NOVEL THERMODYNAMIC AND KINETIC INVESTIGATION OF AMMONIUM CARBAMATE DECOMPOSITION INTO UREA AND WATER
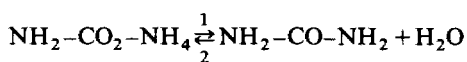
B. CLAUDEL, E. BROUSSE and G. SHEHADEH

Laboratoire de Cinétique et Génie Chimiques, 404-INSA, 20 Avenue A. Einstein, F-69621 Villeurbanne (France)
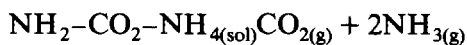
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ABSTRACT

The reversible decomposition of ammonium carbamate into urea and water

$$NH_2-CO_2-NH_4 \underset{2}{\overset{1}{\rightleftharpoons}} NH_2-CO-NH_2 + H_2O$$

has been reinvestigated, from the thermodynamic and kinetic standpoints. The equilibrium conditions have been reached from the right-hand side components. The equilibrium medium is then liquid. From the equilibrium constant relative to molal fractions, an enthalpy variation for the forward reaction of 5.5 kcal mol^{-1} can be derived. The kinetics of this forward reaction have been investigated in conditions where the carbamate remains partly solid. It follows the Prout–Tompkins law, which is interpreted by the ability for water in contact with the solid to create germs of its decomposition. The activation energy of reaction 1 is about 10 kcal mol^{-1}.

INTRODUCTION

Ammonium carbamate $NH_2-CO_2-NH_4$ undergoes a reversible decomposition into carbon dioxide and ammonia, according to the equilibrium

$$NH_2-CO_2-NH_{4(sol)} CO_{2(g)} + 2NH_{3(g)}$$

with a standard enthalpy variation, for the forward reaction equal to 38.3 kcal mol^{-1}. This high value renders ammonium carbamate attractive as an agent of energy storage. Its decomposition requires about 570 Wh per kilogram, this energy being restored when carbon dioxide and ammonia are allowed to recombine. Our laboratory is presently studying the feasibility of this process of energy storage. A side reaction, however, complicates the picture, namely, the reversible decomposition of ammonium carbamate into urea and water, according to the equilibrium
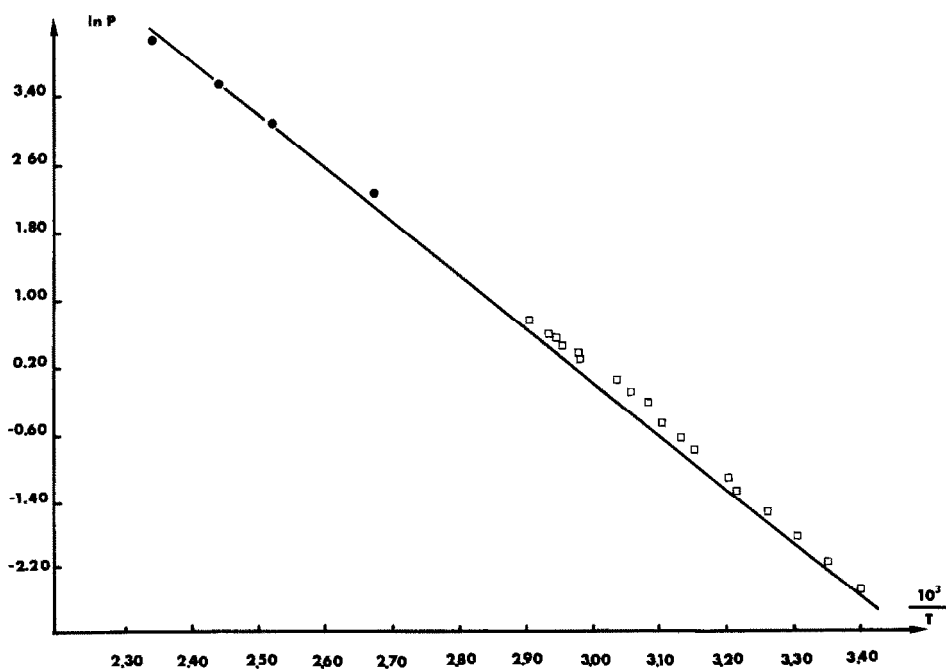
$$NH_2-CO_2-NH_4 \underset{2}{\overset{1}{\rightleftharpoons}} NH_2-CO-NH_2 + H_2O$$

Fig. 1. Variation with temperature of the total pressure P for the equilibrium: $NH_2-CO_2-NH_4 \rightleftharpoons CO_2 + 2NH_3$. In full line: theoretical curve derived from thermodynamic calculations; ($\square$) our experimental points; ($\bullet$) according to ref. 6.

