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Author(s)	MORINO, Shigeru; 森野, 滋; SAKAI, Makoto et al.
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Synthesis of N,N'-Dimethylurea from Monomethylamine and Carbon Dioxide

Shigeru MORINO, Makoto SAKAI*, Isamu KASHIKI*,
Akira SUZUKI* and Masayuki MIKI*

Abstract

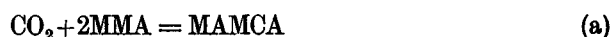
The synthesis of N,N'-dimethylurea from monomethylamine and carbon dioxide is compared with the past works on the synthesis of urea from ammonia and carbon dioxide. They are quite similar, except the former is more favorable from the chemical equilibrium viewpoint but kinetically slower than the latter. Based on the similarity, some general treatments of the multi-component-multiphase reaction and a speculation for the reaction mechanism applicable also for the urea synthesis is made.

Introduction

Organic cationic polymers are known to be effective floccurants for the spent effluent water from fish processing plants. We have attempted to synthesize one from dimethylurea (DMU) and formaldehyde by polycondensation. Unfortunately, the products were in large part, of a cyclic nature, for example, tetramethyldimethylenediureid, $\begin{matrix} \text{CH}_3\text{-N-CH}_2\text{-N-CH}_3 \\ | \qquad \qquad | \\ \text{CH}_3\text{-N-CH}_2\text{-N-CH}_3 \end{matrix}$, and no significant amount of linear products were obtained. We have now synthesized DMU from monomethylamine (MMA) and carbon dioxide, which is of interest in connection with urea (U) synthesis, which, in turn, provides another method for synthesizing soluble floccurant polymer.

Since Bassarov's discovery of U synthesis reaction in 1870, numerous work has been published, of which Matignon et al.¹⁾, Krase et al.²⁾, Clark et al.³⁾, Frèjacques⁴⁾, Tokuoka⁵⁾, Kitawaki et al.⁶⁾, Sakai et al.⁷⁾, Kawasumi⁸⁾ and Otsuka et al.⁹⁾ are of particular interest from the chemical viewpoint. However, no papers, to our knowledge, except a patent granted to B.A.S.F.¹⁰⁾, have ever been presented on the synthesis of DMU, a close homologue of U.

The reactions relevant to the DMU synthesis are:



where MAMCA is methylammonium methylcarbamate, $\text{CH}_3\text{NHCOONH}_3\text{CH}_3$, MAMCO is methylammonium methylcarbonate, $(\text{CH}_3\text{NH}_3)_2\text{CO}_3$, and MAHMCO

* Laboratory of Chemical Engineering, Faculty of Fisheries, Hokkaido University
(北海道大学水産学部化学工学講座)

is methylammonium hydrogen methylcarbonate, $\text{CH}_3\text{NH}_3\text{HCO}_3$. At temperatures above 150°C , however, only Eqs. (a) and (b) seem to be important⁸⁾. For U synthesis, read NH_3 and ammonium carbamate (ACA), $\text{NH}_2\text{COONH}_4$, for MMA and MAMCA, respectively. For U synthesis, the heat of reaction calculated thermodynamically and proven experimentally based on:



is about -12.3 kcal/kg-mol CO_2 ⁸⁾. By analogy, that for DMU synthesis based on:



should be around the value.

Due to its low vapor pressure, no significant amount of DMU or U can exist in the gas phase. Nevertheless, the high pressure, and accordingly the high density, exerted by the chemical system and the inequality of composition between gas and liquid phases due to the vapor liquid equilibrium, make it critical for determining the product composition, to see to what extent the gas or liquid phase prevails. In this context, two new terms are introduced; phase weight means weight fraction of a phase to phase-total weight, and an adjective "lumped" implies "summed up as alike disregarding phase difference", such as lumped density or lumped concentration. Lumped density has been called loading density²⁾, or weight volume ratio³⁾.

Theoretical Section

Two physico-chemical problems which are closely related to DMU and U syntheses, but have not been made clear enough, must be dealt with prior to a general discussion, of more general multicomponent multiphase reaction systems.

1. Degree of Freedom (D.F.) of Lumped Properties in Comparison with Gibb's D.F.

As an example of the lumped properties, lumped concentration is taken up. By definition,

$$C_i = M_i \sum_j f_j X_{i,j} \quad (1)$$

$$\sum_j f_j = 1 \quad (2)$$

$$X_i = \sum_j f_j X_{i,j} = C_i / M_i / (\sum_i C_i / M_i) \quad (3)$$

Suppose that the chemical reaction which takes place is expressed as

$$\sum_i r_i R_i = \sum_{i'} p_{i'} P_{i'} \quad (4)$$

First, Gibbs' D.F. is determined.

