

A new process for preparing dialdehyde by catalytic oxidation of cyclic olefins with aqueous hydrogen peroxide

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A novel peroxo-niobophosphate was synthesized for the first time and used as a catalyst in the oxidation reaction of cyclic olefins with aqueous hydrogen peroxide to prepare dialdehydes. The catalyst was characterized by elemental analysis, thermographic analyses, IR, UV/vis, ^{31}P NMR and XPS spectra as $[\pi\text{-C}_5\text{H}_5\text{N}(\text{CH}_2)_{13}\text{CH}_3]_2[\text{Nb}_4\text{O}_6(\text{O}_2)_2(\text{PO}_4)_2] \cdot 6\text{H}_2\text{O}$ (TPNP). It showed high selectivity to glutaraldehyde in the catalytic oxidation of cyclopentene with aqueous hydrogen peroxide in ethanol.

Keywords Peroxo-niobophosphate, catalytic oxidation, hydrogen peroxide, glutaraldehyde

Since aqueous hydrogen peroxide is cheap, environmentally clean and easy to handle, the oxidation of organic substrates with aqueous hydrogen peroxide catalyzed by transition metal compounds is very attractive either by industrial technology or synthetic organic chemistry. Some early efforts have been devoted to the direct epoxidation of olefins by aqueous hydrogen peroxide.¹ When excess hydrogen peroxide was present, 1,2-diols were formed and would further be cleaved to form carboxylic acids.² The common catalysts are polyacids or heteropolyacids containing VI B metals. V B metals were not considered to be good catalysts.^{3,4,5} But recently, some heteropoly-niobotungstates were reported to be a kind of new catalyst for the oxidation of olefins, which showed some different catalytic behavior from the heteropoly-tungstates.^{6,7} Since metal peroxides are involved in the reaction intermediates in the catalytic oxidation of olefins with H_2O_2 ,⁸ it is interesting to investigate the catalytic properties of peroxy niobium complexes in such procedure.

We report here the catalytic oxidation of alkenes

using a novel niobic complex, tetradecanepyridinium peroxo-niobophosphate, $[\pi\text{-C}_5\text{H}_5\text{N}(\text{CH}_2)_{13}\text{CH}_3]_2[\text{Nb}_4\text{O}_6(\text{O}_2)_2(\text{PO}_4)_2] \cdot 6\text{H}_2\text{O}$ (TPNP), which exhibited high selectivity in the oxidation of cyclopentene to glutaraldehyde with aqueous hydrogen peroxide.

TPNP was prepared by the following procedures: $\text{Na}_8\text{Nb}_6\text{O}_{19} \cdot 15\text{H}_2\text{O}$ (1.0 g, 0.76 mmol) and $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (0.9 g, 2.3 mmol) were dissolved in 10 mL of 30 wt% aqueous H_2O_2 solution at 0°C . The reaction mixture was adjusted to pH 1 with hydrochloric acid. At this time, the color of the solution turned to bright yellow. After two hours of stirring, 15 mL of tetradecanepyridinium chloride aqueous solution (10 wt%) was added dropwise and a yellow precipitate formed immediately. The precipitate was collected on a sintered glass filter and washed with water, ethanol and acetone, dried in air. The yield was 82% (1.3 g).

Anal. $\text{C}_{38}\text{H}_{80}\text{N}_2\text{Nb}_4\text{P}_2\text{O}_{24}$. Calcd: C, 32.99; H, 5.83; N, 2.03; Nb, 26.89; P, 4.48. Found: C, 33.02; H, 5.47; N, 2.02; Nb, 26.93; P, 4.43. TGA ($20^\circ\text{C}/\text{min}$ under N_2) confirmed the presence of six H_2O molecules (calcd. % wt. loss 7.8%, obsd. 8.0%) in TPNP. Iodometry determination⁹ found 2.0 ± 0.1 equivalents of O_2^{2-} per equivalent of TPNP, showed that the mole ratio of Nb to peroxy group was 2:1 (calcd. for $(\text{O}_2)^{2-}$ 4.63%, found $(\text{O}_2)^{2-}$ 4.69%). IR spectrum showed a typical stretching frequency of $\nu(\text{O}-\text{O})^{10,11}$ at 875 cm^{-1} and $\nu(\text{P}-\text{O})^{12}$ at $1096, 1026\text{ cm}^{-1}$. No $\nu(\text{M}=\text{O})^{13}$ absorption was found in the range of $1000\text{--}900\text{ cm}^{-1}$. UV spectrum showed a characteristic MLCT band at 330 nm, similar to the characteristic band found in some peroxo-niobo-complexes.¹⁴ ^{31}P NMR spectrum of a solid sample of TPNP with MAS technique

