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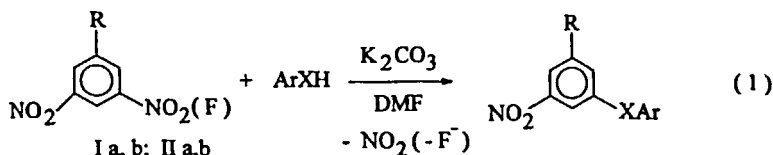
## The Reactivity of Sulfur Nucleophiles in the Substitution Reactions of Nitro Group and Fluorine in Meta-Substituted Arenes

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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  $k_{\text{NO}_2}/k_{\text{F}}$  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



R = H (Ia,b), CF<sub>3</sub> (IIa,b)    X = S, O    Ar = Ph, 4-MeOC<sub>6</sub>H<sub>4</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 2-C<sub>10</sub>H<sub>7</sub>, 3-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>

considerable rise of  $k_{\text{NO}_2}/k_{\text{F}}$  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<sup>-</sup> 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  $\rho_{\text{HMc}}$  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.

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

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

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

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

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<sub>2</sub>CO<sub>3</sub> in DMF and Eyring parameters of these reactions.

ArSH	pK*	$k_{\text{NO}_2} / k_F$				$\Delta\Delta H^\ddagger$ kcal/mol	$\Delta\Delta S^\ddagger$ e.u.
		40°C	50°C	60°C	70°C		
4-MeOC <sub>6</sub> H <sub>4</sub> SH	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 <sub>10</sub> H <sub>7</sub> SH	9.5	0.95	2.8	7.5	13.4	18.4	0.3
4-MeC <sub>6</sub> H <sub>4</sub> OH	18.9	-	-	-	1.05	3.4	-48.9
PhOH	18.0	-	-	-	1.11	3.5	-48.4
3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OH	14.4	-	-	-	1.36	3.7	-47.4

\* In DMSO [3].

## References

- [1] F. Terrier, Nucleophilic Aromatic Displacement: the Influence of the Nitro Group, VCH, Weinheim, 1991, p. 21 - 32.
- [2] G. Bartoli, P. Todesco, *Acc. Chem. Res.* 1977, v. 10, p. 125 - 132.
- [3] G. Bordwell, J.-P. Cheng, *J. Am. Chem. Soc.* 1991, v. 113, N 5, p. 1736 - 1743.
- [4] C. F. Bernasconi, R. B. Killion, Jr., *J. Am. Chem. Soc.* 1988, v. 110, N 22, p. 7506 - 7512; M. R. Crampton, J. A. Stevens, *J. Chem. Soc. Perkin Trans. 2*, 1990, p. 1097 - 1103.