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MECHANISMS OF SUBSTITUTION AT SULFINYL SULFUR. III. THE RELATIVE NUCLEOPHILICITY OF SOME COMMON NUCLEOPHILES TOWARD SULFINYL SULFUR[1]

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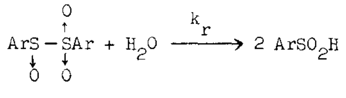
The relative reactivity of a series of nucleophiles Nu^- in a substitution reaction of the type

$$Nu^- + S-X \longrightarrow Nu-S + X^-$$

depends markedly on the character of the center in the substrate which is undergoing nucleophilic attack.[2] Thus, substitutions at carbonyl carbon[3] or tetrahedral phosphorous[4] are much more sensitive to the basicity of the attacking nucleophile than to its polarizability, while just the reverse is true of substitutions at divalent oxygen[5] or sp^3 carbon.[6,7] In a classic paper Edwards and Pearson[7] have attempted both to assess and explain the relative importance of basicity, polarizability and other effects for substitution reactions at these and other centers in protic solvents.

One center for which no quantitative or even semi-quantitative data of this type exist is sulfinyl sulfur. This seems particularly unfortunate in view of the widespread current interest in substitution reactions at sulfinyl sulfur.[8-11] We have now been able to obtain such data from a study of the catalytic effects of various common nucleophiles on the hydrolysis of aryl sulfinyl sulfones (I).

In 60% aqueous dioxane sulfinyl sulfones hydrolyze readily to the corresponding sulfinic acid (eq. 1). The progress of the reaction can be

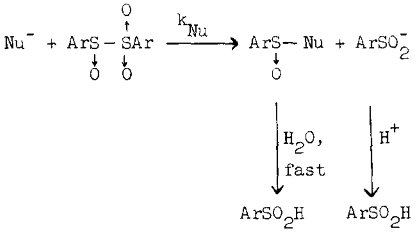


$$\underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{ArS}}-\underset{\substack{\downarrow\\ \mathrm{O}}}{\overset{\substack{\mathrm{O}\\ \uparrow}}{\mathrm{S}}}\mathrm{Ar} + H_2O \xrightarrow{k_r} 2\ \mathrm{ArSO_2H} \qquad (1)$$

I

followed by previously described[12] spectrophotometric procedures. Unlike the situation in acetic acid-1% water solvent[12] the hydrolysis of I in 60% dioxane is not subject to detectable acid catalysis in the concentration range 0.001 - 1.0 M $HClO_4$. It is, however, markedly catalyzed by the addition of small amounts ($\sim 10^{-4}$ M) of various nucleophiles such as halide ions, thiocyanate ion, etc. That the catalyzed hydrolysis is in each instance first order in the catalyzing nucleophile is shown by the constancy of the quantity $[k_r - k_r^\circ/(\mathrm{Nu})]$ with variations in nucleophile concentration under otherwise constant reaction conditions (k_r° equals the rate of hydrolysis of I in the absence of the added nucleophile).

Comparison of the present catalytic effects with the previously observed catalysis of the solvolysis of I by alkyl sulfides[12] makes it clear that the catalyzed hydrolyses involve the following mechanism:



$$\begin{tikzcd}
\mathrm{Nu}^- + \underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{ArS}}-\underset{\substack{\downarrow\\ \mathrm{O}}}{\overset{\substack{\mathrm{O}\\ \uparrow}}{\mathrm{S}}}\mathrm{Ar} \arrow[r, "k_{Nu}"] & \underset{\substack{\downarrow\\ \mathrm{O}}}{\mathrm{ArS}}-\mathrm{Nu} \arrow[d, "{H_2O,\ \mathrm{fast}}"] & + \ \mathrm{ArSO_2^-} \arrow[d, "H^+"] & (2) \\
 & \mathrm{ArSO_2H} & \mathrm{ArSO_2H} &
\end{tikzcd}$$

In solutions containing enough perchloric acid to repress completely the ionization of $ArSO_2H$ one encounters no interference from the reverse of the k_{Nu} step, i.e. $ArSO_2^- + ArS(O)Nu \longrightarrow I + Nu^-$. However, in acetic acid-acetate buffers this reaction does become significant. Nevertheless, since its importance under a given set of conditions can be quantitatively determined by a series of runs involving different concentrations of initially added ArSO$_2^-$, one can still obtain accurate values of k_{Nu} for nucleophiles under such conditions.

