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The Ring-Opening Reactivities of Three-Membered Cyclic Compounds. I. The Ring-Opening Reactions of Three-Membered Cyclic Compounds by Hydrogen Chloride

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There have been many reports about the relative reactivities of cyclic ethers in cationic copolymerizations,[1-3] and these reactivities have been evaluated as linear combinations of the basicity of the ring and the ring strain[2] or the radical dissociation energy of the broken bond.[3]

There have, however, been few reports discussing how the changes in the heteroatoms of the rings influence the reactivities of heterocyclic compounds.[4,5] In this paper, the ring-opening reactions of three-membered cyclic compounds by hydrogen chloride will be studied in toluene in order to discuss their relative reactivities. As three-membered rings, methyl cyclopropane (MCP), propylene oxide (PO), propylenimine (PI), and propylene sulfide (PS) will be used.

Results and Discussion

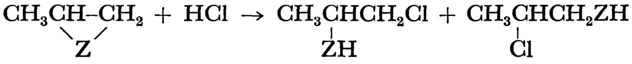
Ring-opening reactions of MCP were carried out at 40 °C and 60 °C. In these reactions, isobutyl chloride, **1a**, could not be observed; only *sec*-butyl chloride, **1b**, could be detected by gas chromatography. The ring-opening reaction rate was so slow that the kinetic study was difficult.

Table 1. Rate constants for the ring-opening reactions by HCl

Reaction temp. (°C)[a]	PO 10^2k_2 (l/mol s)	PI 10^2k_2 (l/mol s)	PS 10^4k_2 (l/mol s)
40			4.83 4.81 5.02
30	10.1 10.3	4.49 5.29	3.14 3.04 3.06
20	3.62 4.05	3.23 3.80	2.00 2.09 1.91
10	2.77 2.59	2.52 2.21	1.53
0	1.46 1.48 1.34	1.52 1.70	

a) ±0.1°C

The ring-opening reactions of three-membered heterocyclic compound by HCl obey second-order kinetics, depending on the first order both in the heterocyclic compound concentration and in the HCl concentration. The kinetic results are shown in Table 1. According to the Eyring equations, the activation parameters were calculated; they are shown in Table 2. In these reaction systems, two kinds of reaction products were produced:



$$\underset{\diagdown Z \diagup}{CH_3CH\text{–}CH_2} + HCl \rightarrow CH_3\underset{ZH}{\underset{|}{C}}HCH_2Cl + CH_3\underset{Cl}{\underset{|}{C}}HCH_2ZH$$

Z=O	**2a**	**2b**
Z=NH	**3a**	**3b**
Z=S	**4a**	**4b**

The ring-opening reaction products of PO were separated into their components, **2a** and **2b**, by gas chromatography, and each of them was analyzed by NMR spectroscopy. In the gas chromatogram, two peaks of the reaction products were observed with retention times 8.7 and 11.4 min, respectively. The chemical shift of the methyl protons of the former is 8.70 τ, and that of those of the latter, 8.50 τ. Considering the difference between the shielding effect due to a substituent in the β-position to methyl protons, the former is **2a**, and the latter, **2b**.[6]

Two kinds of aminopropanols in the PI–HCl reaction system were analyzed by NMR(D_2O) spectroscopy. The methyl-proton spectra of two kinds of reaction products were separated into 1.35 and 1.55 ppm, respectively; the lower-field absorption in the signals was assigned to the abnormal product, **3b**.

In the ring-opening reaction of PS, two kinds of chloropropanethiols were analyzed by both gas chromatography and NMR(C_6H_6) spectroscopy according to the modified method of Schwarz.[7]

The results of product analyses (Table 2) show that the ring-opening reactions of three-membered heterocyclic compounds proceed *via* an S_N2-type mechanism and that the normal products, **2a**, **3a**, and **4a**, are produced in larger amounts.[5,8] The reaction rate decreases in the following order: PO, PI, PS, and MCP. The order of the reactivity corresponds to neither that of the basicity[9] nor that of the ring strain[10]

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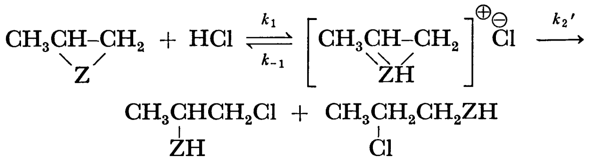
TABLE 2. THE ACTIVATION PARAMETERS AND THE PRODUCT RATIOS IN THE RING-OPENING REACTION OF THREE-MEMBERED CYCLIC COMPOUNDS BY HCl

