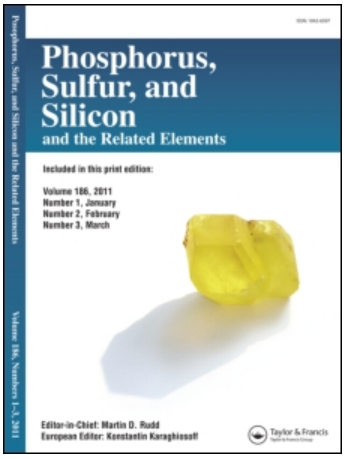

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KINETIC STUDY OF THE REACTIONS OF TRIARYLPHOSPHINES WITH α-HALO SULFONES

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KINETIC STUDY OF THE REACTIONS OF TRIARYLPHOSPHINES WITH α-HALO SULFONES

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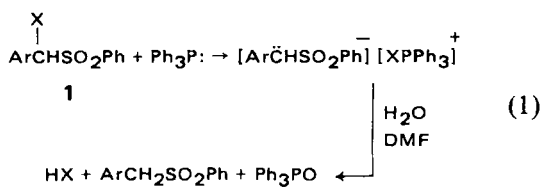
ABSTRACT

Reaction of a series of triarylphosphines with α-halo-*m*-cyanobenzyl phenyl sulfones gives the following Hammett ρ values: (Cl) $\rho = -1.84$; (Br) $\rho = -3.03$; (I) $\rho = -3.36$.

In a continuing investigation of S_N2 reactions on halogen atoms,[1-3] we wish to report the effect of systematic variation of the nucleophile in the reduction of α-halo sulfones. The reactions of triphenylphosphine with α-halo sulfones[1,2] (eq 1) has been shown to be markedly sensitive to both the halogen atom (X) present and the substituents on the benzyl ring in the sulfone **1**. For this reaction it was observed that $k_{Br} > k_I \gg k_{Cl}$, contrary to the typical S_N2 order of reactivity. This can be rationalized in terms of the relative strengths of the bonds formed and broken in the transition states.[1,2]

Hammett plots, which correlated with σ^- constants, gave the following ρ values: (Cl) +2.23, (Br) +5.97 and (I) +6.29. The large ρ's for the reactions of the α-bromo and α-iodo sulfones indicate a great deal of carbon-halogen bond breaking in the transition states.

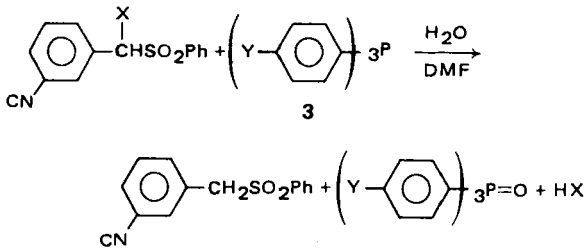


(1)

1a, X = Cl
1b, X = Br
1c, X = I

We have now examined the rate of reaction of α-halo-*m*-cyanobenzyl phenyl sulfones **2** as a function of the substituents on the triarylphosphines in order to measure the degree of phosphorus-halogen bond making.

As can be seen from Table I, the rates vary considerably with the halogen atom as well as with the substituents on the phosphine. Again the observed order of reactivity is $k_{Br} > k_I \gg k_{Cl}$.



(2)

2a, X = Cl
2b, X = Br
2c, X = I

The Hammett ρ's given in Table I can be contrasted with those determined for a) the acidity of triarylphosphines, $\rho = -1.11$[4]; b) S_N2 reactions of diethyl arylphosphines with ethyl iodide, $\rho = -1.11$[5], and triarylphosphines with α-bromoacetophenone, $\rho = -1.2$[6]; and c) the initial step in the reactions of triarylphosphines with azides (Staudinger reaction), $\rho = -1.07$.[7] Clearly, reaction (2) is significantly more sensitive to changes in the triarylphosphine than were

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TABLE I

Rate Constants for the Reaction of α-Halo-*m*-cyanobenzyl Phenyl Sulfone, 2, with *p*-Substituted Triarylphosphines, 3, in 90% Aqueous Dimethylformamide (DMF) at 25°

X	Y	$k\ M^{-1}\ sec^{-1}$ [a]	ρ [b]
Cl	$-N(CH_3)_2$	5.76×10^{-3}	
Cl	$-OCH_3$	1.06×10^{-4}	
Cl	$-CH_3$	2.73×10^{-5}	
Cl	−H	2.75×10^{-6}	−1.84 (Cl)
Br	$-OCH_3$	4.57×10^{-1}	
Br	$-CH_3$	6.83×10^{-2}	
Br	−H	2.07×10^{-3}	
Br	−Cl	1.48×10^{-5}	−3.03 (Br)
I	$-OCH_3$	4.06×10^{-2}	
I	$-C(CH_3)_3$	7.37×10^{-3}	
I	$-CH_3$	2.61×10^{-3}	
I	−H	7.76×10^{-5}	−3.36 (I)

[a] Determined in a manner previously reported with the same degree of accuracy.[1]

[b] Determined from Hammett σ constants: $\log k_X/k_H = \rho(\Sigma\sigma)$.

the above reactions.[8] This strong interaction between the phosphorus and halogen atoms, particularly for bromine and iodine, in the transition states can be accounted for by the principle of hard and soft acids and bases.[9]

Experimental Section

The synthesis of the α-halo-*m*-cyanobenzyl phenyl sulfones and the kinetic measurements (by conductance) of their reactivity toward triarylphosphines have been described previously.[1] The triarylphosphines were synthesized as previously described.[10,11]

8. The reactions of triarylphosphines with 7,7,8,8-tetracyanoquinodimethane and tetracyanoethylene [M.P. Naan, R. L. Powell and C. D. Hall, *J. Chem. Soc.*, (*B*), 1683 (1971)] exhibit a rather large negative ρ (−3.2), also. However, these reactions appear to involve the radical cations $Ar_3P^{\cdot+}$. We have no evidence that such species are involved in our reactions, but this point is being studied further.
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