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Short Communication

Selective catalysis for the oxidation of alcohols to aldehydes in the presence of cucurbit[8]uril

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ABSTRACT

Efficient selectivity for the supramolecular catalysis by cucurbit[8]uril (Q[8]) for the oxidation of aryl, allyl, and alkyl alcohols to corresponding aldehydes by *o*-Iodoxybenzoic acid (**IBX**) in aqueous solvent is reported. The relationship between the catalytic ability of Q[8] and the structure of the substrate has revealed that the catalyst prefers aryl and allyl alcohols to alkyl alcohols, and the conversions of most aryl and allyl alcohols have been increased by 30–50% in the presence of Q[8]. The catalytic selectivity suggests that the **IBX** oxidation proceeds via a stabilized α-Carbanion intermediate and the supramolecular catalysis should be mechanistically related to the electron density and reactivity of the α-Carbanion.

1. Introduction

The oxidation of alcohols to their corresponding aldehydes [1,2], especially the dependence of selectivity on the structure of the substrate [3,4], is one of the most important synthetic processes in organic chemistry. Numerous investigations into the easy isolation of the product and recycling of the catalyst emphasise the importance of the development of an efficient heterogeneous catalysis system [5,6]. From the economical and environmental viewpoint, such stoichiometric, safe and eco-friendly oxidizing reagents are thus extremely valuable [7,8]. *o*-Iodoxybenzoic acid (**IBX**, Scheme 1), a precursor in the preparation of Dess–Martin periodinane, was already known in 1893 [9], but it had little use in synthetic chemistry until an awareness of its solubility in DMSO was observed [10].

In the last 5 years, **IBX** has attracted amazing attention due to its unique combination of a mild and extraordinarily efficient oxidizing reagent with high selectivity to perform a number of oxidation reactions, especially alcohol oxidation [11,12]. In fact, **IBX** can carry out the oxidation of alcohols as a suspension in many common solvents besides DMSO. Finney et al. observed that the suspended **IBX** showed a satisfying capability to transform primary and second alcohols to the corresponding carbonyl compounds in ethyl acetate, trichloromethane, acetone and so on, close to the refluxing temperature of the solvent [13]. Chen and co-workers described the oxidation of alcohols to carbonyl products with IBX in a mixed solvent of ionic liquid and water in spite of the stoichiometric excess of **IBX** [14]. Rao et al. described an efficient oxidation of various alcohols by **IBX** with β-cyclodextrin catalysis in water/acetone mixture [15]. **IBX** has been proved to be able to carry out the efficient oxidation of various substrates other than alcohols, such as phenols [16,17], ethers [18], amines and sulfides [19,20]. Since most of these oxidations have inevitably been carried out in organic solvents, since a hydrophobic solvent can promote the removal of water in the oxidation reaction, we have recently built a clean oxidation process with this hypervalent iodine reagent via cucurbituril-mediated catalysis for the transformation in water of benzylic alcohols into the corresponding aldehydes [21].

Cucurbit[*n*]uril (Q[*n*], $n = 5$–8 and 10, Scheme 1) are macrocyclic compounds with carbonyl groups on both portals and a hydrophobic cavity enclosed with the glycoluril wall [22]. The cavity can be filled with organic molecules involving amino groups, alcohols, phenols and some small biomolecules with weak ion-dipole, hydrogen binding, hydrophobic or hydrophilic properties [23,24]. Depending on the host–guest chemistry, cucurbituril-induced supramolecular catalysis has made a significant contribution to organic synthesis [25]. The cucurbit[8]uril host, in particular, is always able to accommodate sizeable guests in its cavity to form ternary complexes in a ratio of 1:2 or 1:1:1 [26,27], giving the unique property of stereoselective cycloaddition reactions within the "*nano*-reaction vessels" of Q [8] [28,29]. The encapsulation of substrates within Qs has been considered to be mechanistically connected to the easy formation of a transition state, since the distance between reagents was expected

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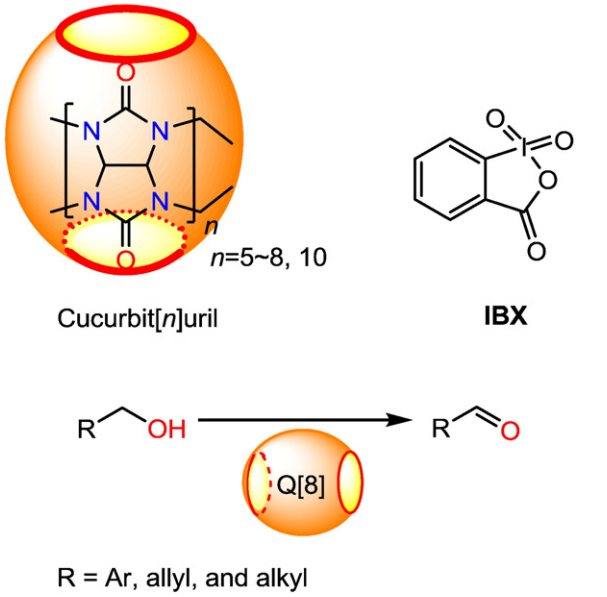


Scheme 1. Structures of cucurbiturils and *o*-Iodoxybenzoic acid, and Q[8]-catalyzed oxidation of alcohols.

