Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

H_2O_2 Oxidation by Ce(IV) Contained Weakley-Type Heteropolyoxometalate for Various Alcohols

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To cite this article: Ryuji Shiozaki , Hiroshi Kominami & Yoshiya Kera (1996) H_2O_2 Oxidation by Ce(IV) Contained Weakley-Type Heteropolyoxometalate for Various Alcohols, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 26:9, 1663-1668, DOI: 10.1080/00397919608002603

To link to this article: http://dx.doi.org/10.1080/00397919608002603

SYNTHETIC COMMUNICATIONS, 26(9), 1663–1668 (1996)

H_2O_2 OXIDATION BY Ce(IV) CONTAINED WEAKLEY-TYPE HETEROPOLYOXOMETALATE FOR VARIOUS ALCOHOLS

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ABSTRACT: Catalytic activity of Ce(IV) contained Weakley-type heteropoly-oxometalate for the H_2O_2 oxidation of primary and secondary alcohols was evaluated for the first time. It was found that this catalyst exhibited a mild and thus quite selective activity, especially for benzylalcohols.

INTRODUCTION: A large number of recent reports concerning the catalytic activities of Keggin-type polyoxometalates for the oxidation of organic substrates using H_2O_2 have been fruitfully submitted,[1-3] whereas that of lanthanidedecatungstate, Weakley-type polyoxometalate ($LnW_{10}O_{36}^{n-}$, abbreviated as LnW10 below) has not been reported.[4] According to the crystallographic determination of sodium salt of CeW10 (Na-CeW10), a tetravalent cerium square antiprismatically coordinates two units of polytungstates

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($W_5O_{18}^{6-}$) in which five octahedral tungstates are bonded with edge sharing (see the FIG).[5] From the structural feature, Weakley-type heteropolyoxometalate must be expected to posses catalytic activities like other isopoly and heteropolyoxometalates. Here we wish to report the CeW10 catalyzed oxidative dehydrogenation of various primary and secondary alcohols in the presence of H_2O_2.

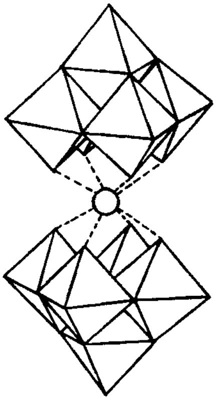
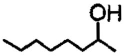
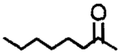
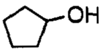
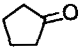
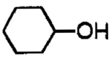
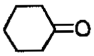
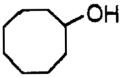
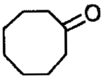
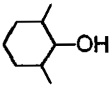
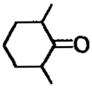
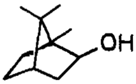
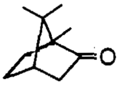
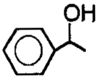
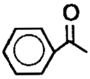
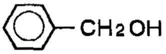
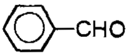
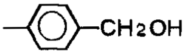
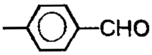
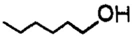


FIG
Octahedral presentation of CeW10. The central circle represents Ce(IV) atom.

RESULTS AND DISCUSSION: In order to be dissolved in an organic media, cation of Na-CeW10 was stoichiometrically replaced with cetylpyridinium ion. We abbreviate the resulting salt as cetyl-CeW10 hereafter. However, tetraethyl, tetrapropyl, and tetra-n-butyl ammonium salts of CeW10 were not satisfactorily prepared unlike Keggin-type polyoxometalates. The reaction was conducted under the biphase system using chloroform as an organic solvent at various amount of H_2O_2 and reaction time. During the reaction, cetyl-CeW10 was completely dissolved predominantly in the organic phase. The results are listed in the table. For saturated acyclic alcohols, secondary alcohol such as 2-octanol was converted to 2-octanone in 78 % yield (entry 1), whereas the oxidized product was not obtained for the primary alcohol such as hexanol (entry 10). Saturated cyclic alcohols were also highly converted to the corresponding ketones (entries 2-6). Especially, sterically hindered alcohols, 2, 6-dimethylcyclohexanol (entry 5) and borneol (entry 6) were smoothly oxidized to give the corresponding ketones. For both secondary and primary arylalcohols, the corresponding ketones and aldehydes were easily obtained without any further oxidation products

