the free thioamide. Rotational barriers have been calculated as a function of the medium acidity.

Influence of the Solvent on the Anionic Reactivity of Quaternary Onium Salts in Nucleophilic Aliphatic Substitutions. Leaving Group Effects

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Kinetics of nucleophilic substitutions by anions of phosphonium quaternary salts have been measured as a function of the solvent [1, 2], and of the leaving group [3].

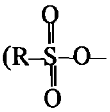
$$n\text{-}C_8H_{17}X + Q^+Y^- \xrightarrow[\text{solv.}]{60\ ^\circ C} n\text{-}C_8H_{17}Y + Q^+X^-$$

$Q^+ = C_{16}H_{33}P^+Bu_3$

$Y^- = N_3, CN, Cl, Br, I, SCN$

$X^- = Cl, Br, I, Tos, Mes$

solv. = MeOH, DMSO, PhCl, cyclohexane.

When the leaving group is a sulphonate ( $R{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}O{-}$; R = Me, Tol), anionic reactivity increases up to 10^3 fold by diminishing the solvent polarity ($k_{MeOH} < k_{DMSO} < k_{PhCl} < k_{cyclo\ hexane}$).

On the contrary, when the leaving group is a halogen (Cl, Br, I) the highest reactivities are found in DMSO and the reactivity scale becomes ($k_{MeOH} < k_{cyclohexane} \leqslant k_{PhCl} < k_{DMSO}$).