Kinetics and Mechanism of the Reaction of Phenyl Phenylmercury Sulphide with Picryl Halides

By **Carlo Dell'Erba,* Giuseppe Guanti, Marino Novi,** and **Giuseppe Leandri,** Istituto di Chimica Organica dell'Università, Palazzo delle Scienze, Corso Europa, 16132 Genova, Italy

The rates of the reaction of phenyl phenylmercury sulphide with picryl halides to give phenyl 2,4,6-trinitrophenyl sulphide have been measured in various aprotic solvents (benzene, chlorinated hydrocarbons, nitromethane, dioxan, tetrahydrofuran, and acetone). The rate increases on passing from picryl chloride to bromide and to iodide. The reaction rate is only slightly affected by solvent change. Very large negative activation entropy values were found and there is a satisfactory linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. A four-centre, concerted mechanism is suggested for the reaction.

THE chemistry of aryl arylmercury sulphides (1) has been investigated by many workers.[1-3] In some reactions the sulphur atom reacts as a nucleophilic centre, *e.g.* (1) reacts with various acid halides (2) according to equation (1), yielding the sulphides (3).[3d] A dependence of the reactivity on the nature of the halogen present in (2)

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[1] G. Sachs, *Annalen*, 1923, **433**, 158.

[2] S. Takagi, H. Tsukatani, and H. Tanaka, *Bull. Inst. Chem. Res.*, 1951, **27**, 71.

[3] (*a*) G. Leandri and D. Spinelli, *Ricerca sci.*, 1959, **29**, 541; (*b*) G. Leandri, D. Spinelli, and A. Salvemini, *ibid.*, p. 2618; (*c*) G. Leandri, D. Spinelli and G. Monaco, *Ann. Chim.* (*Italy*), 1960, **50**, 156; (*d*) D. Spinelli and A. Salvemini, *ibid.*, 1961, **51**, 1296.

has been observed, *e.g.* in contrast to toluene-*p*-sulphonyl iodide, the chloro-analogue is unreactive toward (1).

$$\underset{(1)}{\mathrm{Ar^1\text{-}Hg\text{-}S\text{-}Ar^2}} + \underset{(2)}{\mathrm{Ar^3\text{-}X\text{-}Hal}} \longrightarrow \underset{(3)}{\mathrm{Ar^3\text{-}X\text{-}S\text{-}Ar^2}} + \mathrm{Ar^1\text{-}Hg\text{-}Hal} \quad (1)$$

$$\mathrm{X = CO, SO_2, or\ S}$$

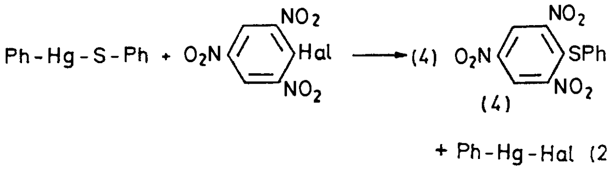
However, the mechanism of these reactions has not been studied and no measurement of rate constants has been reported, although the particular nature of the Hg–S bond of (1), which is considerably different from that of an ionized arenethiolate, makes this research stimulating. From spectrophotometric investigations[4] and from descriptions of the Hg–S bond in inorganic compounds,[5] it is possible to describe (1) as the hybrid structure *A* which has some positive charge on the sulphur atom. The reactivity of (1) with nitro-activated aromatic halides has not been reported.

$$\mathrm{Ar^1\text{-}Hg\text{-}S\text{-}Ar^2} \longleftrightarrow \mathrm{Ar^1\text{-}\overset{-}{Hg}{=}\overset{+}{S}\text{-}Ar^2}$$

A

We have investigated the reactivity of phenyl phenylmercury sulphide (1, $Ar^1 = Ar^2 = Ph$) with some aromatic halides and found that (1; $Ar^1 = Ar^2 = Ph$) reacts with picryl halides in various aprotic solvents affording the sulphide (4), characterized by its physical properties [reaction (2)] in almost quantitative yield. Under the same conditions, no reaction occurs between (1; $Ar^1 = Ar^2 = Ph$) and 2,4-dinitrohalogenobenzenes.

We report the results of a kinetic investigation of the reaction with picryl halides which includes studies of the effects of halogens and of the solvent on the reaction rate.



RESULTS

Kinetic runs, followed by u.v. spectroscopic techniques, gave results fitting a second-order rate equation, first order in (1; $Ar^1 = Ar^2 = Ph$) and first order in the picryl halide. The majority of runs were followed up to 80—90% completion; Table 1 lists the specific rate constants found for the reaction of (1; $Ar^1 = Ar^2 = Ph$) with picryl iodide in benzene, carried out at different initial concentrations. Table 2 summarizes the rate data for the reactions between the various picryl halides and (1; $Ar^1 = Ar^2 = Ph$) in benzene at different temperatures along with the corresponding activation parameters. The rate of the reaction between picryl iodide and (1; $Ar^1 = Ar^2 = Ph$) was measured at different temperatures in various solvents and the corresponding activation parameters were evaluated (Table 3).

