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Short Communication

Baeyer–Villiger oxidation of cyclic ketones with aqueous hydrogen peroxide catalyzed by transition metal oxides

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ABSTRACT

The Baeyer–Villiger oxidation of cyclic ketones to the corresponding lactones using aqueous hydrogen peroxide as an oxidant over transition metal oxides was investigated. MoO_3 and WO_3 were found to exhibit higher catalytic activity than TiO_2, Fe_2O_3, Co_3O_4, ZnO and ZrO_2. The high catalytic activity was attributed to the interaction of MoO_3/H_2O_2 and WO_3/H_2O_2. Additionally, the reaction mechanism on MoO_3 and WO_3 was proposed.

1. Introduction

Baeyer–Villiger oxidation in organic unit process is considerable interest to the preparation of lactone and ester intermediates in perfumes, agrochemicals, pharmaceuticals etc. [1–3]. Choice of the oxidants determines the practicability and efficiency of the oxidation reactions, traditional Baeyer–Villiger reaction is carried out with various peroxyacids, the performance of this process on an industrial scale is associated with some technological problems caused by the necessity of synthesis and isolation of peroxyacids [4], the oxidants produce toxic, environmentally and economically unacceptable by-products. Three alternative oxidants, organic hydroperoxides [5,6], molecular oxygen [7] and aqueous hydrogen peroxide [8], have been used in Baeyer–Villiger reaction to solve some environmental problems. When molecular oxygen and aqueous hydrogen peroxide are used as oxidizing agents, catalysts are obligatory for active transfer of oxygen from the oxidizer to the substrate. Low concentration aqueous hydrogen peroxide is a promising oxidant for Baeyer–Villiger reaction, because the only by-product is environmentally benign water [9]. The application of hydrogen peroxide for Baeyer–Villiger reaction is started by Mares and co-workers, using Mo^{VI} picolinate and dipicolinate complexes as catalyst [10]. Subsequently, an efficient catalytic system involving Sn-zeolites is used by Corma et al. for Baeyer–Villiger reaction of cycloketones with aqueous hydrogen peroxide [11]. Later, compounds of other metals are used to catalyze the Baeyer–Villiger reaction, such as Re [12], Fe [13–15], Co [15], Ni [15], Cu [15], Pt [16], Zn [17], Li [18], W [19], Sn [20], Mg [21,22], and Mo [23].

Transition metal oxides have attracted much attention because they have widely been used as catalysts for the oxidation of alkanes [24], olefins [25], alcohols [26], phenols [23,27], aldehydes [28], sulfides [29] etc., using alkyl hydroperoxides, aqueous hydrogen peroxide or molecular oxygen as oxidant. Since the oxidation of cyclic ketones to the corresponding lactones with aqueous hydrogen peroxide catalyzed by transition metal oxides has scarcely been reported, the aim of the present study is to accumulate data on the catalytic activity of a wide range of transition metal oxides in the Baeyer–Villiger oxidation with aqueous hydrogen peroxide.

2. Experimental section

2.1. Materials

All chemicals used in this present work are analytic grade reagents and are used as received from Aladdin.

2.2. Catalytic activity

The catalytic activity of the transition metal oxides is measured in a 25 mL round bottom flask equipped with condenser. In a typical procedure for the oxidation of cyclic ketones is as follows. Tungsten oxide (50 mg) is mixed with 2-heptylcyclopentanone (2.5 mmol, 450 mg), the oxidizing agent of aqueous hydrogen peroxide (30 wt.%; 6.2 mmol) is slowly added dropwise to this mixture with stirring at 40 °C. The resultant mixture is stirred for 12 h. The catalyst is separated by filtration. Conversion of 2-heptylcyclopentanone and selectivity of δ-dodecalactone are determined by quantitative GC analyses of the organic phase. The organic phase is evaporated under reduced pressure

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Table 1
Catalytic performance of transition metal oxides for oxidation of 2-heptylcyclopentanone to δ-dodecalactone with aqueous hydrogen peroxide.

