

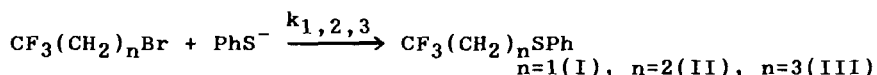
INFLUENCE OF  $\alpha$ -,  $\beta$ - AND  $\gamma$ -CF<sub>3</sub>-GROUPS UPON THE KINETICS OF  
THE S<sub>N</sub>2 BROMINE SUBSTITUTION IN ALKYL BROMIDES. ROLE OF  
TRANSITION STATE SOLVATATION

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As known the activation barrier rises and the reaction rate decreases for S<sub>N</sub>2 halogene substitution in Alk-Hal, containing  $\alpha$ -CF<sub>3</sub> substituent. This effect was discussed in terms of destabilization electronic influence of  $\alpha$ -CF<sub>3</sub>-group and the increasing of the steric hindrances for S<sub>N</sub>2 attach [1,2].

We have investigated the kinetics of the S<sub>N</sub>2 bromine substitution in CF<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>Br (n=1,2,3), containing of CF<sub>3</sub>-group at  $\alpha$ -,  $\beta$ - and  $\gamma$ -position correspondingly



There is the insignificant difference in constant rates for compounds III (k<sub>3</sub>) and II(k<sub>2</sub>). However for compound I the magnitude of k<sub>1</sub> 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<sup>-</sup> + R-Br show that the appearance of CF<sub>3</sub>-group at  $\alpha$ -position of R-Br decreases the enthalpy of barrier:  $\Delta H^\ddagger = \Delta H(\text{RBr}_2)^\ddagger - \Delta H(\text{RBr} + \text{Br}^-)$ ;  $\Delta H^\ddagger$  for C<sub>2</sub>H<sub>5</sub>Br +4,7 and CF<sub>3</sub>CH<sub>2</sub>Br +3,9, for CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br +5,2 and CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br +1,6 kcal/mol.

However evaluation of solvation energy contributions (CH<sub>3</sub>CN,  $\epsilon$  =37) indicates that the increasing of activation barrier and the strong braking effect of  $\alpha$ -CF<sub>3</sub> group arise from the significant difference between solvation energies of starting reagents and transition state:  $\Delta H^\ddagger$  for CH<sub>3</sub>CH<sub>2</sub>Br +14,7 and CF<sub>3</sub>CH<sub>2</sub>Br +33,1; for CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br +16,2 and CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br +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