The interplay of both equilibria provides the basis of urea production from a mixture of CO_2 and NH_3 [1]. However, whereas the former equilibrium is rather well documented [2–4] the references on the latter are surprisingly ancient and scanty [5–7]. In particular, the data from refs. 5 and 6 are conflicting: the authors claim that their system is made of two phases, liquid and gas. If, however, the values that they report for the total pressure P are plotted in the coordinates $\ln P$, $\dfrac{10^3}{T(\mathrm{K})}$, the corresponding points lie quite well on the straight line determined for the first equilibrium (Fig. 1). This means that in their experiments, part of the carbamate is in the solid state. This fact was acknowledged in a later study [7].

From the kinetic viewpoint, Matignon and Frejacques [6] give results that we represent in Fig. 2. At their operating temperatures, the occurrence of the component reactions of the first equilibrium is likely. Moreover, they measure a net effect, due to the occurrence of the two opposite reactions 1 and 2. Finally, no quantitative treatment of curves of Fig. 2 is given. This is why we attempted to re-examine, both from the thermodynamic and kinetic viewpoints, the reversible conversion of ammonium carbamate into urea and water. A priori, it seemed advisable to operate at lower temperatures: a rough estimate of the activation energy of its decomposition into carbon
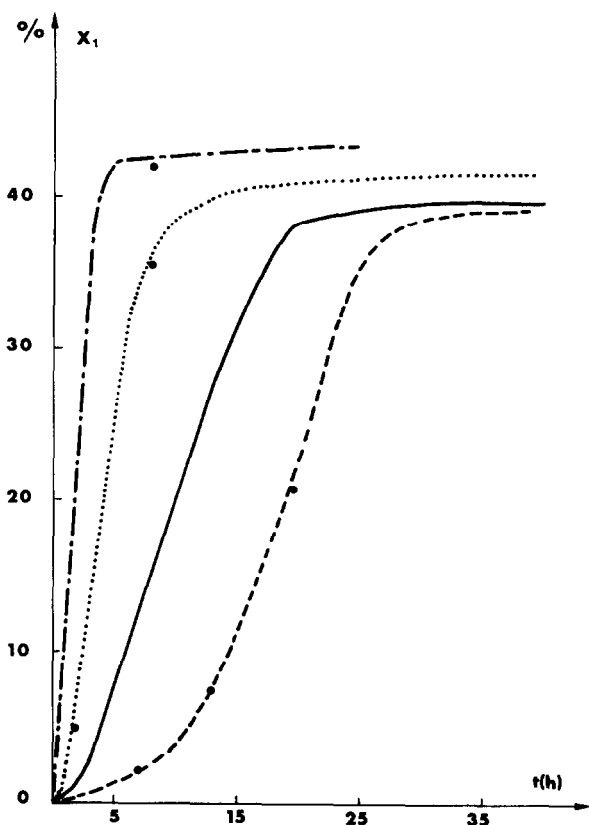
Fig. 2. Fractional conversion of ammonium carbamate into urea as a function of time, according to ref. 6: (— — —) 130°C; (———) 134°C; (······) 140°C; (·—·—·) 145°C.

dioxide and ammonia gives, according to Janjic's data [4] about 19 kcal mol^{-1}, whereas our own determination of the activation energy of reaction 1 yields 10 kcal mol^{-1}. Therefore, it is legitimate to think that the first equilibrium does not interfere at lower temperatures.

EXPERIMENTAL

The initial components, either pure carbamate or an equimolar mixture of urea and water, are put in glass tubes (1.5 mm in wall thickness), which are cooled down to liquid nitrogen temperature, evacuated for the gas phase, and sealed under vacuum. The tubes are then put in stoves at set temperatures, between 68 and 100°C, for determined times. When this time has elapsed, the tube is quenched at 0°C and analyzed for its urea content using

the Fosse's method [8]. It consists in condensing urea with xanthydrol, according to the reaction
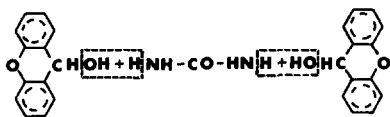
which forms a product "dixanthylurea" of high molecular weight, $M = 420$ g mol^{-1}, and thus allows an accurate gravimetric determination. The analytical procedure is the following: after quenching, the tube is broken, its content is dissolved in 20 cm^3 of distilled water to which are added 20 cm^3 of glacial acetic acid and 3 cm^3 of a 10 wt% solution of xanthydrol in methanol. The mixture is allowed to react for 6 hours with magnetic stirring. The insoluble dixanthylurea is filtered off, washed with 20 cm^3 of pure ethanol, dried at 105°C and finally weighed.

