Reaction-Controlled Phase-Transfer Catalytic Oxidative Cleavage of Cyclopentene to Glutaraldehyde over Peroxy-niobic Acid

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(Received September 13, 2001; CL-010909)

The oxidative cleavage of cyclopentene to glutaraldehyde with aqueous H_2O_2 was performed over a peroxy-niobic acid catalyst with high yield (72%) and complete conversion of cyclopentene under mild reaction conditions. Peroxy-niobic acid has been shown as a ‘‘reaction-controlled phase-transfer’’ catalyst, which has the advantages of both homogeneous and heterogeneous catalysts.

Glutaraldehyde (GA) is now commonly used in sterilization and disinfection fields, whose large-scale utilizations are restricted by its complicated and expensive process in the case of using propenal as raw material.[1] H. Furukawa *et al.* reported an interesting one-step route for the preparation of GA by the oxidative cleavage of cyclopentene (CPE) in 1987.[2] Unfortunately, the advantages of lowering the cost by short-cutting the conventional multi-step reaction and using the cheap raw material are far outweighed by the inefficiency of the noble catalysts as well as the dangerous anhydrous H_2O_2 involved in the reaction. We have previously developed another new system,[3,4] which has made great improvements to this one-step route against those drawbacks mentioned above, using environmentally benign and clean aqueous H_2O_2, instead of dangerous anhydrous H_2O_2, as oxygen donor and cheap tungstic acid as catalyst. However, the new route has not yet succeeded in industry because of two factors: the relatively expensive solvent—tert-butanol and the problem in homogeneous catalytic systems: the difficulty of separation and reuse of the tungstic acid catalyst.

We herein first report the novel catalytic system in which CPE was oxidized to GA by aqueous H_2O_2 when using ethanol as the solvent and peroxy-niobic acid as the catalyst. Complete conversion of CPE and a very high yield of GA (72%) were obtained. The unique characteristic of this system is the use of peroxy-niobic acid as a ‘‘reaction-controlled phase-transfer’’ catalyst,[5] which overcame all the drawbacks of our previous tungstic acid system. Thus, the present catalytic reaction system may open new promising route for the preparation of GA commercially.

Peroxy-niobic acid was synthesized according to the following procedure: 1 g of $Na_8Nb_6O_{19}\cdot 9H_2O$ was dissolved in 10 mL of 30 wt% aqueous H_2O_2 at 268 K, then cooled concentrated HCl was slowly added into the solution under gentle stirring until the pH of the solution was adjusted to about 1.0. A yellow solid precipitate was collected after the further stirring at room temperature for another 1 hour. The as-prepared precipitate was washed by distilled water, and dried in air for further study.

The selective oxidation of CPE to GA in the presence of peroxy-niobic acid catalyst was carried out as follows: 66 mg of peroxy-niobic acid was added into the mixture of 1 mL of CPE, certain amount of ethanol and aqueous H_2O_2. The yellow solid catalyst gradually dissolved and the system gradually changed from turbid to clear during the reaction, demonstrating that homogeneous oxidation took place. After the H_2O_2 was consumed, peroxy-niobic acid was self-precipitated slowly and could be removed from the system for its reuse.[6] This phenomenon suggested a solid-liquid-solid phase transfer of the catalyst, which was controlled by the reaction. After stirring at 308 K for 24 hours, the mixture was sampled and analyzed by GC-MS, according to the details found elsewhere.[3,4] There were several by-products in the product mixture, such as the solvated compounds (2-*R*-1-cyclopentanol (R=methoxy, ethoxy, iso-propoxy, tert-butoxy, *etc.*), cyclopentane-1,2-diol, and other little amounts of by-products: cyclopentanone, cyclopentenone and cyclopentene oxide. Details are shown in Tables 1–3.

