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Selective Catalytic Oxidative Cleavage of Oximes to Carbonyl Compounds with H_2O_2 over TS-1 +

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Abstract: *Catalytic system of TS-1-H_2O_2 combination has been shown to display remarkable reaction selectivity in the liquid-phase oxidative cleavage of oximes to carbonyl compounds in excellent yields.*

The oximes of aldehydes and ketones not only represent a convenient series of derivatives of carbonyl compounds but also may be used as intermediates for the preparation of amides by the Beckmann rearrangement.[1] Since many useful reactions have been developed to prepare oximes from other than carbonyl compounds (such as Barton reaction[2]), an efficient catalytic cleavage of oximes assumes great importance leading to new methods of preparing carbonyl compounds. Methods so far developed to regenerate carbonyl compounds from oximes consist of hydrolytic (acid-catalysed[3]) ,or oxidative[4] or reductive[5] reactions and most of them are non-catalytic. In view of current thrust on catalytic processes[6],it merits to develop a true catalytic oxidative cleavage of oximes using inexpensive and non-polluting reagent.

The discovery of titanium silicalite-1(TS-1) of MFI structure zeolite has, in recent years, led to remarkable progress in the field of oxidations of organic substrates with H_2O_2[7]. As part of comprehensive ongoing programme on zeolite-mediated organic reactions at this laboratory,[8] we wish to report a new catalytic method for selective oxidative cleavage of oximes to aldehydes and ketones using TS-1 and dilute H_2O_2 employing acetone as solvent (equation 1)

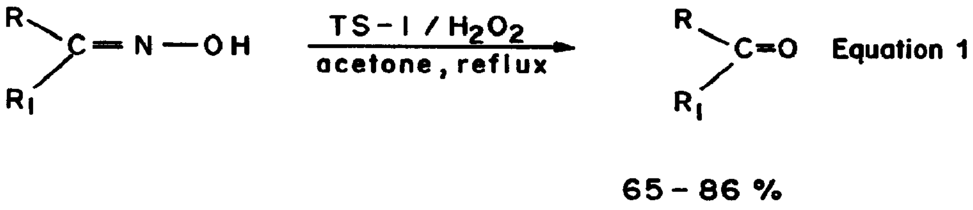

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TABLE 1: Oxidative cleavage of Oximes with H_2O_2 catalysed by zeolite, TS-1.

Entry	Substrate	Time/h	Product[a]	Yield[b](%)
1	Cyclohexanone oxime	4	Cyclohexanone	75
2	4-t-Butylcyclohexanone oxime	4	4-t-Butylcyclohexanone	70
3	Acetophenone oxime	4	Acetophenone	77
4	4-Methylacetophenone oxime	4	4-Methylacetophenone	70
5	4-Methoxyacetophenone oxime	4	4-Methoxyacetophenone	75
6	1-Tetralone oxime	4	1-Tetralone	70
7	Camphor oxime	4	Camphor	65
8	4-Nitrobenzaldoxime	3	4-Nitrobenzaldehyde	70
9	4-Methoxybenzaldoxime	3	4-Methoxybenzaldehyde	72
10	Cinnamaldehyde oxime	3	Cinnamaldehyde	71
11	3-Methylcyclohex-2-enone oxime	3	3-Methylcyclohex-2-enone	86

[a] characterized by IR, ^1H and ^{13}C NMR and MS.

[b] isolated after chromatographic purification ; the rest is essentially unreacted oxime.

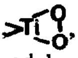
TS-1(Si/Ti=35)[9] and VAPO-5[10] were synthesized following literature procedure. In a typical reaction, a mixture of cinnamaldehyde oxime (0.441g; 3 mmol), TS-1 (44 mg ; 10% by wt.) and 30% H_2O_2 (0.67 ml; 6 mmol) in acetone (15 ml) was refluxed for 3h. After the reaction was complete, the catalyst was filtered off and the product purified by flash chromatography to afford cinnamaldehyde in 71% yield.

Several examples illustrating this novel and rapid procedure for the conversion of oximes to parent carbonyl compounds are illustrated in **TABLE-1.** Notably, aldehydes, regenerated from aldoximes, did not undergo further oxidation under the reaction conditions(GC). Even the sterically hindered camphor oxime had been successfully converted to camphor in good yields. Interestingly, the unsaturated oximes underwent deoximation very efficiently and the reaction is essentially chemoselective [entries 10 & 11].The efficiency and effectiveness of the catalytic system is demonstrated in the case of acetophenone oxime where 5% by wt of TS-1 is sufficient to bring about the deoximation in excellent yield **[Table-2]**. It may also be noted that vanadium-containing aluminophosphate (VAPO-5) catalyzes the deoximation selectively, though in moderate yield (**Table-2**). The zeolite catalyst was recovered ,calcined at 573K and reused several times with no loss of activity and selectivity.

