

NUCLEOPHILIC DISPLACEMENTS ON HALOGEN ATOMS. I. REACTIVITY OF
 α -HALOBENZYL PHENYL SULFONES TOWARD TRIPHENYLPHOSPHINE

Bruce B. Jarvis and John C. Saukaitis

Department of Chemistry, University of Maryland

College Park, Maryland 20742

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In general the ease of reduction of alkyl halides increases as the series progresses, $RCI < RBr < RI$. Although the literature in this area contains many references to reductions which occur via displacement by nucleophiles on the halogen atom in alkyl halides¹, there have been few kinetic studies made. Recently, a study of the reaction of 1-halo-1-alkynes with thiolate ions as nucleophiles² has substantiated the mechanism involving displacement on the halogen atom in that system. The iodides reacted ca. 10^3 - 10^4 times faster than the bromides which reacted ca. 10^3 - 10^4 faster than the chlorides.

We have studied the kinetics of the reductions of α -halobenzyl phenyl sulfones (1, X=Cl, Br and I and Ar is p-H, p-NO₂, p-Cl, p-CN, m-CN and m-Cl substituted) with triphenylphosphine (Ph₃P) in 90% aqueous dimethylformamide (DMF) to give the benzyl phenyl sulfones (2) in quantitative yield. A Hammett $\sigma\rho$ correlation (using σ^- constants) gives a $\rho=+2.23$ ($r=0.988$) for the chloro series (1, X=Cl), $\rho=+5.97$ ($r=0.998$) for the bromo series (1, X=Br) and $\rho=+6.29$ ($r=0.993$) for the iodo series (1, X=I).³ The rates of reaction⁴ at 25° for the bromo sulfones are 10^2 - 10^6 faster than those for the chloro sulfones. Surprisingly, the α -iodobenzyl phenyl sulfones (1, X=I) react 2-40 slower than the corresponding bromides (see Table I)⁶. Our data as well as others^{1a-d} are consistent with the following mechanism:

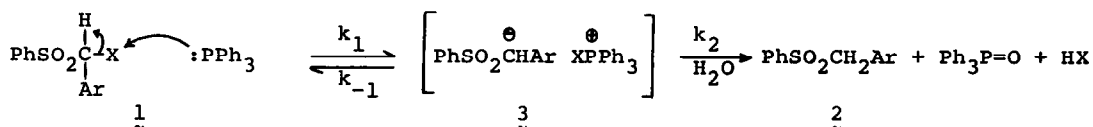
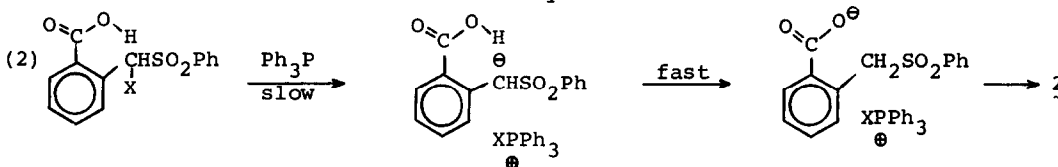


Table I. Second Order Rate Constants for the Reaction of α -Chloro, α -Bromo and α -Iodobenzyl Phenyl Sulfones with Triphenylphosphine in 90% Aqueous DMF at 25°.

Substituent	k_I (l mol ⁻¹ sec ⁻¹) ⁴	k_{Br} (l mol ⁻¹ sec ⁻¹) ⁴	k_{Cl} (l mol ⁻¹ sec ⁻¹) ⁴
H	4.09×10^{-7}	1.07×10^{-6}	4.79×10^{-8}
p-Cl	2.76×10^{-6}	8.06×10^{-6}	3.19×10^{-7}
m-Cl	4.30×10^{-6}	1.75×10^{-4}	4.14×10^{-7}
m-CN	7.76×10^{-5}	2.07×10^{-3}	2.75×10^{-6}
p-CN	9.90×10^{-3}	1.61×10^{-1}	9.20×10^{-6}
p-NO ₂	4.36	23.5	2.80×10^{-5}

The unusual observation that the iodides undergo reduction with Ph_3P less easily than the bromides might be due to a number of effects. Internal return⁹ of $\bar{3}$ to $\bar{1}$ (k_{-1}) seems to be unimportant for several reasons: a) since the acidity of the media increases with increasing reaction time, the rates of these reactions should show an upward drift from linearity if k_{-1} is important (this is not observed) and b) attempts to trap $\bar{3}$ intramolecularly (eq 2) failed to reverse the order of reactivity for the iodides and bromides.



$\bar{4a}$, X=Br ($k_{60^\circ} = 3.46 \times 10^{-3}$ l mol⁻¹sec⁻¹)

$\bar{4b}$, X=I ($k_{60^\circ} = 1.18 \times 10^{-3}$ l mol⁻¹sec⁻¹)

In light of the previously observed "normal" order of reactivity of sulfide ion toward the alkynyl halides², a possible explanation for our results can be based on the relevant bond dissociation energies. The bond dissociation energies decrease going from chlorides to bromides to iodides, but the drop is particularly large going from P-Br to P-I.¹² Since in the transition states for these reactions, a P-X bond is being made as well as a C-X bond being broken, the stronger P-Br bond (cf. P-I) being made more than compensates for the stronger C-Br bond (cf. C-I) being broken. Presumably, other nucleophiles

(e.g. RS^-) will exhibit different orders of reactivity with $\underline{1}$. This point is currently being tested.

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2. M. C. Verploegh, L. Donk, H. J. T. Bos and W. Dreuth, *Rec. Trav. Chim. Pays-Bas*, **90**, 765 (1971).
3. The reaction of Ph_3P with α, α -dichloro-phenyl-N-methylacetanilids which goes via displacement on the α -chlorine atom, gives a $\rho = +2.58$ ($r = 0.993$) in acetonitrile [A. J. Speciale and L. J. Taylor, *J. Org. Chem.*, **31**, 2450 (1966)]. The large positive ρ values for the reactions of the bromo and iodo compounds are some of the highest reported. These ρ 's are even larger than those reported for reactions known to involve carbanionic intermediates such as nucleophilic aromatic substitution [A. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953)] and base catalyzed polymerization of substituted styrenes [C. H. DePuy *et al.*, *J. Amer. Chem. Soc.*, **87**, 2421 (1965)].
The ρ given in the text for $\underline{1}$, $X = I$ was determined without including the point for the parent α -iodobenzyl phenyl sulfone ($\underline{1}$, $X = I$, $Ar = Ph$) since the point fell so far off the line. Inclusion of this point gives a ρ of +5.74 ($r = 0.986$).
4. The rates were followed by several equally precise (+5%) techniques: potentiometric titration for liberated halide, conductometrically for formation of ions and by use of an acid-base indicator (phenol red) using a Cary 15 uv-visible spectrometer fitted with a thermostated curvette holder. The three methods gave good agreement (+5%) when applied to the reaction of α -bromo-m-cyanobenzyl phenyl sulfone with Ph_3P in 90% aqueous DMF. The reaction was run under pseudo first order reaction conditions ($[Ph_3P] \geq 10$ [$\underline{1}$]), and the second order rate constants were determined by dividing k_{obs} by $[Ph_3P]$. The reactions were shown to be first order in both $\underline{1}$ and Ph_3P .
The compounds in this study were made by variations of standard procedures⁵. All new compounds gave correct elemental analyses and ir and nmr spectra consistent with their structures.

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