TABLE 1

Second-order rate constants for the reaction between phenyl phenylmercury sulphide (1; $Ar^1 = Ar^2 = Ph$) and picryl iodide in benzene at 30 ± 0·1°

[Sulphide]/M	[Picryl iodide]/M	10^4k/l mol^{-1} s^{-1} [a]
$2 \cdot 10^{-2}$	$1 \cdot 10^{-3}$	1·96
$1 \cdot 10^{-3}$	$1 \cdot 10^{-2}$	1·85
$1 \cdot 10^{-2}$	$1 \cdot 10^{-2}$	1·89

[a] Each value is the average of three or more independent runs; standard deviation 3—4%.

DISCUSSION

Compound (1; $Ar^1 = Ar^2 = Ph$) reacts with the picryl halides in the same way as sodium or potassium arenethiolates to give the normal product of thiophenoxy-dehalogenation. However, kinetic results indicate that (1; $Ar^1 = Ar^2 = Ph$) is a rather poor nucleophilic reagent.

The general features of the reaction may be summarized as follows. (i) The rate depends on the nature of the aromatic substrate; under the same conditions 2,4-dinitrohalogenobenzenes are unreactive. (ii) The rate in benzene increases on passing from picryl chloride to bromide and to iodide. (iii) Change of solvent affects the rate only slightly. (iv) The reactions show a quite large and negative activation entropy which is not appreciably influenced by the nature of the solvent.

On comparing these results with those reported for the reaction of sodium benzenethiolate with aromatic halides, some interesting differences can be observed. The reactivity order found I > Br > Cl (Table 2) is similar to that observed (I ≥ Br > Cl) for the reactions in methanol of sodium benzenethiolate with *p*-nitrohalogenobenzenes and 2,4-dinitrohalogenobenzenes.[6] However, the reactivity ratios for the reaction of (1; $Ar^1 = Ar^2 = Ph$) with picryl halides ($k_I : k_{Cl} = 185$ and $k_I : k_{Br} = 2{\cdot}6$ at 30° in benzene) are much greater than those reported for the reaction of sodium benzenethiolate with nitro-activated halogenobenzenes. For example, the reactivity ratios for the reactions of *p*-nitrohalogenobenzenes (at 49·2°) and 2,4-dinitrohalogenobenzenes (at 14·9°) in methanol are respectively $k_I : k_{Cl}$ 2·47 and 1·32, and $k_I : k_{Br}$ 1·18 and 0·85.[6] Such differences are too significant to be ignored as depending just on the change of solvent and therefore they indicate, in our opinion, that in the reaction of (1; $Ar^1 = Ar^2 = Ph$) with picryl halides the nature of the halogen influences the reaction rate to a greater extent than that observed in the usual aromatic thiophenoxy-dehalogenation reactions. The activation parameters for the three picryl halides show very large, negative entropy values, which are similar in all cases. The variations in reactivity can be essentially attributed to variations in activation enthalpy.

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Table 2

Rate constants and activation parameters for the reactions between the various picryl halides [a] and (1; $Ar^1 = Ar^2 = Ph$) [b] in benzene

	10^4k/l mol^{-1} s^{-1} [c]					
Hal	20°	30°	40°	50°	$\Delta H^‡$/kcal mol^{-1} [d]	$-\Delta S^‡$/cal mol^{-1} K^{-1} [e]
Cl		0·011	0·024	0·053	15·1	45·4
Br	0·36	0·75	1·33		11·5	48·9
I	1·01	1·96	3·65		11·2	47·7

[a] [Picryl halide] = $1\cdot10^{-3}$M. [b] (1; $Ar^1 = Ar^2 = Ph$)] = $2\cdot10^{-2}$M. [c] Mean values of three or more independent runs for each temperature; error 3—4%. [d] At 30°; accurate to ±0·4 kcal mol^{-1}. [e] At 30°; accurate to ±1·5 cal mol^{-1} K^{-1}.

