Synthetic Zeolites as Catalysts for the Ring Conversion of γ-Butyrolactone into 1-Substituted 2-Pyrrolidinones

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Synthetic zeolites were found to be effective catalysts for the synthesis of 1-substituted 2-pyrrolidinone by the reaction of γ-butyrolactone with amines. 1-Propyl-2-pyrrolidinone was obtained in the equilibrium yield with practically 100% selectivity over copper exchanged Y-zeolite at 280 °C. The effects of reaction temperature, contact time and partial pressures of the reactants were examined. A reaction mechanism is proposed for the ring transformation based on the kinetic studies of the reaction of γ-butyrolactone with propylamine.

Transformation of heterocycles into compounds containing a ring system differing from that of starting substance provides a convenient method for the synthesis of some heterocycles. As an example, 2-pyrrolidinone can be obtained by the reaction of γ-butyrolactone and ammonia.[1] Usually, the reaction is carried out in a liquid phase under pressure. The ring transformations of cyclic ethers or lactones into the corresponding cyclic imines or lactams can be effectively carried out in a vapor phase by using synthetic zeolites as catalysts.[2-7] Over copper-exchanged Y zeolites, 2-pyrrolidinone was obtained from γ-butyrolactone in 80—90% yield.[4] We have carried out the synthesis of 1-substituted 2-pyrrolidinones from γ-butyrolactone in a vapor phase with use of zeolites as catalysts. A detailed study has been carried out on the kinetics of the reaction and a reaction mechanism is proposed in the case of the reaction of γ-butyrolactone with propylamine to form 1-propyl-2-pyrrolidinone.

Experimental

Measurements.   All the boiling points are uncorrected. The determination of infrared spectra was made on a Shimadzu IR-6 spectrophotometer. The NMR spectra were recorded in tetrachlorometane solution with a spectrometer using tetramethylsilane as an internal reference. Gas chromatograms were obtained using a 2 m column packed with a 10% PEG-6000 on Shimalite-F operating at 200 °C.

Materials.   γ-Butyrolactone (Tokyo Chemical Industry) was distilled just before each reaction. Amines (Wako Pure Chemical Industry) were used without purification.

Catalyst.   NaY-zeolite (Linde SK-40) was used as the starting material for all the catalysts. Various cation forms of zeolites were prepared by the conventional cation exchange procedure using salt solutions. The cation exchanged zeolites were pelleted without a binder and crushed and sized into 9—16 mesh.

Apparatus and Procedure.   A continuous flow reactor was used under atomspheric pressure. The reactor is a silica tubing (13 mm i.d.) placed in a vertical furnace. Prior to the reaction, the catalyst in the reactor was heated in an air stream at 500 °C (or 450 °C for HY) for 60 min. The liquid reactants were pumped with microfeeders into the preheating zone of the reactor containing 10 ml quartz or α-alumina (about 24 mesh). The gaseous materials were fed through flowmeters. Nitrogen was used as a diluent for

regulating the initial pressure of reactants. Reaction products collected in the receiver maintained at 0 °C was withdrawn at certain intervals during the run and were analyzed by gas chromatography. 2-Pyrrolidinone, 1-methyl-2-pyrrolidinone and 1-ethyl-2-pyrrolidinone were identified by comparison of their infrared spectra with that of authentic samples. Other products were assignd by IR, NMR, and the elemental analysis methods.

1-Propyl-2-pyrrolidinone.   Bp 94—96 °C, 9 mmHg. C=O band 1693 cm⁻¹. NMR (CCl₄, δ) 0.80—1.00 (t, 3H), 1.24—1.80 (m, 2H), 1.90—2.40 (m, 4H), 3.06—3.47 (m, 4H). Found: C, 66.33; H, 10.46; N, 11.27%. Calcd for C₇H₁₃NO: C, 66.10; H, 10.30; N, 11.01%.