Entry	Catalyst	Conversion (%)[a]	Yield (%)[a]
1	–	Trace	Trace
2	TiO_2	3	3
3[b]	TiO_2	4	4
4	Fe_2O_3	2	2
5[b]	Fe_2O_3	2	2
6	Co_3O_4	Trace	Trace
7[b]	Co_3O_4	1	1
8	ZnO	6	5
9[b]	ZnO	21	19
10	ZrO_2	2	2
11[b]	ZrO_2	4	3
12	MoO_3	53	41
13[b]	MoO_3	98	78[c]
14	WO_3	11	9
15[b]	WO_3	87	72[c]

Reaction conditions: 2-heptylcyclopentanone (2.5 mmol), catalysts (50 mg), experiments performed at 40 °C for 12 h, and aqueous hydrogen peroxide (30 wt.%) (6.25 mmol).

[a] Calculated by GC.

[b] Aqueous hydrogen peroxide (50 wt.%) (6.25 mmol).

[c] Isolated yield.

and further purified by column chromatography over silica gel using 1:5 ethyl acetate–hexane as eluent to furnish the pure δ-dodecalactone.

3. Results and discussion

As Table 1 shows, the absence of transition metal oxides effect in the Baeyer–Villiger oxidation of 2-heptylcyclopentanone indicates that the formation of δ-dodecalactone is not predominantly caused by aqueous hydrogen peroxide. Among the transition metal oxides used for the Baeyer–Villiger oxidation of 2-heptylcyclopentanone with different concentration of aqueous hydrogen peroxide, MoO_3 and WO_3 were significantly more active than other transition metal oxides. We repeated the experiments (entries 13 and 15) for three times, the conversion of 2-heptylcyclopentanone and yield of δ-dodecalactone was changed a little. The differences in the conversion of 2-heptylcyclopentanone and yield of δ-dodecalactone for entries of 12–13 and 14–15 in Table 1 can be explained by the different amount of water in the reaction system. Water in the reaction system hinders hydrogen peroxide/2-heptylcyclopentanone interaction. The catalytic activity of the other transition metal oxides is considerably lower than MoO_3 and WO_3, they show only slightly different reactivity in the conversion of 2-heptylcyclopentanone and yield of δ-dodecalactone except ZnO.

The differences in the catalytic activities of the studied oxides are obviously related to the differences in their catalytic mechanisms. When aqueous hydrogen peroxide is mixed with TiO_2, Fe_2O_3, Co_3O_4, ZnO or ZrO_2, we find the rapid decomposition of hydrogen peroxide, while for MoO_3 and WO_3, the decomposition of hydrogen peroxide is not found. Presumably, TiO_2, Fe_2O_3, Co_3O_4, ZnO and ZrO_2 are associated with the possible reactions (R1, R2). H_2O_2 will first adsorb molecularly onto the surface of the transition metal oxides according to the reaction R1 and then undergo decomposition according to the reaction R2.

$$H_2O_2(aq) + MxOy \rightarrow H_2O_2{-}MxOy \tag{R1}$$

$$H_2O_2{-}MxOy \rightarrow 1/2O_2 + H_2O + MxOy. \tag{R2}$$

Along with the decomposition of hydrogen peroxide in the presence of TiO_2, Fe_2O_3, Co_3O_4, ZnO or ZrO_2, the concentration of aqueous hydrogen peroxide is decreased, and then the difficulty of interaction between hydrogen peroxide and 2-heptylcyclopentanone is gradually increased. The different catalytic activities of TiO_2, Fe_2O_3, Co_3O_4, ZnO and ZrO_2 indicate that the catalytic capabilities of these oxides toward decomposition of H_2O_2 are very different. Phenomena such as hydrogen bonding between H_2O_2 and the hydroxylated surfaces of the transition metal oxides; the degree of interaction between the O atoms of H_2O_2 and the surface exposed on the transition metal oxides; the adsorption energies of the products formed—all these parameters will determine the pathway that the catalytic process for the H_2O_2 decomposition will follow [30]. The conversion of 2-heptylcyclopentanone and the yield of δ-dodecalactone are higher on the ZnO than on the TiO_2, Fe_2O_3, Co_3O_4 and ZrO_2, it is because the decomposition of H_2O_2 on ZnO is slower than on the TiO_2, Fe_2O_3, Co_3O_4 and ZrO_2. The rapid decomposition of H_2O_2 on the TiO_2, Fe_2O_3, Co_3O_4 and ZrO_2 might explain why the catalytic activities of these transition metal oxides in different concentration of aqueous hydrogen peroxide are low and similar. The Baeyer–Villiger reaction mechanism proceeding on TiO_2, Fe_2O_3, Co_2O_3, ZnO and ZrO_2 may be similar to which Paul et al. have supposed [22].

