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Priority communication

The selective catalytic oxidation of terminal alcohols: a novel four-component system with MTO as catalyst☆

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Dedicated to Professor Dietmar Seyferth on the occasion of his 70th birthday

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Abstract

A four-component system (H_2O_2, MTO, HBr, TEMPO) in acetic acid catalyzes the selective oxidation of terminal alcohols to the corresponding aldehydes with excellent selectivity and yield. The system allows the oxidation of alcohols with hydrogen peroxide as oxidants either selectively to aldehydes or to the corresponding acids, depending on the reaction parameters. The new technique is especially applicable to the oxidation of carbohydrates.

Keywords: Methyltrioxorhenium; TEMPO; HBr; Oxidation; Carbohydrates; Starch; Catalysis; Renewable resources

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1. Introduction

The development of new catalytic methods for the selective oxidation of alcohols applying simple and cheap oxidants like hydrogen peroxide is still challenging. Usually, strong oxidizing agents ($KMnO_4$, MnO_2, SeO_2, etc.) in stoichiometric amounts are necessary to perform this reaction [1]. Since the first reports on the catalytic applications of organorhenium(VII) compounds have appeared in 1990 [2–8], a growing number of publications and patents have shown that methyltrioxorhenium(VII) (MTO, CH_3ReO_3) exhibits a high catalytic activity in a variety of organic reactions [9–11]. Recently it has been reported that MTO also catalyzes the conversion of alcohols to aldehydes in the presence of hydrogen peroxide [12,13]. It is known that the oxidation of primary and secondary alcohols can be accelerated upon addition of bromide as a co-catalyst [13]. We now report an improved, highly selective oxidation of terminal alcohols to aldehydes using a novel four-component catalytic system consisting of H_2O_2, MTO, HBr and TEMPO. Acetic acid is used as solvent.

2. Results and discussion

Parallel to our studies, Espenson et al. observed an MTO/HBr-catalyzed oxidation of alcohols by hydrogen peroxide [13]. They found that the addition of HBr accelerates the catalytic oxidation of different alcohols to aldehydes or ketones. The addition of HBr decreases the reaction time by a factor of 1000 [13]. This is in agreement with our own results. A disadvantage of this

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☆ Multiple bonds between transition metals and main-group elements Part 175; preceding communication: W.A. Herrmann, J. Fridgen, G. Lobmeier, M. Spiegler, New J. Chem. 23 (1999) 5.

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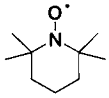
catalytic system, however, is its selectivity failure in the oxidation of terminal alcohols like benzyl alcohol. The use of the stoichiometric amount as well as an excess of hydrogen peroxide leads to a mixture of the corresponding aldehyde and the acid [13].

It is well known [14–16] that the selective oxidation of primary alcohols in the presence of secondary ones is preferred when the stable organic nitroxyl radical 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, **1**) is used as a mediator. The nitrosonium ion **2** is the intermediately observed oxidizing species; it becomes reduced to the hydroxylamine **3** during the oxidation process while it regenerates to **1** during further reaction [15].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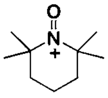
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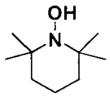
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Van Bekkum and Besemer found that the C6-primary alcohol group in carbohydrates can be oxidized selectively by the in situ generation of the nitrosonium ion **2** using hypochlorite as oxidant and the bromide/hypobromide co-catalyst in water [15,16]. An analogous system was applied to monosaccharide by Flitsch et al. [17].

We now found that the oxidizing nitrosonium agent **2** is also generated with H_2O_2 and HBr in the presence of methyltrioxorhenium (MTO) as catalyst. In our studies we first used benzyl alcohol and its derivatives as a model system. The results will be transferred to aliphatic alcohols, especially to carbohydrate derivatives as technically interesting substrates.

2.1. Oxidation of benzyl alcohol derivates

In a typical run, 0.52 ml (5 mmol) of benzyl alcohol, 37 mg of MTO (3 mol%) and 23 mg of TEMPO (3 mol%) are dissolved in 5 ml of acetic acid and treated with 0.1 ml (10 mol%) of a solution of HBr (30 wt.%) in CH_3COOH. The addition of 2 ml (25 mmol) of H_2O_2 (30%) starts the oxidation process. The catalytic results for two model systems on different time scales are summarized in Table 1. The selective oxidative formation of aromatic aldehydes, without unselective further oxidation to carboxylic acid, is of high interest for the efficient production of fine chemicals.

