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Oxidations of Olefins Adsorbed on Molecular Sieves

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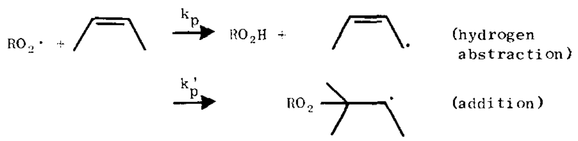
Cyclopentene and 1- and 2-butenes have been adsorbed on synthetic zeolites ("molecular sieves") and reacted with oxygen at temperatures from 25 to 90°. Rates of oxidation are from 5 to 600 times faster than in homogeneous systems at the same temperature, but a multiplicity of products, some tightly bound to the sieves, are formed. The most prominent volatile products from the butenes are methyl ethyl ketone, crotonaldehyde, and 2-butene-1-ol, whereas the principal products of homogeneous oxidations are hydroperoxides.

INTRODUCTION

We have previously shown (*1*) that the products of olefin oxidations depend on the two competing propagation reactions:



Further investigation (*2*) showed that the relative values of k_p and k'_p are nearly independent of temperature and solvent. Consequently, other methods of controlling the products from olefin oxidation were sought. Oxidation of an olefin in a (presumably) physisorbed state offered an interesting possibility. The strong electrostatic field which binds the olefin to the adsorbent should influence the allylic bond dissociation energy and render the double bond more resistant to electrophilic attack. Because of their large capacity, about 10 wt % at 1 atm for 1-butene, "molecular sieves" were chosen as adsorbents. Our approach was empirical and left unanswered the question of the mechanism of the oxidation.

The use of molecular sieves as catalysts, principally as Lewis acids, has been well explored and a recent review (*3*) lists 183 references on the subject. However, no mention is made of their use in oxidation of organic compounds; and another review (*4*) by Turkevich lists only one reference (*5*) to the use of zeolites as oxidation catalysts. We initially expected zeolites, with their large olefin adsorption capacity, to offer a different reaction than the classic transition metal oxide (*6*) oxidation catalysts. Our limited findings do, in fact, indicate that zeolites give products corresponding to substantial attack at the double bond rather than at the allylic position as is the case with metallic oxides or in homogeneous free radical oxidations.

EXPERIMENTAL METHODS

a. *Materials*

Sieves. The sieves, either type **5A or 13X,** were the commercial products of Linde

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Division, Union Carbide. For most of the experiments the $\frac{1}{16}$-in. pellet form containing 20% "inert clay binder" was used. For a few experiments the 100% zeolite powder was used. Little difference was found in the catalytic effect of the two materials. Cobalt-exchanged sieves were made by successive treatments of the sieves (100 g) with aqueous cobaltous nitrate solutions (10 g of $Co(NO_3)_2 \cdot 6H_2O$ in 300 ml of H_2O) at 100° until no more cobalt was exchanged, as determined visually from the color of the solutions (7).

Olefins. Both 1-butene and *trans*-2-butene were Phillips research grade. Cyclopentene was from Aldrich, distilled before use. All olefins were distilled from neutral Al_2O_3 in the vacuum line immediately before use.

b. *Procedure*

The sieves were dried in an air oven at ~150°, then loaded into a glass bulb with a neck that could be connected to an oxygen supply through a Swagelok connection. The bulb was then evacuated to ~0.1 Torr and heated with an oil bath to 210°C. After 2 hr of baking, the butene (~10% of the wt of the sieves) was adsorbed at room temperature up to a final equilibrium vapor pressure of ~400 Torr. The bulb was detached from the vacuum line, filled with air to a total of 1 atm, weighed accurately, then attached to the oxygen reservoir. The bulb was either thermostated or kept at room temperature at an oxygen pressure of up to ~50 psig. In some cases a short period of accelerating rate was obtained before the maximum rate was observed. In others, the initial rate was the maximum and the rates then decreased with conversion. At conversions of 5 to 10% the reactions were stopped by closing all valves of the apparatus and cooling the reaction bulb to −78°. The consumption of oxygen was determined from both the pressure drops at the oxygen reservoir and the weight gain of the bulb at the end of the experiment. Agreement was usually within 5–10%.