The weight w of dixanthylurea is known with an uncertainty $\delta w = 10^{-4}$ g at the most. The uncertainty δn_2 in the mole number of urea is, therefore:

$\dfrac{\delta w}{M} = \dfrac{10^{-4}}{420} \simeq 2 \times 10^{-7}$. The initial number of moles of urea is determined

from the weight w_2^0 and the molal mass $M_2 = 60$ g. Hence,

$\delta n_2^0 = \dfrac{\delta w_2^0}{60} = \dfrac{10^{-4}}{60} \simeq 2 \times 10^{-6}$. If a conversion X is calculated from:
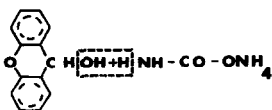
$$1 - X = \frac{n_2}{n_2^0}$$

$$\frac{\delta X}{1 - X} = \frac{\delta n_2}{n_2} + \frac{\delta n_2^0}{n_2^0}$$

If X remains low, $X \ll 1$, $n_2 \simeq n_2^0 = 2.6 \times 10^{-3}$ mol. Hence,

$$\delta X = \frac{2.2 \times 10^{-6}}{2.6 \times 10^{-3}} \simeq 10^{-3}$$

It can be noticed that ammonium carbamate also reacts with xanthydrol through its amide group

However, this condensation product, of molecular weight inferior to that of dixanthylurea, dissolves in washing ethanol.

THERMODYNAMICS

Owing to the fact that reaction 2 is faster than reaction 1, the equilibrium state is reached more rapidly when the initial components are urea (denoted 2 in the following) and water (denoted 3).

TABLE 1

System composition

Component	Carbamate 1	Urea 2	Water 3	Total
Initial number of moles	0	n_3^0	n_3^0	
At equilibrium — number of moles	$n_3^0 X_{3e}$	$n_3^0(1 - X_{3e})$	$n_3^0(1 - X_{3e})$	$n_3^0(2 - X_{3e})$
At equilibrium — molal fractions	$\dfrac{X_{3e}}{2 - X_{3e}}$	$\dfrac{1 - X_{3e}}{2 - X_{3e}}$	$\dfrac{1 - X_{3e}}{2 - X_{3e}}$	

Repartition of the components between the phases

Visual observations show that the system is made up of two phases: liquid and gas. We shall show that the major part of each component lies in the condensed phase. We shall make this calculation for water, the most volatile component. The composition of the system is indicated by Table 1.

In the absence of data about the activities in solution, we shall assume ideality. Therefore, the partial pressure of water vapour above the solution is

$$P_3 = x_3 P_{3sat}$$

Let us assume that the molal fraction x_3 of water in the liquid is its overall molal fraction (which anticipates on the computation result). Then

$$P_3 = \frac{1 - X_{3e}}{2 - X_{3e}} P_{3sat}$$

If we take from Table 2 the values $T = 341.4$ K, $X_{3e} = 1.2 \times 10^{-2}$, then $P_{3sat} = 218$ Torr, and, given an internal volume of about 5 cm³, $n_{3g} = 2.6 \times 10^{-5}$ mol. Whereas $n_3 \simeq n_3^0 = 2.6 \times 10^{-3}$ mol. Therefore, only 1% of water is in the vapour state, and the preceding computation is valid at this approxi-

TABLE 2

Experimental measurements of X_{3e}

T (K)	$\dfrac{10^3}{T}$	X_{3e}	K_x	$\ln K_x$	$\dfrac{\delta K_x}{K_x}$
341.4	2.929	11.5×10^{-3}	42.73	3.755	0.09
346.0	2.890	9.9×10^{-3}	49.96	3.911	0.10
352.0	2.840	9.6×10^{-3}	51.33	3.938	0.10
359.0	2.786	9.3×10^{-3}	53.01	3.970	0.13
361.4	2.767	8.7×10^{-3}	56.72	4.038	0.13
367.5	2.721	6.5×10^{-3}	76.17	4.333	0.16
371.4	2.693	6.0×10^{-3}	82.58	4.414	0.17

mation. In the following equilibrium calculations, we shall restrict ourselves to the consideration of the liquid phase.