showed only one sharp peak at -3.87 . TPNP can be dissolved in the mixed solution of H_2O_2 and alcohol. When $(\text{CH}_3)_3\text{COH}$ was used as solvent, the ^{31}P NMR spectrum of the mixed solution showed only one sharp peak at 0.6669 . When CH_3OH was the solvent, electrospray ionization mass spectrometry (ESI-MS) of the mixed solution gave peak at 315 for $[\text{Nb}_4\text{O}_6(\text{O}_2)_2\{(\text{OH})(\text{O}_2)\}_2]^{2-}$, showing a skeleton of Nb_4O_6 in TPNP.¹⁵ A suggested structure of TPNP is depicted by Fig. 1.

Catalyzed by TPNP, cyclic olefins can be oxidized to dialdehydes with stoichiometric amount of H_2O_2 . In the case of cyclopentene, glutaraldehyde (**a**) was ob-

tained as the major product, while α -ketocyclopentene (**b**), 2-ethoxy-1-cyclopentanol (**c**), and 1,2-cyclopentanediol (**d**) were obtained as the by-products.¹⁶ Table 1 shows the results of the catalytic oxidation of cyclopentene in various solvents.

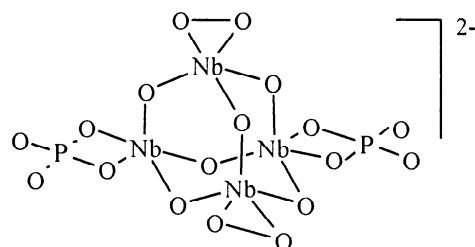


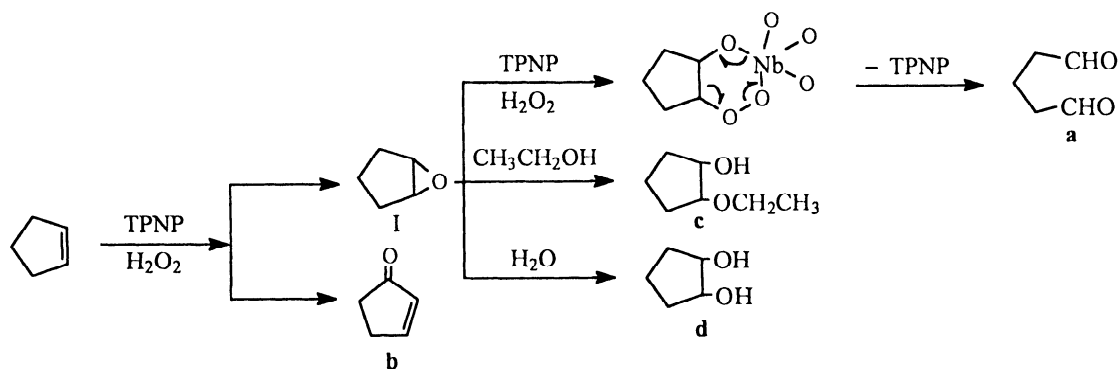
Fig. 1 A suggested structure of TPNP anion.

Table 1 Oxidation^a of cyclopentene with H_2O_2 in various solvents^b

Entry	Solvent	Conv. (%)	Selectivity (%)			
			a	b	c	d
1	Ethanol	99	80	7	5	8
2	<i>t</i> -Butanol	88	68	22	1	9
3	Methanol	82	59	6	22	13
4	Dioxane	82	70	17		13
5	Ethylene dichloride	10	36	64		
6	<i>iso</i> -Propanol	95	72	19	1	8
7 ^c	Ethanol	99	80	7	5	8

^a Reaction conditions: Cyclopentene (0.5 mL, 5.6 mmol), solvent (2.0 mL), 35°C , 24 h, 1.15 mL of 30% aqueous H_2O_2 (11.2 mmol), TPNP (0.0277 g, 0.02 mmol). ^b The products were analyzed with GC-MS and GC. ^c Catalyzed by recovered TPNP.¹⁷

Scheme 1



A typical plot of the cyclopentene, glutaraldehyde and other products vs. time at 35°C , using TPNP as a catalyst and 30% aqueous hydrogen peroxide as oxidant in ethanol is showed in Fig. 2. It indicated that cyclopentene was epoxidized to form 1,2-epoxycyclopentane (**I**) in the first step of the reaction, some α -ketocyclopentene (**b**) was also produced. **I** was either catalyti-

cally oxidized by second equivalent of H_2O_2 to form **a**, or attacked by H_2O or solvent molecules to form by-products **c** and **d** (Scheme 1). Though dialdehydes and diols were reported to be easily oxidized with excess H_2O_2 ¹⁸, we did not find dicarboxylic acid or even half carboxylic acid in the products under our reaction conditions. Cyclopentanediol was found unable to be catalyti-

cally oxidized by TPNP at 35°C, although it can be catalytically oxidized by tungstophosphate under the same conditions.¹⁹ It was attributed to the relatively low reaction temperature (35°C) and the better selectivity of the catalyst we used.

