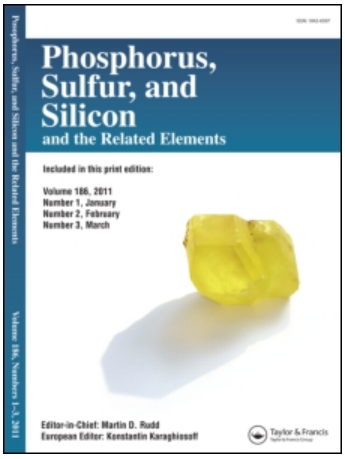

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The Reactivity of Sulfur Nucleophiles in the Substitution Reactions of Nitro Group and Fluorine in Meta-Substituted Arenes

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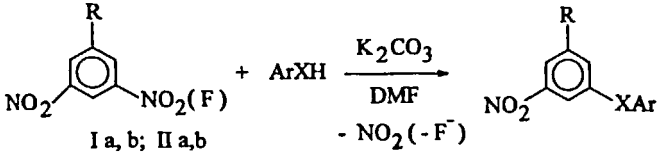
It is well known that nitro group and fluorine are the best leaving groups in activated nucleophilic aromatic substitution reactions [1]. Therewith comparing the rate of these reactions with soft sulfur and hard oxygen nucleophiles is a standard method reasonable to predict leaving nitro group and fluorine mobility [2].

The relative mobility of nitro group and fluorine k_{NO2} / k_F in low activated arenes such as meta - benzene derivatives under the action of both thiophenolate and phenolate ions [reaction (1)] has been studied. We have found that the rise of a substrate electrophilicity leads to a



(1)

I a, b; II a,b

R = H (Ia,b), CF_3 (IIa,b) X = S, O Ar = Ph, 4-$MeOC_6H_4$, 4-MeC_6H_4, 2-$C_{10}H_7$, 3-$NO_2C_6H_4$

considerable rise of k_{NO2} / k_F ratio, in particular for sulfur nucleophiles (from 1.3 for compounds Ia,b to 52.4 for compounds IIa,b under the action of PhS^- at 95°C). The reason of this effect can be associated with poor solvation of sulfur nucleophiles relative to oxygen ones and favourable soft - soft interaction in the transition state through polarisable sulfur atom and nitro group (cf. [4]).

The displacement selectivity of nitro group and fluorine depends on the reaction temperature and the nucleophile basicity too (Table 1). There are good correlations between Brønsted coefficient β_{Nuc} and inverse temperature 1/T, enthalpy and entropy changes (equations 2 - 5) that suggested isokinetic ratios in these reactions. The isokinetic temperatures are equal to 38°C

and 47°C for sulfur and oxygen nucleophiles correspondingly that is lower than the experimental field.

$\beta_{Nuc} = 986.6 \times 1/T - 3.17$ $r = 0.998$ for ArS^- (2)

$\beta_{Nuc} = 137.4 \times 1/T - 0.43$ $r = 0.999$ for ArO^- (3)

$\Delta\Delta H^{\neq} = 310.7\,\Delta\Delta S^{\neq} + 18322.7$ $r = 0.999$ for ArS^- (4)

$\Delta\Delta H^{\neq} = 322\,\Delta\Delta S^{\neq} + 19083$ $r\ 0.993$ for ArO^- (5)

Therefore the displacement selectivity is controlled by entropy, in particular for sulfur nucleophiles.

Table 1. Relative rate ratios of nitro group and fluorine displacements in 3,5-dinitro-(IIa) and 3-fluoro-5-nitrobenzotrifluorides (IIb) under the action of ArXH in the presence of K_2CO_3 in DMF and Eyring parameters of these reactions.

ArSH	pK*	k_{NO2}/k_F				$\Delta\Delta H^{\neq}$	$\Delta\Delta S^{\neq}$
		40°C	50°C	60°C	70°C	kcal/mol	e.u.
4-$MeOC_6H_4SH$	11.2	0.89	1.75	3.1	4.4	10.8	-24.3
PhSH	10.3	0.95	2.2	5.2	9.5	15.9	-7.8
2-$C_{10}H_7SH$	9.5	0.95	2.8	7.5	13.4	18.4	0.3
4-MeC_6H_4OH	18.9	-	-	-	1.05	3.4	-48.9
PhOH	18.0	-	-	-	1.11	3.5	-48.4
3-$NO_2C_6H_4OH$	14.4	-	-	-	1.36	3.7	-47.4

* In DMSO [3].

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