The mechanism of Baeyer–Villiger oxidation proceeding on MoO_3 is of considerable interest in view of its high catalytic activity. It is worthwhile mentioning that the solubility of MoO_3 in water and aqueous hydrogen peroxide. When mixed MoO_3 (50 mg) with water (0.6 mL) and stirred for 12 h at 40 °C, MoO_3 is separated from the mixture without loss by filtration, the water is still in the normal color; when mixed MoO_3 (50 mg) with aqueous hydrogen peroxide (30 wt.%, 0.6 mL) with stirring at 40 °C, 2 h later, the powder of MoO_3 disappears and a

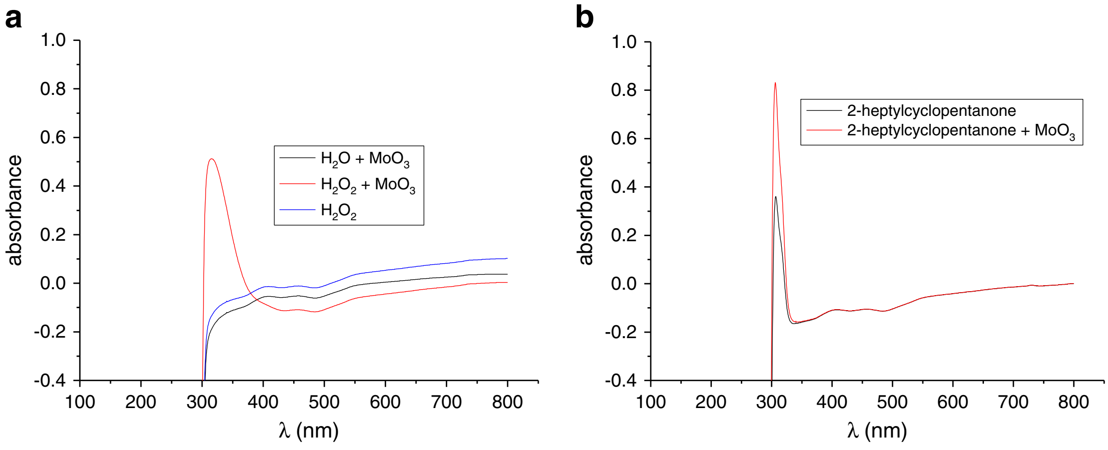


Fig. 1. UV/visible absorption spectra of the mixture of MoO_3 and aqueous hydrogen peroxide (a), the mixture of MoO_3 and 2-heptylcyclopentanone (b).