We have studied the catalytic effect of seven different nucleophiles on the hydrolysis of p-methoxybenzenesulfinyl p-anisyl sulfone (Ia, Ar = p-$CH_3OC_6H_4$) and of three of the same nucleophiles on the hydrolysis of p-toluenesulfinyl p-tolyl sulfone (Ib, Ar = p-$CH_3C_6H_4$). Suitable analysis[13] of the kinetic data yields the values of k_{Nu} shown in Table I.

Table I

Nucleophilic Reactivity Toward Sulfinyl Sulfur in I[a]

	k_{Nu}, $M^{-1}sec^{-1}$		(k_{Nu}/k_{Cl^-})	
Nucleophile	Ia	Ib	Ia	Ib
F^-	4.0	---	0.33	---
CH_3COO^-	9.0	---	0.75	---
Cl^-	12	34	(1.0)	(1.0)
Br^-	64	170	5.3	5.0
SCN^-	160	---	13	---
I^-	1060	3050	90	90
thiourea	3350	---	280	---

[a] All data are for 60% dioxane as solvent at 21.4°.

It is of particular interest to compare the values of (k_{Nu}/k_{Cl^-}) in Table I with those in Table II for the reactivity relative to chloride ion of some of these same nucleophiles in displacements at (1) peroxide oxygen[5] and (2) saturated carbon.[6,7] Edwards and Pearson[7] have concluded that in nucleophilic displacements on peroxide oxygen the polarizability of the nucleophile is all important and that discrimination between nucleophiles is large. On the other hand, for displacements at saturated carbon they believe that both polarizability and basicity are important, with the

Table II

Relative Reactivity of Nucleophiles in Displacements at Bivalent Oxygen and Saturated Carbon

	(k_{Nu}/k_{Cl^-})		
		saturated carbon[b]	
Nucleophile	peroxide oxygen[a]	ref. 6	ref. 7
F^-	---	0.10	---
CH_3COO^-	[c]	0.48	---
Cl^-	(1.0)	(1.0)	(1.0)
Br^-	210	7.0	4.5
SCN^-	4.7×10^3	54	29
I^-	5.5×10^6	100	100
thiourea	[d]	11	230

[a] Ref. 5. [b] Both sets of data are for reaction of a methyl substrate with the nucleophiles. Except for thiourea agreement between the two sets of data is satisfactory. [c] Too slow to measure. [d] Too rapid to measure accurately.

former being more significant. The results for sulfinyl sulfur are clearly much more closely comparable to those for sp^3 carbon than to those for peroxide oxygen. In fact, if one uses the Edwards and Pearson[7] value for the reactivity of thiourea, rather than that of Swain and Scott[6], the response of the sulfinyl sulfur in I and saturated carbon is remarkably similar. One concludes that displacements at sulfinyl sulfur show a sensitivity to the polarizability and basicity of the attacking nucleophile which is very similar to that exhibited by displacements at a simple saturated carbon, as in methyl bromide.

Comparison of the present results with similar data for displacements at sulfenyl and sulfonyl sulfur would be particularly interesting, but unfortunately suitable quantitative data for these systems are not as yet available.

REFERENCES AND FOOTNOTES

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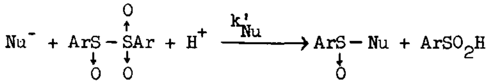
13. Besides the reaction shown in eq. 2 there is also an acid-catalyzed reaction of the nucleophile with I,



$$Nu^- + \underset{\downarrow\atop O}{ArS}-\overset{O\atop\uparrow}{\underset{\downarrow\atop O}{S}}Ar + H^+ \xrightarrow{k'_{Nu}} \underset{\downarrow\atop O}{ArS}-Nu + ArSO_2H$$

which becomes important in more strongly acid solutions (0.05 - 0.5 M $HClO_4$). For nucleophilic catalysis of the hydrolysis of I in such media one has

$$k_r - k_r^\circ = [k_{Nu} + k'_{Nu}(H^+)]\ (Nu^-)$$

Values of k_{Nu} in such cases are obtained from the intercept of a plot of $(k_r - k_r^\circ)/(Nu)$ *vs.* (H^+). Such values agreed well in all cases tested with those obtained directly in less acidic solutions.