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Preliminary communication

Sulphinate complex intermediates in the Peters reaction

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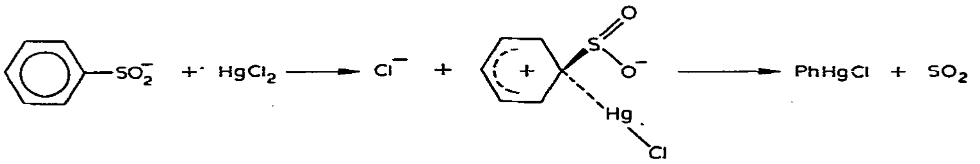
The observation that mercuric arenesulphinates[1,2] and arylmercuric arenesulphinates[3] yield diarylmercurials and sulphur dioxide on thermal decomposition, provides some support for the suggestion[3,4] that the Peters reaction[5,6],

$$RSO_2M + HgCl_2 \xrightarrow{H_2O/100^\circ} MCl + SO_2 + RHgCl \qquad (1)$$

(R = aryl; M = Na or H)

proceeds via intermediate formation of sulphinate complexes. Alternatively, it has been suggested[4] that reaction may proceed by direct electrophilic attack, *e.g.*



We now present evidence that chloro(arenesulphinato)mercury(II) complexes are intermediates in the Peters reaction, and discuss the structures of the complexes.

The complex, (p-$ClC_6H_4SO_2$)HgCl, was precipitated analytically pure (yield, ca. 45%) on reaction of sodium *p*-chlorobenzenesulphinate with mercuric chloride (mole ratio 1/2) in aqueous solution at ambient or lower temperature.

$$p\text{-}ClC_6H_4SO_2Na + HgCl_2 \longrightarrow (p\text{-}ClC_6H_4SO_2)HgCl\downarrow + NaCl$$

Use of a 1/1 mole ratio in the preparation gave a mixture of mercuric *p*-chlorobenzenesulphinate[2] and (p-$ClC_6H_4SO_2$)HgCl. From preparations at ca. 0° and at ca. 20°, (p-$ClC_6H_4SO_2$)HgCl was isolated in two different forms (designated A and B respectively), which have different X-ray powder photographs, but similar, though distinguishable, infrared spectra (Table 1). Powder photographs and far infrared spectra established that neither form is a mixture of mercuric chloride and mercuric *p*-chlorobenzenesulphinate.

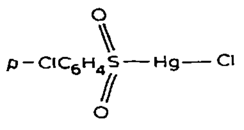
TABLE 1

SULPHUR-OXYGEN STRETCHING FREQUENCIES AND FAR INFRARED SPECTRA OF FORMS A AND B OF CHLORO(*p*-CHLOROBENZENESULPHINATO) MERCURY(II) [a]

	$\nu_{as}(SO_2)$ (cm^{-1})	$\nu_s(SO_2)$ (cm^{-1})	Infrared absorption (cm^{-1}) (650–250 cm^{-1})		Raman [b] (cm^{-1})
				ν(Hg–Cl)	ν(Hg–Cl)
A	1210, 1200vs(br)	1045vs(br)	630m 611s 551s 501m 461s 400w	339s(br)	339m
B	1195vs(br)	1041vs(br)	615s 551s 483w 461s	345s(br)	341m

[a] Compounds examined as Nujol mulls. [b] Solid samples examined.

The $\nu(SO_2)$ frequencies of A and B (Table 1) are indicative[3,4,7] of *S*-sulphinate coordination, and the ν(Hg–Cl) frequencies are in the range[8-10] for mercury complexes with digonal two coordination (*e.g.*, ν(Hg–Cl) of p-ClC_6H_4HgCl 330 cm^{-1})[8]. Accordingly, both forms are considered to have structures based on I, the different powder photographs possibly arising from different arrangements of the molecules of I in the solid state and different



(I)

weak interactions between neighbouring molecules. The coincidence between the infrared and Raman ν(Hg–Cl) frequencies of A and B (Table 1) rules out their formulation as weak adducts between mercuric chloride and mercuric *p*-chlorobenzenesulphinate, since this would give widely separated ν(Hg–Cl) frequencies in the infrared and Raman spectra (see *e.g.*, $(Et_4N)_2Hg_3Cl_8$, which has weakly bonded $HgCl_3^-$ and $HgCl_2$ units in the complex anion[11]).

Thermal decomposition of A and B under vacuum at 100–200° gave *p*-chlorophenylmercuric chloride in 40% yield* and near quantitative yields of sulphur dioxide. Decomposition

$$(p\text{-}ClC_6H_4SO_2)HgCl \longrightarrow SO_2 + p\text{-}ClC_6H_4HgCl$$

of A and B for 2 h in boiling water gave *p*-chlorophenylmercuric chloride in 35% yield*. Accordingly, chloro(*p*-chlorobenzenesulphinato)mercury(II) is probably an intermediate in the preparation of *p*-chlorophenylmercuric chloride** by the Peters reaction (1) in boiling water. Further confirmation was provided by the observation that (p-$ClC_6H_4SO_2$)HgCl (form B) and *p*-chlorophenylmercuric chloride were coprecipitated when boiling aqueous solutions of sodium *p*-chlorobenzenesulphinate and mercuric chloride were mixed.

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* p-ClC_6H_4HgCl was purified by crystallization from benzene/hexane or toluene/hexane and was characterized by analysis, melting point[12] and far infrared spectrum[8].

** Obtained in yields of 24% and 56% using mole ratios p-$ClC_6H_4SO_2Na/HgCl_2$ = 1/1 and 1/2, respectively.

The reaction of sodium benzenesulphinate with mercuric chloride (mole ratios, 1/1, 1/2, or 1/3) in aqueous solution at $\leqslant 20°$ gave a product with the stoichiometry $[(PhSO_2)HgCl]_2HgCl_2$, which was also isolated in different forms (powder photographs and far infrared spectra) from preparations at ca. 20° and ca. 0°. Both forms gave sulphur dioxide, phenylmercuric chloride, and mercuric chloride on being heated at 100–220° under vacuum, and gave phenylmercuric chloride on decomposition in boiling water, hence the species $[(PhSO_2)HgCl]_2HgCl_2$ is probably an intermediate in the synthesis of phenylmercuric chloride by the Peters reaction[5,6]. Reactions of further arenesulphinate ions with mercuric chloride are being studied.

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