Taft's Plot for the Co-pyrolysis of 2-Chloroethyl Compound and Methanol on Activated Alumina

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Synopsis. For the co-pyrolysis of 2-chloroethyl compounds with methanol on activated alumina, the ρ^* value was +0.49, indicating a nucleophilic reaction mechanism.

For the pyrolysis of chloroethanes on activated alumina, ρ^* values were negative, indicating an electrophilic reaction mechanism.[1] On the other hand, positive ρ^* values were observed for the elimination of hydrogen chloride from chloroethanes with sodium hydroxide in ethanol, as well as in the co-pyrolysis with methanol on activated alumina.[1,2]

The effect of the molecular structure on the consumption rate of the substrate was studied by carrying out the co-pyrolysis of 2-chloroethyl compounds and methanol on activated alumina.

Results and Discussion

It has been reported that the co-pyrolysis of organic chlorides and methanol on activated alumina proceeded according to good first-order kinetics.[3] Even if two organic chlorides were competitively co-pyrolyzed with methanol on activated alumina, it seemed reasonable to assume that the consumption rates were first-order in each substrate.

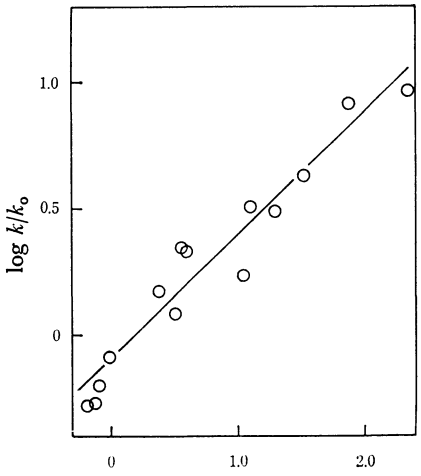

Fig. 1. Taft's plot for co-pyrolyses of 2-chloroethyl compounds and methanol on activated alumina at 250 °C.

In order to investigate the effect of the polar nature of the substituent upon the reactivity in the co-pyrolysis of organic chlorides with methanol on activated alumina, Taft's plot was applied to this heterogeneous catalysis:

$$\log k/k_0 = \rho^*\sigma^*, \quad (1)$$

where k/k_0 is the relative rate constant with respect to the standard reaction (1,1,2,2-tetrachloroethane in this case) and where σ^* represents the polar substituent parameter, which is a measure of the inductive effect.[4] A linear free-energy relationship was found to exist between the reactivity and Taft's σ^*, as is shown in Fig. 1. A value of ρ^* was calculated by the method of least squares to be +0.49.

Experimental

Materials. The 4-chlorobutyronitrile was prepared by the reaction of 1-bromo-3-chloropropane and potassium cyanide described in the literature.[5] The 1-chloro-3-methoxypropane was prepared from 1-bromo-3-chloropropane by modifying the method of Henne and Haeckl.[6] All of the other reagents used in this work were purchased from the Tokyo Kasei Kogyo Co. except for methanol and ethanol, which were obtained from Nakarai Chemicals. All the chemicals were used without further purification. The activated alumina used as catalyst (KHD-24) was supplied by the Sumitomo Chemical Co.: the particle diameter was in the range from 2 to 4 mm.

General Procedure for Co-pyrolysis. The flow-type reaction system of a previous work[7] was used. The organic chlorides were mixed with methanol in the volume ratio of 1.0 : 1.0 : 5.0. In all runs, two organic chlorides were competitively pyrolyzed at 250 °C to check the balance of such volatile products as propylene and to keep the effect of the time factor and the concentration of methanol constant.

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