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KINETICS OF PHASE-TRANSFER-CATALYZED OXIDATIONS OF *p*-SUBSTITUTED BENZYL ALCOHOLS WITH AQUEOUS HYPOCHLORITE

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Abstract

A series of *p*-substituted benzyl alcohols have been oxidized to their corresponding aldehydes using aqueous hypochlorite and phase-transfer catalyst (PTC) conditions. The reaction constant, ρ, has been determined to be +1.03. Possible mechanisms are suggested.

Keywords: Phase-transfer catalyst, hypochlorite, benzyl alcohol

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INTRODUCTION

Numerous methods have been developed to selectively oxidize benzyl alcohol to benzaldehyde, but many suffer from tedious work-ups and low product yields. Work by Lee and Freedman in the mid-1970's established that aqueous hypochlorite solutions used with PTCs provided a convenient and highly effective method of oxidation for alcohols and amines [1]. Since that time, other groups have found aqueous hypochlorite to be a versatile method to readily oxidize other functional groups under PTC conditions [2-4].

Although the nature of the PTC is well understood, the actual mechanism of the oxidation of benzyl alcohol to benzaldehyde by the hypochlorite anion is less clear. Oxidations of benzyl alcohol and its derivatives using a chloramine-T in perchlorate solution [5], acid dichromate [6], and permanganate in perchloric acid [7] have been studied and the reaction mechanisms proposed. In all cases, it has been found that the presence of electron releasing substituents in the *para*-position of the benzene ring tends to increase the rate of oxidation to the aldehyde, while electron-withdrawing groups serve to retard the reaction. The authors' Hammett treatment of the kinetic data gave negative ρ values for each of these examples, indicating the importance of an electron-poor carbon in the rate determining step. However, results from Lee and Freedman's work [8], where the oxidation of benzyl alcohol and some *p*-substituted derivatives were carried out using PTC/hypochlorite in CH_2Cl_2, were in direct opposition to these findings. Their results seem to indicate that the reactivity of the substituted benzyl alcohols decreased in the order $-Cl > -H \sim -OCH_3 > -CH_3$. We sought to further investigate the kinetics and reaction mechanism for the PTC/hypochlorite oxidation of *p*-substituted benzyl alcohols.

In selecting reaction conditions, it was important to choose a system in which the formation of the aldehyde is maximized, while the formation of side-products is eliminated. Abramovici, Neumann, and Sasson found that both the concentration of the organic phase and the pH of the aqueous phase influenced the product composition, in the PTC oxidation of benzyl alcohol by sodium hypochlorite [9]. When the organic phase was concentrated, they observed large amounts of benzyl benzoate. However, when the solvent:benzyl alcohol volumetric ratio was diluted (~25:1), benzyl benzoate was no longer formed and only benzaldehyde was isolated. The researchers also reported that the pH of the aqueous phase had a pronounced effect on the oxidation reaction rate, the optimum value being an initial pH of 9. This observation was attributed to optimal extraction of the hypohalite species at lower pH. The extraction of hypochlorite anion in this pH range was also evaluated with respect to the choice of PTC [10]. It was determined that tetrabutylammonium hydrogen sulfate (TBAHS) efficiently extracted the hypochlorite anion at pH 9-10.

EXPERIMENTAL

The oxidation of *p*-substituted derivatives of benzyl alcohol (Aldrich) were carried out in a 100 mL round-bottomed flask equipped with a magnetic stirring bar. Ethyl acetate (10.0 mL), benzyl alcohol (9.7 mmol), and TBAHS catalyst (100 mg, 0.295 mol, 3 mole %) were added to the flask, stirred and cooled in an ice water bath (4°C). Pre-cooled sodium hypochlorite solution (20.0 mL, 5.25%, 14.1 mmol, commercially available Clorox bleach) was added to the flask and the resulting two-phase system was stirred at 4°C. Samples were regularly taken from the reaction mixture and analyzed by a Hewlett-Packard 5970 gas chromatograph/mass spectrometer.

RESULTS AND DISCUSSION

For the reaction conditions used in these experiments, it was determined that the oxidation reaction followed second order kinetics - first order with respect to the concentration of benzyl alcohol, and hypochlorite. Solvent participation by ethyl acetate has been proposed to occur by Lee and Freedman [1]. The formation of a tetrahedral intermediate between ethyl acetate and hypochlorite or possibly the product of its disproportionation (ethyl hypochlorite) has been suggested to be the rate-limiting step in the overall oxidation process. Thus, our observation of a second order reaction, where both the benzyl alcohol and hypochlorite oxidizing species are significant, is reasonable under the conditions of this reaction. The initial rates of oxidation were observed for several *p*-substituted benzyl alcohols (see Table 1), and the second order rate constants were calculated from the slope of the linear plot of 1/[alcohol] *vs*. time (s). The results indicate that the reactivity of *p*-substituted benzyl alcohols decrease in the order $-CF_3>-Br>-F>-H>-CH_3>-OCH_3$. In general, the presence of electron-donating groups in the aromatic ring lowered the oxidation rates, while electron-withdrawing groups accelerated the rates. In the case of *p*-trifluoromethylbenzyl alcohol, the rate was enhanced to the extent that over-oxidation to the carboxylic acid occurred after one hour's reaction time. In order to postulate a possible reaction mechanism, these data were submitted to Hammett treatment.

