NOTE

Epoxidation of Styrene over a Titanium Silicate Molecular Sieve TS-1 Using Dilute H₂O₂ as Oxidizing Agent

The epoxidation of styrene was studied using a titanium silicate molecular sieve TS-1 as catalyst and dilute (25%) H_2O_2 as oxidizing agent. Mainly two types of reactions were observed: The major reaction (~75–85 mole%) was epoxidation and its further isomerization into phenylacetaldehyde. The other reaction was oxidative cleavage into benzaldehyde (~10–20 mole%). While generally the products were analyzed by capillary GC and GCMS, in certain cases, the products were separated and isolated by column chromatography and analyzed by ^1H and ^{13}C NMR spectroscopy. Polar and nonpolar solvents have marked influence on product distribution in styrene epoxidation. In methanol, a significant part of styrene epoxide undergoes alcoholysis through the addition of methanol forming 2-methoxy-2-phenyl-ethanol. The influence of reaction time, temperature, and styrene/H_2O_2 molar ratio on the conversion and product distribution was also studied.   © 1995 Academic Press, Inc.

Epoxidation of olefinic compounds over titanium silicate molecular sieves TS-1 ([Ti]-MFI] (1,2) or TS-2 ([Ti]-MEL) (3,4), and H_2O_2 has gained considerable interest recently (5–7). Neri and Buonomo (8) have claimed the styrene epoxidation over TS-1 and H_2O_2. However, no details about this reaction using TS-1 as catalyst and dilute H_2O_2 as oxidizing agent are available, particularly in the open literature.

In present communication, we report detailed studies on styrene epoxidation using [Ti]-MFI (TS-1) as catalyst and dilute H_2O_2 (25%) as oxidizing agent in a batch reaction. The influence of various reaction parameters such as time, temperature, and styrene/H_2O_2 molar ratio, as well as effect of protic and aprotic solvents on the activity and product selectivity is studied.

TS-1 was synthesized and characterized according to literature procedure (2). The Si/Ti molar ratio of the sample was 29. The X-ray powder pattern of the calcined sample of TS-1 is characteristic of MFI structure. The Al-free titanium silicate (TS-1) retained orthorhombic symmetry after calcination indicating the incorporation of Ti in silicate network. The scanning electron micrograph of TS-1 sample exhibited the absence of amorphous material. The particle size of cuboid shaped crystallites ranged between 0.2 and 0.3 μm. The UV–VIS spectrum of TS-1

sample exhibited a charge transfer band at 209 nm (Fig. 1), characteristic of framework, isolated Ti^{4+}. An absence of any absorption at 320–340 nm suggests the absence of extra framework TiO_2 (2–5). The framework region IR spectrum of TS-1 sample exhibited a band at 960 cm^{-1}, characteristic of titanium silicate molecular sieves (1–6), in addition to other structural bands (inset in Fig. 1). This 960 cm^{-1} band exhibited by titanium silicate molecular sieves is commonly attributed to "O_3–Si–O–TiO_3" moieties. The equilibrium sorption capacity (wt%) of our sample for n-hexane, cyclohexane and water was 11.6, 7.1, and 5.2% respectively, comparable with those reported in the literature for TS-1 (2), indicating the absence of any extralattice occluded material.

Styrene (Aldrich) and hydrogenperoxide, 25% (National Peroxide) were commercially obtained. Fresh styrene (vacuum distillation) was used during the reaction, which was carried out batch wise in a two necked flask fitted with a condenser. Styrene (1.04 g, 10 mmol) in solvent (5 ml) was added to the catlayst (0.2 g). Aqueous H_2O_2 (25 wt%) solution was added slowly and stirring was continued for 6–8 h. Products were separated from catalyst and analyzed using HP 5890A series gas chromatograph (50 m × 0.2 mm i.d. silicon gum capillary column) and GCMS (Shimadzu, GCMS-QP 2000A). In certain cases, the products were isolated through column chromatography and characterized by ^1H and ^{13}C NMR spectroscopy.

