

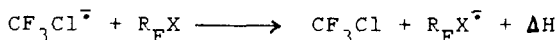
REDUCTION POTENTIAL AND RELATIVE ELECTRON AFFINITY AS
 REACTIVITY INDEXES OF PERFLUOROALKYL HALIDES

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Reduction potentials of perfluoroalkyl halides ($R_F X$) 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-methyl-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 $R_F X$
 were determined as the enthalpy of the reaction (ΔH) :



To define ΔH we performed the quantum chemical AM1 calculations
 of the heats of formation for all participants of the above
 reaction ($R_F X$ 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:

