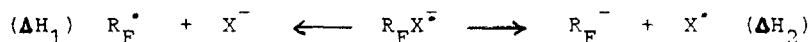


O27

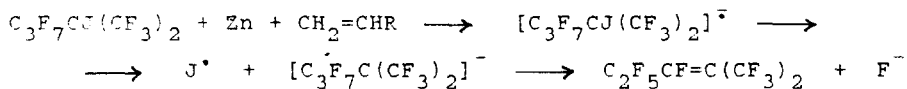
## NEW PATHWAY OF PERFLUOROALKYL HALIDE RADICAL ANIONS DISSOCIATION

I. Rozhkov\*, S. Igumnov, S. Pletnev, G. Rempel and Yu. Borisov  
 Institute of Organo-Element Compounds, Vavilov str. 28, Moscow (U.S.S.R.)

Two different pathways for dissociation of perfluoroalkyl halide radical anions were proposed on the basis of quantum-chemical calculations (method AM1 with completely optimized geometry) of the enthalpies ( $\Delta H_1$  and  $\Delta H_2$ ).



The dissociation pathway is determined by a relation of the electron affinities of  $R_F^\bullet$  and  $X^\bullet$ . In the gas phase, any  $R_F J^-$  dissociates with F-carbanion formation:  $(CF_3)_3CJ$   $\Delta H_1=64.9$  and  $\Delta H_2=5.2$  kcal/mol. However the high energy of halide solvation (particularly for  $Br^-$  and  $Cl^-$ ) may change the correlation between  $\Delta H_1$  and  $\Delta H_2$  in solvents and turn the reaction to the 'radical' pathway. Thus F-tret.hexyl iodide does not add to the hexene double bond in the presence of electron donor (Zn) in EtOAc at 30° and yields F-alkene only.



On the contrary, F-tret.hexyl bromide readily adds to hexene double bond under the same conditions with high yield. This result supposes the 'radical' pathway for the dissociation.

