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$NiBr_2$ Catalyst for the Oxidation of Alcohols and Aldehydes using NaClO: Kinetic Studies

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Abstract

By exposing to NaClO aqueous solution (commercial bleach), $NiBr_2$ is transformed quantitatively into an insoluble nickel oxide hydroxide species. This compound contains large surface area and is a beneficial heterogeneous catalyst for oxidizing numerous organic materials. The oxidation of aldehydes and primary alcohols to carboxylic acids and secondary alcohols to ketones is showed with 1 mol % of $NiBr_2$ catalyst and NaClO as the terminal oxidant. It is demonstrated that the controlled and selective oxidizing of numerous organic compounds with this system resulting in 55-95 % separation yields and 87-95 % purity. In most cases, the oxidations can be carried out with no organic solvent, causing this method attractive as a “greener” substitute to traditional oxidations.

Keywords: Heterogeneous catalyst, NaClO, $NiBr_2$, Oxidation, Alcohols, Aldehydes

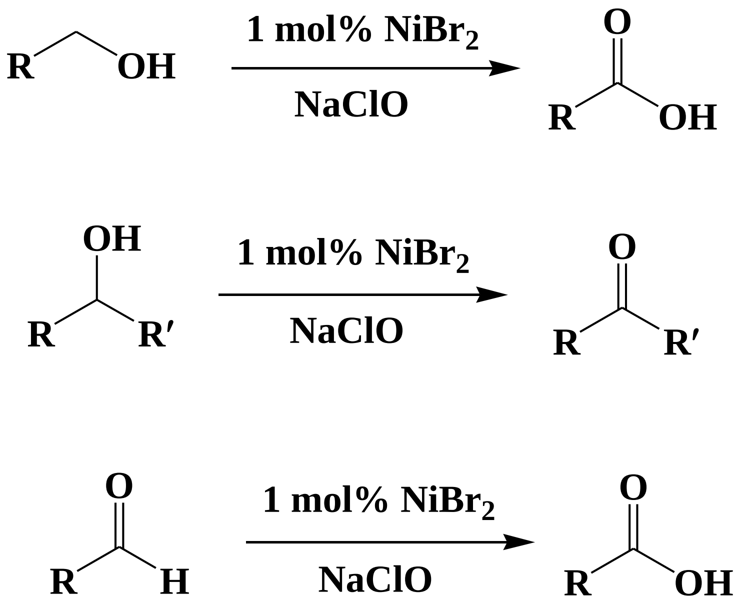
Introduction

NiO(OH) is an oxidant with ability to oxidize an organic substrates host. Several substrates that NiO(OH) is able to oxidize them are alcohols, aldehydes, phenols, amines, and oximes. Initial reports revealed oxidations of organic compounds with 1-1.5 equiv of nickel. In 1975, George et al. reported a widespread review covering main reactions that can be performed with stoichiometric nickel peroxide [1]. There are limited studies on the catalytic application of NiO(OH) on organic substrates with excess NaClO aqueous solution (bleach) as the oxidant. In 1996, Bekkum et al. showed that greater quantity of nickel peroxide (120 mol %) and excess NaClO would cleave the diols in numerous sugars to result in carboxylic acids [2]. In 1945, Weijlard et al. provided the first example; oxidation of nicotine and vitamin C was performed with a catalytic quantity of a $NiCl_2$ (3-5 mol %) and excess NaClO [3]. Nakagawa et al. had proposed that the black oxide of nickel created by treating NaClO using Ni_2SO_4 was responsible for this kind of oxidation [4]. Since then, numerous workers have utilized this reagent for oxidization of diverse organic substrate.

It was reasoned that a large number of the reactions performed with stoichiometric NiO_2 [2] could be performed in the presence of a smaller NaClO instead of a catalytic amount of nickel. The famous stoichiometric reactions provide significant literature precedent, however their catalytic analogues [3, 4] are basically not studied. This reasoning resulted in our outcomes corresponding to the other catalytic example using this oxidation system. $NiBr_2$ (1 mol %) and NaClO aqueous solution (commercial bleach) were used for oxidization of numerous primary and secondary alcohols to the relating carboxylic acids. Dichloromethane was used for dissolving the reactant.

