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ELECTROCHEMICAL FLUORINATION OF ACETAMIDE AND FORMAMIDE IN A MOLTEN KH_2F_3

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The electrofluorination of acetamide ($\mathrm{CH_3CONH_2}$) and formamide ($\mathrm{HCONH_2}$) on the anode was studied in a molten $\mathrm{KH_2F_3}$ at 120°C. Amorphous carbon was used as the anode and Pt rod as the reference electrode. Anodic products were analyzed by both gas chromatography and infrared spectroscopy.

In the both CH₃CONH₂ and HCONH₂, the anode effect did not occur in the current density range of 3-llmA/cm and anode gas was then composed of N₂(+O₂), NF₃, CF₄, C₂F₆, N₂O, CO₂(+COF₂) and so on. The addition of 1.0w% Lif to the electrolyte was available for prevention from the anode effect. From these results, it is suggested that CH₂CONH₂ and HCONH₂ would react chemically with fluoring radical produced by the discharge of fluoring radical produced b

From these results, it is suggested that CH₃CONH₂ and HCONH₂ would react chemically with fluorine radical produced by the discharge of fluoride ion and that the change of the C_mF_n [(CF)_n-I] film on the anode to (CF)_n [(CF)_n-II] film was prevented specially in the case of HCONH₂. The mechanism of electrofluorination of CH₃CONH₂ in the melt is as follows; CH₃CONH₂ CH₃COF, ·NH₂ N₂, NF₃, CF₄, C₂F₆, CHF₃, COF₂(CO₂), N₂O.

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ELECTROPHILIC SUBSTITUTION OF DEACTIVATED HYDROGENS BY ELEMENTAL FLUORINE

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We have shown that under certain conditions, elemental fluorine diluted with nitrogen can be a powerful and yet selective reagent for substitution of unactivated tertiary hydrogens. A correlation between the bond indices of carbon and hydrogen as calculated by CNDO method, and the efficiency and the selectivity of the electrophilic substitution was established. For example high p and low s character in C-H bonds and high charge density on the hydrogen atomic orbital correlate with ease of fluorination.

The influence of the distance, type and number of electron-withdrawing groups on fluorination of tertiary hydrogens as well as the effect of strain in certain cyclic compounds will be discussed.

Dehydrofluorination of fluorinated compounds results in the formation of double bonds at sites where almost no alternative synthetic pathway exists.