Thermodynamic calculations

For the equilibrium considered in the liquid phase, $\varphi = 1$, the number n of physical factors is 1 (no influence of pressure in the liquid), and the number c of independent components is 1, since, in our case, the concentration of urea always equals that of water. It then results from the Gibbs phase rule

$$v = c + n - \varphi$$

that the variance v is one: it means that the two variables on which the system at equilibrium depends, composition and temperature, are interrelated.

This interrelationship is derived from the variation of Gibbs free enthalpy

$$\Delta G = \sum_i v_i \mu_i \tag{1}$$

in which the chemical potentials μ_i in a solution which is supposed to be ideal are expressed by

$$\mu_i = \mu_{i1}^0 + \mathscr{R}T \ln x_i \tag{2}$$

the reference state being the pure component i in the liquid state at temperature T. Hence

$$\Delta G = \Delta G_T^0 + \mathscr{R}T \ln \frac{x_2 x_3}{x_1}$$

by putting

$$\Delta G_T^0 = \mu_{21}^0 + \mu_{31}^0 - \mu_{11}^0 \tag{3}$$

At equilibrium, $\Delta G = 0$, and

$$\ln K_x = -\frac{\Delta G_T^0}{\mathscr{R}T} \tag{4}$$

with:

$$K_x = \frac{x_2 x_3}{x_1} \tag{5}$$

Having regard to Table 1, we obtain

$$K_x = \frac{(1 - X_{3e})^2}{X_{3e}(2 - X_{3e})} \tag{6}$$

which allows one to exploit the experimental measurements of X_{3e} according
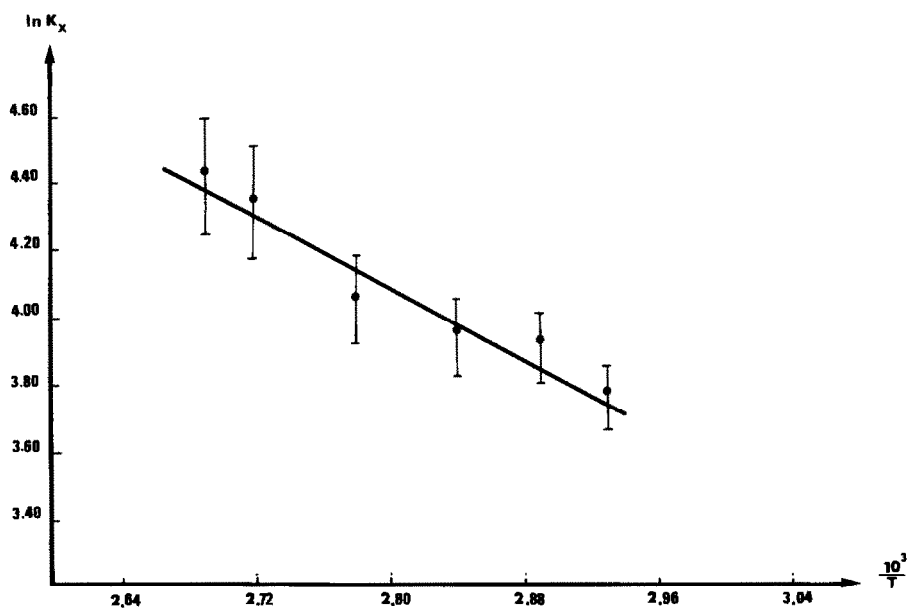
Fig. 3. Variation with temperature of the equilibrium constant K_x.

to Table 2, in which the uncertainty $\dfrac{\delta K_x}{K_x}$ has been derived from eqn. (6)

$$\frac{\delta K_x}{K_x} = \frac{2\delta X_{3e}}{X_{3e}(1 - X_{3e})(2 - X_{3e})}$$

The usual plot of ln K_x vs. $\dfrac{1}{T}$ gives a fairly good straight line (Fig. 3) from which the enthalpy variation for reaction 1 can be deduced: $\Delta H \simeq 5.5$ (± 0.5) kcal mol^{-1}, corresponding to an endothermal dehydration of ammonium carbamate. This result fits well with earlier determinations [6]. More interestingly, it is in agreement with values of heats of formation found in the literature [9]. These values take as reference state for components 1 and 2 their solutions in water at molality $m_i = 1$. The molal fraction is related to the molality by

$$x_i = \frac{m_i}{\sum m_i + \frac{1000}{18}}$$

If we assume that $\sum m_i$ is reasonably less than $\dfrac{1000}{18}$, then

$$x_i \simeq m_i \times \tfrac{18}{1000}$$

For the solutes 1 and 2, the chemical potential given by expression (2), is therefore

$$\mu_i = \mu_{i1}^0 + \mathscr{R}T \ln \tfrac{18}{1000} + \mathscr{R}T \ln m_i$$

an expression in which a reference potential appears

$$\mu^0_{i\,\text{diss}} = \mu^0_{i1} + \mathscr{R}T \ln \tfrac{18}{1000}$$

The ΔG^0_T given by eqn. (3) can then be rewritten

$$\Delta G^0_T = \mu^0_{21} + \mathscr{R}T \ln \tfrac{18}{1000} + \mu^0_{31} - \mu^0_{11} - \mathscr{R}T \ln \tfrac{18}{1000} = \mu^0_{2\,\text{diss}} + \mu^0_{31} - \mu^0_{1\,\text{diss}}$$