Of specific interest to our group is the simplistic oxidation of alcohols with relatively benign and cost-effective catalysts. Usually, oxidations can be performed in the lab via the stoichiometric application of Collins reagent [5], pyridinium chlorochromate [6-11], or potassium permanganate [12, 15]. These mechanisms are commonly unwanted because of the large quantity of toxic-metal-comprising waste that creates through them. In addition, the reagents are always utilized in excess to warrant reaction completion. They do, but, tend to be selective and very reliable. A large number of industrial organic oxidations can be performed using O_2 or H_2O_2 with heterogeneous catalysts; however the reaction conditions can mostly cause over-oxidation of the product to result in CO_2 and H_2O [16-22]. However, heterogeneous systems are applicable in industries to synthesize commodity chemicals from abundant feedstocks as modest selectivity is mostly compensated by the cheap price of the oxidant, typically oxygen gas. Though, with complex and costly alcohols, a more selective path is desirable.

This study reports the facile oxidation of primary, secondary alcohols and aldehydes to provide the relating ketones and carboxylic acids with rather cost effective and usually accessible reagents. The oxidation proceeds quickly in the presence of $NiBr_2$ and NaClO under environment conditions and seems to be quite general, resulting in predictable products with excellent yields (55-95 %) and excellent purities (87-95 %) in most cases (Scheme 1). These oxidations can be carried out without using an organic solvent. To oxidize water-insoluble organics, a little amount of added dichloromethane greatly eases the reaction.



Scheme 1. Oxidation of primary and secondary alcohols and aldehydes with Catalytic $NiBr_2$ and NaClO

Experimental Section

Material and Instrument

All chemicals and solvents purchased from Merck and Sigma-Aldrich Company and were used without further purification. Thin-Layer chromatography (TLC) was performed for determination of purity of the synthesized compounds using n-hexane/ethyl acetate (3:17) mixture. The yields of ketones and carboxylic acids were determined by Gas Chromatography analyses; carried out with a HP 6890 AGILENT, Flame ionization detector (FID) instrument. The reaction products were determined by comparison with the commercially available compounds.

General Procedure for the Oxidation of Primary Alcohols and Aldehydes

$NiBr_2$ anhydrous (0.11 g, 0.50 mmol) and water (2.5 mL) were poured into a 250 mL flask. A primary alcohol or an aldehyde (25 mmol) was poured followed by dichloromethane (10 mL). The reaction flask was placed in an ice bath to be cooled, and cold NaClO aqueous solution (150 mL) was added in a steady stream during 5 min. Fine black sediment created immediately. The obtained slurry was agitated for 2 h at temperature of 0 °C and 2 h at ambient temperature. Then, acidifying the slurry was performed with 2 M HCl until the aqueous layer was strongly acidic by pH paper. The aqueous layer was removed using diethyl ether (3×50 mL). Drying the organic extracts was performed over $MgSO_4$ and then, they were filtered. The solvent was removed using rotary evaporation and brief high vacuum resulted in the crude product. In general, the purities could be enhanced to >98% via distilling the crude product or via crystallization of solids.

General Procedure for the Oxidation of Secondary Alcohols

$NiBr_2$ anhydrous (0.11 g, 0.50 mmol) and water (2.5 mL) were poured into a 250 mL flask. A secondary alcohol (25 mmol) was added after adding dichloromethane (10 mL). The reaction flask was placed in an ice bath to be cooled, and cold NaClO aqueous solution (150 mL) was added in a steady stream during 5 min. Fine black sediment created immediately. The obtained slurry was agitated for 2 h at temperature of 0 °C and 2 h at ambient temperature. The aqueous layer was removed using diethyl ether (3×50 mL). Drying the organic extracts was performed over $MgSO_4$ and then, they were filtered. The solvent was removed using rotary evaporation and brief high vacuum resulted in the crude product. In general, the purities could be enhanced to >98% via distillation the crude product or via crystallization of solids.

