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Characterization of Acid–Base Properties of Oxides via the Selective Ring-Opening of 2-Methyloxirane

Certain literature data on the transformations of monosubstituted oxiranes on acidic catalysts indicate that the ratio of aldehyde to ketone, the two products of isomerization, varies with the properties of the catalysts (*1*). On zeolites, the activity was correlated with the acidity of the catalysts (*2, 3*), while the results on phosphates (*4*) revealed the importance of both acidic and basic sites. In the selective transformation of epoxystyrene to phenylethanal on natural silicates and on silica–alumina, both Si–OH and Al^{3+} proved to participate in the ring-opening (*5*). On mixed $MgO–SiO_2$, the acidity and basicity were found to be responsible for the isomerization of 2-methyloxirane to propanal and acetone, respectively (*6*). The exact function of the catalytic effects of the two kinds of sites was not given, and the by-products formed under the applied reaction conditions complicated the interpretation of the results.

Correlations have been recently established between the activity of oxides in certain catalytic transformations and the electronegativity of the metals in the oxides. The activity and selectivity of oxides in the double-bond migration and skeletal isomerization of alkenes (*7–9*) were found to parallel the ratio n/r (n is the formal charge and r is the radius of the metal ion), a measure of electrophilic character (*10*).

Our interests in the transformations of cyclic ethers (*11–17*) and in the activity of metal oxides in different reactions (*7–9, 17*) led us to study the effects of a number of oxides on the ring-opening reaction of 2-methyloxirane. CaO, ZrO_2, BeO, Al_2O_3, Nb_2O_5, and WO_3 were chosen for investigations of the correlation between the acid–base properties of the oxides and the regioselectivity of the ring-opening.

The preparation, characterization, and pretreatment of the oxides were described earlier (*8*). 2-Methyloxirane (a Fluka product, 100% pure by GC) was studied at 423–673 K by using the GC pulse microreactor technique (Carlo Erba Fractovap Mod G equipment, hot wire detector, quartz microreactor). The quantity of catalyst used in each experiment was equivalent to about 1 m^2 BET surface area. The carrier gas was helium (20 ml min^{-1}) purified with an Alltech Oxy-Trap + Indicating Oxy-Trap. Experimental data were determined in the steady-state activity region reached after the injection of 3–5 1-μl pulses (GC parameters: column: 0.5 m 15% Reoplex-400 + 0.5 m 20% β,β'-oxydipropionitrile on Merck Kieselguhr; 333 K).

Deuterium-labeled compounds were studied in a flow reactor at 523 K by the saturation technique (GC analyses: column: 1.2 m 15% 1,2,3-*tris*(2-cyanethoxy)propane on Merck Kieselguhr; 373 K; helium carrier gas: 30 ml min^{-1}). Treatment of 2-hexanone with D_2O according to (*18*) yielded 2-hexanone-[1,1,1,3,3-$^2H_5$]. Dehydration on Al_2O_3 of 1-hexanol-[1,1-$^2H_2$] prepared from ethyl hexanoate with $LiAlD_4$ gave 1-hexene-[1,1$^2H_2$], which was transformed into 2-butyloxirane-[3,3-$^2H_2$] with monoperphthalic acid (*19, 20*). Deuterium-labeled compounds were analyzed by ^1H and ^{13}C NMR spectroscopy (Bruker AC 250 equipment) and mass spectrometry (a Hewlett–Packard 5890A GC instrument coupled with a 5970 MSD quadrupole mass spectrometer; conditions: 12-m HP-1 column, 303–473 K; EI source, 70 eV, 1-s

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TABLE 1

Transformation of 2-Methyloxirane to Propanal and Acetone on Oxide Catalysts

Catalyst	Temperature (K)										
	423	448	473	498	523	548	573	598	623	648	673
WO_3	2.5/0[a]	10/0	24/1	39/2	60/3		90/5				
Nb_2O_3			5/0	13/0.5	13/1	25/1.5	38/3				
Al_2O_3			3/1	5/3.5	14/3.5	24.5/6	39.5/10				
BeO			5.5/2	6.5/2.5	7/3.5	7/4.5	7.5/5				
ZrO_2							2.5/1.5	7/3	12/5	23/6	28/6
CaO							0.5/1.5	2/5	5.5/7.5	14/7	21/10

[a] Quantities of propanal and acetone, respectively, in mol%. The sum of the two values at a given temperature gives the conversion.

scans, HP 59970 MS ChemStation data system).

The results of the transformation of 2-methyloxirane (Table 1) demonstrate that only two products, propanal and acetone, are formed; i.e., only ring-opening involving isomerization takes place. The total activity of the oxides increases with increasing acidity.

As regards selectivity, the formation of propanal is favored by increasing acidity, while the formation of acetone shows an opposite trend, giving the highest selectivity on CaO (Fig. 1). Supposing the mutual action of Lewis acid and base site pairs, i.e., electron pair acceptor (EPA) and electron pair donor (EPD) sites (*21*), the formation of the two products can be interpreted as shown in Schemes 1 and 2.