Pumping on the sieves to ~0.1 Torr at room temperature desorbed some of the unreacted butenes, which are partly isomerized (*8*) but, apparently, none of the oxidation products. Heating the bulb seemed only to decompose these products. The most satisfactory recovery of products was obtained by placing an aliquot of the sieves in a Soxhlet thimble and extracting, first with dry ether (60 ml), then with 5–10 ml of water added to the reflux pot. The extract, usually a single phase, was found to be free of hydroperoxide and was analyzed directly by glpc. Distillation showed the amounts of nonvolatile products present for the butene oxidations. If excess water was used in the extraction, nonvolatile material seemed to concentrate in the aqueous phase. Oxidations of 2-butene seemed to produce larger proportions of water soluble products than 1-butene. In Expt. 7, 80–20 dioxane–water by weight was used for extraction. The extract was treated with Drierite before glpc analysis.

RESULTS AND DISCUSSION

The results of the oxidation experiments are summarized in Table 1. The first experiment serves as a rate control. It shows that a given quantity of butene in benzene reacts slower at 70° than the same quantity adsorbed on a sieve; cf. Expt. 1 to Expts. 2 and 3. On cobalt-exchanged sieves, Expt. 4, oxidations are faster at 25° than on sodium sieves at 90°, Expt. 3.

a. *Sieve Type*

Comparison of Expts. 2 and 3 indicates that type 5A sieve promotes the oxidation of 1-butene more than type 13X. However, product removal from 5A sieves is very difficult. For nearly identical loadings, it was necessary to use a 20° higher reaction temperature to obtain the same rate with the 13X sieve.

The products from the oxidation of 1-butene on 13X sieve were determined by the wet ether extraction process. Distillation showed a substantial amount of nonvolatile material in the extract. The principal volatile product is methyl ethyl ketone, presumed to arise from acid-catalyzed rearrangement of the epoxide (*9*). Less important volatile products are the butenols and crontonaldehyde. The remaining third of the volatile products is made up of six to eight unidentified components.

A considerable amount of products apparently remains on the sieves. Combustion analyses on some of the extracted sieves show the number of milligram atoms of bound carbon. If the nonextractable material is also classified as nonvolatile, then the sieve oxidation of 1-butene produces more residue and less volatile product than the homogeneous oxidation. The acidic character of the sieves may be responsible for the increase in high molecular weight material; polymerization of the olefin reactants has been demonstrated (*8*) at higher temperatures.

When 13X sieves with the sodium ions exchanged for cobalt are used, the oxidation becomes much faster. At 25°, the rate of oxygen uptake is five times that for the unexchanged sieve at 90; assuming a temperature coefficient of 2/10°, rate enhancement is about 600-fold (cf. runs 3 and 4). An induction period of ~20 min was observed. There seems to be much less nonvolatile and sieve-bound product than with the sodium 13X sieve oxidation, but the composition of the volatile products is more complex. The methyl ethyl ketone and butenols make up only 47% of the volatile product, and the remainder is divided among 14 other compounds.

b. *Effect of Ammonia Presorbed*

In an effort to reduce the number of products by neutralizing (*10*) some of the acid sites of the zeolite, small amounts of gaseous ammonia were adsorbed on the catalysts before the hydrocarbon was adsorbed. Experiment 5 with 1-butene shows that the maximum oxidation rate obtainable with this system is one eighth that without ammonia. The product selectivity, however, seems to have been increased: methyl ethyl ketone and the butenols now make up 77% of the volatile product. Yields of nonextractable products appear to be the same. Comparison of Expts. 7 and 8 with 2-butene suggests that as the ammonia loading is increased the rate of oxidation drops but the product selectivity increases, with a substantial drop in sieve-bound material.

c. *Effect of Double Bond Position*

The 1- and 2-butenes were oxidized under approximately the same conditions, Expts. 5 and 8, and the cyclopentene oxidation, Expt. 9, can be compared with the 1-butene oxidation, Expt. 4. Qualitatively, the olefin reactivity on sieves parallels the homogeneous composite rate constants (*1*), $k_p/(2k_t)^{1/2}$, but the reactivity difference between the butenes is more pronounced on sieves.

