# Substituent Effect in the Reaction of Aryl Arylmercury Sulphides with Picryl Iodide

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The rates of the reaction of a series of substituted aryl arylmercury sulphides (Ar^1HgSAr^2) with picryl iodide in benzene at 30° have been measured. Electron-donating substituents located in Ar^1 and in Ar^2 enhance the reaction rate whereas electron-withdrawing substituents have the opposite effect. The logarithmic plots of rate against σ constants give ρ values of -0.966 (substituents in Ar^1) and -3.67 (substituents in Ar^2). o-Methyl groups in Ar^1 have little steric effect whereas o-methyl groups in Ar^2 strongly depress the reaction rate.

WE have previously reported [1] that phenyl phenylmercury sulphide (1c) reacts with picryl halides (2) in aprotic solvent in the same way as sodium or potassium arenethiolates to give phenyl picryl sulphide (3c) and phenyl mercury halide (4c) according to equation (1).

$$Ar^1HgSAr^2 + O_2N\langle\rangle Hal \longrightarrow O_2N\langle\rangle SAr^2 + Ar^1HgHal \quad (1)$$

(1)   (2)   (3)   (4)
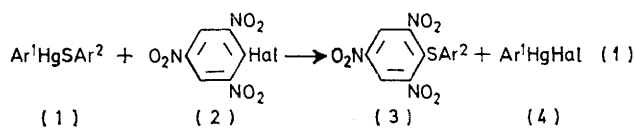
	Ar¹	Ar²
a;	$p\text{-}MeC_6H_4$	Ph
b;	$m\text{-}MeC_6H_4$	Ph
c;	Ph	Ph
d;	$p\text{-}ClC_6H_4$	Ph
e;	$m\text{-}ClC_6H_4$	Ph
f;	$o\text{-}MeC_6H_4$	Ph
g;	$2,4,6\text{-}Me_3C_6H_2$	Ph
h;	Ph	$p\text{-}MeC_6H_4$
i;	Ph	$m\text{-}MeC_6H_4$
j;	Ph	$p\text{-}ClC_6H_4$
k;	Ph	$m\text{-}ClC_6H_4$
l;	Ph	$o\text{-}MeC_6H_4$
m;	Ph	$2,4,6\text{-}Me_3C_6H_2$

The influence of the leaving group * and of the solvent on the reaction rate as well as that of the activation parameters led us to suggest a four centre, concerted mechanism for the reaction with the formation of an active complex (5) with partial dipolar character in the transition state.

* By an independent method we have found that under conditions similar to those used for picryl halides no reaction occurs between phenyl phenylmercury sulphide (1c) and p-nitrophenyl picryl ether. This fact strongly supports our suggestion of the importance of electrophilic assistance of mercury in the removal of the leaving group in these reactions. The mercury assists the removal of the halogens but not of the p-nitrophenoxy-group since halogen–mercury bonds are stronger [2] than oxygen–mercury bonds.

In order to obtain information on the sensitivity of the reaction rate to the polar and steric effects of substituents present in the nucleophile and therein on the

(5)
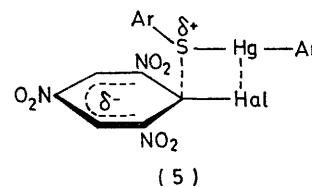
degrees of bond forming and breaking in the rate-limiting transition state, we have studied the kinetics of the reaction between some substituted aryl arylmercury sulphides (1a—m) and picryl iodide (2; $Hal = I$) in benzene.

RESULTS AND DISCUSSION

Kinetic runs, followed by a u.v. spectroscopic technique, gave results fitting a second-order rate equation, first order in both aryl arylmercury sulphide and picryl iodide. The majority of runs were followed up to 80—90% completion. The Table lists the specific rate constants found for the reactions of (1a—m) with picryl iodide at 30° in benzene. The results are discussed by examining separately the effect of the substituent Ar^1 bonded to mercury (1a—f) and in Ar^2 bonded to sulphur (1g—m).