The total number of state variables of the system is $(I_r + I_p)Ph + 2$, in which the first term refers to phase concentration and the second, temperature and pressure. To cope with these variables, there are constraints due to:

a chemical equilibrium which is represented by one in the j th phase:

$$\sum_j p_i' \ln (\gamma_{i',j} X_{i',j}) - \sum_j r_i \ln (\gamma_{i,j} X_{i,j}) = \ln K_j \quad (5)$$

$(I_r + I_p)(Ph-1)$ phase equilibria which are given as:

$$\begin{aligned} \mu_{i,1} + RT \ln \gamma_{i,1} X_{i,1} &= \mu_{i,2} + RT \ln \gamma_{i,2} X_{i,2} = \dots, & i &= 1, 2, \dots, I_r \\ \mu_{i',1} + RT \ln \gamma_{i',1} X_{i',1} &= \mu_{i',2} + RT \ln \gamma_{i',2} X_{i',2} = \dots, & i' &= 1, 2, \dots, I_p \end{aligned} \quad (6)$$

To find material balance constraints, it is necessary to assume, without losing generality, that the system contains no products at the beginning. Thus, there exist (I_p-1) constraints given as

$$X_{1'}/p_{1'} = X_{2'}/p_{2'} = \dots = X_{I_p'}/p_{I_p'} (= X_c) \quad (7)$$

Further, there are Ph more constraints resulting from the use of mole fractions which are shown as:

$$\sum_i X_{i,j} + \sum_{i'} X_{i',j} = 1 \quad j = 1, 2, \dots, Ph \quad (8)$$

The number of constraints is in total, $1 + (I_r + I_p)(Ph-1) + (I_p-1) + Ph = (I_r + I_p)Ph + Ph - I_r$. The D.F. based on Gibbs' phase rule is the difference between the number of variables and the number of constraints, given as

$$\text{D.F. (Gibbs)} = I_r + 2 - Ph \quad (9)$$

The important point is that Gibbs' D.F. of multicomponent multiphase reaction systems depends merely on the number of reactants and the number of products is irrelevant.

For lumped properties, there are $(Ph-1)$ more constraints arising from the relation of Eq. (1) and (2), so that their D.F. decreases by $(Ph-1)$ than Gibbs' D.F., i.e.

$$\text{D.F. (lumped properties)} = I_r + 1 \quad (10)$$

Thus the D.F. of lumped properties is greater than the number of reactants by unity irrespective of the number of products and phases. This coincides with Gibbs' D.F. when the system is, or becomes a single phase.

For U synthesis, Matignon et al.¹⁾ stated that Gibbs D.F. was 2, but later, it was pointed out that his treatment was incorrect²⁾. Kawasumi et al. claimed the D.F. is 3³⁾, but his D.F. was not Gibbs' D.F. but the D.F. of lumped density as defined here. The true situation is: the number of independent components is 2 (reactants NH_3 and CO_2), the number of phases is 2, Gibbs' D.F. is 2 and the D.F. of lumped properties is 3.

In cases where more than one reaction take place, an increase in variables due to an increase of products is always equal to the increase in constraints which result from chemical equilibria similar to Eq. (5), and phase equilibria and material balances similar to the latter half of Eq. (6) and Eq. (7), respectively, so that Eq. (9) and (10) invariably hold.

2. Compositions which give Maximum Conversion and Minimum Pressure
In U synthesis, a representative multicomponent multiphase reaction, it has

been known experimentally that the composition which makes the conversion maximum and that which makes the pressure minimum are different from one another. Kawasumi⁸⁾ attempted to explain the phenomenon by the solubility product in which the existence of another liquid phase is tacitly assumed. If his view is correct, the system becomes univariant by Eq. (9), and once the temperature is specified, the pressure should be independent of composition, which is clearly not the situation.

The general treatment which follows assumes only one liquid phase and a gas phase and depends merely on the theory of real solution.

It is assumed that the reaction system does not contain products at the beginning and the equilibrium conversion is significant only in the liquid phase as is the case for DMU synthesis.

Noticing only the liquid phase, substitution of Eq. (7) into Eq. (5) gives

$$F_1 = \sum_i p_i' \ln(\gamma_i' X_c) - \sum_i r_i \ln(\gamma_i X_{i,iq}) - \ln K_{liq} = 0 \quad (11)$$

$$F_2 = \sum_i X_{i,iq} + (\sum_i p_i') X_c - 1 = 0 \quad (12)$$

To make the conversion X_c maximum subject to the constraints of Eqs. (11) and (12), Lagrange's undetermined multipliers λ_1 and λ_2 are introduced. Simultaneous solution of Eqs. (11), (12) and the following (13) gives the necessary condition.

$$f(X_c + \lambda_1 F_1 + \lambda_2 F_2) = 0 \quad (13)$$

In practice, however, $\gamma_{i,iq}$ and γ_i' are complex functions of $X_{1,iq}, \dots, X_{I_r,iq}, X_{1,iq}', \dots, X_{I_r,iq}'$ to which no methods of general prediction have ever been presented. If $\gamma_{i,iq}$ and γ_i' are assumed to be a function of only $X_{i,iq}$ and $X_{i,iq}'$, respectively, the necessary conditions are reduced to

$$r_i \frac{d \ln(\gamma_{i,iq} X_{i,iq})}{d X_{i,iq}} = \text{const} \quad \text{irrespective of } i \quad (14)$$

If $\gamma_{i,iq} = 1$, the conditions coincide with the stoichiometric ratio. Otherwise, they are different from it.

