BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1496—1498 (1973)

A Kinetic Study on the Decomposition of Benzyl *N*-(Hydroxymethyl)carbamate in Alkaline Solution[1]

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(Received August 11, 1972)

The decomposition of benzyl *N*-hydroxymethylcarbamate (*N*-BHMC) by potassium hydroxide was carried out in a mixed solvent dioxane–water. The following rate equation was obtained. $R_0 = k[N\text{-BHMC}]_0[\text{KOH}]_0$, where $[N\text{-BHMC}]_0$ and $[\text{KOH}]_0$ denote the initial concentrations of *N*-BHMC and potassium hydroxide, respectively. The equation is analogous to that of Ugelstadt[2] obtained for the hydrolytic decomposition of *N*-hydroxymethylbenzamide. Thus the reaction was assumed to proceed *via* the three steps:

1) $C_6H_5CH_2OCONHCH_2OH + OH^- \rightleftarrows C_6H_5CH_2OCONHCH_2O^- + H_2O$

2) $C_6H_5CH_2OCONHCH_2O^- \rightleftarrows C_6H_5CH_2OCONH^- + CH_2O$

3) $C_6H_5CH_2OCONH^- + H_2O \rightleftarrows C_6H_5CH_2OCONH_2 + OH^-$

We studied the reaction of benzyl carbamate (BC) with formaldehyde (F) in an aqueous dioxane solution using potassium hydroxide as a catalyst.[3] It was found that the rate equation is given by

$$R_0' = k'[\text{BC}]_0[\text{KOH}]_0[\text{F}]_0^{1 \text{ or } 0}$$

and the reaction order of formaldehyde changes from 1 to 0 with its concentration.

The following rate equation was obtained for the rate of decomposition of benzyl *N*-hydroxymethylcarbamate (*N*-BHMC) by potassium hydroxide.

$$R_0 = k[N\text{-BHMC}]_0[\text{KOH}]_0$$

where $[N\text{-BHMC}]_0$ and $[\text{KOH}]_0$ denote the initial concentrations of *N*-BHMC and potassium hydroxide, respectively.

The mechanism for decomposition of *N*-BHMC might be the same as Ugelstadt's in the reaction of the hydrolytic decomposition of *N*-hydroxymethylbenzamide.

Experimental

Materials. Benzyl carbamate was prepared by the method of Kraft[4] and recrystallized from toluene. Commercial toluene was used without further purification. Commercial dioxane was distilled at 101 °C.

Preparation of N-*BHMC.* To 15.1 g (0.1 mol) of benzyl carbamate in a 300 ml three-necked flask equipped with a stirrer, thermometer and condenser were added 12.2 g (0.15 mol) of 37% formaldehyde and 100 ml of water. The reaction mixture was stirred for 30 min at 60 °C at pH 8.6. Subsequently, the mixture was dissolved in 30 ml of methanol and cooled in a refrigerator. The solid separated was recrystallized from toluene to give *N*–BHMC as white needles; 10.2 g (5.6%), mp 86.5—87.5 °C. A test with a Tollens reagent was positive. IR (cm^{-1}); 3330 (ν(NH), ν(OH)), 1690 (ν(C=O)), 1520 (ν(CN)+δ(NH)). NMR (ppm); 7.94 (1H, –NH–), 7.39 (5H, $-C_6H_5$), 5.5—5.7 (1H, –OH), 5.1 (2H, $-CH_2-$), 4.4—4.64 (2H, $-N-CH_2O-$).

Found: C, 59.22; H, 6.38; N, 7.81%. Calcd for $C_8H_9NO_2$: C, 59.35; H, 6.59; N, 7.69%.

Measurement of the Rate of Decomposition. The rate was derived by measurement of the quantity of formaldehyde formed from the hydrolytic decomposition of *N*–BHMC.

A mixture of fixed amount of *N*–BHMC and 35 ml of dioxane was placed in a 50 ml volumetric flask and kept at constant temperature. After 20—30 min, a fixed amount of an aqueous solution of potassium hydroxide and then water were added up to the marked line, the time when the potassium hydroxide was added being taken as the starting time. 5 ml of the reaction mixture was then taken out at intervals. The concentration of the formaldehyde caused by the decomposition of *N*–BHMC was estimated by the KCN–

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[1] The preceding paper: S. Takeuchi, M. Kinoshita, K. Kō, and M. Imoto, *Makromol. Chem.*, **157**, 63 (1972).

