May, 1986] © *1986 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 59, 1331—1335 (1986)*

Proton-Catalyzed Formation of Methyl Carbamate in the Reaction of Isocyanic Acid in Methanol

Hitoshi YASHIRO,† Jun-ichi TAKESHITA,†† Akitsugu OKUWAKI,* and Taijiro OKABE
Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Sendai 980

(Received August 14, 1985)

The rate of formation of methyl carbamate has been measured by a determination of the HNCO concentration. It can be expressed as follows: $r_c=k_c[\mathrm{HNCO}][\mathrm{H}^+]$. This rate equation was confirmed in the concentration range of HCl(0.76—1.53×10^{-3} mol dm^{-3}). Consequently, this reaction was subjected to a proton catalysis. However, at a H^+ concentration lower than 4×10^{-4} mol dm^{-3}, the observed rate was lower than that calculated by the rate equation, especially at a high HNCO concentration. This was explained by a reduction of the free HNCO concentration due to an association of HNCO with the formed carbamate.

Isocyanic acid reacts with alchohols to afford carbamates and allophanates.[1–2] The mechanism of the formation of carbamates via a rearrangement of the adduct without any consideration of catalysis was postulated by Blohm and Becker.[3] A detailed kinetic study of the HNCO–alcohol reaction, however, has been difficult since HNCO is produced in situ[4–6] because of its instability. Also a suitable method for determining HNCO or carbamates has not been developed.[7–8] The present authors have developed a method for a rapid determination of HNCO.[9] In this paper, the effects of HCl and triethylamine on the rate of formation of methyl carbamate are examined using the rapid method in a low-concentration range of HNCO($<$ 1.3 M) where the formation of methyl allophanate was negligible. Kinetic analyses show a proton-catalyzed mechanism for the reaction between MeOH and HNCO and a reduction mechanism regarding the rate by the formation of a complex.

Experimental

Reagents: Isocyanic acid was prepared and purified by Linhard's method.[10] The purity attained was 99.4% or greater. Methanol was purified by the usual method using magnesium activated by iodine. Methanolic hydrogen chloride solutions were prepared by bubbling HCl gas into MeOH. Sodium methoxide solution, 0.5 mol dm^{-3}, was prepared by addition of metallic Na pieces into MeOH.

Determination of HNCO: Excess MeONa was titrated with a standard HCl solution after adding a known amount of MeONa into a sample solution containing HNCO and filtering precipitated NaNCO.

Procedure: Methanol(20—30 cm^3) was placed in a 100-cm^3 round-bottomed flask with a ground-glass stopper and immersed in a thermostated bath. Isocyanic acid (0.7 g) was withdrawn with a pipet under a $\mathrm{N_2}$ stream from a storage tube immersed in a Dry Ice–MeOH bath and added into the flask. After rapid agitation, a 2-cm^3 sample was quickly removed and the initial HNCO concentration was determined. Samples were then taken at certain intervals. The reaction mixture was not stirred during the reaction because no precipitate formed and the rate of formation of the carbamate was not altered by agitation.

Results

Effect of Isocyanic Acid, Triethylamine, and Hydrogen Chloride Concentrations. Isocyanic Acid Concentration: Figure 1 shows the effect of the initial HNCO concentration on the decrease in the HNCO concentration at 293 K. The rate of formation of methyl carbamate in MeOH, r_c, can be written as follows:

$$r_c = \mathrm{d}[\mathrm{CH_3OCONH_2}]_\mathrm{T}/\mathrm{d}t = -\mathrm{d}[\mathrm{HNCO}]_\mathrm{T}/\mathrm{d}t = k[\mathrm{HNCO}]_\mathrm{T}^{\alpha}, \quad (1)$$

