

## Correlation Analysis of Reactivity in the Oxidation of Para and Meta-Substituted Benzyl Alcohols by Benzimidazolium Dichromate in Non-Aqueous Media: A Kinetic and Mechanistic Aspects

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**Abstract :** An observed correlation of the reaction rates with the changes in the nature of substituent present on one of the reactants often reveals the nature of transition state. Selective oxidation of organic compounds under non-aqueous media is an important transformation in synthetic organic chemistry. Inorganic chromates and dichromates being drastic oxidant and are generally insoluble in most organic solvents, a number of different chromium (VI) derivatives have been synthesized. Benzimidazolium dichromate (BIDC) is one of the recently reported Cr(VI) reagents which is neither hygroscopic nor light sensitive being, therefore, much stable. Not many reports on the kinetics of the oxidations by BIDC are seemed to be available in the literature. In the present investigation, the kinetics and mechanism of benzyl alcohol (BA) and a number of para- and meta-substituted benzyl alcohols by benzimidazolium dichromate (BIDC), in dimethyl sulphoxide, is reported. The reactions were followed spectrophotometrically at 364 nm by monitoring the decrease in [BIDC] for up to 85-90% reaction, the temperature being constant. The observed oxidation product is the corresponding benzaldehyde. The reactions were of first order with respect to each the alcohol and BIDC. The reactions are catalyzed by proton, and the dependence is of the form:  $\log k_{obs} = a + b[H^+]$ . The reactions thus follow both, an acid-dependent and acid-independent paths. The oxidation of [1,1-<sup>2</sup>H<sub>2</sub>]benzyl alcohol exhibited the presence of a substantial kinetic isotope effect ( $k_H/k_D = 6.20$  at 298 K). This indicated the cleavage of a  $\alpha$ -C-H bond in the rate-determining step. An analysis of the temperature dependence of the deuterium isotope effect showed that the loss of hydrogen proceeds through a concerted cyclic process. The rate of oxidation of BA was determined in 19 organic solvents. An analysis of the solvent effect by Swain's equation indicated that though both the anion and cation-solvating powers of the solvent contribute to the observed solvent effect, the role of cation-solvation is major. The rates of the para and meta compounds, at 298 K, failed to exhibit a significant correlation in terms of Hammett or Brown's substituent constants. The rates were then subjected to analyses in terms of dual substituent parameter (DSP) equations. The rates of oxidation of the para-substituted benzyl alcohols show an excellent correlation with Taft's  $\sigma_I$  and  $\sigma_{RBA}$  values. However, the rates for the meta-substituted benzyl alcohols show an excellent correlation with  $\sigma_I$  and  $\sigma_{R0}$ . The polar reaction constants are negative indicating an electron-deficient transition state. Hence the overall mechanism is proposed to involve the formation of a chromate ester in a fast pre-equilibrium and then a decomposition of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state, involving hydride-ion transfer, leading to the product. The first order dependence on alcohol may be accounted in terms of the small value of the formation constant of the ester intermediate. An another reaction mechanism accounting the acid-catalysis involve the formation of a protonated BIDC prior to formation of an ester intermediate which subsequently decomposes in a slow step leading to the product.

**Keywords :** benzimidazolium dichromate, benzyl alcohols, correlation analysis, kinetics, oxidation

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