1-Butyl-2-pyrrolidinone.   Bp 116—118 °C, 10 mmHg. C=O band 1686 cm⁻¹. NMR (CCl₄, δ) 0.80—1.85 (t, 3H), 1.16—1.61 (m, 4H), 1.86—2.41 (m, 4H), 3.09—3.46 (m, 4H). Found: C, 67.83; H, 10.79; N, 10.30%. Calcd for C₈H₁₅NO: C, 68.04; H, 10.71; N, 9.92%.

1-Isobutyl-2-pyrrolidinone.   Bp 96—98 °C, 10 mmHg. C=O band 1676 cm⁻¹. NMR (CCl₄, δ) 0.80—0.91 (d, 6H), 1.64—2.40 (m, 5H), 2.92—3.02 (d, 2H), 3.20—3.40 (t, 2H). Found: C, 67.82; H, 10.69; N, 9.77%. Calcd for C₈H₁₅NO: C, 68.04; H, 10.71; N, 9.92%.

1-s-Butyl-2-pyrrolidinone.   Bp 102—103 °C, 10 mmHg. C=O band 1677 cm⁻¹. NMR (CCl₄, δ) 0.75—0.96 (t, 3H), 1.04—1.16 (d, 3H), 1.25—1.70 (m, 2H), 1.86—2.37 (m, 4H), 3.12—3.33 (t, 2H), 3.70—4.21 (m, H). Found: C 68.31; H, 10.89; N, 10.20%. Calcd for C₈H₁₅NO: C, 68.04; H, 10.71; N, 9.92%.

1-t-Butyl-2-pyrrolidinone.   C=O band 1672 cm⁻¹.

1-Pentyl-2-pyrrolidinone.   Bp 124—126 °C, 14 mmHg. C=O band 1676 cm⁻¹. NMR (CCl₄, δ) 0.80—0.99 (t, 3H), 1.15—1.59 (m, 6H), 1.86—2.34 (m, 4H), 3.09—3.44 (m, 4H). Found: C, 69.60; H, 11.14; N, 8.99%. Calcd for C₉H₁₇NO: C, 69.63; H, 11.04; N, 9.02%.

1-Hexyl-2-pyrrolidinone.   133—134 °C, 10 mmHg. C=O band 1681 cm⁻¹. NMR (CCl₄, δ) 0.80—0.99 (t, 3H), 1.15—1.60 (m, 8H), 1.80—2.35 (m, 4H), 3.07—3.45 (m, 4H). Found: C, 71.55; H, 11.46; N, 8.45%. Calcd for C₁₀H₁₉NO: C, 70.96; H, 11.23; N, 8.28%.

1-Phenyl-2-pyrrolidinone.   Mp 67—68 °C. C=O band 1676 cm⁻¹. NMR (CCl₄, δ) 1.86—2.64 (m, 4H), 3.68—3.91 (t, 2H), 7.03—7.70 (m, 5H). Found: C, 74.60; H, 6.83; N, 8.79%. Calcd for C₁₀H₁₁NO: C, 74.51; H, 6.88; N, 8.69%.

Results and Discussion

Catalytic Activity of Various Cation Forms of Zeolite.
The catalytic activities of various cation forms of Y-zeolite for the reaction of γ-butyrolactone and propylamine were compared under the following conditions:

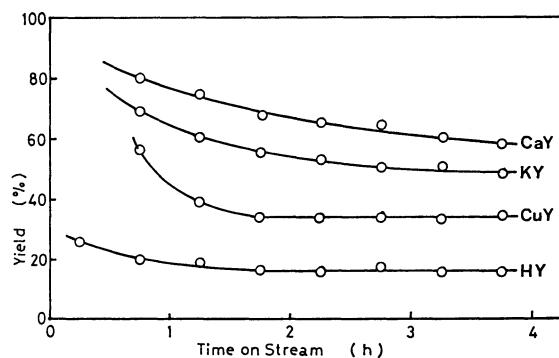* Present address: Faculty of Education, Saitama University, Urawa, Saitama 338.