Substituents in Ar^1.—As the Table shows electron-donating substituents located in Ar^1 increase the reaction rate, whereas electron-withdrawing substituents

[1] C. Dell'Erba, G. Guanti, M. Novi, and G. Leandri, *J.C.S. Perkin II*, 1973, 1879.

[2] R. E. Dessy and F. E. Paulik, *J. Amer. Chem. Soc.*, 1963, **85**, 1812.

have the opposite effect. A logarithmic plot of the rate constant against σ values [3] (Figure) gives a straight line

Rate constants for the reaction of various aryl arylmercury sulphides Ar^1HgSAr^2 (1a—m) with picryl iodide in benzene at 30°

Compound	$10^6 k/l \, mol^{-1} \, s^{-1}$
(1a)	240
(1b)	227.5
(1c)	196.2
(1d)	100
(1e)	81.15
(1f)	158
(1g)	215
(1h)	981.5
(1i)	279.5
(1j)	28.1
(1k)	8.8
(1l)	50.2
(1m)	5

with the slope ρ —0.966 (r 0.986; s 0.042). The low negative value of ρ can be rationalized by taking into account the opposing effects of substitution in Ar on the factors affecting the reaction rate. Electron-donating substituents enhance the nucleophilicity of the
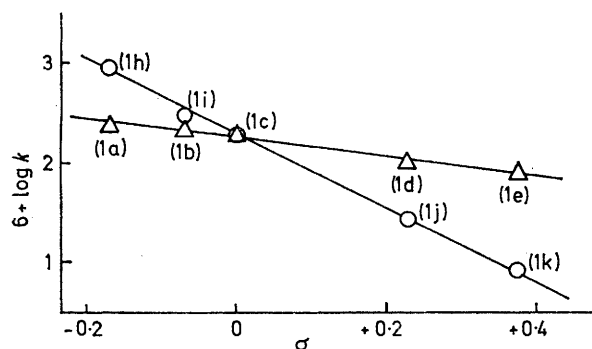
Logarithmic plot of the rate constants of the reaction of a series of substituted aryl arylmercury sulphides [(1a—g), ○], [(1g—m), △] with picryl iodide in benzene at 30° against σ constants. The slope calculated for substituents in Ar^1 is —0.966 (r 0.986); for substituents in Ar^2 —3.67 (r 0.997)

sulphur * and facilitate the breakage of the Hg–S bond in the rate-determining transition state (provided that this breakage occurs) but on the other hand they decrease the availability of the mercury as electrophilic assistor for the loss of the iodine. The value of ρ indicates that the first two effects play a role more important than that of the latter. Another consideration which emerges by the examination of the data in the Table is that o-methyl groups in Ar^1 have a minimal steric effect. Models [4] indicate that steric hindrance by ortho-substituents in Ar^1 should not be an important factor in these reactions since the reaction site is sufficiently removed from the ortho-position.

Substituents in Ar^2.—As found for substituents in Ar^1 in this case also the reactivity of (1c) with picryl iodide is enhanced by electron-donating substituents and

* Evidence [4] that electronic effects of substituents can be transmitted through the mercury atom has been used to interpret the increase of the rate of cleavage of Et–Hg bond by HCl in going from Et_2Hg to EtHgPh.

