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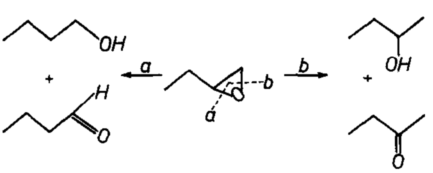
LETTERS TO THE EDITORS

The Role of Acidic Centers in the Isomerization and Hydrogenolysis of Oxiranes

Davidová and Kraus (*1*) recently studied the isomerization and hydrogenolysis of 1,2-epoxybutane on Pt/C and Pt/Cr_2O_3 catalysts, with particular attention to the kinetics of the two parallel processes. They found that the transformation on Pt/C was accompanied by the formation of much more butanal and 1-butanol than 2-butanone and 2-butanol.



Sénéchal and Cornet (*2*) reported that butanal was not formed in the hydrogenolysis of 1,2-epoxybutane on Pt/pumice as catalyst, and that the amount of 1-butanol produced was much lower than the amounts of 2-butanol and 2-butanone.

Our own earlier investigations (*3*) led us to the conclusion that the isomerization of oxiranes and oxetanes to aldehydes results from the action of the acidic centers of the catalyst. These mutually contradictory data relating to the selectivity of the ring-opening, together with the need for the role of the metal to be clarified, stimulated us to make a comparison of support-free catalyst and various types of supported catalysts.

The experimental method, apparatus, chromatographic conditions, identification, and evaluation were described previously (*4*). Investigations were carried out with a pulse microreactor technique, in a carrier gas stream of hydrogen at 50 ml/min, in the presence of 2–20 mg catalyst, with a dose of 2 μl substance.

Our studies began with a support-free Pt catalyst prepared by alkaline reduction. When the hydrogenolysis of methyloxirane was examined, it was found that the ring-opening occurred mainly on the less sterically hindered side (*4*), and propanal could not be detected. Data characterizing the selectivity of ring-opening are given in Table 1.

Supported catalyst were prepared by two methods: impregnation with H_2PtCl_6 and subsequent reduction (*5*); reduction of the $Pt(NH_3)_4^{2+}$ ion bound to the surface by ion-exchange (*6*). We also produced a catalyst similar to the latter from H_2PtCl_6, by the method of Lorimer (*7*). The decomposition of methyloxirane on the catalysts was studied at 100 and at 190°C. The results are to be found in Table 2. Selectivity ratios reported in Tables 1 and 2 refer to initial conversions.

The results permit the conclusion that the selectivity is independent of the metal particle size, as the support-free Pt, with low dispersity, and the ion-exchange catalyst, with very high dispersity, had almost the same selectivities. At the same time, the *S* value for the 3% Pt/Cab-O-Sil catalyst is very low. This catalyst was prepared by impregnation, and it appears that this method gives rise to a catalyst of an acidic nature. Propanal, the formation of which could be demonstrated, is produced on the acidic centers and subsequently hydrogenated to 1-propanol on the Pt. Our earlier work (*3*) showed that oxiranes and oxetanes are very sensitive to such acidic centers, and an acidic support is also able to isomerize them to aldehyde. From this aspect they behave similarly to cyclopropanes (*8*). The isomerization of methyloxirane to propanal can even be utilized to establish the acidity of catalyst supports. The above test reaction indicates that pro-

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TABLE 1

Selectivity of Transformation of Methyloxirane on Pt Catalyst

Temperature (°C)	Acetone (x_1)	2-Propanol (x_2)	1-Propanol (x_3)	Propanal (x_4)	$S = \frac{x_1 + x_2}{x_3 + x_4}$
100	0.02	0.85	0.13	0.00	6.7
125	0.12	0.73	0.15	0.00	5.6
150	0.25	0.57	0.18	0.00	4.6

panal is not formed below 300°C on supports of Cab-O-Sil and Aerosil types. In the same way as the acidity of a support may be characterized by the quantity of propanal produced, the acidity of a supported Pt catalyst may be characterized by the deviation of the *S* value from that for support-free Pt.

The catalyst acidity was studied in an experimental series in which a mixture of methyloxirane and pyridine was used. Table 3 lists the results.