Fig. 1. Change in the yield of 1-propyl-2-pyrrolidinone over various zeolites at 280 °C.

reaction temperature 280 °C, catalyst weight 1 g, flow rate of reactants; γ-butyrolactone 24×10^{-3} mol/h, propylamine 122×10^{-3} mol/h, flow rate of nitrogen 99×10^{-3} mol/h. The catalytic activities decreased with time (Fig. 1). The activity and selectivity for the production of 1-propyl-2-pyrrolidinone on various cation forms of zeolites are given in Table 1. The values refer to the data obtained after the reaction had proceeded for 3 h. Besides 1-propyl-2-pyrrolidinone, a small amount of N-propyl-4-hydroxybutyramide was produced. Selectivity is defined as follows.

$$\text{Selectivity (\%)} = \frac{\text{mol of pyrrolidinone produced}}{\text{mol of } \gamma\text{-butyrolactone reacted}} \times 100.$$

The highest yield of the pyrrolidinone was obtained over CaY (calcium exchanged Y zeolite), followed by alkaline cation forms (Table 1). The best selectivity for the pyrrolidinone was observed for CuY, the most stable catalyst for the reaction (Fig. 1). Thus, CuY was used exclusively for further investigations. Though the activity decreased gradually with stream hours, it is completely recovered by calcining the used catalyst under air stream at 500 °C.

Reaction of γ-Butyrolactone with Various Amines.
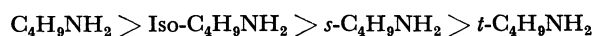The reactions of γ-butyrolactone (I) with various primary amines were carried out with CuY as a catalyst

TABLE 1. ACTIVITY AND SELECTIVITY FOR THE REACTION OF γ-BUTYROLACTONE OVER VARIOUS Y-ZEOLITES

Cation	Conversion of I %	Yield of III %	Selectivity for III %
H	23	15	65
Li	47	36	77
Na	38	30	80
K	58	50	86
Rb	54	46	85
Cs	54	44	81
Mg	24	15	63
Ca	73	62	85
Sr	20	10	50
Ba	16	6	38
Cu	37	34	92
Ni	35	27	77
Co	23	16	70
Zn	16	6	38

Catalyst 1 g. Reaction temperature 260 °C. Feeding rate of I 24.0×10^{-3} mol/h. Reactant ratio II/I=5.08. Total feed (I+II+N$_2$) 225×10^{-3} mol/h.

at 280 °C. The results are summarized in Table 2. The yield of 2-pyrrolidinones depends on the nature of the amines, but the selectivity of the reaction is quite high. In addition to neat amines, the amine in aqueous solution can be used for the synthesis.

The yield of 2-pyrrolidinone in the reaction of I with ammonia was lower than that with primary amines. This may be caused by the difference in the basicity of ammonia and primary amines. The steric effect also seems to be important for the reactions; the yield of 2-pyrrolidinones depends on the starting amine in the following order.

$CH_3NH_2 \approx C_3H_7NH_2 > C_4H_9NH_2 >$

$C_5H_{11}NH_2 > C_6H_{13}NH_2 > PhNH_2$

$C_4H_9NH_2 > \text{Iso-}C_4H_9NH_2 > \text{s-}C_4H_9NH_2 > \text{t-}C_4H_9NH_2$

Since the basicity of alkylamines hardly depends at

TABLE 2. ACTIVITY AND SELECTIVITY FOR THE REACTION OF γ-BUTYROLACTONE WITH VARIOUS AMINES OVER Cu–Y

Amine	P_I (atm)	R_I ($\times 10^{-3}$ mol/h)	P_{amine} (atm)	R_{amine} ($\times 10^{-3}$ mol/h)	Yield of pyrrolidinone (%)	Selectivity (%)
Ammonia	0.098	24	0.497	122	12	68
Methylamine	0.098	24	0.497	122	98	98
Methylamine[a]	0.052	20	0.192	73	56	—
Ethylamine[b]	0.075	20	0.258	67	80	—
Propylamine	0.098	24	0.497	122	96	98
Butylamine	0.098	24	0.409	101	86	94
Isobutylamine	0.098	24	0.508	124	85	96
s-Butylamine	0.098	24	0.404	99	64	92
t-Butylamine	0.098	24	0.571	140	4	88
Pentylamine	0.098	24	0.522	128	60	92
Hexylamine	0.098	24	0.440	108	49	95
Aniline	0.098	24	0.446	109	8	—