		Relative rate, sieves	
Hydrocarbon	$(k_p + k'_p)/(2k_t)^{1/2}$	Co^{2+}, NH_3	Co^{2+}
1-Butene	0.066	1	1
2-Butene	0.106	46	
Cyclopentene	0.61		9

The major products of the butene oxidations seem to be the same except that the unidentified material which elutes close to 2-butene-1-ol on the glpc is formed in larger amounts from 2-butene oxidation. Also, the other unidentified products are different, as judged by glpc retention times. The high yields of sieve-bound products from 2-butene and cyclopentene, experiments 8 and 9, suggest that the products of the 1,2-substituted olefins are more readily polymerized (*8*) by the sieves than the 1-olefins.

d. *Extraction Techniques*

Only Expt. 7 used dioxane–water as extraction solvent. Possibly because of the higher ammonia loading, the portion of oxidation products left on the sieves has been decreased. The higher boiling solvent obscures some of the possible products in the glpc trace, and removing all the water with drying agents is difficult.

About half the sieves of Expt. 7, which had been standing in a capped bottle for ~10 weeks, were extracted by the wet

TABLE 1

Rates and Products of Oxidations of Alkenes on Zeolite Catalysts

							Products (mmole)					
Expt.	Sieve and amount	Alkene (mmole)	Temp (°C)	Maximum rate, $\frac{\text{mole } O_2}{\text{mole RH-hr}}$	Reac. time (min)	Total O_2 absorb. (mmole)	All extractable volatiles (as C_4H_8O)	Methyl ethyl ketone	Crotonaldehyde + 1-butene-3-ol	2-Butene-1-ol + unidentified	Extd. nonvolatiles	Sieve-bound
1	None, 3.3 *M* 1-C_4H_8 in C_6H_6, 0.009 *M* ABN	360.8 1-C_4H_8	70	0.0027	1462	12.5		[a]	[a]	[a]	2.81	
2	5A pellets, 31.6 g	59.8 1-C_4H_8	70	0.011	1780	11.2		Not determined				
3	13X pellets, 30.0 g	59.0 1-C_4H_8	90	0.011	1362	20.2	6.3	2.1	1.0	1.1	6.8[b]	7.1[c]
4	13X, cobalt-exchanged powder, 20.1 g	46.7 1-C_4H_8	25	0.056	475	9.65	6.5	0.81	0.58	1.67	0.6[d]	2.5[c]
5	13X, cobalt-exchanged pellets, 33.8 g, 7.2 mmole of NH_3 presorbed	67.0 1-C_4H_8	25	0.0073	1429	6.43	3.9	1.3	0.3	1.4	—[e]	2.9
6	13X, cobalt-exchanged pellets after extraction in expt. 5, 14.8 g	29.8 1-C_4H_8	70[f]	2.2	18	11.9						

7	13X, cobalt-exchanged pellets, 35.1 g, 11.7 mmole of NH_3 presorbed	57.1 2-C_4H_8	25	0.10	114	7.3	4.7	2.4	[g]	[g]	1.0[h]	1.6[c]
8	13X, cobalt-exchanged pellets, 32.6 g, 5.65 mmole of NH_3 presorbed	57.7 2-C_4H_8	25	0.34	66	10.9	3.8	0.87	0.57	1.4[i]	2.5	11.1
9	13X, cobalt-exchanged pellets, 34.0 g	56.0 *c*-C_5H_8	25	0.50	71	10.6	0.9[j]	0.39[k]				32.2

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[a] 0.60 mmole of 1-epoxybutane + 7.16 mmole of 1-butene-3-hydroperoxide + 2-butene-1-hydroperoxide + crotonaldehyde formed.

[b] 670 mg material analyzing by combustion for $C_4H_{6.95}O_{1.66}$.

[c] Determined by difference assuming 1 mole of O_2/mole of volatile product.

[d] 61 mg of material assuming analyses found in Expt. 2.

[e] Assumed to be small, not determined.

[f] Little reaction at 25°, see Sect. 6.5 in text.

[g] If present, obscured by the dioxane used for extraction.

[h] 83 mg of material assuming analysis found in Expt. 2.

[i] Mostly the unidentified product.

[j] C_5H_8O.