where α is the order of the reaction, k the rate

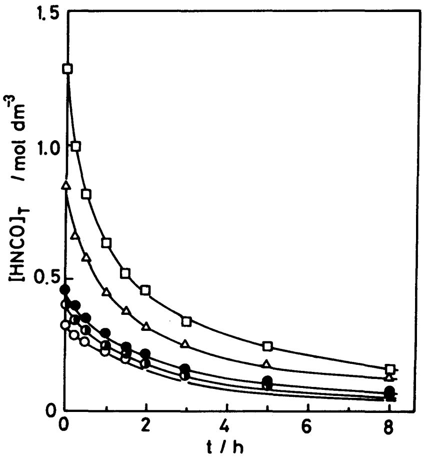

Fig. 1. Decreasing curves of concentration of HNCO at 293 K. $[\mathrm{HNCO}]_0$(mol dm^{-3}): (□) 1.285, (△) 0.830, (●) 0.452, (◑) 0.406, (○) 0.319. Curves are calculated ones.

[†] Present address: Department of Applied Chemistry, Faculty of Engineering, Iwate University, Morioka 020.

[††] Research Division, Japan Chemical Industrial Co. Ltd., Koto-ku, Tokyo 136.

constant for the formation of the carbamate, $[HNCO]_T$ the total HNCO concentration determined and $[CH_3OCONH_2]_T$ the total carbamate concentration. Then,

$$\log \tau_{1/m} = (1-\alpha)\log [HNCO]_0 + \log (m^{\alpha-1}-1)/k(\alpha-1), \tag{2}$$

where $\tau_{1/m}$ is the time required for decreasing the initial HNCO concentration to $1/m$ and $[HNCO]_0$ the initial HNCO concentration. Figure 2 shows plots of $\tau_{1/5}$ vs. $\log[HNCO]_0$. The order of the reaction, α, is 1.5 since the slope of the straight line is -0.5. From this data, we can write

$$2([HNCO]_T^{-1/2} - [HNCO]_0^{-1/2}) = kt. \tag{3}$$

This relationship is shown in Fig. 3. At an early stage, the relationship could be expressed by a dotted straight line. However the plots became lower than the straight line upon increasing the HNCO concentration and for a longer reaction time.

Triethylamine Concentration: In Fig. 4, 3/2 order rate plots are shown in the presence of triethylamine and methyl carbamate. The rate of formation was appreciably suppressed by triethylamine at about 10^{-4} mol dm^{-3}. The tendency is just reversed to the effect of bases on the reaction of phenyl isocyanate with MeOH in which the bases accelerated the formation of carbamates.[11] This discrepancy can be explained by the fact that triethylamine can not act as a base in the presence of a large excess of HNCO. Methyl carbamate also significantly reduced the rate.

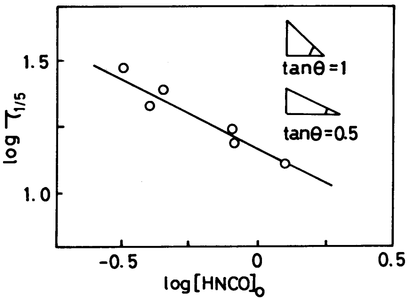

Fig. 2 Plot of log $\tau_{1/5}$ vs. $\log[HNCO]_0$.

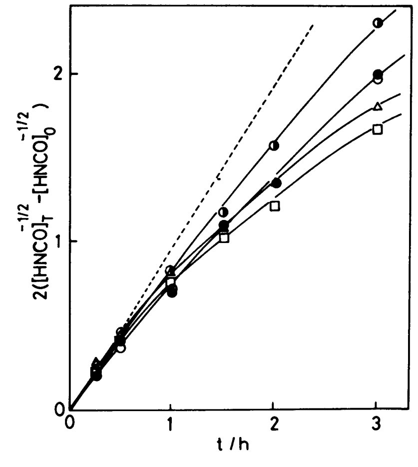

Fig. 3 Plot of $2([HNCO]_T^{-1/2}-[HNCO]_0^{-1/2})$ vs. t. $[HNCO]_0$(mol dm^{-3}): (□) 1.285, (△) 0.830, (●) 0.452, (◑) 0.406, (○) 0.319.