Table 3

Solvent effect on rate constants and activation parameters for the reaction between picryl iodide [a] and (1; $Ar^1 = Ar^2 = Ph$) [b]

Solvent	Dielectric constant [c]	Temp. (°C)	10^4k/l mol^{-1} s^{-1} [d]	$\Delta H^‡$/kcal mol^{-1} [e]	$-\Delta S^‡$/cal mol^{-1} K^{-1} [f]
Carbon tetrachloride	2·24 [g]	20·0	5·91	7·9	55·7
		30·0	9·14		
		40·0	14·9		
1,4-Dioxan	2·21 [g] (at 25°)	20·0	0·12	12·9	46·2
		30·0	0·26		
Benzene	2·28 [g]	20·0	1·01	11·2	47·7
		30·0	1·96		
		40·0	3·65		
Tetrahydrofuran	7·5 [h]	20·0	0·40	12·7	44·3
		30·0	0·87		
		40·0	1·75		
o-Dichlorobenzene	9·93 [g] (at 25°)	20·0	4·67	9·8	49·4
		30·0	8·61		
		40·0	14·5		
Acetone	21·2 [i]	20·0	1·00	8·3	57·6
		25·0	1·36		
		30·0	1·66		
Nitromethane	37·5 [i]	20·0	2·63	11·2	45·8
		30·0	5·09		
		40·0	9·55		

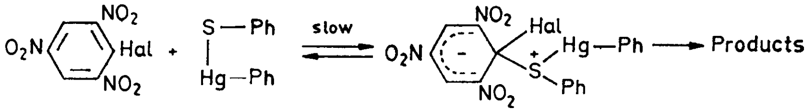
[a] [Picryl iodide] = $1\cdot10^{-3}$M. [b] (1; $Ar^1 = Ar^2 = Ph$) = $2\cdot10^{-2}$M. [c] At 20° unless otherwise stated. [d] Error 3—4%. [e] At 30°; accurate to ±0·4 kcal mol^{-1}. [f] At 30°; accurate to ±1·5 cal mol^{-1} K^{-1}. [g] A. Weissberger, 'Techniques of Organic Chemistry,' Interscience, New York, 1955, vol. VII. [h] F. E. Critchfield, J. A. Gibson, jun., and J. L. Fall, *J. Amer. Chem. Soc.*, 1953, **75**, 6044. [i] J. Hine, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1962.

Moreover, the rate of the reaction between picryl iodide and (1; $Ar^1 = Ar^2 = Ph$) (Table 3) is hardly influenced by the polarity of the solvent, whereas such influences are normally very strong in aromatic nucleophilic substitution with either neutral and anionic reagents.[7]

Table 3 also lists the activation parameters for the reaction of picryl iodide with (1; $Ar^1 = Ar^2 = Ph$) in the different solvents. The values of $\Delta H^‡$ vary from a minimum of *ca.* 8 to a maximum of *ca.* 13 kcal mol^{-1}; the values of $-\Delta S^‡$ vary from a minimum of *ca.* 44 to a maximum of *ca.* 58 cal mol^{-1} K^{-1}. The activation entropies are very large and negative in all cases, indicating a highly ordered transition state. Increases in $\Delta H^‡$ are generally accompanied by increases in activation entropy and there is a satisfactory linear relationship between $\Delta H^‡$ and $\Delta S^‡$. Such a relationship may indicate that the solvents employed perform closely similar roles in the reaction.[8]

The experimental data suggest that the reaction cannot proceed through an initial dissociation or ionization equilibrium of (1; $Ar^1 = Ar^2 = Ph$), $Ph{-}Hg{-}S{-}Ph \rightleftharpoons Ph{-}Hg^+ + Ph{-}S^-$. Such an equilibrium should depend markedly on medium polarity as measured by the dielectric constant;[8] however, the reaction rate is substantially independent of the solvent.

It is also unlikely that the reaction takes place through the formation of a discrete zwitterion intermediate as in route (A). In fact, inspection of the data in Table 3 shows no clear dependence of rates on solvent dielectric constant or on the dielectric function $(\varepsilon - 1)/(2\varepsilon + 1)$.[9-11]



(A)

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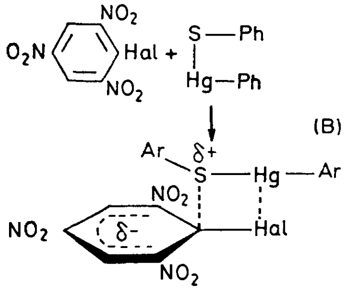
For example, the rates in benzene (ε 2·28) and in nitromethane (ε 37·5) are almost equal. Also, the rate constants are different in dioxan and in carbon tetrachloride, which have similar dielectric constants (ε 2·21 and 2·24 respectively). The lack of dependence on dielectric constant indicates that a mechanism involving charge separation is unlikely.[12-14] Furthermore, route (A) can also be ruled out on the consideration that the sulphur atom of (1; $Ar^1 = Ar^2 = Ph$) is a poor nucleophilic centre and that the divalent sulphur of other sulphides does not seem to be a nucleophilic atom capable of reacting with activated aromatic halides.[15]

