

Kinetics of Oxidation of Triarylsarsines by Potassium Peroxodisulphate

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The kinetics of oxidation of a few triarylsarsines (XC₆H₄)₃As (X = H, *p*-Me, *p*-Cl, *m*-MeO, *o*-Me and *o*-MeO) by potassium peroxodisulphate have been studied spectrophotometrically in 60% acetonitrile-40% water (v/v) mixture at 30°C. The logarithms of second order rate constants give a satisfactory correlation with σ^+ constants ($r=0.954$, $\rho^+ = -0.417$) indicating participation of the π -electron cloud of aromatic rings and the empty *d*-orbitals of arsenic in bonding.

In continuation of our earlier work on the kinetics and mechanism of oxidation of triphenylphosphine, triphenylarsine and triphenylstibine by potassium peroxodisulphate (PS)¹ we are reporting herein the results of the study on the effect of substituents on the kinetics of oxidation of triarylsarsines by PS in 60% acetonitrile-40% water (v/v) mixture.

Substituted triphenylarsines, (XC₆H₄)₃As (X = H, *p*-Me, *p*-Cl, *m*-MeO, *o*-Me and *o*-MeO) were prepared by known methods. The rate studies were carried out at 30 ± 0.1°C under pseudo-first order conditions ([PS] ≫ [(XC₆H₄)₃As]) in 60% acetonitrile-40% water (v/v) mixture at constant ionic strength (maintained by the addition of sodium perchlorate) by monitoring the disappearance of absorbance at 248, 249, 251, 250, 256 and 250 nm for unsubstituted and *p*-Me, *p*-Cl, *m*-MeO, *o*-Me and *o*-MeO substituted triphenylarsines respectively using a Perkin-Elmer model 402 UV-visible spectrophotometer provided with a thermostatic arrangement to control the temperature of the reaction cell with an accuracy of ± 0.1°C. Plots of log (absorbance) versus time were linear ($r > 0.995$) and from the slopes of these plots the pseudo-first order rate constants k_1 were calculated (The errors in rate constants are given in terms of 95% confidence limit of the 'Student *t*'). The second order rate constants were calculated using the equation $k_2 = k_1/[PS]$.

The kinetic data in Table I show that electron-donating substituents accelerate the rate and electron-withdrawing groups retard it. The rate constants for the oxidation of *ortho*-substituted triphenylarsines are lower than those of the *meta*- and *para*-substituted triphenylarsines.

It has been well established that the elements like S, P, Cl, Br and I can expand their valence shells by

Table I—Pseudo-first Order and Second Order Rate Constants for Oxidation of (XC₆H₄)₃As by PS at 30°C

Solvent: 60% CH₃CN-40% H₂O (v/v); $I=0.05$ moldm⁻³;
[PS] (= 0.004 moldm⁻³) ≫ [(XC₆H₄)₃As]

X	$k_1 \times 10^5$ (s ⁻¹)	$k_2 \times 10^3$ (dm ³ mol ⁻¹ s ⁻¹)
H	3.81 ± 0.20	9.52 ± 0.50
<i>p</i> -Me	10.4 ± 0.63	26.0 ± 1.6
<i>p</i> -Cl	3.66 ± 0.36	9.16 ± 0.90
<i>m</i> -MeO	2.95 ± 0.32	7.37 ± 0.80
<i>o</i> -Me	2.75 ± 0.08	6.87 ± 0.19
<i>o</i> -MeO	2.67 ± 0.11	6.68 ± 0.26

utilizing their vacant *d*-orbitals²⁻⁴. Correlations of logarithms of rate constants with substituent constants may be successfully employed to know the *d*-orbital participation. For example, Shulman⁵ in his work on the kinetics of reduction of *t*-butyl hydroperoxide by *para*-substituted triphenylphosphines obtained a reasonable correlation with σ constants ($r=0.967$) and concluded lack of significant $p\pi-d\pi$ bonding in triarylphosphines. The correlation of Shulman's rate data with σ^+ was poor ($r=0.911$). The present kinetic data display a better Hammett correlation with σ^+ ($\rho^+ = -0.417$, $r=0.954$, $s=0.09$) than with σ ($r=0.838$). This is consistent with our earlier proposal¹ that a positive charge is present in M (=P, As, Sb) in the intermediate, Ph₃M-OSO₃⁻, formed in the Ph₃M-PS reaction. This better correlation with σ^+ indicates participation of π -electron cloud of aromatic rings and the *d*-orbitals of arsenic in bonding. The observed rate retardation with *ortho*-methyl and *ortho*-methoxy derivatives may be due to the steric hindrance for the attack by PS as it has been shown that PS oxidation of organic sulphur compounds is susceptible to steric congestion at the reaction centre⁶.

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