Hydrogen Chloride Concentration: The rate of formation of methyl carbamate at 293 K was accelerated upon increasing the HCl concentration and became almost proportional to the first-order of the HNCO concentration at 4×10^{-3} mol dm^{-3}.

Discussion

Mechanism of the Formation of Methyl Carbamate. Rate Equation. The reactions ionvolved in the system can be considered as follows:

$$HNCO \overset{K_1}{\rightleftharpoons} H^+ + NCO^- \tag{4}$$

$$CH_3OH + HNCO \xrightarrow[k_c]{H^+} CH_3OCONH_2 \tag{5}$$

$$CH_3OCONH_2 + HNCO \overset{K_2}{\rightleftharpoons} CH_3CONH_2\cdot HNCO \tag{6}$$

$$HCl \longrightarrow H^+ + Cl^- \tag{7}$$

$$(C_2H_5)_3N + H^+ \longrightarrow (C_2H_5)_3NH^+, \tag{8}$$

where k_c is the rate constant. K_1 and K_2 are the equilibrium constants for Eqs. 4 and 6, respectively.

Figure 5 shows the relationship between the HCl concentration and the slopes of the straight lines ($k_c[H^+]$) obtained from the first-order plots for the

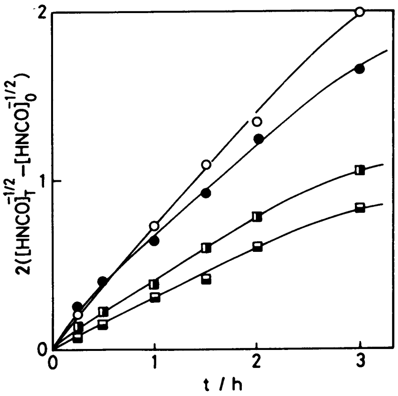

Fig. 4 Suppression of the rate of formation of methyl carbamate in the presence of triethylamine and methyl carbamate at 293 K.

	$[HNCO]_0$	$[(C_2H_5)_3N]$	$[CH_3OCONH_2]$ (mol dm^{-3})
(○)	0.406	—	—
(◨)	0.422	1.01×10^{-4}	—
(⬓)	0.497	2.02×10^{-4}	—
(●)	0.468	—	0.480

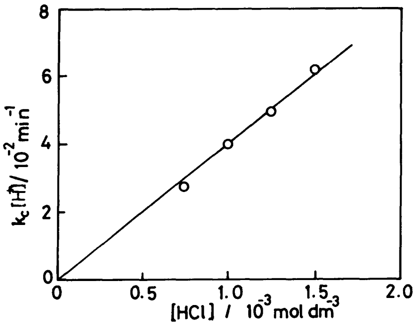

Fig. 5 Relationship between the apparent first-order rate constant($k_c[H^+]$) and concentration of HCl at 273 K.

HNCO concentration at 0.76—1.53×10^{-3} mol dm^{-3} of HCl and 273 K. This result supports the calculation that the rate of formation of the carbamate can be expressed by Eq. 9.

$$r_c = k_c[HNCO][H^+] \tag{9}$$

Rate-Determining Step. Blohm et al.[3] infered from an analogy to the mechanism of conversion of NH_4NCO to urea that carbamates are produced via a zwitterionic intermediate shown by Eq. 10(**a**). However, HNCO can hardly form such stable

$$CH_3OH + HNCO \overset{K_3}{\rightleftharpoons} CH_3\overset{+}{O}H\overset{-}{C}ONH \tag{10}$$

intermediate with MeOH since it is not a base such as NH_3. We considered simply that methyl carbamate was produced by a general acid-catalyzed reaction as shown by Eq. 9(**b**), since there were not enough data to discuss the proton-transfer process in the formation of methyl carbamate.