A strong band at 860 cm^{-1} (ν(O-O)) was observed in the FT-IR spectrum, indicating the presence of a niobic peroxo-group in the prepared solid.[7] The XPS analysis showed that the binding energy of the Nb 3d 5/2 was at 207.3 eV, suggesting that the chemical valence of niobuim in the solid was +5. The niobium content of the solid was determined as 45.3% through elementary analysis. Iodometric titration analysis, based on the literature method,[8] showed that the molar ratio of peroxo-group (O-O) to niobium is almost 1 : 1. TG analysis showed that the content of the released water and oxygen from the as-prepared peroxy-niobic acid was 26.9% and 7.6%, respectively. Accordingly, the simple chemical formula of the solid can be denoted as $Nb_2(O_2)_2O_3\cdot 6H_2O$. Similar formula was also obtained by V. A. Titova *et al.*[9]

As shown in Table 1, the nature of solvents exerted a significant influence on the oxidation. When reaction was carried out in ethanol, the highest yield of GA (59%) was achieved at complete consumption of CPE, using 30% H_2O_2 as the oxidant. Although complete conversion of CPE also ocurred in methanol, the GA yield was only 50%, 9% lower than that of ethanol. When 2-propanol and tert-butanol were used as the solvent, the CPE consumption was low: 80% and 74%, respectively, after 24 hours' reaction, resulting in lower yields of GA: 45% and 40%, respectively. Other non-alcoholic solvents such as dichloro-methane were also used, but the results were not satisfactory: CPE conversion ~70%, GA yield ~32%.

The reaction results as a function of the relative amount of ethanol was also investigated as listed in Table 2. It was shown that

Table 1. The CPE oxidation to GA using different solvents

solvent	Selct. of GA/%	Conv. of CPE/%	Yield/% GA	1,2-diol	a	b
CH_3OH	50	100	50	15	20	15
C_2H_5OH	59	100	59	25	9	7
i-C_3H_7OH	56	80	45	22	8	5
t-C_4H_9OH	54	74	40	19	6	9
CH_2Cl_2	46	70	32	17	—	21

Reaction temperature: 308 K, 1 mL of CPE, 4 mL of solvent, 66 mg of niobium peroxide; Reaction time: 24 hours; a, by-product from the reaction of CPE with the solvnt; b, other by-products, including cyclopentene oxide and cyclopentanone.

Table 2. Effect of ethanol amount on the GA preparation

$V_{ethanol}$ /mL	Conv. of CPE/%	Yield/%			
		GA	**1**	**2**	**3**
2	80	40	30	6	4
4	100	59	25	12	4
6	98	55	22	18	5
8	90	50	16	20	4
10	80	40	12	25	3

Reaction condition: 22.7 mmol of H_2O_2 (30%), 1 mL of CPE, 66 mg of catalyst, reaction temperature: 308 K, reaction time: 24 hours. **1**: cyclopentane-1,2-diol, **2**: 2-ethoxy-1-cyclopentanol; **3**, other little amounts of by-products: cyclopentanone, cyclopentenone and cyclopentene oxide.

an appropriate amount of the ethanol solvent is required for this reaction. H_2O_2 was found to decompose apparently during the reaction when small amount of ethanol was used, while extra amount of ethanol would lead to the low concentrations of the reagents and decrease the reaction rate, both resulting in the low yield of GA in a given reaction time. Based on the experimental data, the optimal volume ratio of ethanol to CPE was determined to be 4 : 1.

The molar ratio of CPE to H_2O_2 has a substantial effect on the oxidative reaction results. Low yield of GA ($<50\%$) would inevitably result from the incomplete conversion of CPE when the ratio of H_2O_2 to CPE was less than 2 : 1. If the ratio was higher than 2 : 1, a co-product, pentanedioic acid would be produced due to the over oxidation of CPE, which also leaded to the low GA yield. As a result, the optimal molar ratio of H_2O_2 to CPE was fixed at 2 : 1. This is in good agreement with the theoretically stoichiometric oxidative cleavage of CPE to GA. The H_2O_2 weight content in its aqueous solution also has an important effect on the oxidative cleavage of CPE, as shown in Table 3. Excellent GA yield (72%) was obtained when a 50 wt% H_2O_2 was used, which was much higher than that reported when niobic acid or niobium oxide was used as catalyst (~10%) and suggested the possibility of the commercial application of the peroxy-niobic acid catalyst. Also, it is obvious to find that the increase of the H_2O_2 concentration leads to the corresponding increase of the GA yield, which can be ascribed to the decrease of the less valuable by-product of cyclopentane-1,2-diol. Similar phenomenon was also observed in our previous work.[3,4]