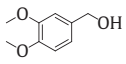
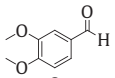
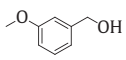
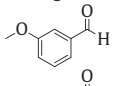
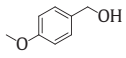
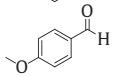
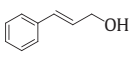
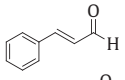
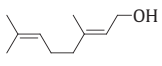
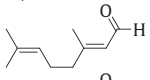
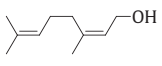
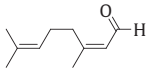
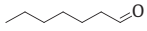
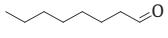
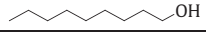
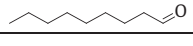
to be reduced as a result of encapsulation [30]. The host–guest interactions between alcohols and Q [6] have been determined in the work of Buschmann's group [31,32], and other pioneering studies have precipitated our previous success in the exploration of the Q [8]-catalyzed oxidation of benzylic alcohol [21]. Further studies of the universality and selectivity of the supramolecular catalysis are reported in this work.

2. Results and discussion

The goal of this work is to develop the supramolecular catalysis of Q [8] as described above, various alcohols, such as aryl alcohols, allyl alcohols and alkyl alcohols, were used to investigate the catalytic efficiency on IBX oxidations by Q[8]. With the optimized reaction conditions of our previous work [21], the oxidation of alcohols with **IBX** in the presence and absence of Q[8] has been carried out, and Table 1 illuminates the scope of the procedures as well as the transformation results of the alcohols.

As a general rule, the Q[8]-induced supramolecular catalysis of the oxidations is clearly affected by the species of aryl and allyl alcohols (entry **1**–**10**). However, the oxidations by **IBX** of the alkyl alcohols (entry **11**–**14**) are very inefficient, for the transformation is barely observable, either in the absence or in the presence of the macrocyclic compound Q[8], and even if the reaction time for the oxidation is extended to as long as 1 h. In each case, for a random selection of alkyl alcohols, the isolated conversion was within 5% of the value determined by gas chromatography. In our previous work [21], we have shown that the equilibrium conversions of veratryl alcohol with catalysis of Q[8] were always higher than those in the absence of Q[8] at different temperatures, indicating that the supramolecular catalysis should be under thermodynamic control. It is impossible to form

Table 1
Q[8]-catalytic oxidation of alcohols with **IBX**.

Entry	Substituent	Product	Time (min)	Conversion(%) to aldehyde	
				With Q[8]	Without Q[8]
1			15	74.6	46.0
2			20	79.6	34.3
3			20	68.8	42.9
4			10	74.9	25.2
5			30	58.3	44.9
6			15	87.1	20.3
7			30	73.6	34.3
8			30	64.2	49.7
9			30	79.4	50.5
10			30	83.7	44.8
11			60	<5	<5
12			60	<5	<5
13			60	<5	<5
14			60	<5	<5

stable alpha-carbanions with alkyl alcohols so that the Q[8]-induced supramolecular catalysis on the **IBX** oxidation is generally invalid to these alcohols.

For the team of aryl alcohols (entries **1**–**7**), the catalysis by Q [8] of the oxidization of an alcohol with IBX is, on the whole, satisfactory. The highest degree of supramolecular catalysis is shown by the improved conversion of 2-furyl alcohol (entry **6**), by up to about 67% in the presence of Q [8], and the oxidizing conversion of 3-methoxybenzyl alcohol (entry 4) is also increased from 25.2% to 74.9% with catalysis by Q[8]. It is evident that the supramolecular catalytic ability of Q [8] on the other aryl alcohols (entries **1**–**3**, **5**, **7**) is very different from the above two species. For veratryl alcohol, benzylic alcohol, 2-methoxybenzyl alcohol (entries **1**–**3**) and 2-thenyl alcohol (entry **7**), the conversions to the corresponding aldehydes are always improved by about 30–40% with Q [8] catalysed oxidation. In particular, for 4-methoxybenzyl alcohol (entry 5), only 13.4% improvement is found when the macrocyclic compound Q[8] is used as supramolecular catalyst, even with a longer reaction time. The above interesting results, namely that the catalytic ability of Q [8] is seriously dependent on the substrate structures of the aryl alcohols, tend to prove that an electronic effect of the substrates seems to exist for these aryl alcohol systems. Taking the methoxybenzyl alcohols, for example, a strong negative inductive effect and weak conjugated effect on the α-C occurs in the 3-methoxybenzyl alcohol, and both positive conjugated effect and negative inductive effect are present in the substituent of 2-methoxybenzyl alcohol, but only the conjugated effect is noticeable in 4-methoxybenzyl alcohol. Obviously, the catalysis of Q [8] for substrates with predominantly negative inductive effect is significantly stronger, and the high conjugated effort generally causes a reduction of Q[8] catalytic activity.

