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Heterogeneous Baeyer–Villiger oxidation of ketones with H_2O_2/nitrile, using Mg/Al hydrotalcite as catalyst

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Abstract—We synthesized a magnesium–aluminium hydrotalcite and used it as a catalyst in the Baeyer–Villiger (BV) oxidation of cyclohexanone with a mixture of 30% aqueous hydrogen peroxide and benzonitrile as oxidant. The hydrotalcite proved an excellent catalyst for the process. The influence of experimental variables was examined in depth in order to bring the working conditions as close as possible to those usable on an industrial scale. We optimized the cyclohexanone/hydrogen peroxide/benzonitrile proportion and used various nitriles, solvents and amounts of catalyst, benzonitrile and methanol proving the most effective nitrile and solvent, respectively, for the intended purpose. The reaction was found to occur to an acceptable extent with other carbonyl compounds as substrates; by exception, α,β-unsaturated carbonyl compounds provided poor results by effect of their undergoing competitive epoxidation of their double bonds.

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1. Introduction

The oxidation of cyclic and linear ketones to their respective lactones and esters with oxidants such as organic peroxides or peroxyoxides, alkyl hydroperoxides or hydrogen peroxide is known as the Baeyer–Villiger (BV) reaction.[1] The BV reaction also includes the oxidation of aldehydes to formate esters. The currently accepted general mechanism for this reaction with organic peroxides involves two steps (see Scheme 1), namely, addition of the peroxyacid to the carbonyl compound to form a Criegee adduct (**1**) and rearrangement of the adduct to the reaction end-product (**2**),[2] which retains the stereochemistry of the migrating site.[3] The BV reaction requires the presence of a catalyst to occur; such a catalyst can be of the acid–base or enzyme type and is usually employed in a homogeneous phase with the reaction ingredients.[4,5] The oxidants used are almost invariably organic peroxides, which can produce large amounts of environmentally hazardous by-products. The environmental concern they have raised and the advantages of heterogeneous catalysts over homogeneous catalysis have propitiated the development of effective heterogeneous catalysts for the BV oxidation with hydrogen peroxide in recent years. Hydrogen peroxide as an oxidant has some advantages such as its ease of use, the large amount of active oxygen it can supply and the decreased production of the sole by-product it generates (water).

The use of heterogeneous catalysts in oxidation processes has been dramatically revolutionized by the discovery of Ti-silicalite (TS-1).[6] This solid consists of a zeolite structure (silicalite) into which titanium is incorporated. It possesses a high oxidizing power, which lies in the ability of titanium metal sites to form Ti-peroxide species that can activate hydrogen peroxide in various oxidation reactions including epoxidation, ammonoxidation and CH oxidation.[7,8] The original catalyst has been refined by inserting other oxidizing metals into the zeolite structure, albeit with poorer results than those obtained with titanium. Corma et al. developed a catalyst consisting of Sn incorporated into a beta zeolite.[9] In subsequent work,[10–15] Corma and co-workers conducted extensive research into Baeyer–Villiger oxidation reactions using their Sn–beta zeolite catalysts. Recently, they proposed a mechanism for the underlying process from a combination of theoretical and experimental data;[16] based on it, tin, which acts as an oxygen transfer agent, activates the carbonyl group in the ketone.

Various other catalysts have been successfully used in BV oxidation reactions. Some are based on hydrotalcite-like structures that are used in combination with other oxidants such as benzaldehyde/O_2 mixtures[17–19] or peroxyacids.[20] Also, a hydrotalcite-supported SnO_2 catalyst was found to effect BV oxidations with hydrogen peroxide[21] in the presence of a nitrile as oxygen transfer reagent. Hydrotalcites constitute a family of natural or synthetic materials, also named layered double hydroxides (LDH), the structure of which derives from hydrotalcite[24] [a magnesium–aluminium hydroxycarbonate of formula $MgAl_2(OH)_{16}CO_3 \cdot 4H_2O$

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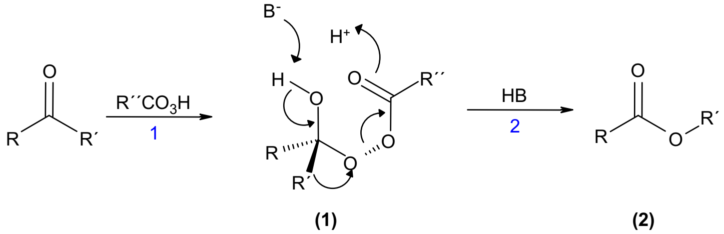


Scheme 1. General mechanism for the Baeyer–Villiger oxidation of ketones with organic peracids.

structurally similar to brucite where some Mg^{2+} ions are replaced with Al^{3+} ions in such a way that positively charged layers are formed and their charge neutralized by carbonate ions in the interlayer region]. The structure of hydrotalcite is compatible with variable Mg/Al ratios and also with the exchange of metal cations and anions; this has facilitated the production of a large family of hydrotalcite-like materials of general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-})A\cdot mH_2O$, with x=M(III)/[M(II)+M(III)].