Table 3. Effect of H_2O_2 concentration on the GA preparation

C_{H2O2} /%	Conv. of CPE/%	Yield/%				Conv. of H_2O_2/%
		GA	**1**	**2**	**3**	
30	100	59	25	12	4	99
36	100	62	23	11	4	100
45	100	68	17	11	4	100
50	100	72	16	9	3	100

Relaction condition: 1 mL of CPE, 4 mL of ethanol, 66 mg of catalyst, 22.7 mmol of H_2O_2, reaction temperature: 308 K, reaction time: 24 hours. **1**: cyclopentane-1,2-diol; **2**: 2-ethoxy-1-cyclopentanol; **3**, small amounts of cyclopentene oxide, cyclopentanone and cyclopentenone.

After each reaction, the novel "reaction-controlled phase-transfer" catalyst was self-precipitated with a $>95\%$ recovery yield (by weight). After 10 cycles of the catalytic reactions, in the FT-IR spectrum, the band at 860 cm^{-1} (ν(O-O)) of the peroxy-niobic acid was still observed, showing that the peroxide group was still preserved in the catalyst after the reactions. Furthermore, the molar ratio of peroxide group (O-O) to Nb in the catalyst was also kept at 1 : 1 after the reactions and the elementary analysis also showed that the element content was almost the same (determined as ~45.1%) as in the fresh catalyst (~45.3%), demonstrating that the catalyst kept its chemical state before and after the oxidative cleavage reaction. Moreover, the catalytic performance of the recovered catalyst after 10 reaction cycles was just the same as those of the fresh catalyst without any addition of fresh catalyst, indicating the excellent stability of catalyst. As compared to the tungstic acid catalyst, this novel catalyst has much longer life time because the tungstic acid catalyst is a homogeneous one and cannot be reused.

The reactivity of several different olefins toward H_2O_2 catalyzed by peroxo-niobic acid under similar reaction conditions is illustrated in Table 4. Acyclic olefins have low reactivity than that of cyclic olefins. However, in all cases the C=C bond is cleaved and the aldehydes are produced.

Table 4. Reactivity of various olefins

Olefin	Conv./%	Yield/%			
CPE	100	$\mathbf{a_1}$(72)	$\mathbf{b_1}$(16)	$\mathbf{c_1}$(9)	$\mathbf{d_1}$(1)
cyclohexene	100	$\mathbf{a_2}$(40)	$\mathbf{b_2}$(15)	$\mathbf{c_2}$(5)	$\mathbf{d_2}$(3)
1-hexene	100	$\mathbf{a_3}$(20)	$\mathbf{b_3}$(15)	$\mathbf{c_3}$(—)	$\mathbf{d_3}$(27)
styrene	84	$\mathbf{a_4}$(22)	$\mathbf{b_4}$(14)	$\mathbf{c_4}$(—)	$\mathbf{d_4}$(1)

Reaction condition: 11.4 mmol of olefin, 66 mg of catalyst, other reaction conditions are the same as in Table 3. $\mathbf{a_1}$, $\mathbf{a_2}$: dialdehydes; $\mathbf{a_3}$: pentanal; $\mathbf{a_4}$: phenyl aledehyde; $\mathbf{b_1} \sim \mathbf{b_4}$: diol; $\mathbf{c_1}$: 2-ethoxy-1-cyclopentanol; $\mathbf{c_2}$: 2-ethoxy-1-cyclohexanol; $\mathbf{c_3}$: 2-ethoxy-1-hexanol; $\mathbf{c_4}$: 2-ethoxy-phenethyl alcohol; $\mathbf{d_1} \sim \mathbf{d_4}$: epoxides.

In conclusion, the catalytic reaction system in the presence of a "reaction-controlled phase-transfer" peroxy-niobic acid catalyst provides an effective method to prepare GA at high yield (~72%) from CPE with complete conversion, which has the advantages of the homogeneous and heterogeneous catalysis. The utilization of environmentally benign and clean aqueous H_2O_2 as the oxygen donor in cheap ethanol solvent makes the reaction process highly promising. A further work is under way to show the actual structure of the catalyst before and during the oxidative cleavage reaction as well as the detailed catalytic mechanism of the reaction system.

This work was supported by the National Natural Science Foundation of China and SINOPEC.

References and Notes

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