The pressure exhibited by the system is represented by

$$\Pi = \sum_i \gamma_{i,iq} \dot{\Pi}_{i,iq} X_{i,iq} + \sum_i \gamma_i' \dot{\Pi}_i' (p_i' X_c) \quad (15)$$

Here, fugacities of respective components are assumed, for simplicity, to be equal to their partial pressures. Using Lagrange's multipliers λ_1 and λ_2 as before, the minimum of Π is found by simultaneous solution of Eqs. (11), (12) and (16) which follows for $X_{i,iq}$, ($i=1,2, \dots, I_r$), X_c , λ_1 and λ_2 .

$$f(\Pi + \lambda_1 F_1 + \lambda_2 F_2) = 0 \quad (16)$$

Again, ignorance of functional forms of $\gamma_{i,iq}$ and γ_i' prevents general solution. If $\gamma_{i,iq}$ and γ_i' equal unity and $\dot{\Pi}_i'$ is negligible, which is a rough approximation of DMU and U synthesis, the problem is simplified considerably. Thus, setting

$$\Pi = \sum_i \dot{\Pi}_{i,liq} X_{i,liq} \quad (17)$$

$$\Pi_i/r_i = \Pi/\sum_i r_i = \text{const} \quad (18)$$

Thus, the partial pressure of any reactant Π_i , divided by its stoichiometric coefficient r_i is constant irrespective of reaction species, as demonstrated in DMU and U synthesis.

Experimental section

MMA and CO₂ were obtained courtesy of Nitto Kagaku K.K. and Seitetsu Kagaku K.K., respectively. Autoclave (A), 52 mm in dia. and 300 ml in vol. was used for experiments in equilibrium, whereas Autoclave (B), 16 mm in dia. and 20 ml in vol. was used exclusively for rate measurement. With Autoclave (A), in order to prevent blockage due to condensation of solid MAMCA, the piping which connects the Bourdon manometer and the inside of the autoclave was filled with liquid paraffin, whereas with Autoclave (B) the pressure was not measured and the piping was closed.

A specified amount of MMA was taken into a glass tube cooled in a methanol-dry ice bath maintained at a temperature between -30-50°C and placed in the autoclave, cooled to -20°C in advance. The reactor was tightly capped, filled with CO₂ to about 50 kg/cm², kept for 24 hr, and released completely to atmospheric pressure. The product was practically pure MAMCA. In cases where more MMA was charged, the reactor was again cooled to -20°C, opened, filled with the prescribed amount of MMA at -30-50°C which was prepared as mentioned, and recapped.

In experiments with Autoclave (A), the reactor was heated electrically at an average rate of 3°C/min, kept at a constant temperature, (reaction temperature), for a specified period of time, (reaction time), the current was turned off and the reactor was left to cool.

In experiments with Autoclave (B), it was immersed in an oil bath held at a reaction temperature, shaken vigorously at 200 r.p.m. for a specified time, removed from the bath and quenched with water. It took about 3 min to raise the temperature inside the reactor, so the reaction time was corrected by that amount.

According to Eqs. (a), (b), (c) and (d), reaction products can contain DMU, MAMCA, MAMCO, MAHMCO and H₂O along with unreacted CO₂ and MMA at room temperature. However, upon dilution with water, MAMCA, MAMCO and MAHMCO hydrolyze into the methyl ammonium cation and carbonate anion, and their respective analyses are quite difficult but not important. And they are shown collectively as unreacted MMA (MMA') and CO₂ (CO₂'). MMA' was determined by titration with 0.2 N-H₂SO₄ at room temperature using methylene blue-methyl red as an indicator, while CO₂' was determined gravimetrically by Kawasumi's method¹¹⁾ after complete decomposition of MAMCA, MAMCO and MAHMCO with conc. H₂SO₄. DMU was calculated as the difference between the charged and the unreacted MMA' and CO₂', and identified by its m.p. of 106°C

and the infrared spectrum, after vacuum condensation and recrystallization from ethyl alcohol. Other substituted ureas were not detected.

Results and Discussion

There are two experimental series for equilibrium and rate. For comparison, data for U synthesis taken from the literature are shown along with the current data. Due to low vapor pressure of DMU and U, the syntheses reaction can never progress to a significant extent in gas phase. With the object of using lumped properties instead of liquid phase properties, experiments were carried out at high lumped densities, except in the case where the effects of lumped density were examined.