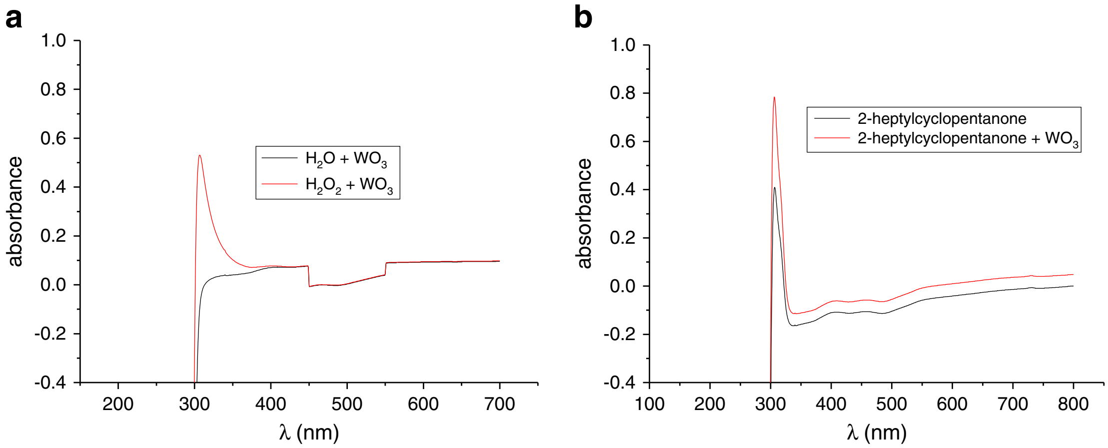


Fig. 2. UV/visible absorption spectra of the mixture of WO3 and aqueous hydrogen peroxide (a), the mixture of WO3 and 2-heptylcyclopentanone (b).

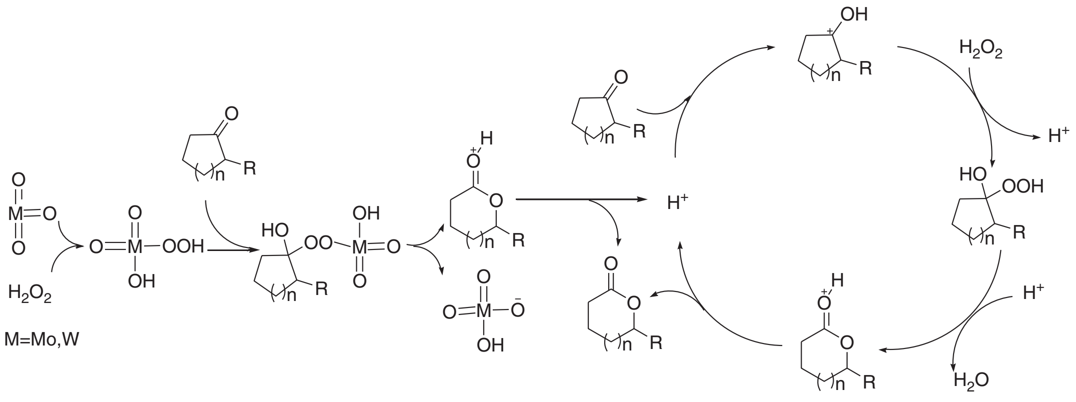
yellow solution is formed. The different solubility of MoO_3 in water and aqueous hydrogen peroxide is a good evidence for the formation of peroxyacid as the reaction (R3) showed.

$$MoO_3 + H_2O_2 \rightarrow HOMoO{-}OOH. \qquad (R3)$$

To verify such intermediate formation, preliminary investigations, UV/visible absorption spectra are used for detecting the interaction of MoO_3/H_2O_2 and MoO_3/H_2O, they are shown in Fig. 1. A new absorption peak appears around 310 nm when MoO_3 is mixed with aqueous hydrogen peroxide. However, nearly no changes happen in the UV/visible absorption spectra when MoO_3 is mixed with water. It means that the intermediate does exist according to the reaction (R3) showed. UV/visible absorption spectra are also used to confirm the interaction of MoO_3/2-heptylcyclopentanone. MoO_3 (50 mg) is mixed with 2-heptylcyclopentanone (2.5 mmol, 450 mg) and stirred for 12 h at 40 °C, MoO_3 is separated from the mixture by filtration. No changes happen in the UV/visible absorption spectra when MoO_3 is mixed with 2-heptylcyclopentanone.

