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Preliminary communication

Oxidation of cyclohexene with t-butyl hydroperoxide catalyzed by transition metal oxide clusters

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Abstract

Organometallic oxide clusters $[(Rhcp')_4V_6O_{19}]$ ($cp' = \eta^5$-C_5Me_5) and $[(Rhcp')Cl(CH_3CN)_2]_2[Mo_6O_{19}]$ catalyze the oxidation of cyclohexene with t-butyl hydroperoxide to give allylic oxidation products mainly and epoxycyclohexane selectively, respectively.

Oxidation of olefins with t-BuOOH catalyzed by transition metal complexes involves two important reaction pathways: allylic substitution triggered by the homolytic cleavage of t-BuOOH and olefin epoxidation caused by the oxygen-atom transfer [1]. Rhodium complexes favor the former pathway [2], while higher-valent vanadium and molybdenum complexes favor the latter [3*]. We report here the oxidation of cyclohexene with t-BuOOH catalyzed by multi-metal oxide clusters, $[(Rhcp')_4V_6O_{19}]$ (**1**) and $[(Rhcp')Cl(CH_3CN)_2]_2[Mo_6O_{19}]$ (**2**) containing rhodium and vanadium atoms, and rhodium and molybdenum atoms, respectively, to compare with that catalyzed by mononuclear transition metal complexes.

Cluster **1** was recently prepared, and has approximately tetrahedral molecules in which each of four $[Rhcp']^{2+}$ cations is bound to a single $[V_6O_{19}]^{8-}$ anion through three bridging oxygen atoms [4]. Complex **2**** has been newly obtained from the reaction of the triple cubane-type cluster $[(Rhcp')MoO_4]_4$ [5] with excess t-BuOOH

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* Reference numbers with asterisks indicate notes in the list of references.

** **2**: Anal. Found: C, 21.62; H, 2.69; N, 3.71. $C_{28}H_{42}O_{19}N_4Cl_2Mo_6Rh_2$ calcd.: C, 21.14; H, 2.66; N, 3.52%. IR (Nujol, 1000–400 cm^{-1}): 956 cm^{-1} (s) [$\nu(Mo–O^t)$]; 800(s), 602 cm^{-1} (m) [$\nu(Mo–O^b)$]; 434 cm^{-1} (m) [$\nu(Mo–O^c)$] (O^t: terminal oxygen, O^b: bridging oxygen, O^c: central oxygen). ^1H NMR (CD_3CN): C_5Me_5 δ 2.20 s. The crystal used in the X-ray study was obtained from an acetonitrile solution. Crystal data: monoclinic, space group $P2_1/c$, a 10.808(3) Å, b 11.016(2) Å, c 19.638(7) Å, β 91.22 (2)°, $Z = 2$, D_c 2.19 g/cm³. Intensity data were collected on an Enraf–Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation in the $2\theta \leq 60°$ range. The structure was solved by a direct method (Multan 78) and refined by a block diagonal least-squares technique. The current R value is 0.076 for 3364 independent absorption-corrected reflections.

