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ELECTRONIC STRUCTURE AND POLAROGRAPHIC REDUCTION POTENTIAL OF FLUOROLEFINES

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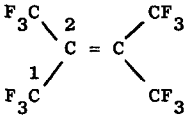
F-Alkenes have the relatively high electron affinities and consequently rather readily undergo electrochemical reduction on Hg in aprotic solvents. The main factor determining the magnitude of reduction potential (RP) of F-alkenes is a quantity of the electron-withdrowing perfluoroalkyl-groups at the double bond: a) CF_2=CF_2 undergoes reduction at the potential more cathodic than -3.0 V (SCE); b) the RP of terminal F-alkenes CF_2=CF-R_F lie in the region of -2.6 V; c) two R_F-groups at the double bond both for terminal and internal F-alkenes fall the RP magnitude to -2.2 V; d) the further increase of the quantity of R_F-groups leads to the more sharp downfall of RP (0.8 V per every additional R_F-group approximately) and F-tetramethylethylene has RP= -0.6 V. The RP of internal F-alkenes does not change noticeable if vinylic fluorine atoms are substituted by hydrogen whereas a vinylic chlorine reduces the potential on 0.45 V. The RP of F-cyclo-alkenes depends on the cycle cize increasing from six- to four-membered ring.

MNDO calculations were performed for the energies of LUMO and HOMO levels and the formal charge distributions in ground states of wide range of F-alkenes. The LUMO level appears to be the π-antibonding orbital for all investigated F-alkenes including also chlorine-containing ones. The π^*-σ^* levels gap for perfluoroalkenes exceeds 2.3 eV, whereas for chlorine-containing F-alkenes this magnitude decreases markedly to 0.3 eV. The linear correlation for the RP and LUMO levels of F-alkenes was established. At the same time the formal positive charge on sp^2-hybridized carbon atom at the double bond does not determine the RP value. Moreover on the base MNDO calculations the increase of the quantity of R_F-substituents at the double bond unexpectedly decreases the formal positive charge on sp^2-carbon atom.



RP = -0.6 V (SCE)

C-1 charge = + 0.680

C-2 charge = - 0.146