March, 1985] © 1985 The Chemical Society of Japan NOTES *Bull. Chem. Soc. Jpn.*, *58, 1065—1066 (1985)* 1065

Tetrabromooxomolybdate(V) Complex. The Catalytic Reactivity for the Reaction of *t*-Butyl Hydroperoxide

Yasuhiko KURUSU,* Yoshiro MASUYAMA, and Mikio SAITA
Department of Chemistry, Faculty of Sciencae and Technology, Sophia University,
7-1, Kioicho, Chiyoda-ku, Tokyo 102

(Received September 21, 1984)

Synopsis. The nature of an ammonium counter cation of tetrabromooxomolybdate complex influences the rate of decomposition of *t*-butyl hydroperoxide(*t*-BuOOH) and oxidation with *t*-BuOOH. The catalytic activity of the ammonium for the decomposition of *t*-BuOOH decreased as the following order; benzyltrimethylammnium, -*N*-methyl pyridinium, -trimethylene bispyridinium, ≫pyridinium, -quinolinium, >1,3-propanediammonium, -1,6-hexanediammonium. However, the reverse order was observed in the catalytic activity for the epoxidation by *t*-BuOOH, and the rate of oxidation of alcohol by *t*-BuOOH was independent of the nature of ammonium cation.

In the synthetic applications of catalytic oxygen transfer process a metal catalyst mediates the selective transfer of an oxygen atom from alkyl hydroperoxides to the substrate.[1] A few examples of this application are epoxidation and other oxidation with alkyl hydroperoxides. For epoxidation of olefin with hydroperoxides molybdenum compounds are effective well-known catalysts.

We have investigated the epoxidation of olefin with *t*-butyl hydroperoxide(*t*-BuOOH) in the presence of various molybdenum compounds.[2] In the process, we found that oxomolybdate complex showed an interesting character for the reaction of *t*-BuOOH; the reactivity of *t*-BuOOH was dependent on the counter cation of the tetrabromooxomolybdate(V) complex. In order to clarify this tendency, we prepared tetrabromooxomolybdate(V) complexes containing benzyltrimethylammonium(**1**), *N*-methylpyridinium(**2**), trimethylene bispyridinium(**3**), pyridinium(**4**), quinolinium(**5**), 1,3-propanediammonium(**6**), and 1,6-hexanediammonium(**7**) as a counter cation.

The decomposition of *t*-BuOOH in the presence of various complexes mentioned above was examined. The results are shown in Table. **1** shows the highest activity in the decomposition of *t*-BuOOH. When an ammonium cation of tetrabromooxomolybdate(V) complex has no hydrogen on the nitrogen atom such as **1**, **2**, and **3**, decomposition of *t*-BuOOH and oxidation of alcohols to carbonyl compounds took place smoothly, but the epoxidation of olefins with *t*-BuOOH did not proceed. On the other hand, the decomposition is rarely found in **6** and **7**. The decomposition of *t*-BuOOH is essentially free-radical-induced decomposition initiated by metal-hydroperoxide interaction,[3] since the addition of 2,6-xylenol, 2,6-xylidine or *N*-phenyl-2-naphthylamine as a radical scavenger depressed the decomposition of *t*-BuOOH. For example, only 4% of *t*-BuOOH were decomposed when a mole of four of 2,6-xylenol to one of **4** was used.

TABLE. DECOMPOSITION OF *t*-BuOOH, EPOXIDATION OF CYCLOHEXENE, AND OXIDATION OF 2-OCTANOL IN THE PRESENCE OF AMMONIUM TETRABROMOOXOMOLYBDATE(V) COMPLEX

Mo complex	Decomposition of *t*-BuOOH conversion/%	Epoxidation of cyclohexene yield of/% cyclohexene oxide	Oxidation of 2-octanol yield of/% 2-octanone[a)]
1	85	0	80
2	96	0	44
3	91	0	46
4	37	66	78
5	35	68	—
6	10	78	77
7	6	85	—

a) The residue compound is only 2-octanol unreacted.