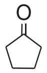
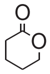
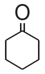
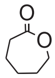
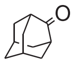
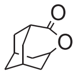
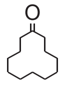
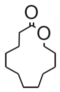
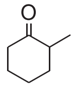
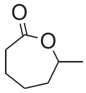
UV/visible absorption spectra are also used for detecting the interaction of WO_3/H_2O_2, WO_3/H_2O and WO_3/2-heptylcyclopentanone. As Fig. 2 shows, the mechanism of Baeyer–Villiger oxidation proceeding on WO_3 may be similar to MoO_3, because a new absorption peak appears around 305 nm when WO_3 is mixed with aqueous hydrogen peroxide, no changes can be found in the UV/visible absorption spectra when WO_3 is mixed with water or mixed with 2-heptylcyclopentanone. The difference between WO_3 and MoO_3 is that most of WO_3 can be separated from the reaction system by filtration, but MoO_3 can't. As results shown in Table 1 (entries 12–15), it is clear that the catalytic activity of MoO_3 in the Baeyer–Villiger oxidation of 2-heptylcyclopentanone is higher than WO_3. It means that the formation of peroxyacid and its solubility in aqueous hydrogen peroxide play an important role in the Baeyer–Villiger oxidation of 2-heptylcyclopentanone. In addition, we have reported that the Baeyer–Villiger reaction can be carried out in the presence of Bronsted acids without transition metal oxides added [31]. The excellent behavior for the oxidation of 2-heptylcyclopentanone with aqueous hydrogen peroxide catalyzed by WO_3 or MoO_3 suggests the possible reaction process as it is shown in Scheme 1.

Table 2 summarizes the reaction of simple cyclic ketones in the presence of MoO_3. The conversion of cyclic ketones is in comparable high values catalyzed by MoO_3. The yields of lactones depend on the sizes of the ring and the alkyl group bonded to the carbonyl carbon. In the case of 2-adamantanone and 2-methylcyclohexanone, the corresponding lactones are obtained in good yields. It is because the alkyl group bonded to the carbonyl carbon is secondary alkyl. When the Baeyer–Villiger reaction for cyclododecanon was carried out at 40 °C for 24 h, the corresponding lactone was not detected; the yields of δ-valerolactone and ε-caprolactone observed in the reaction catalyzed by MoO_3 are low. It is possible that both the reactivity of cyclic ketones and the stability of lactones are different. So the success of the reaction is more due to the reactivity of the substrates rather than that of the oxidant. We believe that our method has great potential for synthetic application.



Scheme 1. A possible mechanism for Baeyer-Villiger oxidation over transition metal oxides.

Table 2
Catalytic performance of MoO_3 for the oxidation of cyclic ketones to lactones with aqueous hydrogen peroxide (50 wt.%).

Ketone	Product	Temperature (°C)	Time (h)	Conversion (%)[a]	Yield (%)[a]
		40	12	83	15
		40	12	92	22
		40	12	99	93[b]
		55	24	75	61[b]
		40	12	99	96[b]

Reaction conditions: Ketone (2.5 mmol), catalyst/substrate = 20 wt.%, aqueous hydrogen peroxide (50 wt.%, 6.25 mmol), and dioxane (3.5 mL).

[a] Calculated by GC.

[b] Isolated yield.

4. Conclusion

In this study we demonstrate the interaction of MoO_3/H_2O_2 and WO_3/H_2O_2, which is beneficial for the Baeyer–Villiger oxidation of cyclic ketones. As a result of the present studies one can conclude that MoO_3 and WO_3 are promising catalysts for the oxidation of cyclic ketones to lactones in aqueous hydrogen peroxide. MoO_3 and WO_3 may react with aqueous hydrogen peroxide to form peroxyacids without decomposition of hydrogen peroxide, the formation of such peroxyacid in the Baeyer–Villiger oxidation had a great effect on the overall rate of the reaction. TiO_2, Fe_2O_3, Co_3O_4, ZnO and ZrO_2 have low catalytic activities in the Baeyer–Villiger oxidation of cyclic ketones with hydrogen peroxide because they catalyze the decomposition of hydrogen peroxide. Clarifying the mechanism of Baeyer–Villiger oxidation would be very helpful to reveal more general and essential features of the mechanism of other oxidations over transition metal oxides with aqueous hydrogen peroxide. Further work for the utility of MoO_3 is on-going in our laboratory since MoO_3 is soluble in aqueous hydrogen peroxide.

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