The Electrochemistry Of Alcohols In Aqueous Phosphate Electrolytes Under Reducing Conditions.

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ABSTRACT

Few methods are available for the routine reduction of alcohols in synthetic chemistry. These few are dominated by reduction with HI/I_2, $LiAlH_4$ or Li/NH_3 and typically involve severe conditions for other functionalities and there is little research into less severe synthetic or electrochemical methods. There is also limited mechanistic or kinetic information available for these reduction methods. This leaves an interesting area for development within fundamental knowledge. The development of an effective process for the reduction of alcohols could have many applications in pharmaceutical and chemical industries along with many environmental and economical benefits.

A preliminary study on a range of electrodes established an electrochemical reduction response observed for a number of water-soluble alcohols on rotating disc copper, tin and lead electrodes in 0.1 M phosphate buffers.

A response was observed for ethanol, propanol, propan-2-ol and butanol on copper rotating disc electrodes in the 0.1 M phosphate buffer. Reduction of the alcohols at the copper disc electrodes was observed at pH 8.1 with the production of a limiting current plateau. The reduction was found to be continuous and reproducible. The observed limiting current was found to increase with both increasing concentration and increasing electrode rotation rate. A Koutecky-Levich study suggested the reduction of the alcohol occurred through both mass transport and kinetic processes.

A discrete, reproducible response was observed for ethanol, propanol and propan-2-ol on tin rotating disc electrodes in the 0.1 M phosphate buffer electrolyte at pH 7.3. A reductive peak was observed at -1.1 V vs Ag/AgCl in cyclic voltammetry. This formation of a reductive peak suggests that the reduction becomes progressively hindered, proposed to be due to a passivating layer forming on the surface of the electrode. The charge associated with the peak is relatively invariant with alcohol concentration (in the range 7–20 mM) and with scan rate (over the range 10–500 mV s^{-1}). In the case of ethanol, the peak charge is typically found to be in the range 2.9–3.6 C m^{-2} suggesting that a passivating layer of reaction products forms with an area of 8.8–10.8 Å^2 for each adsorbed molecule (assuming a 2-electron process and a surface roughness factor of one). This suggests formation of

a monolayer with sparsely located binding sites. The peak charge does not change with increasing electrode rotation rate, not inconsistent with the formation of a passivating layer on the surface of the electrode inhibiting any further reduction.

A discrete response was also observed for ethanol, propanol and propan-2-ol on lead rotating disc electrodes in the 0.1 M phosphate buffer electrolyte at pH 8.1. A reduction peak is observed at −0.9 V vs Ag/AgCl in cyclic voltammetry. This suggests that the reduction becomes progressively hindered due to a proposed passivating layer. The passivating layer is not permanent – employing a > 30 second open-circuit rest period or having an anodic limit more positive than −0.6 V will result in the new reduction peak for each subsequent voltammogram. Multiple-cycle voltammograms exhibit only the background response if these conditions are not met.

The charge associated with the peak decreases with scan rate (over the range 10−500 mV s^{-1}) but is relatively invariant with alcohol concentration (in the range 7−20 mM). In the case of ethanol, the peak charge is typically found to be in the range 0.5−4.0 C m^{-2} suggesting that a passivating layer of reaction products forms with an area of 19−58 Å^2 for each adsorbed molecule (assuming a 2−electron process and a surface roughness factor of one). This suggests formation of a monolayer with sparsely located binding sites.

The peak charge *decreases* with increasing electrode rotation rate. It is proposed that this is due to a surface chemical reaction following the electrochemical process – it is the product of this chemical reaction that results in a transient passivating monolayer. FT−IR analyses of the lead disc systems suggest possible products to be propandiol and butandiol.

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Symbol		Unit
A	area	m^2
A_N	area per molecule	nm^2
A1	first anodic peak	
Ag	Silver	
Au	Gold	
C1	first cathodic peak	
C2	second cathodic peak	
c_b	bulk concentration	mM
c_s	surface concentration	mM
Cu	Copper	
D	diffusion coefficient	$m^2\,s^{-1}$
δ	thickness of the Nernst diffusion layer	
E	potential	mV
E_1	initial potential	mV
E_2	final potential	mV
F	faraday constant	$C\,mol^{-1}$
h	thickness of the insulating layer	cm
I	current	A
I_L	limiting current	A
k_f	kinetic transfer rate constant	

m	mass of product	g
M	molar mass	g mol^{-1}
N_A	Avogadro's number	mol^{-1}
N_{C2}	number of molecules per unit area for peak C2	molecules m^{-2}
n_{C2}	moles of product per area for peak C2	mol m^{-2}
ρ	density	g cm^{-3}
Pb	Lead	
Pb$_{BS}$	Pb electrode binding site	
Pb$_{surf}$	Pb electrode surface	
Pb$_{surf}$-H$_{ads}$	H adsorbed to Pb electrode surface	
Pd	Palladium	
Pt	Platinum	
Q	charge	C
q	charge per unit area	C m^{-2}
Re	Reynold's number	
Sn	Tin	
r	radius	m
V	volume	cm^3
υ	kinematic viscosity of a fluid	m^2 s^{-1}
ω	electrode rotation rate	rad s^{-1}
z	number of electrons	

LIST OF ABBREVIATIONS

CA	Chronoamperometry
CE	Counter Electrode
Cu RDE	Copper Rotating Disc Electrode
CV	Cyclic Voltammetry
FT-IR	Fourier Transform Infrared spectroscopy
MS	Mass Spectrometry
MSCV	Mass Spectrometry Cyclic Voltammogram
Pb RDE	Lead Rotating Disc Electrode
RDE	Rotating Disc Electrode
RE	Reference Electrode
RHE	Reversible Hydrogen Electrode
rpm	revolutions per minute
SCE	Standard Calomel Electrode
SERS	Surface Enhanced Raman Spectroscopy
SHE	Standard Hydrogen Electrode
Sn RDE	Tin Rotating Disc Electrode
THF	Tetrahydrofuran
WE	Working Electrode