Catalyst Cu–Y 3 g. Reaction temperature 280°C. Total feed(I+amine+N$_2$): 245×10^{-3} mol/h. P: partial pressure. R: feeding rate. a) 40% aqueous solution. b) 70% aqueous solution.

all on the kind of alkyl group, the difference in the yield of 2-pyrrolidinone seems mainly to be caused by the steric effect. The bulkier the alkyl group, the less the reactivity of amine toward I. Since propylamine (II) has a high reactivity toward I with high selectivity, the various parameters determining the yield of 1-propyl-2-pyrrolidinone (III) were examined by using propylamine as a strating amine.
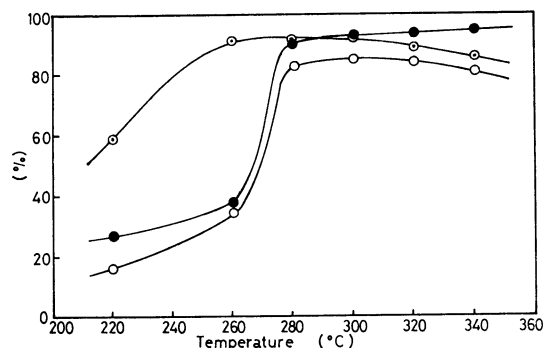

Fig. 2. Effect of reaction temperature on the catalytic behavior of CuY in the reaction of γ-butyrolactone with propylamine.
●: Conversion of γ-butyrolactone, ○: yield for 1-propyl-2-pyrrolidinone, ◉: selectivity for 1-propyl-2-pyrrolidinone.

Influence of the Reaction Temperature.   Figure 2 shows the temperature dependence of the yield of III by the reaction of I with II. The yield of III increases with temperature up to 320 °C, decreasing slightly above 320 °C. Thus, the optimum temperature seems to lie around 300 °C.

Effect of Contact Time.   Effect of the contact time (W/F) on the yield of III from I and II over CaY and CuY was examined. W/F is defined as follows.

$$W/F = \frac{\text{Weight of catalyst (g)}}{\text{Total feed (I+II+N}_2\text{) (mol/h)}}$$

The results are illustrated in Fig. 3. The partial pressure of I was kept constant at 0.098 atm and that of II was varied in the range 0.088—0.497 atm. The yield of III increased with contact time, reaching a constant value which does not depend on the nature of the catalyst. Thus, the reaction seems to proceed until equilibrium is reached. The apparent equilibrium constant (K_P)
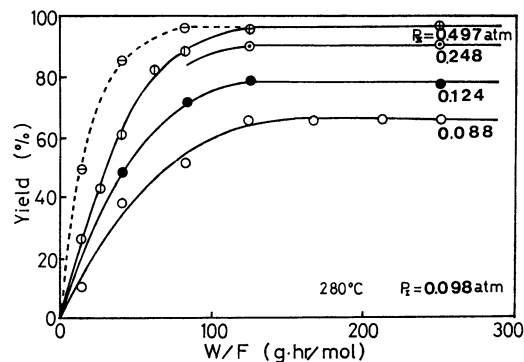

Fig. 3. Effect of contact time (W/F) on the yield of 1-propyl-2-pyrrolidinone over CuY (———) and CaY (------).

values estimated from the data in Fig. 3 are given in Table 3. The K_P value does not depend on the initial reaction conditions, suggesting that the reaction proceeds nearly to equilibrium.

