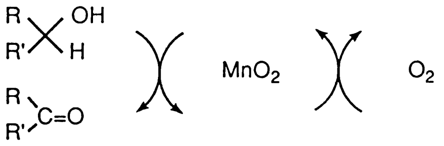
Selectivity in Catalytic Dehydrogenation with Active Manganese Dioxide

Takahide Kimura,* Mitsue Fujita, Hajime Sohmiya,
and Takashi Ando
Department of Chemistry, Shiga University of Medical Science, Seta, Otsu, Shiga 520-21

(Received August 30, 1991)

Synopsis. The selectivities in the competitive dehydrogenation of alcohols, such as benzhydrol and cinnamyl alcohol, with active manganese dioxide under catalytic conditions are different from those under the usual conditions.

Active manganese dioxide has long been ranked among the most useful oxidizing agents in organic synthesis.[1] Although the stoichiometric conversion of the alcohol to ketone or aldehyde with MnO_2 has been well known, a large excess of MnO_2 (5—20 fold by weight) is generally used. During a study of ultrasonically activated MnO_2,[2] we found that Attenburrow's active MnO_2[3] behaves catalytically under an O_2 atmosphere.



As shown in Fig. 1, benzhydrol was quantitatively oxidized to benzophenone with a 1/10 molar equivalent of active MnO_2[3] at 90 °C under an O_2 atmosphere,[4] while under N_2 the reaction stopped at 10% yield of benzophenone. Without MnO_2, benzhydrol was not oxidize by O_2. At room temperature, although the reaction took place catalytically, it occurred very slowly. The other benzenemethanols and cinnamyl alcohol were moderately; 2-octanol, however, was not oxidized under the same conditions.

Although aniline was oxidized to azobenzene (25%, 7 h), diphenyl sulfide was not oxidized at all. This catalytic reaction is therefore dehydrogenation, rather than oxygenation.

Table 1 shows the results of some catalytic competitive reactions together with results obtained under noncatalytic conditions. In the case of the competition of benzhydrol and 2-octanol (Entry 1), although the latter was not oxidized under catalytic conditions, the reaction proceeded slowly under the usual conditions (5 molar excess of MnO_2). The oxidation of aniline was also retarded under catalytic conditions (Entry 2). Interestingly, the oxidation of highly reactive benzhydrol was almost completely inhibited in a competitive reaction with cinnamyl alcohol (Entry 3).

Since the oxidation with active MnO_2 occurs on a solid surface, the nature of adsorption/desorption of substrates onto/from a MnO_2 surface is decisively

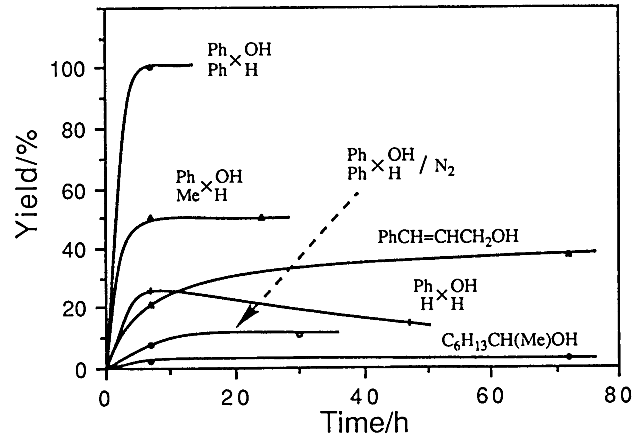


Fig. 1. Reaction profiles of the oxidation of alcohols with active manganese dioxide under an O_2 atmosphere. The reaction conditions are cited in Ref. 4. /N_2 indicates that the reaction was carried out under an N_2 atmosphere.

Table 1. Competitive Oxidations on Active Manganese Dioxide

Entry	Substrates	Yield/% with O_2[a)] Time 2 h	with O_2[a)] 24 h	without O_2[b)] Time 2 h	without O_2[b)] 24 h	without O_2[c)] Time 1 h	without O_2[c)] 24 h
1	Ph_2CHOH	92	100	20	31	99	100
	$C_6H_{13}CH(Me)OH$	<1	4	<1	<1	12	66
2	Ph_2CHOH	50	100	7	18	98	100
	$Ph\text{-}NH_2$	<1	4	1	<1	25	64
3	Ph_2CHOH	1	3	<1	1	71	100
	$PhCH{=}CHCH_2OH$	20	31	14	14	78	66

a) Substrates 2.5 mmol, MnO_2 0.5 mmol, neat, 90 °C, with O_2 bubbling. b) Substrates 1.0 mmol, MnO_2 1.0 mmol, hexane 10 cm³, reflux, without O_2 bubbling. c) Substrates 1.0 mmol, MnO_2 5.0 mmol, hexane 10 cm³, 40 °C, without O_2 bubbling.

important regarding selectivity in competitive oxidations. When a large excess of MnO_2 is used on substrates, as under the usual conditions, the oxidation potentials of the substrates determines the selectivity in competitive reactions. In contrast, when a molar equivalent of MnO_2 was used in a competitive reaction without O_2, although the reaction proceeded slowly, the selectivity showed a tendency to be similar to that obtained under catalytic conditions. (Table 1) This indicates that the catalytic use of MnO_2 changes, selectivity, the adsorption and/or desorption dependency. Thus, the use of catalytic amounts of active MnO_2 under O_2 without a solvent is useful for the selective oxidation of substrates with multi-functional groups.

Pyrolusite (inactive MnO_2) and US-MnO_2[2)] showed no catalytic activity. Active MnO_2 is generally believed to be reduced to either MnO or $Mn(OH)_2$[1)] during the oxidation of alcohols. However, neither MnO, $Mn(OH)_2$ nor Mn_2O_3 showed any oxidizing ability under catalytic conditions. Although $KMnO_4$ is capable of oxidizing four equivalents of benzhydrol, the resulting manganese product does not show any catalytic activity. It has been suggested that there is an active (hydrated) manganese dioxide ($HOMnO_x$) which may act as a surface source of hydroxyl radicals. These radicals never become free, but are detached from the surface by free-radical reactions with adsorbed substrates.[5)] This type of intermediate may well be an active species for recycling.

References

1) For reviews; A. J. Fatiadi in "Organic Syntheses by Oxidation with Metal Compounds," ed by W. J. Mijs and C. R. H. I de Jonge, Plenum Press, New York (1986), Chap. 3, p. 119.

2) T. Kimura, M. Fujita, and T. Ando, *Chem. Lett.*, **1988**, 1387.

3) Active MnO_2 was prepared by following the Attenburrow's method. J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, **1952**, 1094.

4) Typical reaction was carried out as follows: A mixture of substrate (10 mmol) and active MnO_2 (1 mmol) was stirred at 90 °C with O_2 bubbling (10 $cm^3\ min^{-1}$). After an appropriate reaction time, the reaction mixture was cooled and organic materials were extracted with ether.

5) H. B. Henbest and M. J. W. Stratford, *Chem. Ind.* (*London*), **1961**, 1170.