Table 1

Kinetic parameters of *p*-substituted benzyl alcohols

Alcohol	$k \times 10^5$ (s^{-1})	log k/k_o	σ
p-Methoxybenzyl	5.61	-0.187	-0.268
p-Methylbenzyl	5.85	-0.169	-0.170
Benzyl	8.63	0	0
p-Fluorobenzyl	10.8	0.097	0.062
p-Bromobenzyl	18.0	0.318	0.232
p-(Trifluoromethyl)benzyl	32.4	0.574	0.551

The kinetic data in Table 1 and the accepted Hammett constants (σ) for the various substituents [11], gave a linear Hammett correlation, where the reaction constant, ρ, was determined to be + 1.03 (Fig. 1). The positive value of ρ suggests that the rate-determining step is favored by electron-withdrawing groups and indicates the development of negative charge in the transition state. A mechanism consistent with these findings must account for the electron-rich nature of the rate-determining step.

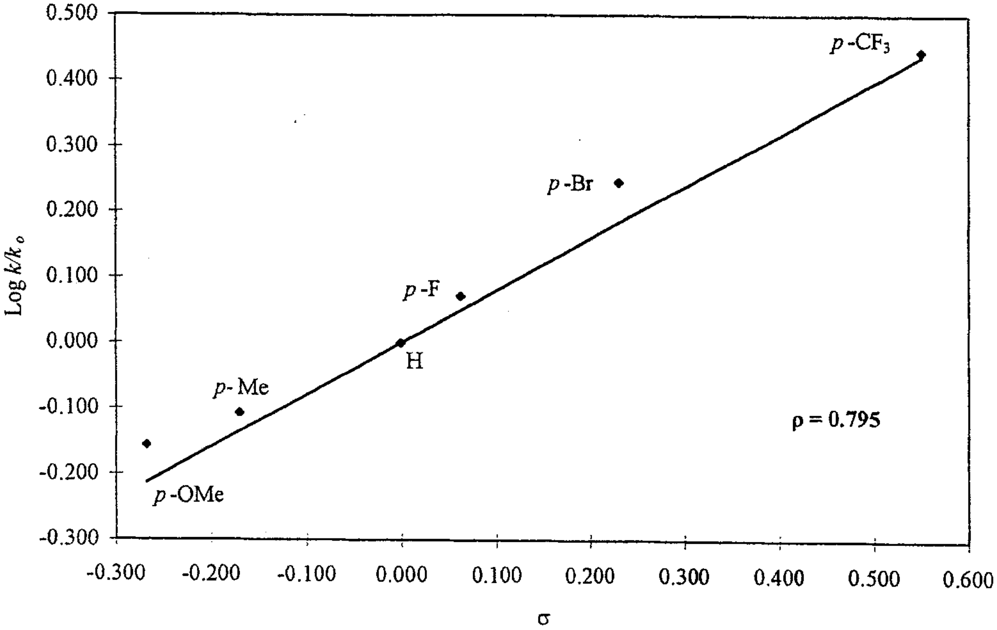

Fig. 1. Reactions of *p*-substituted benzyl alcohols

The theory that a hypohalite species is the primary intermediate in the oxidation of alcohols is not new [12]. Dehydrohalogenation of the unstable hypohalite has generally been attributed to the formation of aldehyde product. This mechanism was consistent with the oxidation results reported by Uma and Mayanna [5], for which a negative reaction constant was determined. However, such a mechanism is not supported by the data presented in this paper, where ρ was found to be positive.

Other mechanisms must therefore be considered. The formation of a chlorohydrin intermediate, reportedly detectable by ^{1}H and ^{13}C NMR, was proposed by Mathur *et al.* in their PTC aqueous hypochlorite oxidations of benzyl alcohol [13]. A mechanism described by Anelli and Montanari [4], in their work involving benzyl alcohol oxidations with oxoammonium salts, has the PTC playing a more active role. In this approach, the PTC is described as delivering the hypochlorite anion, a strong base under the conditions of the reaction, to the benzyl alcohol compound. Abstraction of a benzylic proton leads to a negatively charged carbon intermediate, and ultimately, the aldehyde product. Further experiments, including NMR studies, will be undertaken to further elucidate the nature of the mechanism for the reactions presented.

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