Reaction Kinetics.   The kinetics of the reaction of I and II was studied with CuY as a catalyst. Reaction kinetics was examined in the temperature range 240—280 °C under small contact time conditions for the reaction of I and II. The effect of the partial pressure of I (P_I) on the reaction rate was examined by keeping the partial pressure of II (P_{II}) at 0.348 atm. The partial pressure of nitrogen was adjusted to keep the contact time constant. The result is given in Fig. 4.
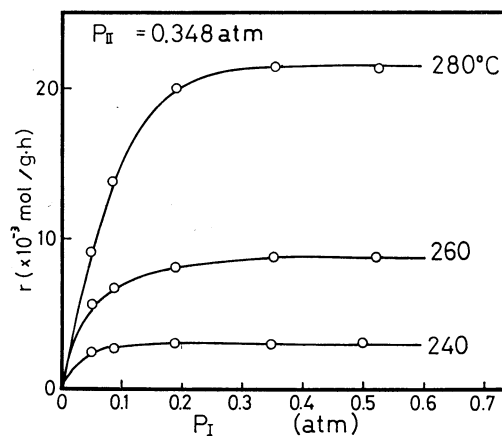

Fig. 4. Dependence of the reaction rate on the partial pressure of γ-butyrolactone.

TABLE 3. APPARENT EQUILIBRIUM CONSTANT OF THE REACTION OF γ-BUTYROLACTONE WITH PROPYLAMINE

| Catalyst | Feeding rate of reactant | | Formation rate of III | Yield of III | Apparent equilibrium constant |
| | I | II | | | |
	$\times 10^{-3}$ mol/h	$\times 10^{-3}$ mol/h	$\times 10^{-3}$ mol/h	%	K_p
CuY, CaY	24.0	121.6	23.0	95.8	5.4
CuY	24.0	60.8	21.6	90.0	5.0
CuY	24.0	30.4	18.5	77.1	5.6
CuY	24.0	21.5	15.8	65.8	5.3

Catalyst 3 g. Reaction temperature 280 °C. Total feed (I+II+N$_2$) 245×10^{-3} mol/h.

$$K_p = \frac{P^*_{III} \cdot P^*_{H_2O}}{P^*_I \cdot P^*_{II}} = \frac{P^{*2}_{III}}{P^*_I \cdot P^*_{II}}$$

P^*: partial pressure at the reactor exit.

The dependence of the rate (r) on the partial pressure of I can be expressed by

$$r = k_I \cdot \frac{K_I P_I}{1 + K_I P_I}, \tag{1}$$

were k_I and K_I are constants. By rearrangement, we have

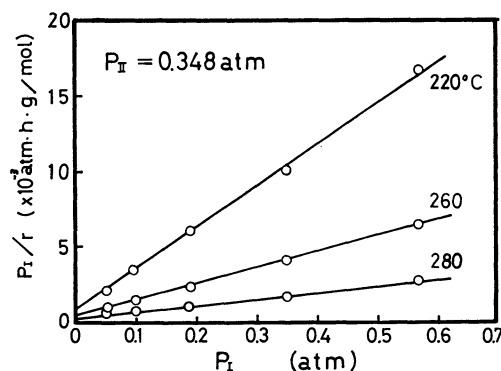$$\frac{P_I}{r} = \frac{1}{k_I K_I} + \frac{P_I}{k_I}, \tag{2}$$
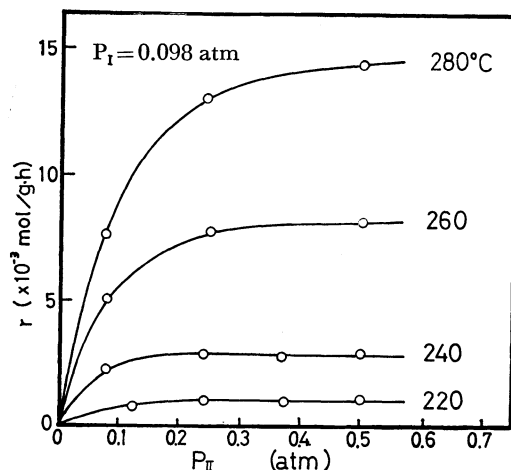

Fig. 5. P_I/r vs. P_I plot.