The tabulated data suggest that the pyridine is reversibly bound on the acidic centers, thereby suppressing aldehyde formation, and the selectivity becomes similar to the values measured for the ion-exchange catalysts.

After being heated in vacuum for 1 day at 400°C, the impregnation catalyst displayed a scarcely changed selectivity. After reduction in hydrogen at 400°C, however, the *S* value increased from 0.6 (Table 2) to 2.6.

TABLE 2

Selectivity of Transformation of Methyloxirane on Supported Pt Catalysts

Catalysts	S	
	100°C	190°C
3% Pt/Cab-O-Sil, impregnation (*5*)	0.8	0.6
0.5% Pt/Cab-O-Sil, ion-exchange (*6*)	4.9	4.5
5% Pt/Aerosil, ion-exchange (*6*)	4.5	4.0
5% Pt/Cab-O-Sil (*7*)	4.8	3.0

With a view to establishing the nature of the active sites, we also examined the adsorption of the pyridine with an infrared spectrometer (*9–11*). It was found that these catalysts are not capable of pyridinium ion formation. On the above basis it may be assumed that the acidity of the impregnation catalysts is caused by the electrophilic centers remaining as a consequence of the incomplete reduction.

Davidová and Kraus found that on a Pt/C catalyst at 190°C $S = 0.2$. In their view, the reason why Sénéchal and Cornet obtained a selectivity in contradiction with this in the deuterolysis of 1,2-epoxybutane is that they studied the reaction at 90°C and the activation energies of the isomerization and the hydrogenolysis are different. However, Sénéchal and Cornet also examined the hydrogenolysis of 1,2-epoxybutane at 132°C, on a Pt/pumice catalyst, and found that $S = 4.6$. They also established that the variation in selectivity is not too high between 100 and 150°C. As a control, we investigated the decomposition of methyloxirane at 190°C as well (Table 2).

Our experimental data clearly demonstrate that the selectivity does not change fundamentally as the temperature is raised. Since the catalyst of Pt/C used by Davidová and Kraus was prepared by an impregnation method, in all probability it was acidic in nature. If so, the results of the kinetic studies relate not merely to the Pt, but also to the system containing the acidic sites. From their examination of the isomerization reaction they concluded that the kinetic equation of this reaction describes two parallel isomerization processes, one

TABLE 3

Effect of Pyridine on Transformation of Methyloxirane[a]

	1	2	3	4
Conversion (%)	15	4	7	2
Propanal (mole%)	6	0	0	2.7
S	0.4	6.2	2.2	0.7

[a] 3% Pt/Cab-O-Sil impregnation; 180°C; 1, 2 μl methyloxirane; 2, 2 μl methyloxirane + 0.5 μl pyridine; 3, 2 μl methyloxirane after process 2; 4, 2 μl methyloxirane after treatment at 350°C.

of which is independent of the hydrogen, but the other not. It is probable that the former process is the isomerization on the acidic centers, while the latter is the Pt-catalyzed isomerization leading to ketone. We are of the opinion that alcohol formation likewise involves the occurrence of two parallel reactions. One of them is hydrogenolysis, which results mainly in 2-butanol, but additionally in 1-butanol, and the other is hydrogenation of the aldehyde, which gives the main bulk of the 1-butanol. It can be attributed to this complex process that the constants of the kinetic equation display an irregular variation as a function of the temperature. Since the product curves showed no indication of a secondary reaction, a proportion of the aldehyde formed on the acidic centers is hydrogenated before desorption. At the same time, readsorption of the already desorbed aldehyde does not take place on the epoxide-covered surface (*2*). The support effort observed by Davidová and Kraus is also indicative of the role of acidity. The initial selectivity of the Pt/Cr_2O_3 is much closer to that of the support-free Pt than the selectivity of the Pt/C. The results of the kinetic investigation demonstrated that the support effect influenced only the value of k_i, which is the rate constant of the acidic isomerization.

What has been said above in connection with the formation and role of the acidic centers reveals that the usual conclusion, that the difference between the support and the supported catalyst is to be ascribed to the processes taking place on the metal, must be applied with due care in the case of Pt catalysts prepared by impregnation.

Finally, we should like to state that our opinion in no way detracts from the important findings of Davidová and Kraus with regard to the cocatalytic role of hydrogen.

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