Mechanism of the Reduction of Rate by Methyl Carbamate. The plots in Fig. 3 became lower than the dotted line as the reaction proceeded. The tendency was enhanced at higher HNCO concentrations and for a longer reaction time. This may indicate that the formed methyl carbamate inhibited the reaction. This was confirmed by the result that the rate of formation decreased in the presence of 0.48 mol dm^{-3} methyl carbamate as shown in Fig. 4. From the rate Eq., there are the following three mechanisms by which the carbamate reduces its rate of formation: **A**) Reduction of the H^+ concentration, **B**) Reduction of the free HNCO concentration, **C**) Reduction of both concentrations. Each mechanism is discussed below.

In the case of **A**, the simplest mechanism is the formation of $CH_3OCO\overset{+}{H}NH_2$ as

$$CH_3OCONH_2 + H^+ \overset{K_4}{\rightleftharpoons} CH_3OCO\overset{+}{H}NH_2 \tag{11}$$

However, the decreasing curves of the HNCO concentration calculated by this mechanism could not be fitted with experimental data. The H^+ concentration was reduced remarkably by this mechanism; hence, the first-order linear relationship in Fig. 5 can not be obtained in such a low HCl concentration. Consequently, we did not consider any model composed of only case **A** as the mechanism of the reduction of rate. In the case of **B**, the simplest mechanism is the formation of a 1:1 complex as shown in Eq. 6. In this case, the H^+ concentration also slightly decreases through Eq. 4. In the case of **C**, the simplest mechanism is a combination of **A** and **B**.

Mechanism of the Formation of Methyl Carbamate. Four models can be made from the combination of the rate-determining step(**a** or **b**) and the mechanism of the reduction of rate(**B** or **C**) as follows: I **b-B**, II **b-C**, III **a-B**, IV **a-C**. In order to determine the optimum model, the decreasing curves of HNCO concentration as a function of time were simulated with these models.

In models III and IV, the decreasing curves could be fitted with the experimental ones only by model III. However, the formation constant (K_3) for the zwitterionic intermediate obtained was too great (1.0×10^{-2} mol^{-1} dm^3). Thus, model III is not reasonable since this value brings about a high concentration of the unstable intermediate.

In models I and II, the decreasing curves could be fitted with the experimental ones only by model I. The agreement could be obtained even in the presence of triethylamine, methyl carbamate, or HCl. In this model there is the problem that the formation of the 1:1 complex has not been confirmed by any other experiment. However, it is considered from the following facts that a weak interaction between an acid and base acts between methyl carbamate and HNCO to form the complex.

Isocyanic acid reacts quantitatively with strong bases such as MeONa or NaOH to precipitate the NaNCO[9] used in this study. An ion pair, $NH_4^+NCO^-$ is formed in DMSO between HNCO and NH_3 which is a weak base, and the formation constant is 79.6 at $\mu=0.0142$.[12] It is known that carbamates promote the formation of those carbamates as base-catalyst.[11] In Fig. 4, it is shown that methyl carbamate is a very weak base.

Simulation. Theoretical Rate Equation. In order to calculate the rate of formation of methyl carbamate by Eq. 9, the concentrations of free HNCO and H^+ based on the model I shown by Eqs. 4—8 are derived as a function of initial and total concentrations of HNCO as follows. It will be shown that the first and 3/2 order rate equations can be derived by this model.

$$[\mathrm{HNCO}] = [\mathrm{HNCO}]_T - [\mathrm{NCO^-}] - [\mathrm{CH_3OCONH_2\cdot HNCO}] \qquad (12)$$

$$= [\mathrm{HNCO}]_T/(1+K_2[\mathrm{CH_3OCONH_2}]) \qquad K_1/[\mathrm{H^+}] \ll 1 \qquad (13)$$

The concentration of free carbamate, $[\mathrm{CH_3OCONH_2}]$, in Eq. 13 can be expressed as follows.

$$[\mathrm{CH_3OCONH_2}] = [\mathrm{CH_3OCONH_2}]_T - [\mathrm{CH_3OCONH_2\cdot HNCO}] \qquad (14)$$