A. Effects of Temperature on Conversion and Pressure

The equilibrium conversion of MAMCA to DMU at a temperature range of 170–200°C is shown in Fig. 1. The conversion increased 65→80% with an increased temperature. Although the conversion was much lower, a similar tendency was observed in U case.

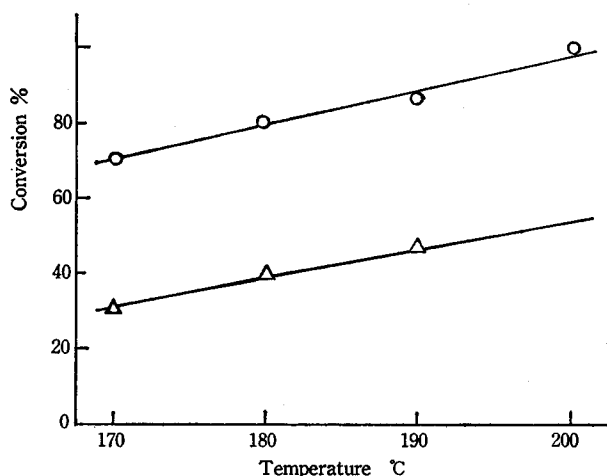


Fig. 1. Effect of temperature on equilibrium conversion of DMU. Data for U were taken from Clark²¹. L.D. (g/ml): 0.7 for DMU, 1.0 for U. Datum pt.: ○ for DMU, △ for U.

As mentioned in the introduction, Eqs. (e) and (f) are exothermic, so, according to Le Chaterier's principle, the equilibrium conversion should always decrease with an increase in temperature. In order for the apparent reverse tendencies to be compatible, it should be assumed that the reacting liquid phase contains at least one more reaction participant in addition to those shown in Eq. (f). The most probable candidate is dissolved MAMCA as shown in the following equilibrium scheme.



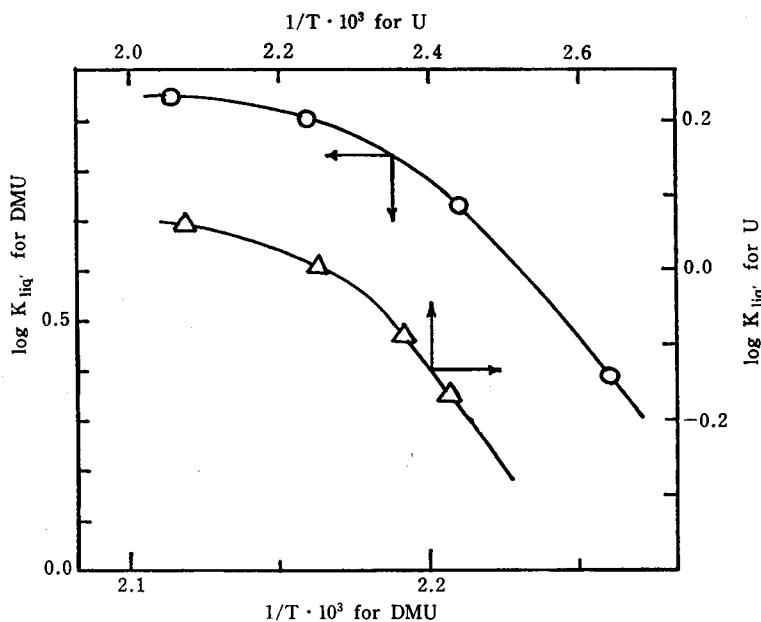


Fig. 2. Relation between logarithm of the apparent equilibrium constant $K_{liq'}$, and $1/T$. Data for U were taken from Kawasumi⁹⁾. L.D. (g/ml): 0.7 for DMU, 0.6 for U. Datum pt.: \circ for DMU, Δ for U.

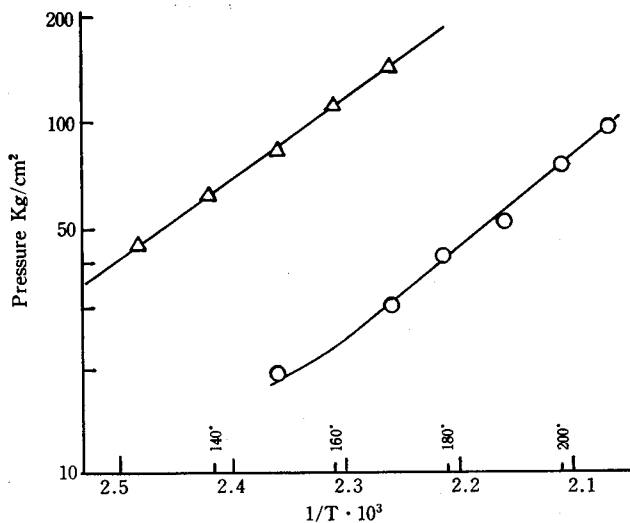


Fig. 3. Effect of temperature on equilibrium pressure. Data for U were taken from Kawasumi⁹⁾. L.D. (g/ml): 0.7 for DMU, 0.8 for U. Datum pt.: \circ for DMU, Δ for U.