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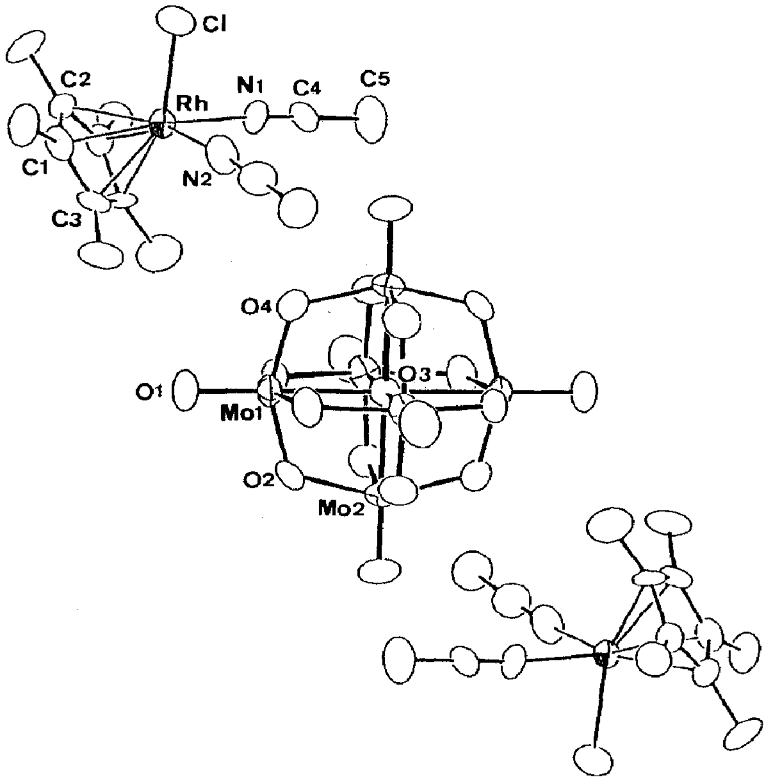
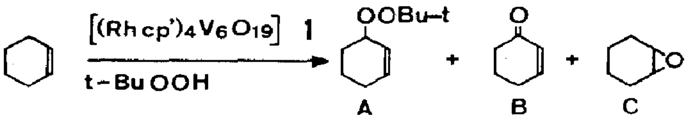


Fig. 1. Perspective view of cluster **2**. Important bond lengths (Å) and angles (deg) are as follows: Mo1–O1, 1.68(1); Mo1–O2, 1.94(1); Mo1–O3, 2.307(2); Rh–Cl, 2.400(5); Rh–N1, 2.13(1); Rh–N2, 2.11(1); C1–C2, 1.41(2); C1–C3, 1.42(2); N1–C4, 1.10(2); C4–C5, 1.47(3); O1–Mo1–O2, 103.4(6); O1–Mo1–O3, 179.0(5); O2–Mo1–O4, 153.4(5); O2–Mo1–O3, 76.0(4); C2–C1–C3, 107(1).

in 1,2-dichloroethane at 70 °C. The acetonitrile molecules in **2** were incorporated as ligands on recrystallization of the product from an acetonitrile solution. Single crystal X-ray diffraction has revealed that **2** is an ionic compound consisting of the $[(\text{Rhcp}')\text{Cl}(\text{CH}_3\text{CN})_2]^+$ cation and the $[\text{Mo}_6\text{O}_{19}]^{2-}$ anion [6*] in a cage-like structure as shown in Fig. 1. Important bond lengths and angles are given in the caption to Fig. 1.

A deep red-brown solution of cluster **1** (0.10 g, 6.0×10^{-2} mmol) in 1,2-dichloroethane containing cyclohexene (0.40 g, 4.8 mmol) and t-butyl hydroperoxide (4 cm^3 of a 3.0 *M* solution in 2,2,4-trimethylpentane, 12 mmol) was stirred under nitrogen at 70 °C for 24 h. GC-Mass analysis revealed the formation of 2-cyclohexen-1-yl t-butyl peroxide (**A**) (2.0 mmol, 42% yield based on cyclohexene), 2-cyclohexen-1-one (**B**) (1.0 mmol, 21%), and 1,2-epoxycyclohexane (**C**) (0.7 mmol, 15%) (eq. 1). The reaction was almost complete within 5 h (Fig. 2), but did not proceed in the absence



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of either the oxide cluster or t-BuOOH under the same conditions. When various amounts of t-BuOOH were used against a fixed amount of cyclohexene, interest-

