

**List of publications:**

1. **Shital A. Kakade**, Nandini P. Hilage, *Transition Metal Chemistry*,  
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2. **Shital A. Kakade**, Amit S. Varale, Vilas Y. Sonawane, Nandini. P.  
Hilage, Accepted for publication in *Journal of Indian Chemical society*  
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## Oxidation of benzyl alcohol by Cr<sup>VI</sup> supported on Ambersep 900 (O<sup>-</sup>H) – a kinetic and mechanistic investigation

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### Abstract

The oxidation of benzyl alcohol was found to proceed through ester formation. In a slow step the ester decomposes and produces chromium(IV). Chromium(IV) formed in a slow step, oxidizes another molecule of benzyl alcohol and our oxidant was supported on polymeric material and generates a free radical in a fast step. The free radical subsequently reacts with another oxidant site in a polymeric reagent in a fast step and forms chromium(V). In a last step the intermediate chromium(V) reacts with benzyl alcohol to produce benzaldehyde. The mechanism was suggested and activation parameters were also determined.

### Introduction

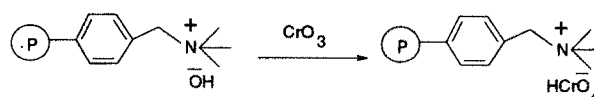
Chromium oxide (chromium trioxide) dissolves in water and forms chromic acid, which is used as a versatile oxidizing agent. The major use of chromic acid in synthetic chemistry is in the oxidation of primary and secondary alcohols to aldehydes and ketones respectively. The primary alcohols are less satisfactorily oxidized because of further oxidation of the aldehyde to the corresponding carboxylic acid. Chromic acid [1, 2] is used to oxidize various alcohols. The present work, namely, oxidation of benzyl alcohol using polymer-supported agent, is quite meager [3]. Although a large number of reagents are known in the literature [4] for such transformation of alcohol to aldehyde, there is still need either to improve the existing oxidation method [5] or to introduce new reagent to obtain better selectivity under milder conditions. In synthetic organic chemistry, oxidation under phase transfer catalysis [7] finds wide application, but using polymer supported oxidizing agents [8] for kinetic and mechanistic studies are limited. The polymer supported oxidizing agent can be used and be reused without loss of capacity, and also very easy work up and safety are the major factors of interest for the present study. By use of polymer supported oxidizing agent the side reaction decreases and the oxidation process stops at the product aldehyde step only. For chemical and mechanical stability, cross-linked polystyrene (with varying % of DVB) is used nowadays, and also because the polymer swells strongly in several solvents. The reactions carried out using such cross-linked polymer result in high yield transformation.

Considering all these advantages the title reaction, in which polymer supported chromic acid is used as an oxidant, was investigated and the results are given below.

### Experimental

#### Preparation of polymer bound – chromium(VI) oxide

The polymer bound chromium(VI) oxide was prepared [9–11]. The hydroxide form of Ambersep 900 (O<sup>-</sup>H) [a macro reticular anion exchange resin] containing a quaternary ammonium group [10 × 10<sup>-3</sup> kg] was stirred with a saturated solution of chromium trioxide [5 × 10<sup>-3</sup> kg] in water [30 × 10<sup>-3</sup> dm<sup>3</sup>] for 30 min at room temperature using a magnetic stirrer. Hydroxide ion was readily displaced and HCrO<sub>4</sub><sup>-</sup> form of resin was obtained in 30 min. The resin was successively rinsed with water, acetone and ether and finally dried in vacuum at 50° for 5 h. The dried form of the resin was stored and used throughout the kinetic study.



#### Determination of the capacity of the chromate form of polymeric reagent

The capacity of the chromate form of polymeric reagent was determined iodometrically.

The capacity of the chromate form of Ambersep 900 resin – 6.55 mmol/g, is used for the kinetic study throughout the work. Other chemicals like 1,4-dioxane (A.R.), chloroform, cyclohexene, carbon tetrachloride, (Merck) and benzyl alcohol used were purified and stored.

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