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ALKANE AND ALKENE OXIDATION IN FLUORINATED SUPERACID MEDIA: ROLE OF THE ACIDITY LEVEL

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The acidity functions of fluorosulfuric, trifluoromethane sulfonic (triflic) acids and monohydrate $HSO_3CF_3 \cdot H_2O$ have been established using voltammetric measurements and tetrafluorobenzoquinone TFQ as electrochemical indicator. The acidity function Ro(H) of triflic acid was observed to range from -16 (1M triflate solution) to -22 (1M SbF_5 solution) and the acidity level of the monohydrate was buffered at: Ro(H) = -12.

The electrochemical oxidation of alkanes (C_1 to C_5) and alkenes has been studied and the results compared to these recently obtained in HF-derived fluorinated superacids (HF-SbF_5 mixtures).

For each alkane, from methane (C_1) to decane (C_{10}) the acidity function and the thermodynamic properties of hydrocarbons resulting from our electrochemical measurements, completed by literature data, have led to the establishment of potential-pH diagrams (Pourbaix type).

These diagrams allow a general interpretation of the chemical behavior of alkanes as a function of the acidity in superacid media : range of stability of carbenium ions, oxidation of alkanes by H^+, acidity constant (pK_A) of alkanes (RH/RH_2^+ couple) and pK_A of alkenes ($R=/R^+$ couple).

These thermodynamic data were used to give an interpretation of the electrochemical oxidation of alkanes (C_2 to C_{10}) and alkenes (C_5 and C_6) in triflic acid and monohydrate at 60°C.

In the monohydrate $HSO_3CF_3 \cdot H_2O$, the presence of water led to the formation of intermediate alcohols and aldehydes. Characterization of aldehydes implies a disproportionation of the carbenium ion resulting from the protonation of the alkene. In the case of hexene, the disproportionation can be written :

$$C_6H_{12} + H^+ \rightarrow C_6H_{13}^+$$

$$2C_6H_{13}^+ + H_2O \rightleftarrows C_5H_{11}CHO + C_6H_{14} + 2H^+$$
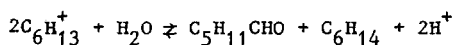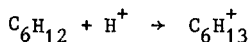
These reactions depend on the acidity level and are favorised by its lowering.