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Mechanism and Kinetics of Electrocarboxylation of Aromatic Ketones in Ionic Liquid

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Abstract

The electrochemical carboxylation of a range of substituted benzophenones was studied in 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid (IL, ([Bmpy][NTf$_2$]). As expected, the aromatic carbonyls exhibited electrochemical reversibility for the first reduction to the radical anion at potentials which were a function of the sum of their Hammett substituent constants ($\Sigma\sigma$). However, in the presence of CO$_2$, the electrochemical reversibility was lost and positive shifts in reduction potentials were observed which were indicative of post-electron transfer chemical reaction which has been attributable to the nucleophilic radical anion/CO$_2$ coupling reaction.

Analysis of the positive potential shift a function of sweep rate (ν) indicated that the mechanism is either ECE or DISP1, or mixed ECE/DISP1. Also from the potential shift with ν, an apparent rate constant (k_{app}), and a pseudo-first order rate constant (k_1), for the coupling reaction was determined and compared to molecular solvent where the rate is over two orders of magnitude lower in IL compared to dimethylformamide (DMF). The low polarity of the IL compared to DMF appears to be the cause of slow kinetics. Finally, plots of k_{app} vs. $\Sigma\sigma$ were strictly linear indicating that IL does not preferentially interact with any of the electrogenerated radical anions thus implying that the electrocarboxylation reaction may be a useful probe of IL environments and structure on radical anion reactions.

Key words ionic liquid; organic electrochemistry; electro-carboxylation; mechanism; kinetics; Hammett