The epoxidation of cyclohexene with *t*-BuOOH was carried out in the presence of a catalytic amount of various ammonium tetrabromooxomolybdate(V) complexes. As can be seen from Table, the tendency in the rate of decomposition of *t*-BuOOH reversely relates to that of the epoxidation, that is, in the case of high activity for epoxidation, decomposition activity is low. For example, **6** and **7** are effective for epoxidation with *t*-BuOOH but not for decomposition. On the other hand, oxidation activity for alcohol is independent of the decomposition activity for *t*-BuOOH. **1**, **2**, and **3** show no activity for epoxidation but have high effectivity for oxidation of 2-octanol. Also, we have already reported that unsaturated alcohols were oxidized to unsaturated carbonyl compounds.[4]

It is worth noting that *t*-BuOOH shows no activity for olefinic compound in the presence of **1**, **2**, and **3**, thus unsaturated alcohol can be oxidized selectively by *t*-BuOOH with **1**, **2**, and **3** without disturbing carbon–carbon double bond. It is interesting that ammonium as a counter-cation of tetrabromooxomolybdate(V) complex profoundly affects the reactivity of *t*-BuOOH.

Experimental

Materials. Pyridinium tetrabromooxomolybdate(V) (**4**) and quinolinium tetrabromooxomolybdate(V)(**5**) were prepared according to the procedure of Allen and Newmann.[5] Similar procedures were used with a little modification for the preparation of other ammonium tetrabromooxomolybdate(V) complexes. These complexes were identified by the elemental analysis (Mo: EDTA method and Br: Volhard method), and spectral measurements. Benzyltrimethylammonium tetrabromooxomolybdate(V)(**1**): Found: Mo, 15.8; Br, 54.6%. Calcd for $C_{10}H_{16}Br_4MoNO$: Mo, 16.5; Br, 54.9%. *N*-Methylpyridinium tetrabromooxomolybdate(V)(**2**): Found: Mo, 18.2%. Calcd for $C_6H_8Br_4MoNO$: Mo, 18.3%. Trimethylenebispyridinium tetrabromoxomolybdate(V)(**3**): Found: Mo, 18.3%. Calcd for $C_{13}H_{16}Br_8Mo_2N_2O_2$: Mo, 18.0%. 1,3-propanediammonium tetrabromooxomolybdate(V)(**6**): Found: Mo, 20.0; Br, 64.0%. Calcd for $C_3H_{12}Br_8Mo_2N_2O_2$: Mo, 20.4; Br,68.1%. 1,6-hexanediammonium tetrabromooxomolybdate(V)(**7**): Found Mo, 19.0; Br, 63.8%. Calcd for $C_6H_{18}Br_8Mo_2N_2O_2$: Mo, 19.6; Br, 65.1%. *t*-BuOOH supplied by Nippon Oils & Fats Co. was used after the purification by vacuum distillation.

General Procedure for Decomposition. In a test tube with a screw cap, benzene(50 cm^3) and *t*-BuOOH(0.05 mol) were mixed with a catalytic amount of molybdenum complex(0.2 meq). Then the tube contents were stirred at 60 °C for 60 min in an aluminum block thermostat. The products were analyzed by GC; column packing material was DOP/Chromosorb PNAW, carrier gas was hydrogen.

General Procedure for Epoxidation. Cyclohexene (0.05 mol) was dissolve in benzene(50 cm^3) and the mixture was stirred at 60 °C. Then molybdenum catalyst(0.2 meq) and *t*-BuOOH (0.05 mol) were added to the solution. The stirring was continued at 60 °C for 60 min. Cyclohexene oxide was separated by GC (DOP/Chromosorb PNAW, carrier gas; nitrogen or helium) and identified by NMR and IR.

General Procedure for Oxidation of 2-Octanol. Molybdenum catalyst(0.15 meq), *t*-BuOOH(5 mmol), and 2-octanol(3 mmol) were added into benzene(3 cm^3) and stirred at 60 °C for 24 h. After evaporation, the product, 2-octanone, was separated by column chromatography(Wako gel C-200/hexane; ethyl acetate (3:1)) and identified by NMR and IR.

References

1) R. A. Sheldon, "Synthesis and Uses of Alkyl Hydroperoxides and Dialkyl Peroxides" in "The Chemistry of Peroxides" ed by S. Patai, John Wiley & Sons, Chichester-New York-Brisbane-Toronto-Singapore (1983) pp. 161—200.

2) M. Yamazaki, H. Endo, M. Tomoyama, and Y. Kurusu, *Bull. Chem. Soc. Jpn.*, **56**, 3523 (1983).

3) R. Hiatt, T. Mill, K. C. Irwin, and J. Castleman, *J. Org. Chem.*, **33**, 1421 (1968).

4) Y. Masuyama, M. Takahashi, and Y. Kurusu, *Tetrahedron Lett.*, **25**, 4417 (1984).

5) J. F. Allen and H. M. Newmann, *Inorg. Chem.*, **3**, 1612 (1964).