INFLUENCE OF α-, β- AND γ-CF_3-GROUPS UPON THE KINETICS OF THE S_N2 BROMINE SUBSTITUTION IN ALKYL BROMIDES. ROLE OF TRANSITION STATE SOLVATATION

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As known the activation barrier rises and the reaction rate decreases for S_N2 halogene substitution in Alk-Hal, containing α-CF_3 substituent. This effect was discussed in terms of destabilization electronic influence of α-CF_3-group and the increasing of the steric hindrances for S_N2 attach [1,2].

We have investigated the kinetics of the S_N2 bromine substitution in $CF_3(CH_2)_nBr$ (n=1,2,3), containing of CF_3-group at α-, β- and γ-position correspondingly

$$CF_3(CH_2)_nBr + PhS^- \xrightarrow{k_{1,2,3}} CF_3(CH_2)_nSPh$$

n=1(I), n=2(II), n=3(III)

There is the insignificant difference in constant rates for compounds III (k_3) and II(k_2). However for compound I the magnitude of k_1 fall down sharply. The quantum-chemical calculations(method AM1), polarographic and NQR-spectra studies show the absence of any dramatic differences in charge distribution and energy levels of frontier orbitals for ground states of compound I and II, III.

Moreover, AM1 calculations of transition state of the reaction Br^- + R-Br show that the appearance of CF_3-group at α-position of R-Br decreases the enthalpy of barrier: $\Delta H^{\neq} = \Delta H(RBr_2)^{\neq} - \Delta H(RBr + Br^-)$; $\Delta H^{\neq}$ for C_2H_5Br +4,7 and CF_3CH_2Br +3,9, for $CH_3CH_2CH_2Br$ +5,2 and $CF_3CH_2CH_2Br$ +1,6 kcal/mol.

However evaluation of solvatation energy contributions (CH_3CN, ε =37) indicates that the increasing of activation barrier and the strong braking effect of α-CF_3 group arise from the significant difference between solvatation energies of starting reagents and transition state: $\Delta H^{\neq}$ for CH_3CH_2Br +14,7 and CF_3CH_2Br +33,1; for $CH_3CH_2CH_2Br$ +16,2 and $CF_3CH_2CH_2Br$ +17,4 kcal/mol.

1 McBee E., Battershel R., J.Am.Chem.Soc. 1962, **84**, 3157
2 Bordwell F.G., Brannen W.T., ibid., 1964, **86**, 4645