$[\mathrm{CH_3OCONH_2}]_T$: total concentration; $[\mathrm{HNCO}]_0 - [\mathrm{HNCO}]_T$ (or $[\mathrm{CH_3OCONH_2}]_0 + [\mathrm{HNCO}]_0 - [\mathrm{HNCO}]_T$)

$$[\mathrm{CH_3OCONH_2}] = [\mathrm{CH_3OCONH_2}]_T/(1+K_2[\mathrm{HNCO}]) \qquad (15)$$

This relationship is substituted in Eq. 13 and the expression is arranged.

$$K_2[\mathrm{HNCO}]^2 + (1+K_2[\mathrm{HNCO}]_0 - 2K_2[\mathrm{HNCO}]_T)[\mathrm{HNCO}] - [\mathrm{HNCO}]_T = 0 \qquad (16)$$

Thus, the HNCO concentration is expressed by Eq. 17 as the reasonable solution for Eq. 16.

$$[\mathrm{HNCO}] = [-(1+K_2[\mathrm{HNCO}]_0 - 2K_2[\mathrm{HNCO}]_T) + \{(1+K_2[\mathrm{HNCO}]_0 - 2K_2[\mathrm{HNCO}]_T)^2 + 4K_2[\mathrm{HNCO}]_T\}^{1/2}]/2K_2 \qquad (17)$$

On the other hand, the concentration of $\mathrm{H^+}$ can be expressed in the presence of HCl or triethylamine as follows.

In the Presence of HCl:

$$[\mathrm{H^+}] = [\mathrm{HCl}] + [\mathrm{NCO^-}] \qquad (18)$$

Consequently, the concentration of $\mathrm{H^+}$ can be expressed by Eq. 19.

$$[\mathrm{H^+}] = \{[\mathrm{HCl}]+([\mathrm{HCl}]^2+4K_1[\mathrm{HNCO}])^{1/2}\}/2 \qquad (19)$$

In the Presence of Triethylamine:

$$[\mathrm{H^+}] = [\mathrm{NCO^-}] - [(\mathrm{C_2H_5})_3\mathrm{NH^+}] \qquad (20)$$

This can be solved similarly in the case of HCl, and the concentration of $\mathrm{H^+}$ is expressed by Eq. 21.

$$[\mathrm{H^+}] = \{-[(\mathrm{C_2H_5})_3\mathrm{N}]_T+([(\mathrm{C_2H_5})_3\mathrm{N}]_T^2 + 4K_1[\mathrm{HNCO}])^{1/2}\}/2 \qquad (21)$$

Only HNCO: Hydrogen ion concentration can easily be derived from Eq. 19 or Eq. 21 as follows:

$$[\mathrm{H^+}] = K_1^{1/2}[\mathrm{HNCO}]^{1/2} \qquad (22)$$

Thus, r_c can be expressed as Eq. 23.

$$r_c = k_cK_1^{1/2}[\mathrm{HNCO}]^{3/2} \qquad (23)$$

This Eq. is the differential form of Eq. 3 and k is equal to $k_cK_1^{1/2}$. Blohm and Becker[3] pointed out that if $\mathrm{H^+}$ catalyzed the formation of carbamates, HNCO itself behaved as a catalyst. This was confirmed by the present work. In the presence of 10^{-3} mol dm^{-3} of HCl, the $\mathrm{H^+}$ concentration is nearly equal to that of HCl since K_1 is very small and the free HNCO concentration can be replaced by that of the total HNCO at an early stage. Consequently, a first-order rate equation can be obtained. Thus, the two experimental rate equations could be derived from this mechanism.

Calculation of Rate and Equilibrium Constants. Generally, the rate equation is an ordinary differential equation

$$r_c = f([\mathrm{HNCO}]_T,\ [\mathrm{HCl}],\ [(\mathrm{C_2H_5})_3\mathrm{N}],\ k_c,\ K_1,\ K_2). \qquad (24)$$

These constants can be determined by solving Eq. 24 using the Runge-Kutta numerical-integration method to obtain the total concentration of HNCO at each reaction time by assuming these values.