[2] J. Ugelstadt, *Bull. Soc. Chim. Fr.*, **1955**, 138.

[3] S. Takeuchi, M. Kinoshita, K. Kō, and M. Imoto, *Kogyo Kagaku Zasshi*, **72**, 1362 (1969).

$Hg(NO_3)_2$ method.[5]

Results and Discussion

Reaction Order of N-*BHMC in the Hydrolytic Decomposition.* With the concentration of potassium hydroxide kept at 8.55×10^{-4} mol/l, the concentration of *N*-BHMC varied from 0.01 to 0.08 mol/l. A linear relationship was obtained between $\log a/(a-x) \times 10^{-3}$ and t, where the initial concentrations of *N*-BHMC and formaldehyde resulting from the reaction were given as a and x. Figure 1 shows the relationship between $\log a/(a-x) \times 10^{-3}$ and t.

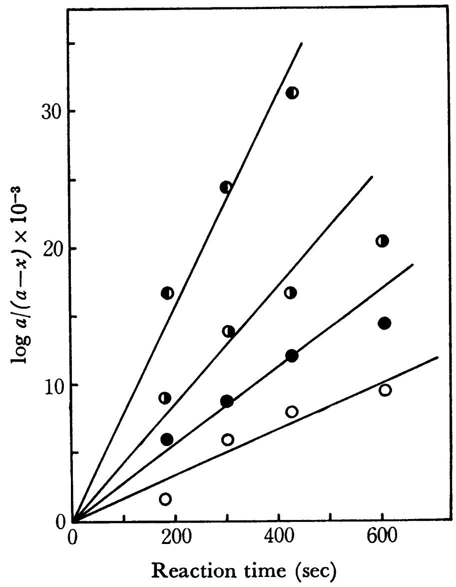

Fig. 1. The relationship between $\log a/(a-x)$ and t.
a=initial concentrations of *N*-BHMC.
x=consumption of *N*-BHMC.
N-BHMC in mol/l: -○- 0.01; -●- 0.02; -◑- 0.04; -◐- 0.08.

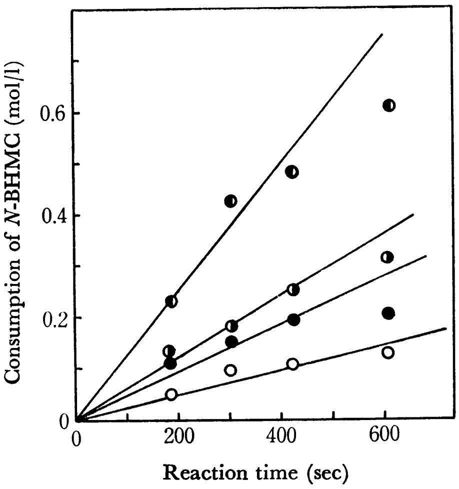

Fig. 2. The consumption of *N*-BHMC *vs.* reaction time at 35 °C.
The reaction conditions were as follows:
N-BHMC 0.04 mol/l. KOH 2.57—12.82×10^{-4} mol/l.

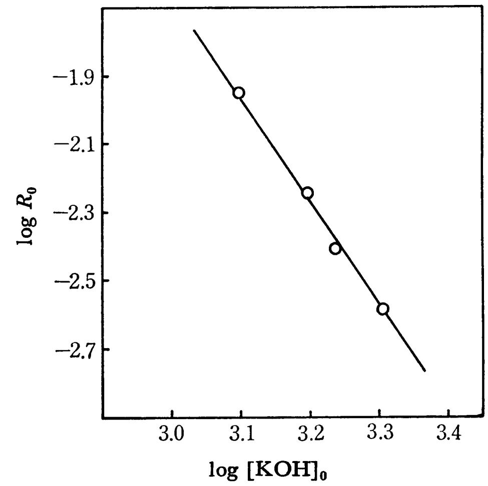

Fig. 3. The relationship between the rate and the concentration of KOH.

The reaction order of *N*-BHMC on the formation of formaldehyde is concluded to be 1.