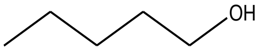
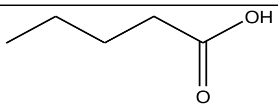
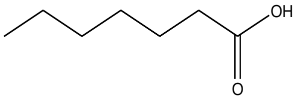
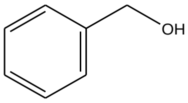
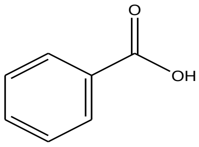
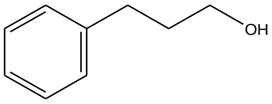
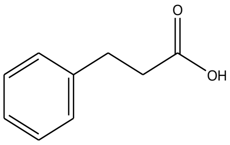
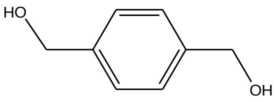
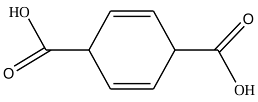
Results and Discussion

To achieve data relating to activity and selectivity comparisons, it was decided to carry out each oxidation reaction under our conditions that are named for a little amount of dichloromethane for dissolving the organic alcohols. As the active form of the nickel oxide hydroxide catalyst is not soluble our reaction conditions of this study, it can be assumed that the oxidation occurs on the surface of catalyst. Therefore, it is surmised that oxidation of liquid alcohols occurs without using an organic solvent, whereas water-insoluble solid alcohols would need dissolution in an organic solvent. In most cases, this prediction holds true. An organic substrate that is either a liquid or water-soluble can be oxidized without using organic solvents. This is obviously helpful as it decreases the amount of waste created and it removes the necessity for a potential harmful organic solvent. This reaction seems to be relatively general, oxidizing both aliphatic and aromatic alcohols quite cleanly. Moreover, aldehydes are easily oxidized to carboxylic acids with this catalytic system.

Oxidation of Primary Alcohols

The oxidation of primary alcohols proceeds under the standard reaction conditions to provide the relating carboxylic acids following acidic action. Isolated yields corresponding to these reactions were mostly good in the range of 62-88%, and initial purities were excellent (92-98% by GC), signifying that the reaction produces limited byproducts (Table 1). As these alcohols are all liquids and/or water soluble, same outcomes were expected by excluding the organic solvent from the reaction. Actually, the diverse reaction conditions led to very similar isolated yields and GC purities. These five studied substrates are easily oxidized to the carboxylic acids without using organic solvent.

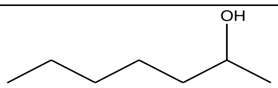
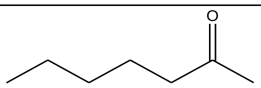
Table 1. Oxidation of primary alcohols under the reaction conditions

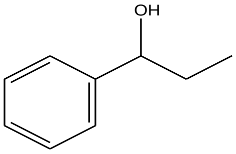
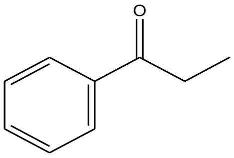
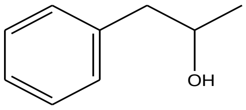
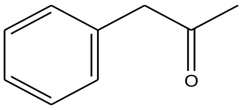
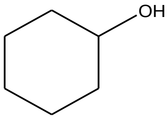
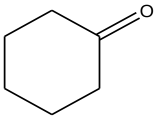
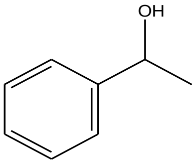
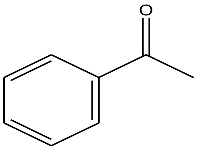
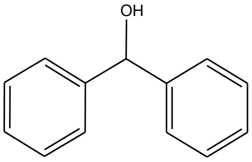
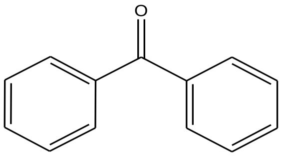
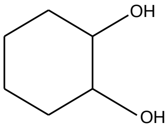
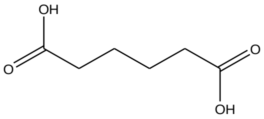
Entry	substrate	product	% Crude Yield	% GC Purity	% Isolated Yield
1			78	92	62
2			84	98	77
3			82	95	78
4			68	95	65
5			88	97	88

Oxidation of Secondary Alcohols

In most cases, secondary alcohols are oxidized to ketones in excellent yields and purities (Table 2). Again, no organic solvent is needed for liquid alcohols or water-soluble alcohols, with one exception. The oxidizing sec-phenethyl alcohol resulted in only 59% conversion after 4 h without using organic solvent (Table 2, entry 5). The material balance was measured to be starting material with GC. Curiously, performing this reaction for longer times did not enhance the yield or the conversion. By using organic solvent, the GC purity is excellent; however a low isolated yield is achieved for the relevant ketone. Furthermore, the substrate in Table 2 entry 6 did not react under either of the reaction conditions, proposing that excessive steric bulk strictly impedes oxidation. Lastly, the cyclic vicinal diol 1,2-dihydroxycyclohexane (Table 2, entry 7) experiences carbon-carbon bond cleavage for affording the dicarboxylic acid in excellent yield (87% isolated).

