NEW APPROACH TO PERFLUOROALKYL HALIDES CHEMISTRY. INTERACTION OF $R_{\rm F}X$ with unsaturated hydrocarbons as a set-process

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The sharp increase of electron affinity and the corresponding rise of oxidative properties of perfluoroalkyl halides as compared with unfluorinated analogues have been demonstrated by means of polarography and quantum-chemical calculations. Tertiary perfluoroalkyl iodides possess a rather strong oxidative ability associated with a very high speed of intermediate anion radical dissociation. F-tret.hexyl iodide (1) does not react with unsaturated hydrocarbons at 80°. However in the polar solvents (DMF), single electron transfer (SET) occurs at the interaction of (1) with C_6H_6 or with hexene and F-alkene and/or monohydroalkane are produced. (1) + $CH_2=CHR$ /or $C_6H_6 \longrightarrow [C_3F_7CI(CF_3)_2]^{\frac{1}{2}}$ (2)

$$(2) \longrightarrow I' + [C_3F_7C(CF_3)_2] \longrightarrow C_2F_5CF=C(CF_3)_2 + C_3F_7CH(CF_3)_2$$

In less polar solvents (EtOAc, 80⁰) iodide (1) readily adds to alkenes, butadiene and acetylene.

R _F I	+	CH2=CHR	\rightarrow	R _F CH ₂ CHIR
R _F I	+	CH2=CH-CH=CH2	\longrightarrow	R _F CH ₂ CH=CHCH ₂ I trans-
R _F I	+	HC≡CH	\rightarrow	R _F CH≃CH⊥ trans-

The relatively mild conditions for these addition reactions allow to propose the realization of the SET-process in the case of non-polar solvents with the formation of the intermediate contact ion-radical pair. In polar solvents SET-process takes place through the distance with the formation of completely separated radical ions.