Figure 2 depicts the reaction progress where conversion of styrene (mole% of theoretical maximum, curve (a)) or yield (mole%) of the products (Y = conversion % × selectivity %/100, curves (b)–(e)) are plotted against reaction time. Phenylacetaldehyde (curve (b)), probably formed through the rearrangement of styrene epoxide, is a major product while styrene epoxide (curve (c)) and benzaldehyde (curve (d)) constitute relatively minor products. The curve (e) represents the yield of epoxidation products, i.e., styrene epoxide + phenylacetaldehyde. As expected, styrene conversion increased steadily with the reaction time and leveled off at about 80 mole% in 6–8 h (Fig. 2, curve (a)). This limiting value of styrene conversion is due to the complete exhaustion of
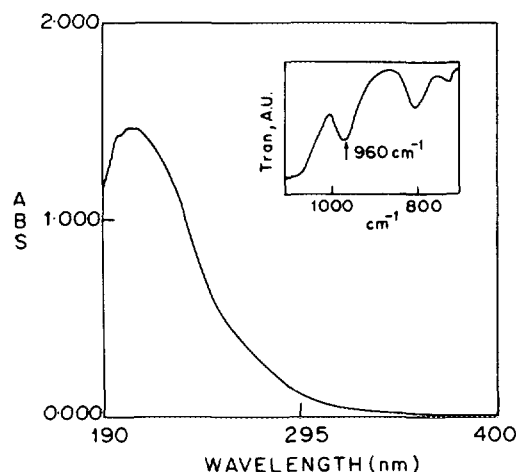
FIG. 1. UV–VIS and IR (inset) spectra of TS-1 sample.

H₂O₂ in the reaction mixture. The total yields of epoxidation products (curve (e)) and the yield of phenylacetaldehyde (curve (b), Fig. 2) also followed similar path and reached the maximum value of ca. 68 and 64 mole%, respectively. The yield of styrene epoxide (curve (c)) increased slowly and then decreased after passing through a maximum. This is mainly because of the isomerization of primarily formed epoxide into phenylacetaldehyde.

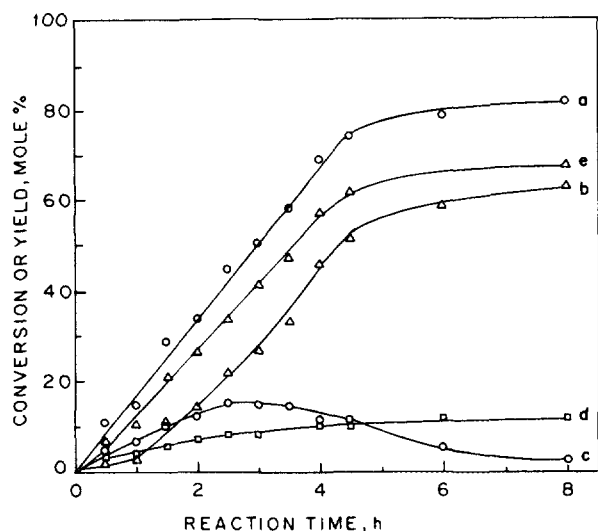In Fig. 3 the product selectivities (mole%) are plotted

FIG. 2. (a) Styrene conversion (mole% of theoretical conversion calculated on the basis of styrene/H₂O₂ molar ratio in the reaction mixture) and product yields of (b) phenylacetaldehyde, (c) styrene epoxide, (d) benzaldehyde, and (e) styrene epoxide + phenylacetaldehyde. ((selectivity, mole% × conversion, mole%)/100) as a funciton of reaction time. Styrene/H₂O₂ (25% aq.) mole ratio = 4, reaction temperature = 333 K.
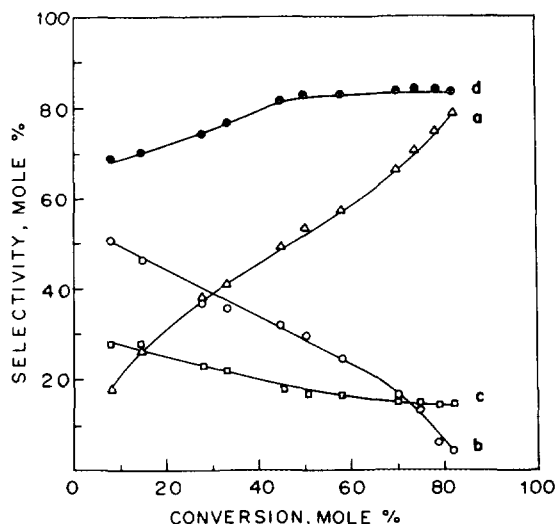

FIG. 3. Product selectivities (mole%) against styrene conversion (mole%): (a) phenylacetaldehyde, (b) styrene epoxide, (c) benzaldehyde, and (d) styrene epoxide + phenylacetaldehyde.

against styrene conversion (mole%). With the increase in styrene conversion, the selectivities for (i) styrene epoxide (curve (b)), a major product at low conversion and in the beginning of the reaction, decreased sharply (from 50% to 5%), (ii) the selectivity for phenylacetaldehyde (curve (a)) increased linearly and reached around 78%, mainly at the cost of epoxide, and (iii) benzaldehyde (curve (c)), probably a cleaved product of C=C double bond (9), decreased slowly from 28 to 16%. These observations clearly suggest that the styrene epoxidation is a major reaction in the beginning and the isomerization of epoxide takes place very efficiently into phenylacetaldehyde as the reaction progresses. Cleavage of C=C double bond, a minor reaction, decreases with conversion as exhibited by the selectivity profile of benzaldehyde (Fig. 3, curve(c)).