Table 2. Oxidation of Secondary alcohols under the reaction conditions

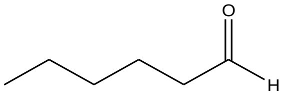
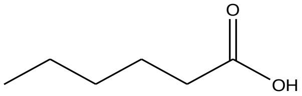
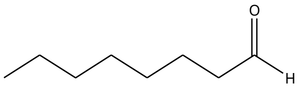
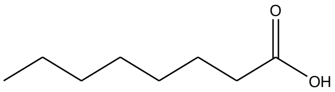
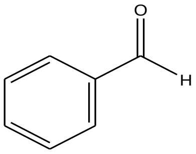
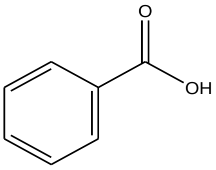
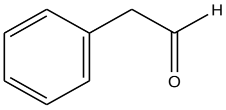
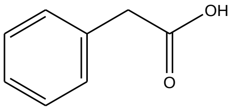
Entry	substrate	product	% Crude Yield	% GC Purity	% Isolated Yield
1			78	98	78

2			92	99	91
3			87	96	85
4			72	79	68
5			59	93	58
6			-	-	-
7			87	91	87

Oxidation of Aldehydes

As predicted, aldehydes are easily oxidized to the relating carboxylic acids under the reaction conditions. The four entries in Table 3 appropriately show this conversion, which results in the carboxylic acids in excellent yield and excellent purity. In addition, the oxidation proceeds rather well without applying organic solvent. Remarkably, even very bulky aldehydes (Table 3, entry 4) are oxidized with facility. The similar oxidation of pivaldehyde with conventional oxidants oxone or H_2O_2 [16-22] happens with lower yields: 45 or 40%, respectively.

Table 3. Oxidation of Aldehydes under the reaction conditions

Entry	substrate	product	% Crude Yield	% GC Purity	% Isolated Yield
1			88	69	55
2			76	91	82
3			94	98	95
4			79	96	89

Preliminary Kinetic Studies

To gain a better understanding of this catalyst system, oxidizing benzyl alcohol was studied in more detail. Gas chromatography was used for determination of the distribution of existing organic components as a function of time at intervals of 5 min for a reaction at 25°C. In the case of benzyl alcohol, the reaction proceeds easily via a benzaldehyde intermediate, which is subsequently oxidized to benzoic acid. The initial amount of benzoic acid is trace, however the quantity of benzaldehyde gradually enhances, reaching its peak abundance about 38-42 min (Figure 1). The benzyl alcohol is fully oxidized to benzoic acid in almost 60 min at ambient temperature.

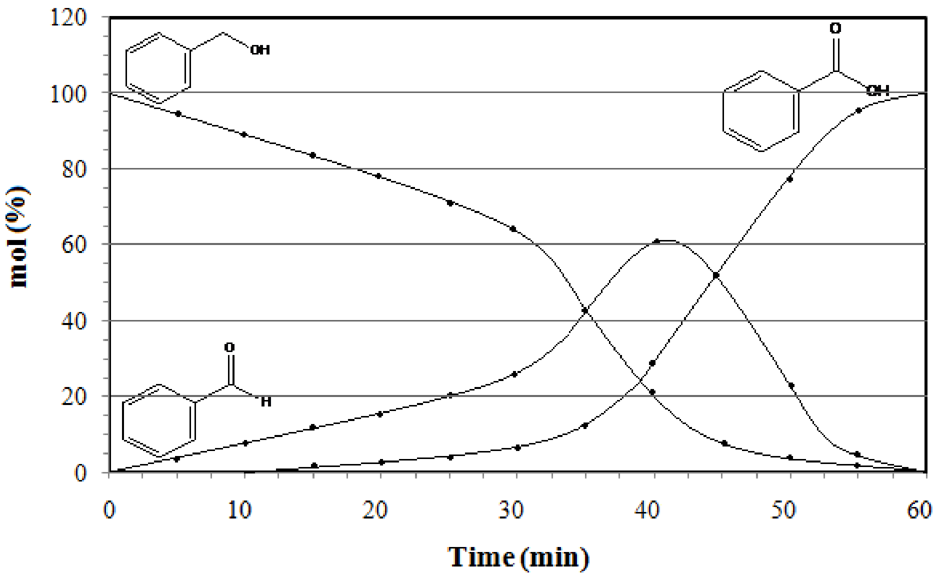


Figure 1. Distribution versus time in the oxidation of benzyl alcohol with $NiBr_2$/NaOCl system