The application of the four-component system (H_2O_2, MTO, HBr, TEMPO) in this reaction reduces the conversion time (Table 1) significantly as compared to the analogous reaction without TEMPO (Table 2). In contrast to the oxidation process without TEMPO, where benzoic acid is formed as a by-product (Table 2), we observed a selectivity of > 99% and no formation of the corresponding acid (Table 1).

Table 1
MTO/HBr/TEMPO catalyzed oxidation of terminal alcohols

Substrate	Time (min)	Conversion (%)[a]	Selectivity (%)[a]
Benzyl alcohol	1	51	>99
Benzyl alcohol	15	70	>99
Benzyl alcohol	120	81	>99
4-Isopropyl benzyl alcohol	1	62	>99
4-Isopropyl benzyl alcohol	15	78	>99
4-Isopropyl benzyl alcohol	120	>90	>99

[a] Determined by GC-MS.

Several research groups dealt with mechanistic investigations of the TEMPO-mediated oxidation of alcohols. In this context, Semmelhack and coworkers excluded a radical mechanism as well as a direct hydride abstraction for this type of reaction [19]. Furthermore, van Bekkum et al. discussed the different mechanisms in the TEMPO-catalyzed oxidation of alcohols under alkaline as well as under acidic reaction conditions [14]. However, only differences in the oxidation rate of secondary alcohols but not of primary alcohols are found. The mechanistic details of the TEMPO-catalyzed oxidation of primary alcohols, which are proposed in the literature [15,18], are agreeable with our mechanistic understandings. A simplified catalytic cycle of the novel H_2O_2/MTO/HBr/TEMPO system is shown in Fig. 1.

We found that all four components of the catalyst system are essential to reach the reported results. Without MTO, hydrogen peroxide does not activate bromide or TEMPO efficiently (low conversion of benzyl alcohol even after 2 days). This means that MTO is the 'endorsement catalyst' for the oxidation of bromide to hypobromite with hydrogen peroxide as oxidant. If TEMPO is not applied, the system H_2O_2/MTO/HBr gives both the aldehyde and the carboxylic acid unselectively. The oxidation of aromatic aldehydes with the system MTO/H_2O_2 generates the corresponding benzoic

Table 2
MTO/HBr-catalyzed oxidation of terminal alcohols

Substrate	Time (min)	Conversion (%)[a]	Selectivity (%)[a]
Benzyl alcohol	1	2	
Benzyl alcohol	15	59	~80[b]
Benzyl alcohol	120	63	~80[b]

[a] Determined by GC-MS.

[b] ~20% formation of the corresponding acid (benzoic acid).

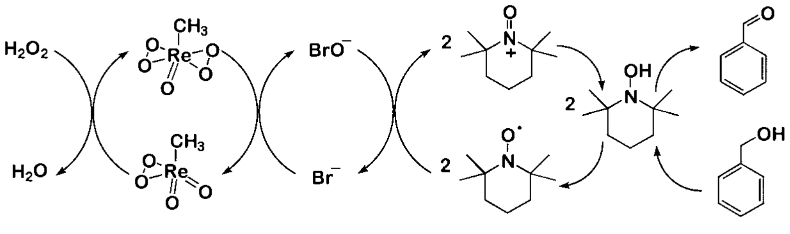

Fig. 1. Proposed cascade-type mechanism of H_2O_2/MTO/HBr/TEMPO catalyzed oxidation [15,18].

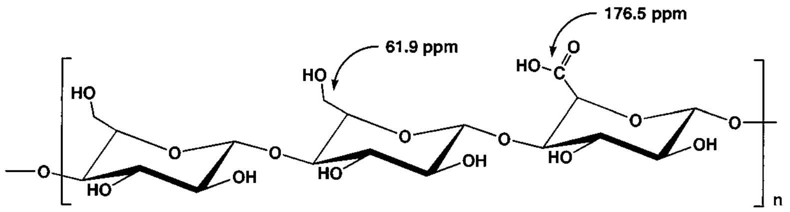

Fig. 2. Partial oxidation (with respect to the content of hydroxymethyl groups at position C6) of the C6-group by the three-component system H_2O_2/MTO/HBr.

acid derivatives. However, in the bromide- and TEMPO-free system the selectivity is low and the formation of phenols as by-products was observed (MTO-catalyzed 'Dakin reaction' [20]). The selectivity of the oxidation of aromatic aldehydes is also dependent on the electronic character of the substituents of the aromatic system (92% formation of *o*-nitro benzoic acid starting from the corresponding aldehyde) [21]. The system we found permits the oxidation of aromatic as well as aliphatic alcohols with hydrogen peroxide either to the corresponding aldehydes with very high selectivity, or to the corresponding acid depending on the applied reaction parameters (hydrogen peroxide amount, presence of TEMPO, reaction time).