As the temperature rises, the left side endothermic equilibrium shifts to the right, with the result that the amounts of MMA and CO₂, and consequently, DMU increase.

The relation between the logarithm of the apparent equilibrium constant defined by $K_{liq}' = X_{DMU} \cdot X_{H_2O} / X_{MMA}' \cdot X_{CO_2}'$, and the reciprocal absolute temperature is shown in Fig. 2. Here X_{MMA}' and X_{CO_2}' stand for the mole fraction based on unreacted MMA and CO₂ including those in MAMCA, respectively. As expected, the relation is curvilinear convex upward, and this suggests that, at higher temperatures, the relation eventually becomes a line with a positive slope, provided that no side reactions occur. Kitawaki⁶⁾ explained the nonlinearity by assuming the existence of one more independent liquid phase of MAMCA. We and Kawasumi⁸⁾ explained it by assuming the existence of dissolved MAMCA. The existence of MAMCA will be supported further by reaction rate considerations.

The effect of temperature upon the pressure exerted by the reaction system is shown in Fig. 3. The pressure increased with an increase of temperature, as is the

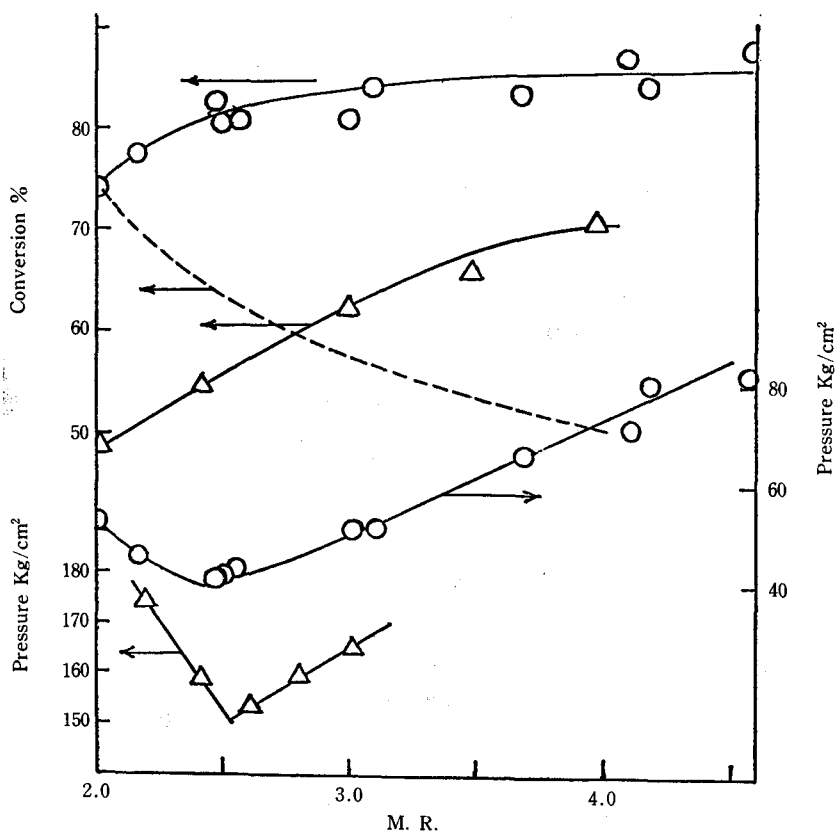


Fig. 4. Effect of M.R. on equilibrium conversion and equilibrium pressure. Data for U were taken from Kawasumi⁸⁾. L.D. (g/ml): 0.7 for DMU, 0.6 for U. Temp. (°C): 190 for DMU, 190 for U. Datum pt.: ○ for DMU, △ for U. Solid line, based on MAMCA, chain line, based on MAMCA and MMA.

case for U. Mathematically, the relation for DMU is represented by a Clausius-Clapyeron type equation:

$$\log \Pi = -2648/T + 7.484 \quad (\Pi \text{ in kg/cm}^2)$$

The corresponding equation for U was presented by Kawasumi⁸⁾:

$$\log \Pi = -2369/T + 7.503 \quad (\Pi \text{ in kg/cm}^2)$$

The slope is somewhat larger for DMU, which is understandable, because the boiling points of the reaction participants for DMU are generally higher and Trouton's law says that the entropy increase at the normal boiling point accompanying evaporation is constant irrespective of materials.

