as said $[\mathrm{H^+}] = K_1^{-1}$, giving $K_{1(\mathrm{TMM})} = 10^{4.0}$ and $K_{1(\mathrm{DMM})} = 10^{4.5}$.

These values are in good agreement with literature values determined by other methods [1].

With DMM having a max point at pH 4.5 we get:

$$k = k_3 K_2 \frac{10^{-4.5}}{(1 + 10^{+4.5} \times 10^{-4.5})^2} = \frac{k_3 K_2}{4} \times 10^{-4.5} \tag{23}$$

With TMM having a maximum point at pH 4.0 we get:

$$k = k_3 K_2 \frac{10^{-4.0}}{\left(1 + 10^{+4.0} \times 10^{-4.0}\right)^2} = \frac{k_3 K_2}{4} \times 10^{-4.0} \tag{24}$$

From Eqs. (23) and (24) we finally get:

$$\frac{k_{\mathrm{TMM}}}{k_{\mathrm{DMM}}} = \frac{10^{-4.0}}{10^{-4.5}} = 3.2$$

The theoretical treatment is in accordance with the experimental result.

3. Conclusion

Experimental results given in the literature on the hydrolysis of methylol melamines as well as condensation of methylol melamines in acid solution may be explained by a model assuming that side group activated species are the reactive ones. Ring protonation on the other hand leads to deactivation.

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