2.2. Oxidation of carbohydrates

From an industrial point of view, the complete oxidation of the C6-hydroxymethyl-group of potato starch yielding the corresponding carboxylic acid would be preferred since such biopolymers can be used in a variety of applications, e.g. as superabsorbing agents. Thus, the task was to generate carboxylated starch exclusively. Therefore, to achieve extensive oxidation of the hydroxymethyl groups of the starch molecules to carboxylic acid units, we used the three-component system (H_2O_2, MTO, HBr) without TEMPO; further oxidation of the intermediate aldehyde was thus expected to occur.

The water soluble starch used contains 27% amylose and 73% amylopectin. In a typical run, 700 mg of potato starch and 12.5 mg of MTO (0.05 mmol) were dissolved in 5 ml of acetic acid and treated with 0.05 ml of a solution of HBr (30 wt.%) in CH_3COOH. Addition of 2 ml (25 mmol) of H_2O_2 (30%) started the reaction with concomitant gas evolution over almost 2 h. After that the sample was prepared for ^{13}C-NMR by removal of the solvents in vacuo. The NMR-spectroscopic measurements were carried out in methanol-d_4/D_2O (60/40). As expected the NMR data showed a partial oxidation of the C6-group (Fig. 2). The characteristic signal for the carboxylic C6-group [15] was monitored at $\delta =$ 176.5 ppm. Signals due to the corresponding aldehyde-groups were not seen.

In agreement with the mechanistic proposals of Espenson et al. [13] for the oxidation of alcohols with MTO/H_2O_2 and HBr as a co-catalyst, we suggest the mechanistic considerations shown in Fig. 3. Like van Bekkum et al. [15] we believe that further formation of hypobromite in the presence of excess hydrogen peroxide during the oxidation process takes place. We believe this is a reasonable explanation for the observation that no aldehyde, but only the preferred carboxylic acid is formed.

3. Conclusions

The four-component system MTO, H_2O_2, HBr and TEMPO in acetic acid is efficient for the selective catalytic oxidation of terminal alcohols. An important advantage—apart from the accessibility, the mild conditions, and the short reaction times—is the amazing highly selective formation of aldehydes. We succeeded in the desired substitution of bleach (NaOCl) as primary oxidant by the application of environmental friendly hydrogen peroxide in BrO^-/TEMPO-mediated oxidation reactions. Furthermore, the catalytic system (MTO, H_2O_2, HBr) without TEMPO allows oxidation of the C6-atom to the corresponding carboxylic acid of

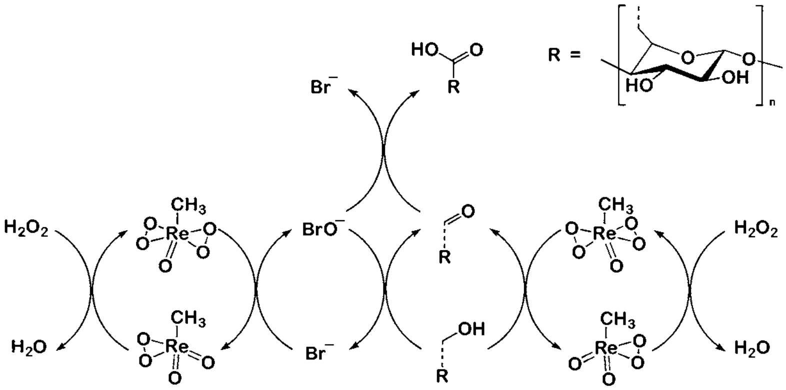

Fig. 3. Proposed simplified mechanism of the starch oxidation by H_2O_2/MTO/HBr.

carbohydrates as demonstrated for starch. The MTO-based oxidation of terminal alcohol groups in carbohydrates opens perspectives for broadly desired industrial applications in this area.

Currently we are investigating the potential of this novel catalyst/co-catalyst system, especially in the field of the selective oxidation of carbohydrates and related substrates derived from renewable resources.

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[21] (a) R. Kratzer, PhD Thesis, Rhenium- und Rutheniumverbindungen als Katalysatoren in der organischen Synthese, Technische Universität München (1998). (b) In further studies we will investigate the substitution of benzyl alcohols as substrates by their corresponding methyl-arene counterparts. This change will probably need at least one oxidation step, mediated by a radical reaction, e.g. the formation of benzylic radicals applying Co(III) as co-oxidant.