Since the isomerization of styrene epoxide can yield both phenyl acetaldehyde and acetophenone, it was quite interesting that no acetophenone was formed during the course of the reaction. This very high regioselectivity towards phenylacetaldehyde vis-a-vis acetophenone during rearrangement of styrene epoxide may be due to the reason that the formation of α-cation, adjacent to phenyl ring is stabilized (10), thus favoring the formation of phenylacetaldehyde.

After completion of the reaction (6h), the products were also analyzed by GCMS, which could separate and identify styrene, benzaldehyde, styrene epoxide, and phenylacetaldehyde. The fragmentation patterns of all the compounds mentioned above matched perfectly well with those reported for standard compounds (11).

The progress of the reaction mixture was also moni-

TABLE 1

Epoxidation of Styrene with H_2O_2 Over TS-1: Effect of Reaction Temperature

Temp (K)	TON (h^{-1})[a]	Styrene conv. (mole%, theoretical)	Products, mole%			
			Styrene epoxide	Phenylacetaldehyde	Benzaldehyde	Others[b]
313	9.1	54.6	13.3	58.3	29.0	1.4
333	12.8	76.8	6.2	75.8	16.1	1.9
353	13.0	78.0	5.5	77.5	13.5	3.5

Note. Solvent: acetone; styrene/H_2O_2 (mole ratio) = 4; Time = 6 h; acetone/styrene = 5 (wt/wt).

[a] TON: moles of styrene converted per mole of Ti in the catalyst per hour. One gram TS-1 (Si/Ti molar ratio = 29) contains 5.5×10^{-4} mole of Ti.

[b] High boiling products including diols and some unidentified compounds.

tored by TLC. The usual work up gave the crude product which was purified and fractionated by column chromatography (using ethylacetate as eluent). The total isolated yield of styrene epoxide + phenylacetaldehyde obtained by the separation and purification of the final product through column chromatography was ~65 mole%. The fractions thus obtained were again analyzed by GC and GCMS. The fractions corresponding to styrene epoxide, phenylacetaldehyde and benzaldehyde were then analyzed by ^{1}H NMR confirming the presence of these compounds.

The effect of reaction temperature on the styrene conversion (mole%) and product selectivity (mole%) is recorded in Table 1. As expected, by increasing reaction temperature from 313 K to 333 K, styrene conversion increased from 60 to 86.0%. Further, selectivity for phenylacetaldehyde also increased mainly at the cost of epoxide and benzaldehyde (Table 1). Reddy et al. (9) have observed that the cleavage of C=C (vis-a-vis epoxidation) is higher at lower temperature. At higher temperature, the epoxidation seems to compete more favorably against C=C cleavage. However, a further increase in

the temperature to 353 K did not exhibit any significant change both in the conversion and in the product selectivity.

The influence of styrene/H_2O_2 mole ratio on the conversion of styrene (%, theoretical) and product selectivity is given in Table 2. With the increase in styrene/H_2O_2 mole ratio, the styrene conversion increased considerably due to increased H_2O_2 utilization for styrene oxidation. The selectivity for epoxidation products (epoxide + phenylacetaldehyde) increased mainly at the cost of benzaldehyde (Table 2), indicating that in the presence of excess amount of H_2O_2, the oxidative cleavage of C=C is favored. Sheldon and Dakka (12) have also observed oxidative cleavage during oxidation of 1,2-diols. The initial product is an hydroxy aldehyde which on further oxidation undergoes oxidative cleavage with excess H_2O_2 (12).

In Table 3 the effect of different solvents on styrene conversion and product selectivity are given. Aprotic solvents like acetone and acetonitrile seem to favor the formation of epoxide + phenylacetyaldehyde vis-a-vis protic solvent like methanol (Table 3). Neri and

TABLE 2

Epoxidation of Styrene with H_2O_2 Over TS-1: Effect of Styrene : H_2O_2 Mole Ratio

Styrene/ H_2O_2	TON (h^{-1})[a]	Styrene conv. (mole%, theoretical)	Products, mole%			
			Styrene epoxide	Phenylacetaldehyde	Benzaldehyde	Others[b]
1	5.9	35.4	2.0	74.2	22.8	1.0
2	8.9	53.4	3.2	75.5	19.5	1.8
3	12.8	76.8	6.2	75.8	16.1	1.9

Note. Solvent: acetone; temperature: 333 K, time = 6h, acetone/styrene = 5 (wt/wt).