[k] Cyclopentanone and cyclopentene oxide.

ether procedure. Most of the product was water-soluble, nonvolatile material, 843 mg based on the measured 7.3 mmole of oxygen consumed. The ether extract was principally two volatile materials. Total yield of the volatile products was 554 mg. Apparently further oxidation and/or polymerization took place on standing.

An attempt was made to remove the large quantity of oxidation and polymerization product from the extracted sieves of Expt. 9. The procedure (*11*) of treating with $2N$ HCl, which exchanges hydrogen ions for cobalt and increases the zeolite pore size, allowed recovery of 450 mg of nonvolatile chloroform-soluble oil, corresponding to 5.3 mmole (mol wt $= 84$) of product. The material was not investigated.

e. *Sieve Reuse*

The extracted sieves of Expt. 5 were subjected to the usual baking-out procedure and fresh 1-butene was adsorbed for Expt. 6. When the sieves were pressured with oxygen at room temperature, slow consumption of oxygen seemed to occur for ~45 min, but then halted. When the bulb temperature was then raised to 70°, very rapid consumption of oxygen occurred. Although the sieves are deactivated somewhat by the nonextractable products, they still can be used to accelerate further oxidations.

CONCLUSIONS

Large increases in rates of hydrocarbons can be obtained by the use of transition metal-exchanged sieves. Thus, 2-butene, which oxidizes with difficulty at 70° in the homogeneous system, is converted initially at the rate of 30% per hour at room temperature by cobalt-exchanged sieves. This rate would presumably be even faster without the ammonia. Over a period of time, the catalyst converts 2-butene to water-soluble material. It certainly seems reasonable that a profitable technological application of this rate enhancement can be found.

The relatively nonselective product formation and the substantial quantities of nonvolatile and sieve-bound products do not make this an attractive reaction for a chemical process at this time. However, there are many parameters that can be varied in this system: starting zeolite (different SiO_2, Al_2O_3 ratios), metal exchanged, acid site deactivator, temperature, contact time (use of a flow system instead of a batch process), and hydrocarbon type. From the paucity of open literature data on the use of zeolites as oxidative catalysts, we suspect that effort along these lines must be in progress in industrial laboratories. An optimized system should be of considerable value.

Because of the large amounts of uncharacterized products in these oxidations and possible further transformations of the primary products, it is not possible to decide the extent to which the addition–abstraction ratio of the olefins has been changed by zeolite oxidation. The indication is that on sieves, attack at the double bond (to give epoxide which is isomerized to methyl ethyl ketone) predominates over attack at the allylic position. We have no indication at this time that the oxidation mechanism involves a free radical chain, but the qualitative resemblance of products from 1- and 2-butene oxidations suggests a common intermediate. Isomerization (*8*) of 1-butene to 2-butene by the sieves may also account for the product similarity.

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REFERENCES

1. VAN SICKLE, D. E., MAYO, F. R., AND ARLUCK, R. M., *J. Amer. Chem. Soc.* **87**, 4824 (1965); AND SYZ, M. G., **89**, 967 (1967).
2. VAN SICKLE, D. E., MAYO, F. R., ARLUCK, R. M., AND GOULD, E. S., *J. Amer. Chem. Soc.* **89**, 977 (1967).
3. VENUTO, P. B., AND LANDIS, P. S., *Advan. Catal. Relat. Subj.* **18**, 259 (1968).
4. TURKEVICH, J., *Catal. Rev.* **1**, 1 (1967).
5. BRECK, D. W., AND MILTON, R. M., U. S. Pat. 3,013,985 (1961).
6. VOGE, H. H., AND ADAMS, C. R., *Advan. Catal.* **17**, 151 (1967).
7. Manganese and rare earth exchanged zeolites

are described by Plank, C. J., Rosinski, E. J., and Hawthorne, W. P., *Ind. Eng. Chem.* 3(3), 165 (1964).

8. Ref. 3, p. 315.

9. Ref. 3, p. 351.

10. Benesi, H. A., and Peterson, D. L. (to Shell Oil Co.), U. S. Pat. 3,106,593 (1963); *Chem. Abstr.* **60**, 1519 g (1963).

11. Venuto, P. B., Hamilton, L. A., and Landis, P. S., *J. Catal.* **5**, 484 (1966).