Table

$$\text{Alcohol} + H_2O_2 \xrightarrow[\text{CHCl}_3\text{, reflux}]{\text{2 mol\% cetyl-CeW10}} \text{Product}$$

entry	alcohol /mmol		H_2O_2 /mmol	time / h	product	conv / %	yield / %[a]
1		(5)	540	16		78	78
2		(5)	540	16		82	72[b]
3		(5)	360	9		83	83
4		(5)	360	9		>98	>98
5		(5)	360	10		79	79
6		(5) (10)	180 600	6 8		96	96 99[c]
7		(5) (10)	180 800	6 8		87	87 98[c]
8		(5)	180	6		86	86
9		(5)	180	6		89	86
10		(5)	180	6		5	5

a) GC yield using internal standard method. b) no other peak was detected by GC. c) isolated yields.

(entries 7-9). These reactivities of cetyl-CeW10 are comparable to those of Keggin-type polyoxometalate. In conclusion, it is clarified that this H_2O_2/cetyl-CeW10 system can be satisfactorily used as a selective oxidation method. Additionally, the cetyl-CeW10 can be easily prepared in large quantities without producing any impurities.

It is noteworthy that the FT-IR spectrum of the catalyst collected after the reaction was consistent with that before the reaction, implying that the polyanion structure was left intact during the reaction. However, it was suggested by *in situ* FT-Raman spectroscopy in the H_2O_2/Na-CeW10 catalyst system that some kinds of peroxo complexes existed.[6] Such intermediate peroxo complexes seem to be the key species. We are now investigating the influence of lanthanide ions on the physico-chemical properties of LnW10 and the related peroxo species.

EXPERIMENTAL: Preparation of the catalyst. Na-CeW10 ($Na_6H_2CeW_{10}O_{36}$ $\cdot 30H_2O$) was synthesized according to the literature[7] and was characterized by UV,[8] FT-IR, FT-Raman,[9] ^{183}W-NMR, and ICP analyses. Then the cation of Na-CeW10 was replaced with quaternary alkylammonium to form catalyst. The preparation procedure is as follows:[1] To a stirred solution of Na-CeW10 (1 g, 0.31 mmol) in distilled water (5 ml), an aqueous solution of cetylpyridinium chloride monohydrate (0.9 g, 2.5 mmol; 15 ml) was dropwise added at room temperature (ca. 20 °C). After 2 hours, the resulting pale yellow massive precipitate was filtered, washed with distilled water, and dried *in vacuo* (1.52 g, 98 %). Anal. Calcd for $C_{168}H_{304}N_8CeW_{10}O_{36}$: C, 40.42; H, 6.14; N, 2.25. Found: C, 40.97; H, 6.30; N, 2.26. FT-IR and UV spectra suggested that the product preserved its polyanion structure.

Typical oxidation reaction procedures. In a three-necked round bottom flask (100 ml), the catalyst (0.5 g, 0.1 mmol), alcohol (5 mmol), and $CHCl_3$ (10 ml) were introduced. After ca.10 min of preheating the mixture at 61 °C under a

N_2 atmosphere, the reaction was started by the addition of H_2O_2 (30 %; 20.4 g, 180 mmol). At the end of the reaction, the solution was cooled and extracted with $CHCl_3$. The product yield was determined by GC (0.25 mm × 30 m DBWAX capillary column) using the internal standard method.

ACKNOWLEDGMENTS: The authors thank Dr. Masahiko Maekawa (Kinki University) for the ^{183}W-NMR measurement and also Professor Shigetoshi Takahashi (Osaka University) for his continuous and helpful suggestions. This work was supported by the Ministry of Education, Science and Culture on Priority Areas "New Development of Rare Earth Complexes" (NO. 06241277).

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(Received in Japan 21 July 1995)