It follows that

$$\Delta H = H^0_{2\,\text{diss}} + H^0_3 - H^0_{1\,\text{diss}}$$

By using ref. 9 $H^0_{2\,\text{diss}} = -76.3$ kcal mol^{-1}; $H^0_3 = -68.32$ kcal mol^{-1}; $H^0_{1\,\text{diss}} = -150.4$ kcal mol^{-1} a value $\Delta H = 5.8$ kcal mol^{-1} is obtained, in very close agreement with the experimental one.

KINETICS

General features

Reaction 1 is followed at fixed temperatures starting from ammonium carbamate. Visual observation shows that, for the conversions obtained in these experiments, the system is triphasic: gas, liquid and solid, this last phase consisting of unconverted carbamate.

Conversion is measured by titrating urea as explained above. The experimental results are given in Table 3 and represented by Fig. 4. The isotherms obtained, if the vicinity of origin is discarded, correspond to a self-accelerated reaction, i.e., a reaction the rate of which increases with time, for the observed durations. This is why we tried to check the kinetic influence of the products. We observed that initially added urea did not change the reaction

TABLE 3

Variation of conversion with time

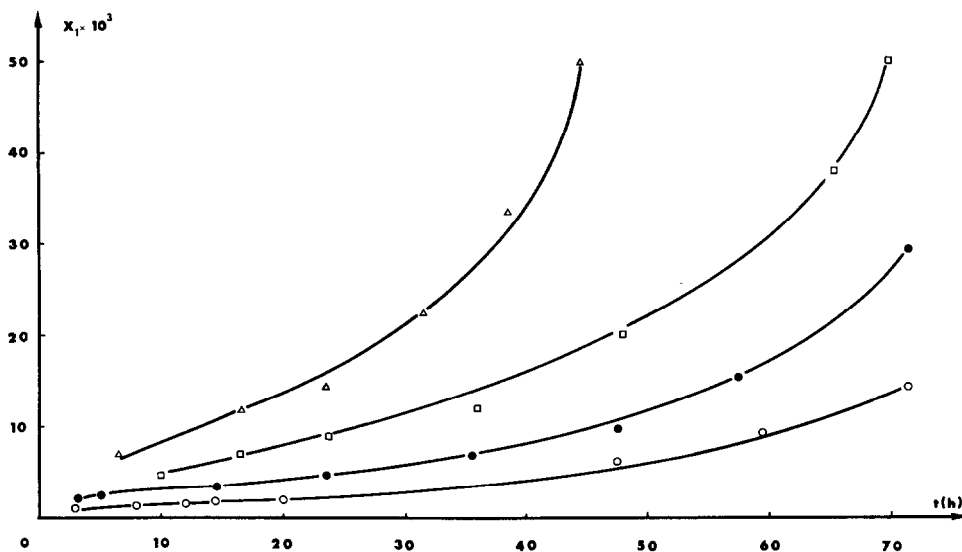| T (°C)							
68.4		78.4		88.4		98.4	
t (h)	X_1	t (h)	X_1	t (h)	X_1	t (h)	X_1
3	0.013	3	0.024	10	0.049	8	0.070
8	0.015	6	0.028	16.5	0.070	16.5	0.118
12	0.016	14.5	0.035	23.5	0.091	23.5	0.148
14.5	0.018	23.5	0.047	36	0.121	31.5	0.223
20	0.019	35.5	0.068	48.5	0.200	38.5	0.331
47.5	0.063	47.5	0.099	65.5	0.382	44.5	0.499
59.5	0.094	57.5	0.154	70	0.500		
71.5	0.143	71.5	0.293				

Fig. 4. Variation with time of fractional conversion of ammonium carbamate into urea: (○) 68.4°C; (●) 78.4°C; (□) 88.4°C; (△) 98.4°C.

course. On the contrary, when we initially introduced water, a drastic change of kinetics was observed.