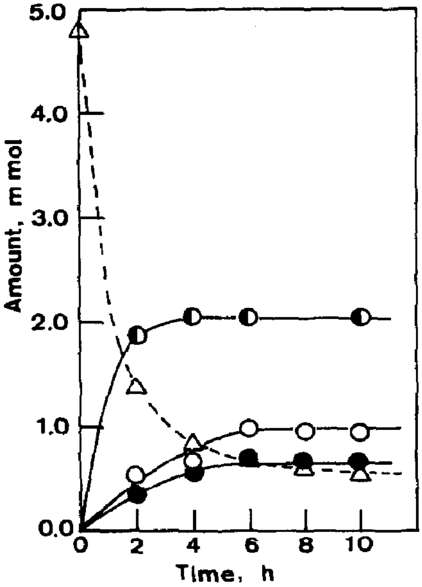

Fig. 2. Oxidation of cyclohexene with t-BuOOH catalyzed by cluster 1 in 1,2-dichloroethane (10 cm^3) at 70 °C. Catalyst, 6.0×10^{-2} mmol; cyclohexene, 4.8 mmol (initial amount); t-BuOOH, 12.0 mmol (initial amount); ◐, 2-cyclohexen-1-yl t-butylperoxide; ○, 2-cyclohexen-1-one; ●, 1,2-epoxycyclohexane; △, cyclohexene.

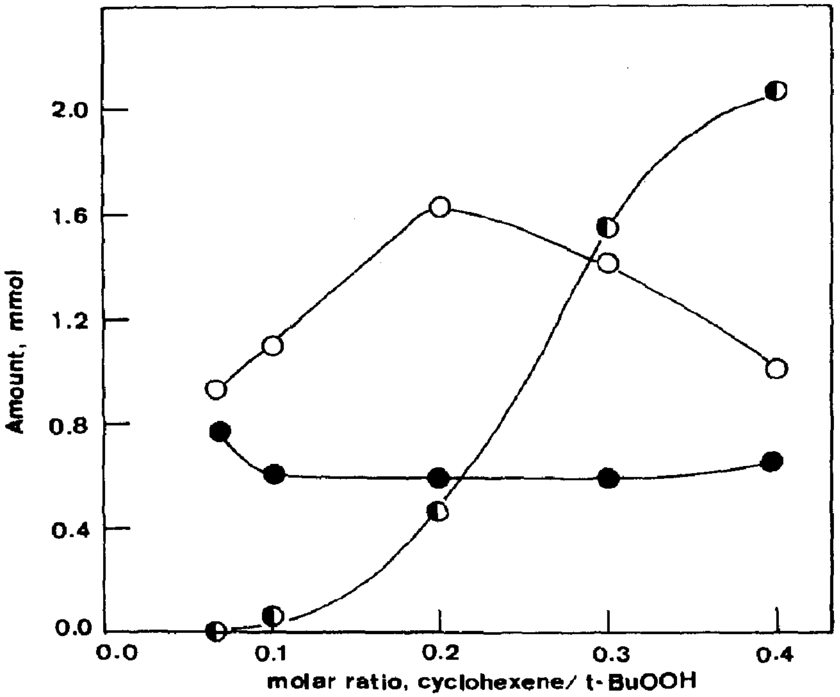

Fig. 3. Effect of the t-BuOOH concentration on the yield of each product after 5 h of the reaction of cyclohexene with t-BuOOH catalyzed by cluster 1 in 1,2-dichloroethane (10 cm^3) at 70 °C. Catalyst, 6.0×10^{-2} mmol; cyclohexene, 4.8 mmol (initial amount). Symbols are the same as those in Fig. 2.