	MCP	PO	PI	PS
$\Delta H^{\ddagger}$(kcal/mol)[a]	—	9.5±0.5	5.5±0.3	6.7±0.3
$\Delta S^{\ddagger}$(e.u.)[a]		−32.0±1.9	−46.3±1.0	−51.8±0.9
Product ratio[b] (a : b)	0 : 100	67 : 33	86 : 14	62 : 38
Ring strain[c] (kcal/mol)	27.43	27.28	26.87	19.78
Association const[d] with phenol K (l/mol)	?	5.95	139	1.081

a) At 30 °C, b) At room temp., c) Ref. 10, d) At 20 °C. See ref. 9. That of PI was calculated from the average value of ethylene imine and 2,2-dimethylethylene imine.

(Table 2). In the protonic acid system, the ring-opening reaction is that of the conjugate acid by the anion, as follows:



Z=O, NH, S

The apparent rate constant, k_2, can, then, be expressed as the product of the equilibrium constant, $K(=k_1/k_{-1})$, and the rate constant of the elementary reaction, k_2'. The former is related to the basicity of the ring, while the latter is influenced by the ring strain of the conjugate acid. However, it is difficult to find the dependence of the ring-opening reactivity on either the ring strain or the basicity of the ring, because the relation between the ring strain of the three-membered ring and that of its conjugate acid is unknown and the equilibrium constant can not be determined.

The details of the reactions of MCP in other protonic acid systems will be reported in the near future.

Experimental

Reagents. Methyl cyclopropane was prepared by the method of Demjanoff[11] and was dried over phosphorus pentoxide. Propylene oxide was a commercial product; it was dried over calcium hydride and then distilled; bp 35.0 °C. Propyleneimine was prepared by the method of Wenker,[12] dried over sodium metal, and distilled; bp 64.0—66.0 °C. Propylene sulfide was prepared by the method of Bordwell *et al*,[13] dried over anhydrous sodium carbonate, and distilled; bp 72.0—75.0 °C. All three-membered cyclic compounds were distilled just before use. Toluene was purified by the usual method, and the anhydrous HCl solution in toluene was prepared by the method of Manson.[14]

Kinetic Measurements. The reaction was carried out in toluene under dry nitrogen in a 200 ml four-necked flask equipped with a thermometer, a stirrer, and a cooler. The gas chromatographic conditions in the MCP–HCl reaction were: internal standard, carbon tetrachloride; column materials, 25 wt% tricresyl phosphate 75 cm×3 mm; column temp., 40 °C; carrier gas, He 50 ml/min. The rate constants for the reaction of PO with HCl were measured in the following manner. At desired time intervals, a constant volume of the reaction mixture was withdrawn and poured into a constant volume of a potassium hydroxide methanol solution (M/10). The conversion of PO was calculated from the amount of the remaining potassium hydroxide, which was determined with a benzoic acid methanol solution (M/25), using phenolphthalein as the indicator. The reaction rate of PO was too fast to determine the conversion of PO by gas chromatography. Kinetic measurements of the reaction of PI with HCl were carried out in the same manner as those of the PO–HCl reaction system except that initial mole ratio, HCl/PI, was controlled at 2. The true residual values of HCl were calculated as twice the apparent values of HCl, because two kinds of aminopropanols act as bases in the back titration. The influence of PI should be negligible, for PI is a weak and it consumes only HCl 1×10^{-5} mol/PI 0.01 mol. The rate constants for the reaction of PS with HCl were measured by determining the residual PS under the following gas chromatographic conditions: internal standard, chlorobenzene; column material, 25 wt% tricresyl phosphate 75 cm×3 mm; column temp., 120 °C; carrier gas, He 50 ml/min. In this reaction, the residual HCl could not be determined because the reaction products, chloropropanethiols, act as acids.

Product Analyses. *sec*-Butyl chloride was prepared as an authentic sample from *sec*-butyl alcohol. The gas chromatographic conditions in the PO–HCl reaction system were: column material, carbowax 1500 300 cm×3 mm; column temp., 80 °C; carrier gas, He 50 ml/min. 2-Chloro-*n*-propylamine hydrochloride was prepared as an authentic sample from 1-amino-2-propanol hydrochloride; mp 186.0—187.0 °C(lit,[15] 187—190 °C). 2-Chloropropane-1-thiol, **4b**, was prepared by the method of Davis *et al.*;[16] it contained about 10% of the isomer, **4a**.

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