NOTES

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (8), 2419—2420 (1978)

The Ring Transformation of Tetrahydrofuran into 1-Propylpyrrolidine over Y-Zeolites

Kou HATADA, Katsuhiro FUJITA, and Yoshio ONO*
Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

(Received February 13, 1978)

Synopsis. The catalytic activities of Y-zeolites for the synthesis of 1-propylpyrrolidine from tetrahydrofuran and propylamine were examined. Aluminum cation exchanged zeolite was found most active, 65% yield of 1-propylpyrrolidine being attained at 360 °C. The kinetics of the reaction was examined and the reaction mechanism suggested.

The ring transformation of tetrahydrofuran (THF) into 1-alkylpyrrolidine proceeds over alumina.[1–2] Reppe and coworkers obtained 1-ethylpyrrolidine in 61% yield by the reaction of THF and ethylamine at 300 °C for 6 h over ThO_2-promoted alumina.[2] Synthetic zeolites are effective catalysts for the ring transformations of γ-butyrolactone into 1-alkyl-2-pyrrolidinones,[3] and THF into pyrrolidine.[4] This note reports that zeolites are effective also for the ring conversion of THF into 1-alkylpyrrolidine: Tetrahydrofuran is converted into 1-propylpyrrolidine by the reaction with propylamine over zeolites with a flow reactor under atmospheric pressure.

Experimental

THF and propylamine were distilled prior to each run. NaY zeolite (Linde Division of Union Carbide Corp.) was used. Various forms of Y-zeolites were prepared by the conventional cation exchange procedure using aqueous solution of the corresponding salt. The cation exchanged zeolites were pelleted without binder and crushed and sized into 9—16 mesh. A continuous flow reactor was used under atmospheric pressure. A silica tube (13 mm i.d.) placed in a vertical furnace was used as a reactor. The reactants were pumped into the preheating zone of the reactor containing 10 ml quarts powder. Nitrogen used as a diluent for regulating the initial pressure of the reactants was fed through a flow meter. Reaction products collected in the reciver were taken out at certain intervals during the course of run and analyzed by gas chromatography.

Results and Discussion

The reaction of THF and propylamine was carried out at 300 °C and at $W/F=5.56$ g h mol^{-1} (W is the weight of catalyst and F the molar flow rate), and the catalytic activities of the various cation forms of Y-zeolites for the ring conversion were examined. The results (Table 1) show that HY and zeolites with trivalent cations except CeY have high activity. Of the zeolites studied, the selectivity to 1-propylpyrrolidine was the highest with AlY, further study thus being made exclusively with AlY.

Figure 1 shows the temperature dependence of the

TABLE 1. ACTIVITY AND SELECTIVITY FOR THE REACTION OF THF AND PROPYLAMINE OVER VARIOUS Y-ZEOLITES

Catalyst	Conversion of THF %	Yield of 1-propylpyrrolidine %	Selectivity %
AlY	61	46	76
FeY	58	42	72
CrY	52	40	76
HY	41	21	50
MgY	33	16	50
CuY	24	10	42
CeY	12	6	50
NaY	10	1	10

Reaction temperature, 300 °C; $W/F=5.56$ g h mol^{-1}, $W=1.0$ g; reactant molar ratio, THF: propylamine: $N_2=1:5.25:2$.

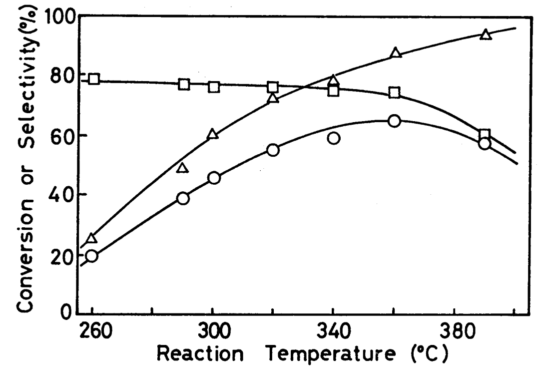

Fig. 1. Effect of reaction temperature on the catalytic behavior of AlY in the reaction of THF and propylamine (△): conversion of THF, (○): yield of 1-propylpyrrolidine, (□): selectivity to 1-propylpyrrolidine.