[3] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

decreased by electron-withdrawing substituents. The observed trend is in line with the proposed mechanism and parallels the substituent effect in the nucleophile in nucleophilic aromatic substitution.[5a,b] Electron-donating substituents in Ar^2 enhance the ability of the sulphur atom of (1) to interact with the substrate and stabilize the positive partial charge developed on the sulphur atom in the rate limiting transition state. The rates have been examined by means of the Hammett relationship. In the Figure the values of log k for the *meta-* and *para-*substituents in Ar^2 are plotted against σ.[3] A good linear correlation has been obtained with ρ —3.67 (r 0.997; s 0.074). It is interesting to compare the present results with those reported for thiophenoxydehalogenation carried out with substituted sodium benzenethiolates on nitro-activated halogenobenzenes. Even though these reactions were carried out in very different solvents (methanol [5a] or ethanol [5b]) and on different substrates the ρ values reported (ca. —1) are sufficiently different not to attribute the differences just to a change of solvent or of substrate. Two other factors are important, (a) the sulphur atom of (1) is a weaker nucleophile than that of benzenethiolate anion and therefore more sensitive to polar substituent effects and (b) in the transition state of the two reactions the charges on the sulphur atom are very different. There is partial negative charge in the case of the reaction of benzenethiolate, a partial positive charge in the case of the reaction of phenyl phenylmercury sulphide. The effect of o-Me groups in Ar^2 on the reaction rate has also been examined. As the Table shows the k value of the p-methylphenyl phenylmercury sulphide is ca. 20 times greater than that of o-methylphenyl phenylmercury sulphide and ca. 200 times greater than that of 2,4,6-trimethylphenyl phenylmercury sulphide. Such a steric effect is in line with the mechanism proposed which involves a particularly crowded transition state in the limiting step. Comparison of these results with those found in the case of the reaction of halogenonitrobenzenes with substituted benzenethiolates can be made. The rate constant for the reaction of substituted thiophenoxides with 1-chloro-2,4-dinitrobenzene in 95% (v/v) ethanol–water at 25° decreases of a factor ca. 3 on going from p- to o-methylbenzenethiolate.[5b] In this case the high polarizability of the negative charged sulphur atom which can interact with the electrophilic centre at great distance to give a not particularly crowded transition state is certainly the main factor responsible for the less important steric effect.

EXPERIMENTAL

Benzene was purified according to a standard procedure.[6] Picryl iodide was prepared as described.[7]

Aryl Arylmercury Sulphides (1).—These compounds were

[4] R. E. Dessy and J. Kim, *J. Amer. Chem. Soc.*, 1961, **83**, 1167.

[5] (a) G. Bartoli, L. di Nunno, L. Forlani, and P. E. Todesco, *Internat. J. Sulfur Chem.* (C), 1971, 77; (b) M. R. Crampton and M. J. Willison, *J.C.S. Perkin II*, 1974, 238.

[6] A. Weissberger, ' Techniques of Organic Chemistry,' vol. VII, Interscience, New York, 1960.

[7] A. H. Blatt and N. Gross, *J. Org. Chem.*, 1957, **22**, 1046.

prepared from the appropriate arylmercury chloride [8] and sodium arenethiolate [9] according to the method of Sachs.[10] *p*-Methylphenylmercury phenyl sulphide (1a) had m.p. 122—123° (lit.,[11] 123°), *m*-methylphenylmercury phenyl sulphide (1b) m.p. 120° (lit.,[11] 118°), phenyl phenylmercury sulphide (1c) m.p. 106° (lit.,[12] 103°), *p*-chlorophenylmercury phenyl sulphide (1d) m.p. 139° (lit.,[12] 139°), *m*-chlorophenyl-mercury phenyl sulphide (1e) m.p. 137° (lit.,[11] 137°), *o*-methylphenylmercury phenyl sulphide (1f) m.p. 112° (lit.,[13] 112°), *phenyl 2,4,6-trimethylphenylmercury sulphide* (1g) m.p. 122° (from ethanol–dioxan) (Found: C, 41.9; H, 3.7. $C_{15}H_{16}HgS$ requires C, 42.0; H, 3.75%), *p*-methyl-phenyl phenylmercury sulphide (1h) m.p. 104° (lit.,[12] 104°), *m*-methylphenyl phenylmercury sulphide (1i) m.p. 152° (lit.,[11] 151°), *p*-chlorophenyl phenylmercury sulphide (1j) m.p. 162° (lit.,[11] 157°), *m*-chlorophenyl phenylmercury sulphide (1k) m.p. 146° (lit.,[11] 145°), *o*-methylphenyl phenylmercury sulphide (1l) m.p. 118° (lit.,[11] 118°), *2,4,6-trimethylphenyl phenylmercury sulphide* (1m) m.p. 210° (from benzene) (Found: C, 41.9; H, 3.7%).