TABLE 2: The effect of the variation of catalytic concentration on the oxidative cleavage of acetophenone oxime to acetophenone.

Catalyst	Weight %	Yield^a(%)
TS-1	0	0
TS-1	1	20
TS-1	5	75
TS-1	10	77
VAPO-5	10	60

a isolated after chromatographic purification.

Mechanistically, the peroxo species , generated in-situ on reaction of silica-bound titanyl (>Ti=O) active site with H_2O_2 followed by elimination of water, is believed[11] to provide the reactive O* species for oxidation of C=N of oxime and the resulting compound subsequently undergoes decomposition generating carbonyl compounds.

In conclusion ,the results described herein demonstrate the novelty of TS-1 catalyst exercising unique selectivity in the oxidative cleavage of oximes to carbonyl compounds by dilute H_2O_2. Besides, the interesting aspect to be noted is that TS-1-H_2O_2 combination is very well-known to effect ammoxidation of cyclohexanone to cyclohexanone oxime in the presence of ammonia.[12]

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References:

1 Donaruma, L. G. and Heldt, W. Z., *Organic Reactions*, **1960**, *11*, 1

2 (a) Barton, D. H. L.,Beaton, J. M.,Geller, L. E. and Pechet, M. M.,*J.Am. Chem. Soc.*,**1961**, *83*, 4076; (b) Barton, D. H. L.,And Beaton, J. M.,*J.Am. Chem. Soc.*,**1961**, *83*, 4083.

3 Donaldson ,R. E.,Saddler, J. C., Byrn ,S.,McKenzie , A. T. And Fuch, P. L.,*J. Org. Chem.*, **1983**, *48*, 2167 and references cited therein.

4 (a) Lee, J. G., Kwak, K. H. And Hwang, J. P., *Tetrahedron Lett.*, **1990**, *31*, 6677; (b) Tamani, B. And Goudarzian, N.,*Eur. Polym. J.*,**1992**, *28*, 1035; (c) Olah, G. A., Liao, Q. Lee, C. S. And Suryaprakash, G. K.,*SYNLETT.*, **1993**, 427.

5 (a) Curran, D. P., Brill, J. F. And Rakiewicz, D. M., *J. Org. Chem.*, **1984**, *49*, 1654; (b) Drabowicz, J., *Synthesis*, **1980**, 125; (c) Corey, E. J., Hopkins, P. B., Kim, S., Yoo, S. Nambiar, K. P. And Falck, J. R., *J. Am. Chem. Soc.*, **1979**, *101*, 7131.

6 Sheldon, R. A, *Chemtech*, **1991**, 566.

7 (a) Davies, M. E., *Acc. Chem. Res.*, **1993**, *26*, 111; (b) Huybrechts, D. R. C, Buskens, P. L., And Jacobs, P. A., *Stud. Surf. Sci. Catal.*, **1992**, 7221.

8 (a) Sonawane, H. R., Pol, A. V., Moghe, P. P., Biswas, S. S. And Sudalai, A., *J. Chem. Soc., Chem. Commun.*, **1994**, In press; (b) Kumar, P., Hegde, V. R., Pandey, B. And Ravindranathan, T., *J. Chem. Soc., Chem. Commun.*, **1993**, 1553; (c) Reddy, R. S., Reddy, J. S., Kumar, R., Kumar, P., *J. Chem. Soc., Chem. Commun.*, **1992**, 84.

9 Taramasso, M., Perego, G. And Notari, B., *US Pat., 4,410,501 (1983)*

10 (a) Inui, T., Matsuda, H., Yamase, O., Nagata, H., Fukuda, K., Ukava, T. And Miyamoto, A. *J. Catal*, **1986**, *98*, 491; (b) Inui, T., Medhanavyn, D., Praserthdam, P., Fukuda, K., Ukava, T., Sakamoto, A., And Miyamoto, A., *Appl. Catal*, **1985**, *18*, 311; (c) Miyamoto, A., Medhanavyn, D., And Inui, T., *Appl. Catal.*, **1986**, *28*, 89.

11 Huybrechts, D. R. C., Buskens, P. L. And Jacobs. P. A., *J. Mol. Catal.*, **1992**, *71*, 129.

12 Roffia, P., Leofanti, G., Cesana, A., Mantegazza, M., Padovan, M., Petrini, G., Tonti, S., And Gervasutti, P., *Stud. Surf. Sci. Catal.*, **1990**, *55*, 43..

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