Effect of an initial addition of water

The results at 78.4°C are indicated by Table 4 and Fig. 5, for 6.2×10^{-4} mole of water added to 3.2×10^{-3} mole of carbamate. This clearly shows the accelerating rôle of water. In order to generalize to variable amounts of water (a mole of water per mole of carbamate), we measured the conversion of carbamate at 78.4°C after a duration of 20 hours. Table 5 gives the obtained results.

Formulation of a kinetic law, and interpretation by a mechanism

—In the initial absence of water

The occurrence of a self-acceleration phase in heterogeneous kinetics is rather common. One of the simplest formulas which accounts for this trend

TABLE 4

Effect of addition of water

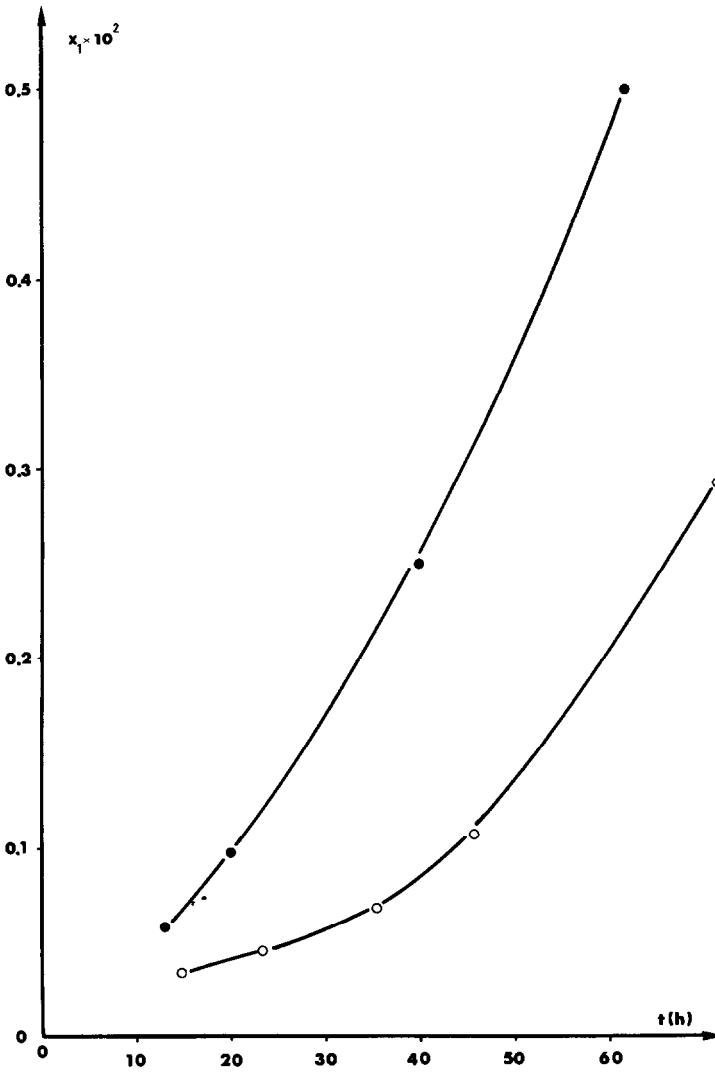| t (h)	13	20	40	50
X_1	0.058	0.097	0.250	0.500

Fig. 5. Variation with time of fractional conversion of ammonium carbamate into urea: (○) without initially added water; (●) with initially added water.

TABLE 5

Results of conversion of carbamate

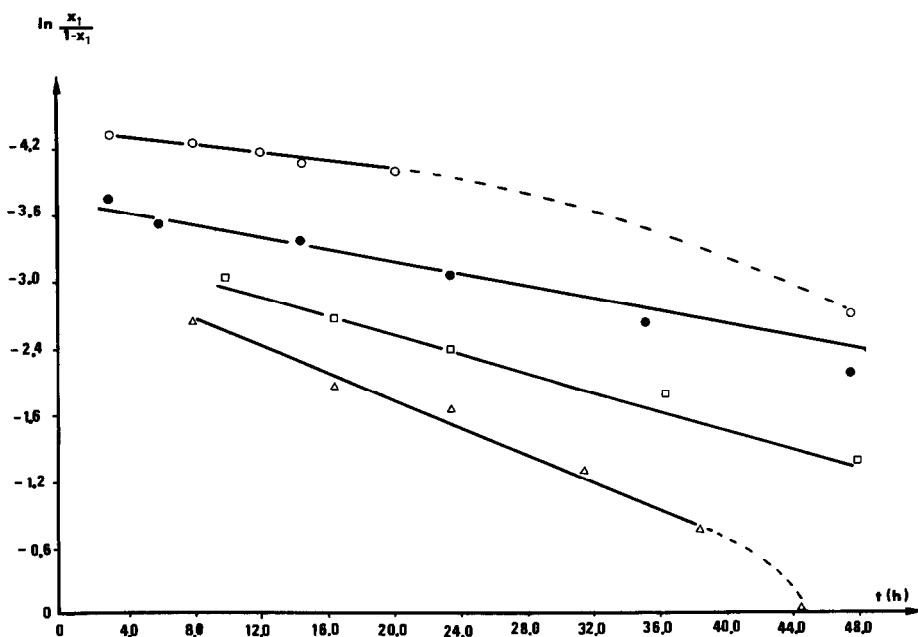| a	0.384	0.469	0.503	0.602	0.740	0.868	0.885	1.076
X_1	0.224	0.229	0.244	0.310	0.340	0.385	0.401	0.432