Aryl Picryl Sulphides (3).—These compounds were prepared from picryl iodide and the appropriate aryl aryl-mercury sulphide (1) as described in ref. 1. Their u.v. spectra were taken in benzene. Phenyl picryl sulphide (3c) had m.p. 120° (lit.,[14] 120°), $\lambda_{max.}$ 374 nm (log ε 3.83), *p*-methylphenyl picryl sulphide (3h) m.p. 154° (lit.,[14] 154°), $\lambda_{max.}$ 380 nm (log ε 3.85), *m*-methylphenyl picryl sulphide (3i) m.p. 112° (lit.,[14] 103°), $\lambda_{max.}$ 378 nm (log ε 3.84), *p*-chlorophenyl picryl sulphide (3j) m.p. 136° (lit.,[15] 133°), $\lambda_{max.}$ 372 nm (log ε 3.85), *m*-chlorophenyl picryl sulphide (3k) m.p. 113° (lit.,[15] 106°), $\lambda_{max.}$ 368 nm (log ε 3.84), *o*-methylphenyl picryl sulphide (3l) m.p. 148° (lit.,[14] 148°), $\lambda_{max.}$ 378 nm (log ε 3.88), 2,4,6-trimethylphenyl picryl sulphide (3m) m.p. 191° (lit.,[16] 191°), $\lambda_{max.}$ 384 nm (log ε 3.93).

Arylmercury Iodide (4).—These compounds were prepared according to standard procedures. *p*-Methylphenylmercury iodide (4a) had m.p. 220° (lit.,[17] 220°), *m*-methylphenyl-mercury iodide (4b) m.p. 162° (lit.,[18] 162°), phenylmercury iodide (4c) m.p. 265° (lit.,[17] 265°), *p*-chlorophenylmercury iodide (4d) m.p. 250° (lit.,[19] 250°), *m*-chlorophenylmercury iodide (4e) m.p. 186° (lit.,[19] 186°), *o*-methylphenylmercury iodide (4f) m.p. 176° (lit.,[20] 176°), *2,4,6-trimethylphenyl-mercury iodide* (4g) m.p. 180° (from benzene) (Found: C, 24.2; H, 2.4. $C_9H_{11}HgI$ requires C, 24.2; H, 2.45%).

Kinetics.—Reactions were followed photometrically by the kinetic technique reported [21] by measuring the appear-ance of the aryl picryl sulphide at its $\lambda_{max.}$. All rate determinations were generally performed with (1) in *ca*. 20-fold excess over the picryl iodide. Quantitative yields of (3) were obtained as indicated by the spectro-photometric data. Pseudo-first-order rate constants were evaluated graphically.[22] The pseudo-first-order rate co-efficients were divided by the initial concentration of (1) to convert them into second-order rate coefficients.

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[15] A. Mangini and R. Passerini, *Atti Accad. Naz. Lincei, Rend. Classe sci. fis. mat. e nat.*, 1949, [8] **7**, 324.

[16] G. Leandri and A. Tundo, *Ann. Chim. (Italy)*, 1954, **44**, 479, 488.

[17] A. Dreher and R. Otto, *Annalen*, 1870, **154**, 109, 173.

[18] A. Michaelis, *Ber.*, 1895, **28**, 589,

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[20] S. Hilpert and G. Grüttner, *Ber.*, 1915, **48**, 906.

[21] D. Spinelli, A. Salvemini, and C. Dell'Erba, *Ann. Chim. (Italy)*, 1962, **52**, 1156.

[22] S. Glasstone, 'Textbook of Physical Chemistry,' Van Nostrand, New York, 1947.