On the basis of our results it is possible to suggest a mechanism involving the formation of an active complex (5) with partial dipolar character in the transition state [route (B)]. In this route the important point is that the nucleophilic attack of the sulphur atom on the reaction centre of the substrate is as important as the electrophilic attack of the mercury on the halogen. Attack by sulphur on the carbon atom is thereby facilitated or assisted by the halogen–mercury interaction, which induces increased nucleophilic reactivity in the adjacent sulphur atom of (1; $Ar^1 = Ar^2 = Ph$). This hypothesis is supported by the known properties of mercury salts as electrophilic assistors in the solvolyses of organic halides.[16-19] In line with route (B) are the very large differences observed in the reaction rate for the various picryl halides. In fact the observed reactivity order (I > Br > Cl) is similar to that reported for the properties as ligands to mercury of iodide, bromide, and chloride anions which are in the order $I^- > Br^- > Cl^-$.[20] In general, since the strength of the mercury–halide interaction can be related to the polarizabilities of the halides,[21] the suggested mechanism is consistent with the kinetic data obtained for the three picryl halides. Moreover, this route would show only a small dependence of reaction rate on the solvent[22] and a very large and negative activation entropy as generally observed in other four-centre, concerted processes, and which is observed here. The lack of reactivity of 2,4-dinitrohalogenobenzenes with (1; $Ar^1 = Ar^2 = Ph$) can be ascribed to the need for large stabilization of the partial negative charge developed in the cyclic transition state.



Therefore, the reaction of the picryl halides with (1; $Ar^1 = Ar^2 = Ph$) can be considered as an aromatic thiophenoxy-dehalogenation, carried out with an undissociated arenethiolate (1; $Ar^1 = Ar^2 = Ph$), assisted by electrophilic catalysis by the metal present in the same reagent.

EXPERIMENTAL

Benzene, carbon tetrachloride, dioxan, *o*-dichlorobenzene, acetone, and nitromethane solvents (Fluka; high purity) were purified according to standard procedures[23] and fractionally distilled. Tetrahydrofuran (Fluka; high purity) was purified according to the procedure reported for the dioxan[23] and fractionally distilled, b.p. 64—65° at 760 mmHg (lit.,[24] 64—65°).

Picryl Halides.—The commercial chloride (Fluka) was crystallized from chloroform to constant m.p. 81—82°. Picryl bromide and iodide were prepared according to literature methods,[25,26] m.p. 124 and 163°, respectively.

Phenyl Phenylmercury Sulphide (1; $Ar^1 = Ar^2 = Ph$).—This was obtained according to the method of Sachs,[1] m.p. 105°.

Phenyl 2,4,6-*Trinitrophenyl Sulphide* (4).—This was prepared from picryl iodide and (1; $Ar^1 = Ar^2 = Ph$) under the same conditions as in the kinetic experiments. A solution of picryl iodide (0·0012 mol) and (1; $Ar^1 = Ar^2 = Ph$) (0·0012 mol) in benzene (40 ml) was kept at room temperature for four or five half-lives. The phenylmercury iodide precipitate (92%) was separated by filtration and crystallized from dioxan, m.p. 268° (lit.,[27] 270°). The filtrate was evaporated under reduced pressure. Phenyl 2,4,6-trinitrophenyl sulphide (90%) was purified by crystallization from ligroin, m.p. 120° (lit.,[28] 120°).

Under the same conditions the reactions of picryl chloride and of picryl bromide with (1; $Ar^1 = Ar^2 = Ph$) produced the sulphide (4) and (respectively) phenylmercury chloride, m.p. 258° (lit.,[29] 258°) and phenylmercury bromide, m.p. 279° (lit.,[30] 280°).

Kinetics.—Reactions were followed photometrically with

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the kinetic technique reported[31] by measuring the appearance of the phenyl 2,4,6-trinitrophenyl sulphide (4) at 374 nm in benzene, at 372 nm in carbon tetrachloride, at 370 nm in dioxan, at 380 nm in *o*-dichlorobenzene, at 370 nm in acetone, at 380 nm in nitromethane, and at 368 nm in tetrahydrofuran. All rate determinations were generally performed with (1; $Ar^1 = Ar^2 = Ph$) in large excess (*ca.* 0·02M : 0·001M) over the picryl halide. Quantitative yields of (4) were obtained as indicated by the spectrophotometric data. Pseudo-first-order rate constants were evaluated graphically.[32] The pseudo-first-order rate coefficients were divided by the initial concentration of (1; $Ar^1 = Ar^2 = Ph$) to convert them into second-order rate coefficients.

The rate constants obeyed the Arrhenius equation and the activation parameters were evaluated by standard methods.[33]

We thank Professor J. O. Edwards for helpful comments and criticisms and the Italian Research Council (C.N.R.) for financial support.

[3/504 *Received, 9th March,* 1973]

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