Fig. 6.   Dependence of the reaction rate on the partial pressure of propylamine.

Straight lines are obtained by plotting P_I/r against P_I (Fig. 5). The slope and the intercept give the values of $1/k_I$ and $1/k_I K_I$, respectively.

The dependence of the reaction rate on the partial pressure of II was examined by keeping P_I at 0.098 atm (Fig. 6). It was found to be represented also by

$$r = k_{II} \cdot \frac{K_{II} P_{II}}{1 + K_{II} P_{II}}, \tag{3}$$

which, on rearrangement, gives

$$\frac{P_{II}}{r} = \frac{1}{k_{II} K_{II}} + \frac{P_{II}}{k_{II}}. \tag{4}$$
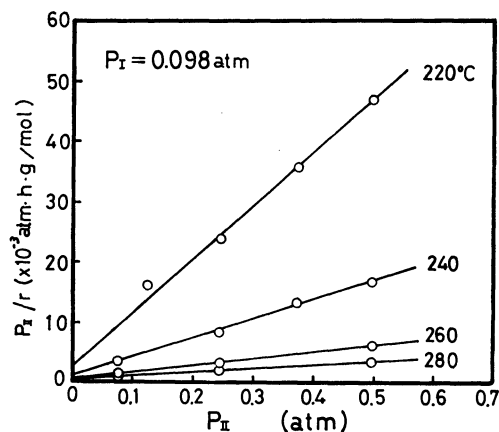

Fig. 7. P_{II}/r vs. P_{II} plot.

The relation was checked (Fig. 7) and the values of k_{II} and K_{II} were obtained.

Thus, the following kinetic expression is obtained from Eqs. 1 and 3:

$$r = k \cdot \frac{K_I P_I}{1 + K_I P_I} \cdot \frac{K_{II} P_{II}}{1 + K_{II} P_{II}}, \tag{5}$$

where

$$k_I = k \cdot \frac{K_{II} P_{II}}{1 + K_{II} P_{II}} \quad \text{and} \quad k_{II} = k \cdot \frac{K_I P_I}{1 + K_I P_I}.$$

From the values of k_I, k_{II}, K_I, and K_{II}, obtained experimentally, the value of k was determined uniquely. The values of K_I, K_{II} are given in Table 4.

Equation 5 indicates that there are independent adsorption sites for I and amine and that the reaction of the adsorbed I and adsorbed amine is rate determining. The activation energy of the reaction, the heats of adsorption of I and II were determined to be 23 kcal/mol, 9.0 kcal/mol, and 9.9 kcal/mol, respectively.

It was also confirmed that rate does not depend on the partial pressure of water or III, by addition of water or III to the feeding reactant.
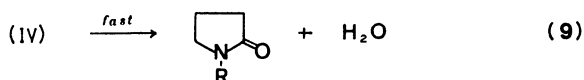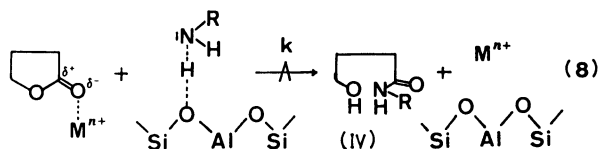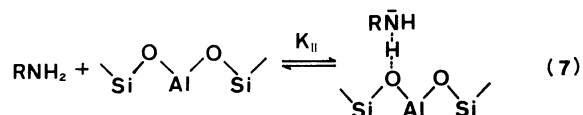
Reaction Mechanism.   The reaction kinetics represented by Eq. 5 suggests that there is an independent adsorption site for each reactant. In a previous work on the reaction of I and ammonia, it was postulated that polarization of the carbonyl group of I to the strong electrostatic field in the neighborhood of the metal cation is essential. The same should hold for the reaction with primary amines. The adsorption sites for I are probably metal cations.

