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Electrochemical Thiocyanation by Two Phase Electrolysis

2상 전기분해를 이용한 전기화학적 티오시안화반응

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The application of two phase electrolysis technique for the electrochemical thiocyanation of organic compounds was examined in this study. Thiocyanogen, $(SCN)_2$, the active thiocyanating species was protected from decomposition in the aqueous phase by its extraction into the nonaqueous solvent. The experimental parameters like the current density, concentration of thiocyanate, electrolysis temperature, nature of the nonaqueous solvent, electrolysis duration, solvent volume ratio etc., were studied and the optimum value of the parameters identified. These parameters were employed for the successful preparation of the $(SCN)_2$ with 70 80% current efficiency. Thiocyano derivates of many aromatic amines and phenols were prepared using the electrochemically prepared $(SCN)_2$. The compounds were characterized using iR and NMR spectral techniques. As the extention of the above study, *in-situ* electrochemical thiocyanation of 2-Methyl phenol (o-cresol) was sucessfully carried out because of its preferential extraction into the nonaqueous solvent. The electro oxidation of 2-Methyl phenol was totally avoided due to its presence in the nonconducting organic phase. The mechanism of electrochemical oxidation of thiocyanate in the aqueous as well as in the nonaqueous electrolyte was studied using cyclic voltammetry, rotating disc electrode voltammetry, rotating ring-disc electrode voltammetry and *in-situ* UV-Visible measurements. The studies lead to the conclusion that the electro oxidation of thiocyanate follows two different path ways in the aqueous as well as in the nonaqueous media. The thiocyanating species produced in the aqueous electrolyte was identified as trithiocyanate, $(SCN)_3^-$ where as $(SCN)_2$ was produced in the nonaqueous solvent. The formation of $(SCN)_3^-$ needs very high concentration of thiocyante where as $(SCN)_2$ can be produced even by employing very low concentration of thiocyante. Suitable mechanistic schemes for the formation of the $(SCN)_3^-$ as well as $(SCN)_2$ were devised.