The following values were obtained: k_c=131 mol^{-1} dm^3 min^{-1}, $K_1=1.57\times10^{-8}$ mol dm^{-3}, K_2=1.11 mol^{-1} dm^3 and σ=0.03622 mol^2 dm^{-6}. The value of $k_cK_1^{1/2}$ calculated from k_c and K_1 obtained is 1.01 h^{-1} and agreed with the observed value of 1.00+0.15 h^{-1} within experimental error. The solid lines in Fig. 1 are the decreasing curves of HNCO concentration calculated using these values. The calculated curves agreed well with the observed values.

Apparent Activation Energy and Dissociation Constant of HNCO. The relationships of Eq. 3 for 0.5 mol dm^{-3} HNCO solution at 273—303 K are shown in Fig. 6. In an early stage, linear relationships were observed. The apparent activation energy was 88 KJ mol^{-1} according to an Arrhenius plot of the slopes. The dissociation constant for HNCO at 273 K

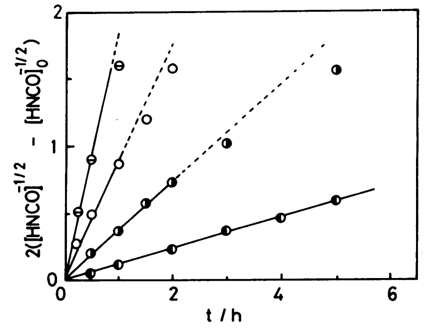

Fig. 6 Effect of temperature on the rate of formation. $[\mathrm{HNCO}]_0$ (mol dm^{-3}): (⊖) 0.471, 303 K, (○) 0.406, 293 K (◑) 0.501, 283 K, (◐) 0.429, 273 K.

can be calculated from the values of $k_cK_1^{1/2}$ and k_c. These were 1.97×10^{-3} mol^{-1} dm$^{3/2}$min^{-1} and 40 mol^{-1} dm^3 min^{-1} from the slopes in Figs. 5 and 6, respectively. Thus, the dissociation constant of HNCO in MeOH is 2.40×10^{-9} mol dm^{-3} at 273 K and 1.57×10^{-8} mol dm^{-3} at 293 K.

Conclusion

In a kinetic study of the formation of methyl carbamate from HNCO in MeOH, we conclude that the rate-determining step is the reaction of MeOH and HNCO under the catalysis of proton and the product, methyl carbamate, reduces the apparent rate of its formation by association with HNCO to afford a complex.

References

1) "Gmelins Handbuch", **14**, C[D1], (1971), p 327.

2) D. J. Belson and A. N. Strachan, *Chem. Soc. Rev.*, **11**, 41 (1982).

3) H. W. Blohm and E. I. Becker, *Chem. Rev.*, **51**, 471 (1952).

4) R. A. Jacobson, *J. Am. Chem. Soc.*, **60**, 1742 (1938).

5) M. Amagasa, Y. Kasuga, Y. Saito, T. Yamaguchi, and H. Takekawa, *Kobunshi Kagaku*, **28**, 42 (1971).

6) E. S. Lane, *J. Chem. Soc.*, **1951**, 2764.

7) M. Spielman, J. D. Barnes, and W. J. Close, *J. Am. Chem. Soc.*, **72**, 2520 (1950).

8) W. J. Close, and M. A. Spielman, *J. Am. Chem. Soc.*, **75**, 4055 (1953).

9) H. Yashiro, J. Takeshita, A. Okuwaki, and T. Okabe, *Nippon Kagaku Kaishi*, **1984**, 1473.

10) M. Linhard, *Z. Anorg. Allg. Chem.*, **236**, 200 (1936).

11) J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, **1947**, 713.

12) K. J. Hall and D. W. Watts, *Aust. J. Chem.*, **30**, 781 (1977).