B. Effects of Mole Ratio (M.R.) of MMA to CO₂ on Conversion and Pressure

Fig. 4 shows the data for DMU along with those for U synthesis. Experiments for M.R. less than 2 were unimportant and omitted. We could expect there the tendency similar to the U synthesis, since it was well established that an excess of CO₂ had little effect upon the conversion when based upon MAMCA. The conversion based upon MAMCA increased with an increased M.R. from 74% at 2 to 85% at 4, but the rate of increase fell off with an increased M.R. A similar tendency is seen in U synthesis, although the conversion is much less. The conversion based

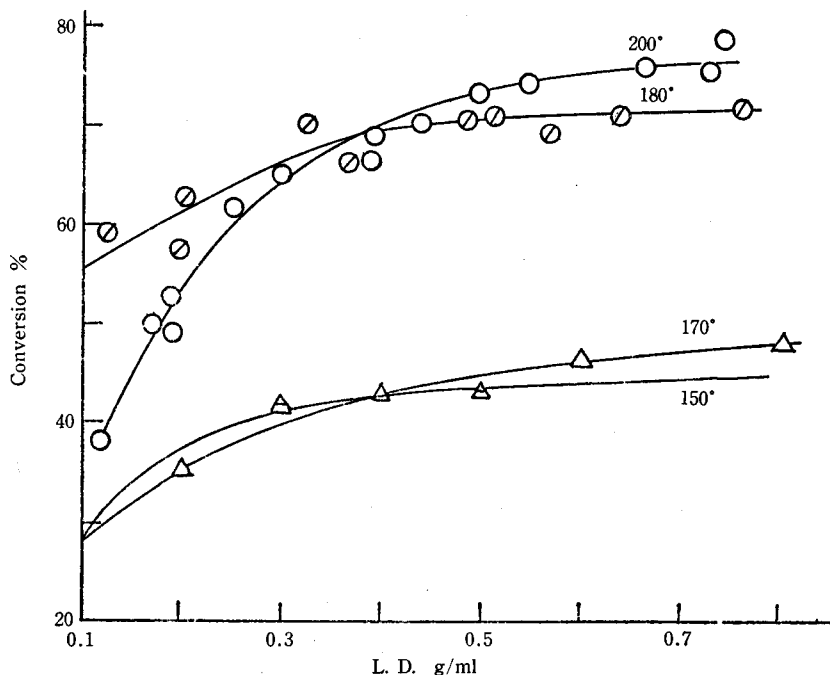


Fig. 5. Effect of L.D. on equilibrium conversion. Data for U were taken from Clark⁹⁾ for 170°C and Tokuoka⁵⁾ for 150°C. M.R.: both 2 to 1. Datum pt.: ○ for DMU, △ for U.

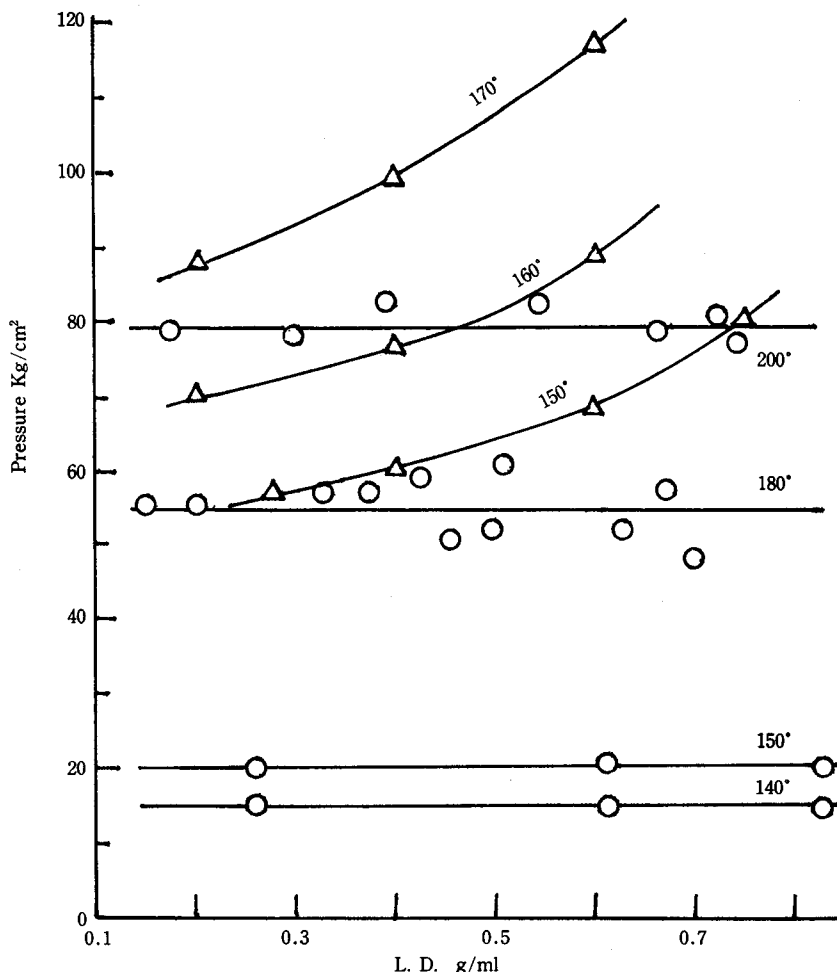


Fig. 6. Effect of L.D. on equilibrium pressure. Data for U were taken from Kawasumi⁹⁾. M.R.: both 2 to 1. Datum pt.: ○ for DMU, △ for U.

