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The Role of Acidic Centers in the Isomerization and Hydrogenolysis of Oxiranes. Reply to Bartók, Notheisz, and Kiss

Bartók *et al.* (*1*) have suggested an explanation for the difference in the ring-opening selectivity of oxirane isomerization and hydrogenolysis on platinum catalysts observed by us (*2*) and by Sénéchal and Cornet (*3*). On the basis of their own experimental results they conclude that platinum catalysts prepared from H_2PtCl_6, which may contain residual Cl atoms due to incomplete reduction, act in the same way as acidic catalysts. We agree with them that this could be the reason for the high butanal to 2-butanone ratios in our experiments with 1,2-epoxybutane (ethyloxirane) as our catalyst was prepared by the reduction at only 200°C. Data on the reactions of 1,2-epoxypropane (methyloxirane) and 1,2-epoxyhexane (1-butyloxirane) on the same catalyst which we have obtained recently seem to support this view.

Table 1 shows the observed selectivities S_c (aldehyde to ketone ratios) and S_a (1-alkanol to 2-alkanol ratios); in the case of 1,2-epoxypropane our values correspond to $S = 0.13$ in the notation of Bartók *et al.* (*1*). The selectivity S_c and the isomerization reactivity (Fig. 1, Table 2) exhibit opposite trends with the change of the alkyl group substituent; however, this is regularly observed in reactions of organic compounds. The reactivity trend corresponds to the electrophilic character of the isomerization, i.e., to acid catalysis, suggested by Bartók *et al.* (*1*). On the contrary, the rate of formation of the alcohols (hydrogenolysis) does not depend on the structure of the oxirane (Fig. 1, Table 2); this confirms the difference in rate-determining steps of the two reaction routes. However, as the selectivities S_a achieve high values and change with the structure of the reactants, there could be a common step in the reaction pathways leading to isomerization and hydrogenolysis products.

On the other hand, high S_c ratios and their independence of partial pressures of the oxiranes and hydrogen, observed with all oxiranes, makes the hypothesis of Bartók *et al.* (*1*) on parallel operation of two types of active centers, consisting of completely and incompletely reduced platinum atoms, improbable. Similarly, we do not see how the "metallic" mechanism as-

TABLE 1

Mean Selectivity Values of Oxirane Ring Splitting at 175°C on Pt/C

Compound	S_c	S_a
1,2-Epoxypropane	7.8	7.7
1,2-Epoxybutane	3.6	7.0
1,2-Epoxyhexane	2.6	5.2

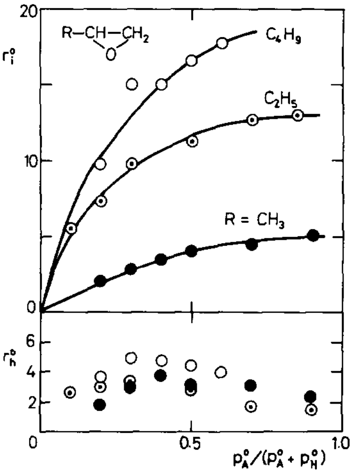

FIG. 1. Dependences of the initial reaction rates of oxirane isomerization r_i^0 and hydrogenolysis r_h^0 (in mol h^{-1} g_{cat}^{-1}) on the composition of the reaction mixture at 170°C on the Pt/C catalyst.

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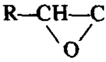
cribed (*1*) to the fresh Pt/Cr_2O_3 catalyst can change to the "acidic" one by aging.

TABLE 2

Constants of the Rate Equations for the Isomerization and Hydrogenolysis of Oxiranes



$R{-}\overset{}{CH}{-}CH_2$ (epoxide, O bridging CH and CH_2)

at 175°C on Pt/C[a]

Constant	R		
	CH_3	C_2H_5	C_4H_9
	Isomerization (Eq. (5) in (*2*))		
k_i	12.7	18.0	27.0
$K_A{}^i$	7	17	20
C_H	4	4	4
	Hydrogenolysis (Eq. (6) in (*2*))		
k_h	150	149	155
$K_A{}^h$	7	14	19
K_H	16	17	16

[a] k_i, k_h in mol h^{-1} $g_{cat}{}^{-1}$; $K_A{}^i$, $K_A{}^h$, C_H, K_H in MPa^{-1}.

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