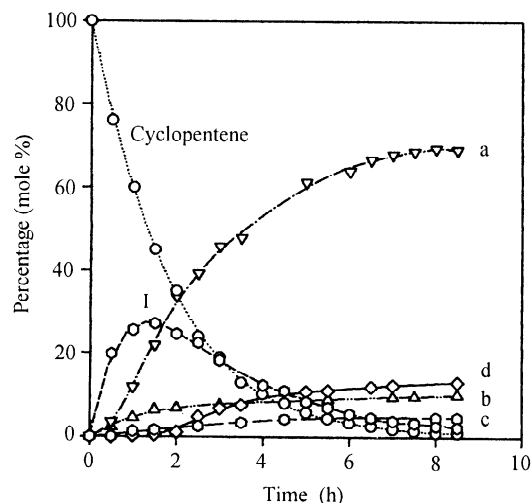


Fig. 2 Oxidation of cyclopentene with aqueous H_2O_2 and TPNP in ethanol at 35°C. Reaction conditions: cyclopentene (0.5 mL, 5.6 mmol), ethanol (2.0 mL), 30% aqueous H_2O_2 (11.2 mmol), TPNP (0.02 mmol) and 35°C, 24 h. The products were analyzed with GC-MS and GC.

Obviously, the highest selectivity of glutaraldehyde occurring in ethanol was really exciting. Under the same reaction conditions cyclohexene gave lower conversion and lower selectivity to adipaldehyde (In ethanol, the conversion was 52% with 42% selectivity when the concentration of H_2O_2 was 1.8 M; the conversion was 62% with 35% selectivity when the concentration of H_2O_2 was 2.8 M.). In *t*-butanol, the conversion was 92% with 52% selectivity. The higher selectivity in cyclopentene was attributed to its ring strain compared to that of the cyclohexene under such a mild reaction condition. Compared to the other catalytic systems, such as $\text{WO}_3 \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$ system²⁰ in Table 2, the TPNP- H_2O_2 system gave the highest selectivity of glutaraldehyde in the cheapest solvent, and was easier to recover the catalyst (The recovered TPNP could be used again without any special treatment, and it showed the same good catalytic performance as the fresh TPNP, see Table 1). The organic cation of TPNP showed better phase transfer ability compared to its sodium analogue.

The system described here is the first example, which uses peroxy-niobophosphate as oxidation catalysts in organic reaction. The system is highly efficient and selective. Further research on the structure of the catalyst and the oxidation mechanism is undergoing.

Table 2 Oxidation of cyclopentene with various catalysts^a

Entry	Catalyst	Solvent	Conv. (%)	Select. (%) ^e
1	$\text{WO}_3 \cdot \text{H}_2\text{O}$	Ethanol	80	9
2	$\text{WO}_3 \cdot \text{H}_2\text{O}$	<i>t</i> -Butanol	100	61
3	$\text{WO}_3 \cdot \text{H}_2\text{O}$	Dioxane	90	62
4	$\text{Nb}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$	Ethanol	100	59
5 ^b	$[\text{Nb}_4\text{O}_6(\text{O}_2)_2(\text{PO}_4)_2]^{2+}$	Ethanol	100	80
6 ^c	$[\text{Nb}_4\text{O}_6(\text{O}_2)_2(\text{PO}_4)_2]^{2+}$	Ethanol	100	80
7 ^d	$[\text{Nb}_4\text{O}_6(\text{O}_2)_2(\text{PO}_4)_2]^{2+}$	Ethanol	80	48

^a Reaction conditions: cyclopentene (0.5 mL, 5.6 mmol), solvent (2.0 mL), 35°C, 24 h, 1.15 mL of 30% aqueous H_2O_2 (11.2 mmol), catalyst (0.08 mmol metal). ^b Tetradecanepyridinium salt. ^c Hexadecanetrimethylammonium salt. ^d Sodium salt. ^e Percentage of glutaraldehyde.

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