upon (MAMCA+MMA) decreased with an increased M.R., and was maximum at the stoichiometric M.R. (Fig. 4). The minimum pressure appeared around 2.5 in M.R., which happened to coincide with the point for U synthesis. The chemical analysis of the gas phase showed that the M.R. is 2 to 1, the same result obtained by Kawasumi⁹⁾ for the U synthesis. As previously discussed, we think this phenomenon is attributable to the gas-liquid equilibrium accompanied by chemical change.

C. Effects of Lumped Density (L.D.) on Conversion and Pressure

Setting aside the theoretical treatment, the importance of the L.D. has been recognized since Fichter et al.¹²⁾, and used almost exclusively as an important

state variable. It is seen from Fig. 5 that the relation of conversion vs. L.D. for DMU is much the same as that for U, except the conversion is much higher for DMU. The reason why lines for higher temperatures and those for lower temperatures intersect each other, are not obvious, but, presumably, can be related to the cooling characteristics of the autoclave. That is, the gas space is cooled faster than the liquid space, and during then MMA and CO₂ vaporize at the liquid phase and condense on the gas space wall to form MAMCA. The result is that equilibrium shifts to reduce DMU. The higher the temperature, the greater the gas density; and consequently, the greater the effect. That the pressure is approximately constant, irrespective of L.D. is shown in Fig. 6. This is in sharp contrast to the tendency for pressure to increase with L.D. in U synthesis. Under the gas-liquid equilibrium theory, if there is no gas space, the fictitious gas is richest in CO₂ content, whereas, if there is gas space only, the gas is the poorest in CO₂ content and should be 2 to 1 in M.R. Presumably, at higher L.D., the CO₂ in the gas phase dissolves

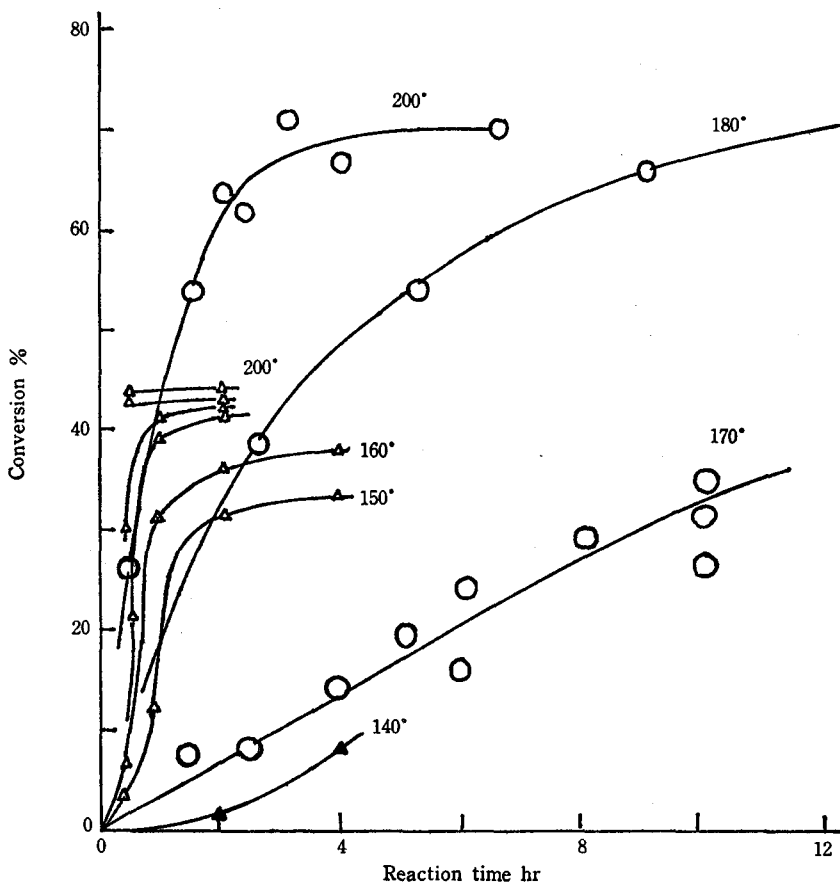


Fig. 7. Effect of reaction time on conversion. Data for U were taken from Sakai⁷⁾. L.D. (g/ml): 0.6 to 0.7 for DMU, not shown for U. M.R.: both 2 to 1. Datum pt.: ○ for DMU, △ for U.

more readily in liquid containing MMA which is more basic than NH_3 ; but at lower L.D., the effect is less because of less liquid fraction. The details will be left to later studies.