Reaction Order of Potassium Hydroxide. With the concentration of *N*-BHMC kept at 0.04 mol/l, the concentration of potassium hydroxide varied from 2.57 to 12.82×10^{-4} mol/l. The rate of formation of formaldehyde increased linearly with progress of the reaction (Fig. 2), and the reaction order in potassium hydroxide was determined to be 1 from the slope of the straight line (Fig. 3).

From these results, the rate equation can be represented as follows.

$$R_0 = k[N\text{-BHMC}]_0[\text{KOH}]_0$$

Activation Energy of the Reaction. The activation energy of reaction of decomposition of *N*-BHMC in the presence of potassium hydroxide was calculated to be 14.4 kcal/mol at 30, 35, 40, 45, and 50 °C (Fig. 4). The value was higher than that of the reaction of formation of *N*-BHMC from benzyl carbamate and formaldehyde (13.8 kcal/mol). The activation entropy was calculated to be −22.24 e.u.

The Reaction Mechanism. Benzyl carbamate and

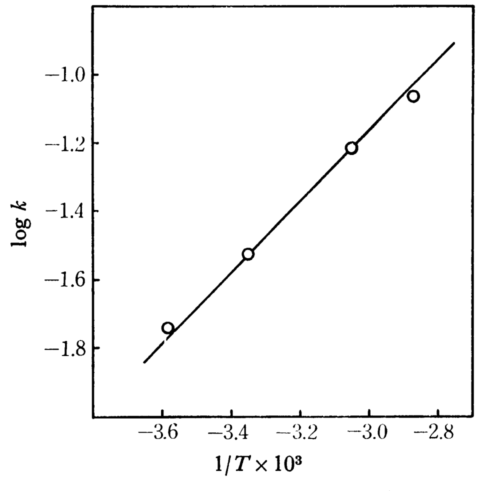

Fig. 4. The relationship between $\log k$ and T.

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[4] W. M. Kraft, *J. Amer. Chem. Soc.*, **70**, 3569 (1948).

[5] J. I. de Jonge and J. de Jonge, *Rec. Trav. Chim. Pays-Bas*, **72**, 356 (1953).

formaldehyde were proved to be obtained from the reaction of decomposition of *N*-BHMC.

$$C_6H_5CH_2OCONHCH_2OH \xrightarrow{OH^-} C_6H_5CH_2OCONH_2 + CH_2O$$

The reaction might proceed *via* the three steps which Ugelstadt showed in the reaction of decomposition of *N*-hydroxymethylbenzamide.

$$(1)\quad C_6H_5CH_2OCONHCH_2OH + OH^- \xrightleftharpoons[k_{-1}]{k_1} C_6H_5CH_2OCONHCH_2O^- + H_2O$$

$$(2)\quad C_6H_5CH_2OCONHCH_2O^- \xrightleftharpoons[k_{-2}]{k_2} C_6H_5CH_2OCONH^- + CH_2O$$

$$(3)\quad C_6H_5CH_2OCONH^- + H_2O \rightleftharpoons C_6H_5CH_2OCONH_2 + OH^-$$

Reactions (1) and (3) are supposed to reach equilibria rapidly. The rate of decomposition is given by

$$R_0 = k_2[C_6H_5CH_2OCONHCH_2O^-] \qquad \text{(a)}$$

From the steady state method we obtain

$$\frac{d[N\text{-BHMC}^-]}{dt} = k_1[N\text{-BHMC}][OH^-] - k_{-1}[N\text{-BHMC}^-] - k_2[N\text{-BHMC}^-] = 0$$

Thus

$$[N\text{-BHMC}^-] = \frac{k_1[N\text{-BHMC}][OH^-]}{k_{-1}+k_2} \qquad \text{(b)}$$

From Eqs. (a) and (b) we get

$$R_0 = \frac{d[F]}{dt} = k_2[N\text{-BHMC}^-] = \frac{k_2k_1[N\text{-BHMC}][OH^-]}{k_{-1}+k_2}$$

$$= \frac{k_2k_1}{k_{-1}+k_2}[N\text{-BHMC}][OH^-] = k[N\text{-BHMC}][OH^-]$$

The author wishes to express his thanks to Prof. Minoru Imoto, Kansai University, for his guidance,to Prof. Masayoshi Kinoshita, Osaka City University, for suggestions and encouragement, and to Dr. Eisaku Ninagawa, for valuable discussions.