Individually, oxidizing benzaldehyde was also explored under these same reaction conditions. Benzaldehyde is oxidized rapidly by the catalyst, achieving complete conversion to benzaldehyde in almost 29 min (Figure 2). This time frame is in accordance with data of oxidizing benzyl alcohol (Figure 1), wherein the reaction is finished in almost 35 min after the peak concentration of benzaldehyde.

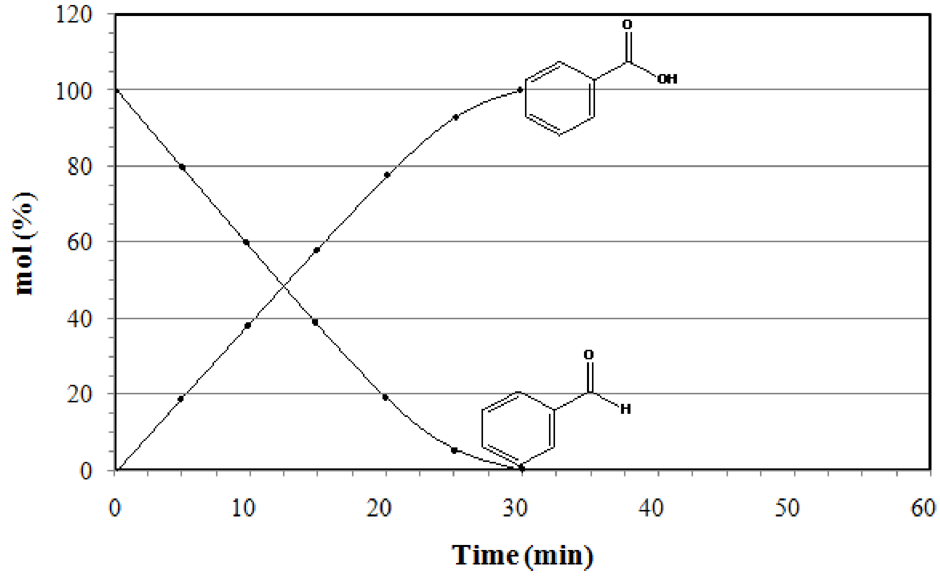


Figure 2. Distribution versus time in the oxidation of benzaldehyde with $NiBr_2$/NaOCl system

Analyzing Figures 1 and 2 should show the relative reactivity for benzyl alcohol versus that of benzaldehyde. The first 30 min of Figure 1 indicates [benzyl alcohol] versus time to be linear. As 25 mmol of substrate was used and 35.1% was consumed over this time, the primary rate can be computed as $k_{alcohol}$=(0.025 mol)(35.1% conversion)/(30 min))=2.925×10^{-4} mol/min. In the same way, the first 15 min of Figure 2 indicates [benzaldehyde] versus time to be linear, and the initial rate can be computed as $k_{aldehyde}$=(0.025 mol)(81.3% conversion)/(20 min)=1.016×10^{-3} mol/min. Accordingly, oxidizing benzaldehyde is somewhat quicker than oxidizing benzyl alcohol under these conditions and $k_{aldehyde}/k_{alcohol}=3.47$.

Conclusions

This study has been presented an extremely effective, useful, and cost-effective approach for oxidation of alcohols and aldehydes with readily accessible $NiBr_2$ and NaClO aqueous solution (commercial bleach). The nickel oxide hydroxide created is known as a selective and high-yielding heterogeneous catalyst, which converts both aliphatic and aromatic substrates to the target product in most cases. These reactions can mostly be carried out without using organic solvents, so developing the ecological influence of these oxidative transformations, which conventionally create much organic and toxic metal waste. Future study will focus on the catalytic oxidation of other functional groups.

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