O32

REDUCTION POTENTIAL AND RELATIVE ELECTRON AFFINITY AS REACTIVITY INDEXES OF PERFLUOROALKYL HALIDES

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

Reduction potentials of perfuoroalkyl halides (R_FX) on Pt in CH_3CN have been determined ($E_{1/2}$, V, SCE) :

CF_3J	-1.10	$(CF_3)_2CFBr$	-1.05
C_3F_7J	-1.00	$(CF_3)_3CBr$	-0.14
$J(CF_2)_4J$	-0.96	$C_3F_7CBr(CF_3)_2$	-0.09
$(CF_3)_2CFJ$	-0.66	F-1-bromo-1-methyl-cyclopentane	+0.12
cyclo-$C_6F_{11}J$	-0.38	F-1-bromo-bicyclo[4.4.0]decane	+0.71
J_2	+0.10	$C_3F_7CCl(CF_3)_2$	-0.97
$(CF_3)_3CJ$	+0.14	F-1-chloro-1-methil-cyclopentane	-1.02
$C_3F_7CJ(CF_3)_2$	+0.32	F-1-chloro-bicyclo[4.4.0]decane	-0.95

The values of the relative electron affinity (REA) of R_FX were determined as the enthalpy of the reaction (ΔH) :

$$CF_3Cl^{\bullet-} + R_FX \longrightarrow CF_3Cl + R_FX^{\bullet-} + \Delta H$$

To define ΔH we performed the quantum chemical AM1 calculations of the heats of formation for all participants of the above reaction (R_FX and corresponding radical anions). The REA (kcal/mol) are :

CF_3Cl	0	CF_3Br	-10.1	CF_3J	-13.7
C_2F_5Cl	-4.5	C_2F_5Br	-14.4	C_2F_5J	-17.6
$(CF_3)_2CFCl$	-6.9	$(CF_3)_2CFBr$	-16.5	$(CF_3)_2CFJ$	-20.8
$(CF_3)_3CCl$	-13.0	$(CF_3)_3CBr$	-22.4	$(CF_3)_3CJ$	-26.3

In accordance with their RP and REA values, perfluoroalkyl halides may be arranged in the following row which is in a good agreement with their reactivity in SET initiated reactions:

$$(R_F)_3CJ > (R_F)_3CBr > (R_F)_2CFJ > R_FCF_2J \simeq (R_F)_2CFBr \simeq (R_F)_3CCl$$