[a] TON: moles of styrene converted per mole of Ti in the catalyst per hour. One gram TS-1 (Si/Ti molar ratio = 29) contains 5.5×10^{-4} mole of Ti.

[b] Styrenediol and some unidentified higher boiling compounds.

TABLE 3

Epoxidation of Styrene with H_2O_2 over TS-1: Effect of Solvent

Solvent	TON[a] (h^{-1})	Styrene conv. (mole%, theoretical)	Products, mole%				
			Styrene epoxide	Phenylacetaldehyde	Benzaldehyde	Ether[b]	Others[c]
Acetonitrile	9.8	58.8	4.1	73.0	22.7	—	0.2
Acetone	12.8	76.8	6.2	75.8	16.1	—	2.1
Methanol	14.8	88.8	0.6	56.2	9.9	32.8	0.5

Note. Styrene/H_2O_2, molar ratio = 4, temp. = 333 K, time = 6 h, solvent/styrene = 5 (wt/wt)

[a] TON: moles of styrene converted per mole of Ti in the catalyst per hour. One gram TS-1 (Si/Ti molar ratio = 29) contains 5.5×10^{-4} mole of Ti.

[b] 2-methoxy 2-phenyl ethanol.

[c] Styrenediol and some unidentified higher boiling compounds.

Buonomo (8) have claimed 85% selectivity for phenylacetaldehyde during epoxidation of styrene in methanol as solvent. Some what contrary to these results we have observed that when methanol was used as solvent, apart from phenylacetaldehyde (sel. 56.2%), another major product, 2-methoxy-2-phenylethanol (~32.8%), characterized through GCMS and ^{13}C NMR spectroscopy, was formed due to its methanolysis (addition of methanol to epoxide).

In summary, it can be stated that the epoxidation of styrene, catalyzed by TS-1/H_2O_2, mainly leads to the formation of first epoxide which quickly isomerizes into phenylacetaldehyde. During epoxide rearrangement, the developing cation at α-position seems to get stabilized by the adjacent phenyl ring resulting in very high selectivity for phenylacetaldehyde (vis-a-vis acetophenone which was not observed during present study). High temperature, higher styrene/H_2O_2 molar ratios and aprotic solvent (like acetone, acetonitrile etc.) favor the epoxidation reaction. In polar solvent, like methanol, epoxide undergoes alcoholysis forming corresponding methyl ether (2-methoxy 2-phenyl ethanol) through the addition of methanol to styrene epoxide.

ACKNOWLEDGEMENT

REFERENCES

1. Taramasso, M., Perego, G., and Notari, B., U.S. Patent 4,578,501 (1983).
2. Thangaraj, A., Kumar, R., Mirajkar, S. P., and Ratnasamy, P., J. Catal. 130, 1 (1991).
3. Reddy, J. S., Kumar, R., and Ratnasamy, P., Appl. Catal. 58, L1 (1990).
4. Reddy, J. S., and Kumar, R., Zeolites 10, 95 (1992).
5. Notari, B., Stud. Surf. Sci. Catal. 37, 413 (1987).
6. Huybrechts, D. R., Bruycker, L. D., and Jacobs, P. A., Nature 345, 240 (1990).
7. Reddy, J. S., Reddy, R. S., Kumar, R., and Kumar, P., J. Chem. Soc. Chem. Commun. 84 (1992).
8. Neri, C. and Buonomo, F., Eur. Patent 102,097 (1984).
9. Reddy, J. S., Khire, U. R., Ratnasamy, P., and Mitra, R. B., J. Chem. Soc. Chem. Commun. 1234 (1992).
10. Hoelderich, W. F., and Van Bekkum, H., Stud. Surf. Sci. Catal. 58, 631 (1991).
11. "Atlas of Mass Spectral Data," (E. Stenhagen, S. Abrahamsson and F. W. McLafferty, Eds.), Interscience/Wiley, New York, 1969.
12. R. A. Sheldon and J. Dakka, in "Selective Oxidation in Petrochemistry," DGMK—Conference (M. Baerns and J. Weitkamp, Eds.), DGMK-Tagungsbericht No. 9204, p. 215. DGMK, Hamburg, Germany, 1992.

Sujit B. Kumar
S. P. Mirajkar
Godwin C. G. Pais[+]
Pradeep Kumar[+]
Rajiv Kumar[*1]

*Catalysis Division
+Division of Organic Chemistry: Technology
National Chemical Laboratory
Pune-411008, India

[1] To whom correspondence should be addressed.