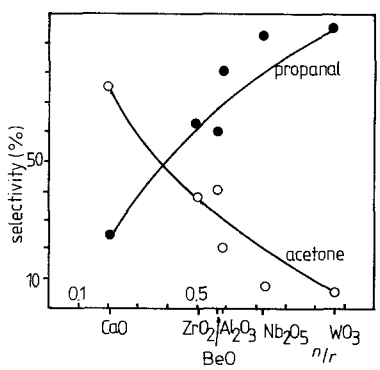
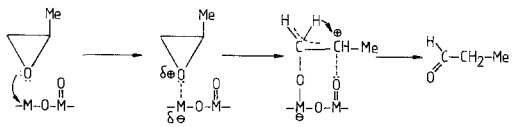


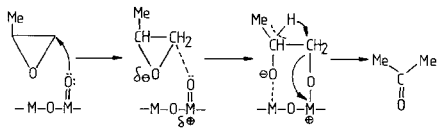
FIG. 1. Selectivity of ring-opening of 2-methyloxirane to propanal and acetone as a function of the n/r value of the oxide catalysts (n is the formal charge and r is the radius of the metal ion. Reaction temperature: 573 K).

During the formation of propanal, an acidic site (metal ion) coordinates with the oxygen atom in oxirane. As a result of the electron withdrawal induced by the positive charge developing on the oxygen in the transition state, the bond between the oxygen and the secondary carbon atom C(2) undergoes rupture. This ring-opening leads to the formation of the more stable secondary carbenium ion, with the basic site assisting in stabilization of the ion. An intramolecular hydride anion migration results in the formation of propanal.

Basic sites play a more important role in the isomerization on basic oxides. Since the metal ions present in these oxides have only a very weak acidic character, the adsorption of 2-methyloxirane starts with coordination between surface O^{2-} and the primary ring carbon atom C(3). Both steric and electronic



SCHEME 1



SCHEME 2

effects lead to the higher probability of this interaction than the coordination of surface oxygen with C(2). The decisive factor is the presence of the methyl substituent on C(2) giving rise to steric hindrance against attack on this carbon. A difference in polarization between C(2) and C(3) induced by the electron-releasing methyl group might also contribute to the favored attack on C(3). Ring-opening therefore takes place through splitting of the C(3)–O bond. The last step is again an intramolecular hydride shift, leading to the formation of acetone.

In the two processes depicted above, the selectivity-determining factors governing the formation of the isomeric carbonyl compounds are different. On acidic oxides, the selectivity is determined by the difference in stability of the possible carbenium ions, resulting in enhanced yields of propanal. In contrast, on basic oxides, the transformation is mainly controlled by steric factors, permitting a higher selectivity for the formation of acetone.

To confirm the proposed reaction schemes, tracer experiments were carried out with 2-butyloxirane-[3,3-$^2H_2$] as substrate. Since the products carbonyl compounds may possibly lose deuterium under the given reaction conditions, 2-hexanone-[1,1,1,3,3-$^2H_5$] was studied under identical conditions.

The results in Table 2 (first three entries) show that the labeled ketone does lose deuterium, presumably via enolization. This observation strongly indicates that the lower deuterium content in the product carbonyl compounds formed from the labeled oxirane (Table 2) can be attributed to consecutive exchange reactions. The positions of the deuterium atoms in the product carbonyl compounds serve as clear evidence of the mechanisms suggested. The deuterium labeling in hexanal testifies to cleavage of the C(2)–O bond, followed by deuterium migration. Fission of the C(3)–O bond and hydrogen migration leads to 2-hexanone labeled with two deuterium atoms exclusively on C(1). It also follows that the mechanisms of aldehyde formation and of

TABLE 2

Tracer Studies with Deuterium-Labeled Compounds

Catalyst	Product	D content per molecule	D loss	% D loss	Labeled positions
	2-Hexanone-[1,1,1,3,3-$^2H_5$] (D content = 4.70 atoms/molecule)				
WO_3	2-Hexanone	4.10	0.60	13	—
Al_2O_3	2-Hexanone	3.53	1.17	25	—
CaO	2-Hexanone	3.14	1.56	33	—
	2-Butyloxirane-[3,3-$^2H_2$] (D content = 1.95 atoms/molecule)[a]				
WO_3	Hexanal	1.70	0.25	13	C(1) 0.95 C(2) 0.75
	2-Hexanone	1.79	0.16	8.2	C(1) 1.79
Al_2O_3	Hexanal	1.70	0.25	13	C(1) 0.90 C(2) 0.80
	2-Hexanone	1.90	0.05	2.5	C(1) 1.90
CaO	Hexanal	1.60	0.35	18	C(1) 0.90 C(2) 0.70
	2-Hexanone	1.78	0.17	8.7	C(1) 1.78

[a] Conversion: 20–30%. No loss of deuterium from the recovered oxirane was observed. No exchange took place between light oxirane and oxides treated with D_2O.

ketone formation are the same on each of the oxides studied. The acid–base properties of the oxide catalysts affect only the regioselectivity of the ring-opening, by altering the relative rates of formation of the two products.

In conclusion, a strong correlation has been found between the regioselectivity of the ring-opening of 2-methyloxirane and the surface acidity and basicity of six oxide catalysts. This correlation may occur when weak and medium strong Lewis acid–Lewis base site pairs are the active center ensembles for the reaction. This is quite common for many reactions on metal oxides without vacant *d* orbitals. Such considerations proved to be useful in predicting the activity of different oxides in the double-bond migration of alkenes (*8*). Within this scope and limitation, 2-methyloxirane can be used as a test molecule to characterize the surface acid–base properties of oxide catalysts and to assess the relative strength and significance of the acidic or basic sites within the site pairs. It is also important to point out that on catalysts with strong Brønsted acidic sites (e.g., zeolites), or if metal ions with vacant *d* orbitals (e.g., Pt^{2+} or Pd^{2+}) are present, the above correlation does not necessarily hold. On zeolites, for instance, the reaction starts with protonation of the ring oxygen atom and, without the assistance of a basic site, results in an opposite selectivity of ring-opening (*2*).

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