Fig. 6. Transformed curves of Fig. 4: (O) 68.4°C; (●) 78.4°C; (□) 88.4°C; (△) 98.4°C.

is that of Prout and Tompkins [10], which can be written, in the initial absence of water

$$\frac{dX_1}{dt} = kX_1(1 - X_1) \tag{7}$$

The integration of this differential equation yields

$$\ln \frac{X_1}{1 - X_1} = kt + \text{const.} \tag{8}$$

The data of Table 3 can be transposed in coordinates t, $\ln \dfrac{X_1}{1 - X_1}$ and the curves of Fig. 6 are obtained, which are reasonably linear for the shorter

TABLE 6

Values of k

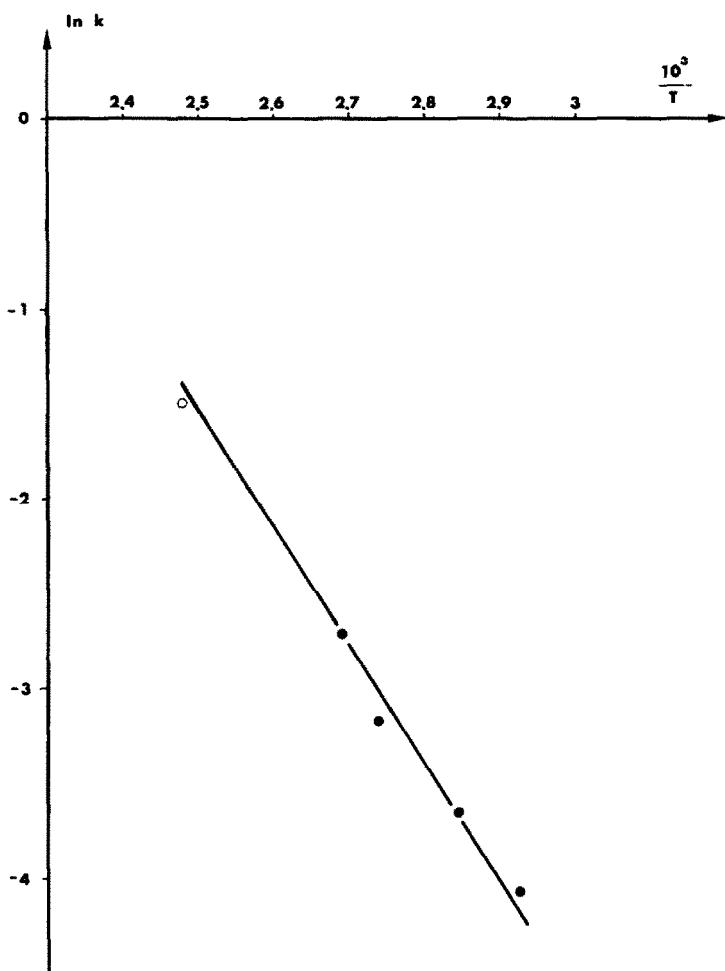| T (°C)	k (h^{-1})
68.4	1.7×10^{-2}
78.4	2.5×10^{-2}
88.4	4.1×10^{-2}
98.4	6.2×10^{-2}
130	0.22

Fig. 7. Variation with temperature of the rate law constant k; (●) our results; (○) point taken from ref. 6.

durations, as expected from expression (8). The curvature observed for the longer durations may be due to the occurrence of the reverse reaction. In order to confirm these results, we exploited, in the same way, the initial part of the curve of Fig. 2 corresponding to 130°C (ref. 6), and found that the points fit fairly well on a straight line. The values of k are obtained by linear regression (Table 6).