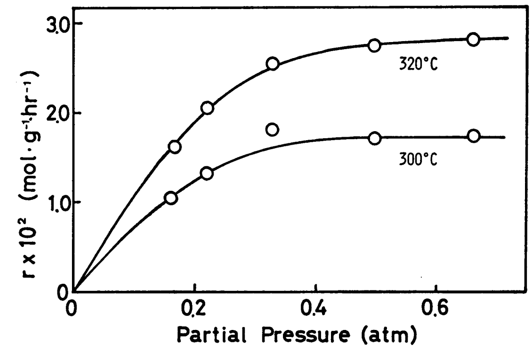

Fig. 2. Dependence of the reaction rate on the partial pressure of propylamine; $W/F=2.78$ g h mol^{-1}, $P_{THF}=0.232$ atm.

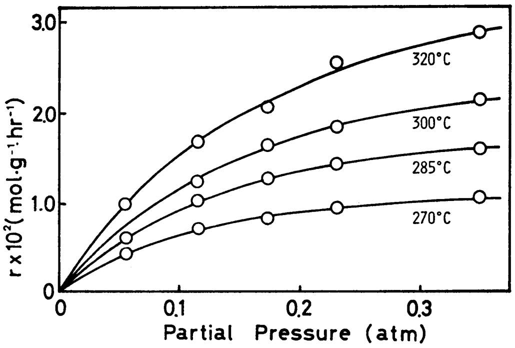

Fig. 3. Dependence of the reaction rate on the partial pressure of THF; $W/F=2.78$ g h mol^{-1}, $P_A=0.334$ atm.

THF conversion, the yield of and the selectivity to propylamine. The maximum yield of propylamine was obtained at 360 °C. A constant selectivity of 75% was obtained in the temperature range upto 360 °C, but the selectivity fell at 380 °C. No attempt was made to identify the byproducts.

The kinetics of the reaction was studied with AlY as a catalyst in the temperature range 270—320 °C under small contact time conditions. Figures 2 and 3 show the dependence of the reaction rate on the partial pressures of propylamine (P_A) and THF (P_{THF}), respectively. In both cases, the rate increases with an increase in the partial pressure of the reactants. The rate (r) is given by

$$r = k\cdot\frac{K_AP_A}{1+K_AP_A}\cdot\frac{K_{THF}P_{THF}}{1+K_{THF}P_{THF}}, \quad (1)$$

where k is the rate constant, and K_A and K_{THF} are the adsorption equilibrium constants of propylamine and THF, respectively. The plots of P_A/r against P_A and P_{THF}/r against P_{THF} give straight lines. The constants k, K_A, and K_{THF} are determined unequivocally. From the temperature dependence of the constants, the activation energy of the reaction, the heats of adsorption of propylamine and THF are determined to be 16 kcal mol^{-1} and 6 kcal mol^{-1}, respectively.

In a previous work,[3] a rate expression similar to Eq. 1 was obtained for the reaction of γ-butyrolactone and propylamine. A mechanism was proposed, in which the lactone and the amine are adsorbed on the metal cation (or proton) and zeolitic oxygen anion, respectively, the reaction of the adsorbed reactants being concluded as the rate determining step.

A similar mechanism may be applied to the reaction of THF and propylamine. Propylamine molecules are adsorbed and dissociated by oxygen anions, while THF molecules open the ring by the interaction with protonic sites, as has been assumed for the reaction of THF and ammonia.[4,5] The fact that the heat of adsorption of propylamine obtained from the kinetics of its reaction with THF (10 kcal mol^{-1}) agrees with that obtained from the kinetics of its reaction with γ-butyrolactone (9.9 kcal mol^{-1})[3] supports the essential similarity of the mechanism of the two reactions.

References

1) Yu. Yur'ev, V. I. Bazan, A. N. Esafova, S. M. Seliverstova, and S. I. Chernyakhover, *J. Gen. Chem. USSR*, **10**, 1839 (1940), *Chem. Abstr.*, **35**, 4377 (1941).

2) W. Reppe and co-workers, *Ann.*, **596**, 143 (1955).

3) K. Hatada and Y. Ono, *Bull. Chem. Soc. Jpn.*, **50**, 2517 (1977).

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

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