A similar electronic effect is also found in the team of allyl alcohols (entries **8**–**10**). Comparing cinnamyl alcohol (entry **8**) to the other allyl alcohols, the improvement of conversion is particularly poor in the presence of Q[8] under the same reaction conditions, which correspond to the conjugated effect of the styryl group in the cinnamyl alcohol. Only about 15% improvement with Q [8] was found. Nerol (entry **9**) and geraniol (entry **10**) are a pair of geometric isomers, and the similar conversion of about 30–35% has been improved in the presence of Q[8]. The identical conversion suggests that the stereo effect of substrates is not relevant to the cucurbituril-induced catalysis system.

Based on the discovered electronic effect on the supramolecular catalysis in the above cases, a plausible mechanism is proposed. The analysis of conjugated and inductive effect drops a hint that the formation of the intermediate of a stable α-Carbanion of substrate and an electron transfer-mediated mechanistic pathway is crucial. Accordingly, the alkyl alcohols, which cannot be stabilized to form an α-Carbanion, exhibit chemical interactions in their oxidation with **IBX**. With powerful manipulation possibilities for the electron on the α-Carbanion, aryl and allyl alcohols always show different improvement of transformation to aldehydes in the presence of Q [8]. It is well known that Q [8] is able to induce electron transfer between electron–donor and acceptor guests in the formation of a ternary supramolecular assembly [27,28]. With this rule, the supramolecular catalysis of Q [8] on the oxidation of alcohols with **IBX** is not difficult to understand, since it means that the electron transfer between the stabilized carbanion and the hypervalent iodine in **IBX** should be enhanced in the cavity of Q [8], and the selectivity of the catalyst is essential to the electron transfer ability of the reaction intermediate.

3. Conclusion

Selectivity of an efficient supramolecular catalysis system for cucurbit[8]uril-mediated oxidation of alcohol with the hypervalent iodine reagent, **IBX**, is investigated in detail. The Q[8]-induced transformation of aryl, allyl and alkyl alcohols into the corresponding aldehydes reveals that the macrocyclic compound catalytically favors benzyl and allyl alcohols but makes no improvement to the oxidation of alkyl alcohols. The catalytic ability of Q[8] for benzyl and allyl alcohols is relevant to the substrate structure. The analysis of the electronic effect of the alcohols indicates that the electron-rich α-Carbanion contributes to the improvement of the supramolecular catalysis. No steric effects have been clearly observed in the above cases.

4. Experimental

4.1. Materials and apparatus

Cucurbit[8]uril was prepared and purified according to the methods developed in our laboratory [33]. Alcohols and aldehydes were purchased from Alfa Aesar (Tianjing) Chemical Co., Ltd. and used without further purification. **IBX** was prepared with 2-iodobenzoic acid and ozone [34]. ^{1}H NMR (d_6-DMSO, δ): 7.20 (t, 1H), 7.44 (t, 1H), 7.66 (d, 1H), 7.94 (d, 1H). Mp: 230–233 °C with explosive decomposition.

Gas chromatography (GC) was performed using an Angilent 6820 with a HP-Innovax quartz capillary column (30 m × 0.32 mm × 0.25 μm) and flame ionization detector (FID) using ultrapure nitrogen as the carrier gas.

4.2. Catalytic oxidation experiments

The alcohol (0.2 mmol) was added to a suspension of 0.2 mmol **IBX** and Q[8] in 25 ml distilled water. The reaction was carried out at a temperature of 95 °C [21]. When cooled to room temperature, the product was separated from the mixture by filtration under vacuum and extracted with ethyl acetate (3 × 5.0 ml). The organic phase was brought to volume (25 ml) before GC analysis. The reaction conversions were determined by gas chromatographic analysis using the external standard. The products were identified by comparing their retention time in GC with the aldehydes obtained commercially.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.03.029.

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