D. Rates of DMU Formation from MAMCA

The conversion of MAMCA to DMU at 170, 180 and 200°C is plotted against time in Fig. 7. Corresponding data for U synthesis can be obtained from the works of Frèjacques⁴), Tokuoka⁵) and Sakai⁷). None of their experimental designs were suitable for the kinetic analysis. However, Sakai's data were used for comparison because of the temperature range of his observation. As can be seen, the reaction rate for DMU is much slower than for U. The fact that an NH_3 molecule and an MMA molecule have 3 and 2 hydrogen atoms, respectively, seems to play an important role in the slow reaction rate. The Arrhenius plot, based on the reciprocal of the time necessary for 20% conversion, is curvilinear and convex upward (Fig. 8). This tendency is similar to the relation between $\log K_{1iq'}$ and $1/T$ shown in Fig. 2. A similar tendency is also seen in Fig. 7 for U synthesis. However, its further kinetic treatment is not possible for U because of the sigmoidal nature of the conversion vs. time curve.

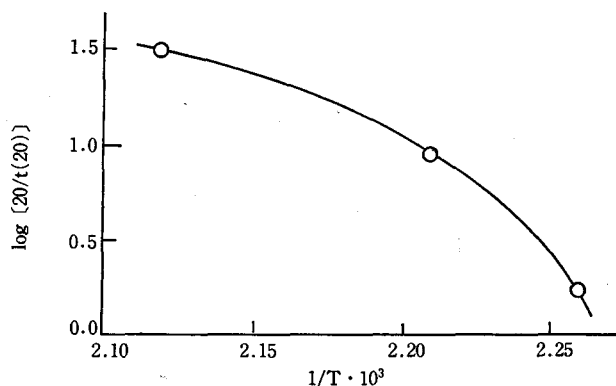
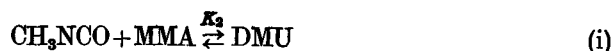
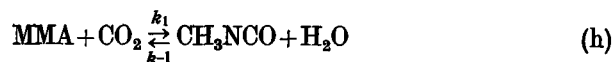


Fig. 8. Arrhenius plot of the reaction rate. Time necessary for 20% conversion is referred to as $t(20)$.

E. Probable Reaction Mechanism

It was inferred in Section A., that the reaction between MMA and CO_2 takes place in the liquid phase and not via MAMCA. That interpretation resulted from the fact that the dependency of the apparent $\log K_{1iq'}$ against the reciprocal absolute temperature is convex upward. It is further supported kinetically by the fact that the Arrhenius plot is also convex upward. Taking Eq. (g) into consideration, the most probable reaction scheme at this point is shown as:





The occurrence of Eq. (i) has been known¹²⁾. Eq. (j) is a side reaction which retards the reaction rate. Intuitively, the rate constant, and probably, the equilibrium constant of Eq. (h) are supposed to be small. In that case, the rate of the overall reaction is shown as:

$$\begin{aligned} \frac{dX_{\text{DMU}}}{dt} &= k_1 X_{\text{MMA}} X_{\text{CO}_2} - k_{-1} X_{\text{CH}_3\text{NCO}} X_{\text{H}_2\text{O}} \\ &= (k_1/K_3) \frac{X_{\text{MAMCA}}}{X_{\text{MMA}}} - (k_{-1}/K_2) \frac{X_{\text{DMU}} X_{\text{H}_2\text{O}}}{X_{\text{MMA}}} \end{aligned} \quad (19)$$

If X_{MAMCA} is significant, the reaction rate can roughly be approximated by an equation which is first order to the unreacted X_{MMA} , and X_{CO_2} , expressed as MAMCA. Eq. (19) can also be applied to U synthesis after necessary substitutions. If Eq. (h) is the rate determining step, the sluggishness of DMU synthesis as compared to U synthesis, is roughly estimated by the number of the active hydrogen atoms, as ${}_2\text{C}_2$ to ${}_3\text{C}_2$, or 1 to 3, which coincides approximately with the situation.

Acknowledgment

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Nomenclature

- C : Concentration
- f : Phase weight, defined as weight fraction of a phase to phase-total weight
- I_p : Number of products
- I_r : Number of reactants
- M : Molecular weight
- P : Chemical symbol for products
- Ph : Number of phases
- p : Stoichiometric coefficient for product
- R : Chemical symbol for reactants
- r : Stoichiometric coefficient for reactant
- X : Mole fraction
- γ : Activity coefficient
- λ : Lagrange's multiplier
- μ : Chemical potential at the standard state
- Π : Pressure exerted by the system
- $\bar{\mu}$: Pressure exhibited by a substance at the standard state
- ∇ : Gradient operator

Subscript:

- c : Conversion
- g : Gas phase
- I_p : The I_p th product

- i : Index referring to reactant
 I_r : The I_r th reactant
 i' : Index referring to product
 j : Index referring to phase, usually used as second subscript
 liq : Liquid phase

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