Drawing $\ln k$ vs. $\dfrac{1}{T}$ allows one to get a fairly good straight line, including the point corresponding to ref. 6, and to derive an activation energy of about 10 kcal mol^{-1} (Fig. 7).

Case of initially added water

According to eqn. (7), the decomposition rate is proportional to the fraction of undecomposed solid and to the fraction of decomposed solid. A
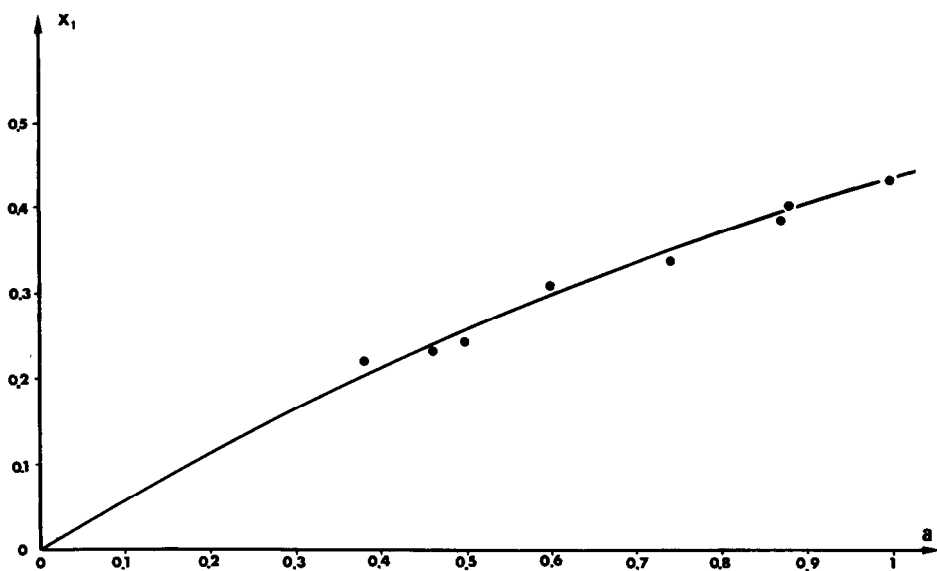
Fig. 8. Variation with the amount of initially added water of fractional conversion of ammonium carbamate: (●) experimental points obtained at 78.4°C; (———) theoretical curve representing eqn. (10).

possible interpretation is that the process is governed by the nucleation rate, which is itself proportional on the one hand to the amount of undecomposed solid, and on the other hand to the amount of a reaction product (here water) which contributes to create decomposition germs in the solid. If such an interpretation holds, when water is initially added in the amount of a moles per mole of carbamate, the kinetic expression (7) should be transformed into

$$\frac{d X_1}{dt} = k(1 - X_1)(a + X_1) \tag{9}$$

where the constant k depends on temperature only, and therefore takes the same value, at the same temperature, as in the preceding case. The integration of (9) gives

$$X_1 = a \frac{\exp k(a + 1)t - 1}{a \exp k(a + 1)t + 1} \tag{10}$$

The check consists in using the data of Table 5 and representing $X_1(a)$ for given k and t. Figure 8 shows that this check is quite satisfactory, the points derived from Table 5 fitting closely the theoretical curve derived from eqn. (10).

In conclusion, the equilibrium between ammonium carbamate, water and urea has been studied in conditions where it is realized in the liquid phase. The heterogeneous kinetics of ammonium carbamate decomposition into

urea and water could be measured and interpreted. This interpretation rests upon the key rôle played by the reaction product water, which appears to contribute to create decomposition germs.

LIST OF SYMBOLS

a	moles of water added per mole of carbamate
c	number of independent components
G	Gibbs free enthalpy
H	enthalpy
k	rate law constant
K	equilibrium constant
ln	Napierian logarithm
m	molality
M	molal mass
n	$\begin{cases} \text{number of moles} \\ \text{number of physical factors} \end{cases}$
P	pressure
$\mathscr{R}$	ideal gas constant
t	time
T	temperature
v	variance
w	weight
x	molal fraction in the liquid phase
X	fractional conversion

Greek letters

δ	uncertainty
Δ	variation
μ	chemical potential
ν	algebraic stoichiometric coefficient
φ	number of phases

Subscripts

1	relative to carbamate
2	relative to urea
3	relative to water
i	relative to any component
e	at equilibrium
l	in the liquid state
sat	value at saturation

sol   in the solid state

x relative to molal fractions

Superscript

0   initial state or reference state

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