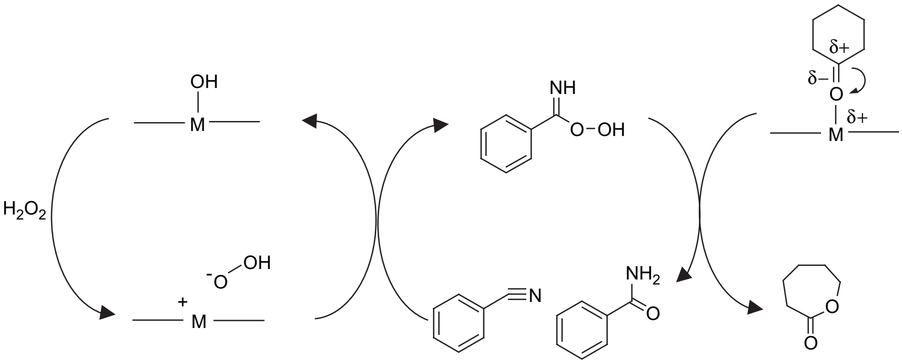
In previous work,[22,23] we used hydrotalcites as effective catalysts for the BV oxidation of cyclohexanone with hydrogen peroxide. Also, we examined the influence of the nature of the catalyst on its activity and proposed a mechanism involving two steps, namely (1) the initial attack of hydrogen peroxide on a Bronsted basic site at the catalyst surface to form a hydroperoxide species, followed by the attack of such a species on benzonitrile to give a peroxycarboximidic acid intermediate and (2) the attack of the previous intermediate on cyclohexanone adsorbed at an acid site of the catalyst to form an intermediate equivalent to the Criegee adduct in homogeneous catalysis processes that undergoes rearrangement to ε-caprolactone, the peroxycarboximidic intermediate being transformed into benzamide (see Scheme 2).

In this work, we expanded the above-described study by examining the influence of some experimental variables including the solvent, nature of the nitrile and amount of catalyst with a view to bringing them as close to those used in large-scale work as possible. All tests were conducted by using an Mg/Al hydrotalcite with a metal ratio of 4, which was previously found to be the best choice for the intended purpose.[22]

2. Results and discussion

In previous work,[22,23] we found hydrotalcites to be effective catalysts for the BV oxidation of cyclic ketones with hydrogen peroxide/benzonitrile mixtures in a large excess with respect to the carbonyl compound. Also, we found the reaction rate to be substantially increased by the addition of a surfactant such as sodium dodecylsulfate. As noted in Section 1, we proposed a mechanism for the reaction based on the results.

We subsequently set to optimize the process with a view to its transfer to a more ‘realistic’ operating scale. We used cyclohexanone as substrate in all tests in order to reduce the amount of benzonitrile and hydrogen peroxide needed, and also that of catalyst. To this end, we used variable benzonitrile/cyclohexanone and hydrogen peroxide/cyclohexanone ratios in order to bring the operating conditions closer to the industrial case and render the process feasible. This additionally involved performing some tests with variable amounts of catalyst that revealed 0.1 g to be appropriate for our purpose. The optimum benzonitrile/cyclohexanone ratio was found to be 4. In order to ensure that the reaction would not be affected by the volume loss resulting from a decreased nitrile/ketone ratio, the reaction vessel was filled with methanol to the volume used in the previous tests. Then, the optimum amount of hydrogen peroxide was determined under the new conditions. As before, the reaction vessel was filled with water as the hydrogen peroxide/cyclohexanone ratio was lowered in order to ensure that the final volume coincided with that used until then. Based on the results obtained with variable hydrogen peroxide/cyclohexanone ratios, an amount of 2 equiv of hydrogen peroxide proved optimal.



Scheme 2. Mechanism for the Baeyer–Villiger oxidation of cyclohexanone with H_2O_2 over HT as catalyst.