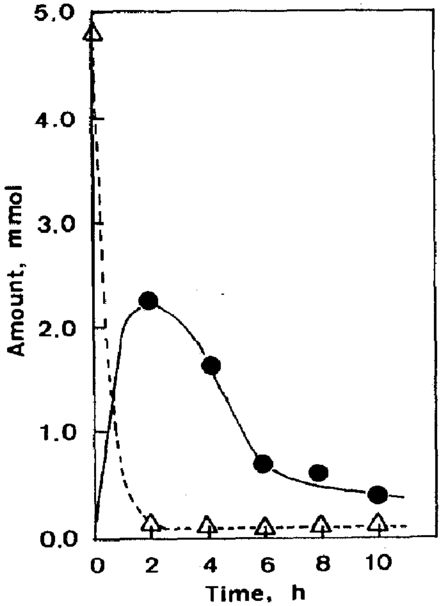

Fig. 4. Oxidation of cyclohexene with t-BuOOH catalyzed by cluster **2** in 1,2-dichloroethane (10 cm^3) at 70 °C. Catalyst, 6.0×10^{-2} mmol; cyclohexene, 4.8 mmol (initial amount); t-BuOOH, 12.0 mmol (initial amount). Symbols are the same as those in Fig. 2.

ingly, the yield of **A** increased with increasing molar ratio of cyclohexene to t-BuOOH and that of **B** has a maximum at the ratio of ca. 0.2, whereas the yield of **C** was not affected appreciably (Fig. 3).

Addition of hydroquinone as a radical scavenger (1.9 mol% to the olefin) to the reaction mixture containing cluster **1** retarded the formation of **A** and **B** anomalously during 1.2 h from the outset of the reaction. Thus an induction period of 1 h was observed before the production of **B**, and thereafter the formation of **A** and **B** proceeded at rates comparable to those recorded in the absence of hydroquinone. In contrast, the formation of **C** was not affected by the scavenger. These results suggest that the reactions that yield **A** and **B** may have the free radical character, whereas **C** is generated by heterolytic cleavage of t-BuOOH [3a].

Oxide cluster **1** and its uncharacterized decomposition products were recovered from the solution after reaction, and we are unable to identify the active catalyst species at this stage. We also examined the catalytic activities of $[(Rhcp')Cl_2]_2$ and $((n\text{-}C_4H_9)_4N)_3[H_3V_{10}O_{28}]$, but both were less efficient with regard to the formation of allylic oxidation products and the total conversion of cyclohexene. Thus the rhodium complex gave mainly **A** in a conversion of ca. 32% during 10 h and the vanadium polyoxometalate mainly **C** in a conversion of ca. 25% during 10 h.

Oxidation of cyclohexene with cluster **2** as the catalyst was carried out under conditions similar to the above and was almost complete within 2 h; 99% of the cyclohexene was consumed to give 1,2-epoxycyclohexane (2.5 mmol, 52%) selectively. Prolonged reaction diminished the yield of product significantly owing to further oxidation (Fig. 4). The molybdenum hexamer $((n\text{-}C_4H_9)_4N)_2[Mo_6O_{19}]$ was also effective as a catalyst and gave 1,2-epoxycyclohexane selectively, but the reaction was very slow and the yield was very low (ca. 4%) after 2 h.

The catalytic oxidation under the action of the mixed metal oxide clusters **1** and **2** has the following characteristic features. Cluster **1** is a more efficient catalyst for the formation of allylic products than $[Rhcp'Cl_2]_2$ and $((n\text{-}C_4H_9)_4N)_3[H_3V_{10}O_{28}]$, but less efficient than the vanadium decamer for the formation of the epoxide. On the other hand, cluster **2** is a powerful catalyst that is superior to $((n\text{-}C_4H_9)_4N)_2[Mo_6O_{19}]$ in affording the epoxide.

It has been reported that when a mixture of two metal complexes such as $[RhCl(PPh_3)_3]$ and $[Mo(O)(O_2)_2(OP(NMe_2)_3(H_2O)]$ is used as a combined catalyst system for the oxidation of cyclohexene with gaseous oxygen, each complex independently plays its own catalytic role [7]. Thus, the rhodium complex catalyzes the formation of 2-cyclohexen-1-yl hydroperoxide, whereas the molybdenum complex assists the oxygen transfer from the peroxide to cyclohexene to produce 1,2-epoxycyclohexane. The present observations may indicate that the roles of mixed metal centers in **1** and **2** differ from those of metals in the combined catalyst system, the mixed metal centers in **1** and **2** working cooperatively in one particular step of the oxidation reaction.

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