The adsorption site for primary amines might be the oxygen ions next to aluminum cations in the zeolitic framework. Dissociative adsorption of ammonia has been observed on the oxide ions of alumina surface.[8]

Table 4.   Kinetic parameters for the reaction of γ-butyrolactone and propylamine over CuY

Temperature (°C)	k_I ($\times 10^{-3}$ mol/g·h)	K_I (atm^{-1})	k_{II} ($\times 10^{-3}$ mol/g·h)	K_{II} (atm^{-1})	k ($\times 10^{-3}$ mol/g·h)
220	—	—	1.11	45.2	—
240	3.66	32.1	3.15	24.9	4.1
260	9.28	26.3	9.62	20.8	12.1
280	23.25	21.5	16.39	15.3	20.9

Thus, we proposed the following reaction mechanism.

$$\text{[structure]} + M^{n+} \xrightleftharpoons{K_I} \text{[structure]} \cdots M^{n+} \quad (6)$$

$$RNH_2 + \text{[Si–O–Al–O–Si structure]} \xrightleftharpoons{K_{II}} \text{[structure with } R\bar{N}H\ H\text{]} \quad (7)$$

$$\text{[structure]} + \text{[structure]} \xrightarrow[A]{k} \text{[structure]} (IV) + M^{n+} \quad (8)$$

$$(IV) \xrightarrow{fast} \text{[lactam structure]} + H_2O \quad (9)$$

Equations 6 and 7 represent the adsorption of I and primary amine on metal cation and oxygen anion in the zeolite framework, respectively. The activated reactants react with each other to form an acid amide like intermediate IV (Eq. 8), the step being rate determining. The dehydration of the intermediate to the lactam is fast. This mechanism is in line with Eq. 5, if we put the adsorption equilibrium constant of I and primary amine, K_I and K_A and the rate constant of the elementary reaction (Eq. 8), k. This mechanism also expresses the effect of the kind of amines on their reactivity toward I. The elementary reaction (Eq. 8) should be faster, if the basicity of the amine increases; primary normal alkylamines react more readily with I than ammonia. The large steric effect is expected since

the reaction occurs on the surface of zeolite. The interaction between the carbonyl group of I and the lone pair of the amine may need very specific special arrangement.

Low activity of hydrogen form of the zeolite (HY) should be noted since the origin of catalytic activity of the zeolite is very often ascribed to the protonic acidity of the zeolite. In the case of the reaction studied, protonic acid probably reacts with amines to form ammonium ions.

$$NH_2R + H^+ \rightleftharpoons NH_3R^+.$$
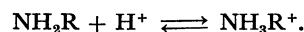
This explains the low activity of HY.

References

1) E. Späth and J. Lintner, Chem. Ber., **69**, 2727 (1936).

2) K. Hatada, M. Shimada, K. Fujita, Y. Ono, and T. Keii, Chem. Lett., **1974**, 439.

3) K. Fujita, K. Hatada, Y. Ono, and T. Keii, J. Catal., **35**, 325 (1974).

4) K. Hatada, M. Shimada, Y. Ono, and T. Keii, J. Catal., **37**, 166 (1975).

5) Y. Ono, K. Hatada, K. Fujita, A. Halgeri, and T. Keii, J, Catal., **41**, 322 (1976).

6) Y. Ono, Y. Takeyama, K. Hatada, and T. Keii, Ind. Eng. Chem., Prod. Res. Dev., **15**, 180 (1976).

7) Y. Ono, M. Kaneko, A. Halgeri, and K. Hatada, "Molecular Sieves-II," ACS Symposium Series, No. 40, ed by J. R. Katzer, American Chemical Society, Washington (1977), p. 596.

8) J. B. Peri, J. Phys. Chem., **69**, 231 (1969).