SULPHUR DIOXIDE INSERTION REACTIONS IN PHENYLMERCURY CHELATES

S. K. PANDIT, SARADA GOPINATHAN and C. GOPINATHAN Inorganic Chemistry Division, National Chemical Laboratory, Poona 411008 (India) (Received October 16, 1978)

Summary

Phenylmercury chelates take up one molecule of sulphur dioxide from a medium of liquid sulphur dioxide to form mono insertion products. Phenylmercury chelates of salicylaldehyde, 8-hydroxyquinoline, benzoylphenyl hydroxylamine, substituted benzophenones and some Schiff bases were studied for the sulphur dioxide insertion reaction. IR studies show that the products are O-sulphinates, the insertion taking place between mercury and the phenyl group.

1. Introduction

The sulphur dioxide insertion reactions in transition [1] and nontransition [2, 3] metal-carbon σ bonds have attracted much attention. The insertion of sulphur dioxide into the M-C bonds (M = Li, Mg, Zn, Cd, Hg, Al, Si, Ge, Pb, Bi, Fe, Mn, W, Ni, Pd, Pt etc.) has been reported by various workers.

According to Kitching [4], the insertion of one molecule of sulphur dioxide into an M-C system by electrophilic attack is a general reaction:

 $RMR' + SO_2 \longrightarrow RMSO_2R'$

Since identical products are obtained from the above reaction and one between the organic metal chloride and sodium organic sulphinate

 $RMCl + NaSO_2R' \longrightarrow RMSO_2R' + NaCl$

the inference has been made that the products of sulphur dioxide insertions are O-sulphinates.

The behaviour of organomercury compounds towards sulphur dioxide was observed as early as 1870 by Otto [5] who reacted molten diphenylmercury with sulphur dioxide gas. More detailed work was initiated by Wojcicki [6] who studied the reaction of diethyl-, diphenyl- and dibenzylmercury with boiling liquid sulphur dioxide. Phenylmercury benzene sulphinate and p-tolylmercury p-toluene sulphinate were also prepared by reacting liquid sulphur dioxide at low temperatures with diphenylmercury and di-*p*-tolylmercury, respectively [7].

$$R_2Hg + SO_2 \longrightarrow RHgSO_2R$$

Only one molecule of sulphur dioxide was found to be inserted. When phenyl p-tolylmercury was subjected to sulphination, the product was phenylmercury p-toluene sulphinate. No insertion took place between sulphur dioxide and phenylmercury chloride, di-(penta-fluorophenyl)-mercury, phenyl(penta-fluorophenyl)-mercury or di-(penta-chlorophenyl)-mercury. Carey and Clark [8] recently reported the reaction between dimethylmercury and sulphur dioxide and isolated a dinuclear compound $(CH_3Hg)_2SO_2$. Products identical with the sulphur dioxide insertion compounds were obtained in some cases by redistribution reactions [9] such as

 $R_2Hg + Hg(SO_2R')_2 \longrightarrow 2 RHg(SO_2R')$

Although the sulphur dioxide insertion reactions in organomercury compounds have been studied in some detail, there is no mention of such reactions with organomercury chelates. Our studies reported here show that chelated phenylmercury compounds undergo insertion cleavage reactions when they are allowed to react with liquid sulphur dioxide at -20 °C. One molecule of sulphur dioxide was inserted between the phenyl group and the mercury atom.

 $PhHg(chelate) + SO_2 \longrightarrow PhSO_2Hg(chelate)$

2. Experimental

Experiments were carried out in dry nitrogen using an apparatus with standard ground glass joints. The apparatus was flame dried and cooled in nitrogen before use. Dried solvents were freshly distilled and were made oxygen-free by bubbling a stream of nitrogen through them before use.

2.1. Preparation of phenylmercury hydroxide

Phenylmercury hydroxide was prepared from phenylmercury acetate (33.63 g; 0.1 mol) and sodium hydroxide (4.4 g; 0.11 mol) as described by Bloodworth [10]. The yield was 26.5 g (90% of the theoretical yield). The fine white crystals melted at 234 °C; the reported melting point is 234 - 236 °C.

2.2. Preparation of salicylaldehydo phenylmercury

Phenylmercury hydroxide (2.95 g; 0.01 mol) and salicylaldehyde (1.34 g; 0.011 mol) were refluxed in benzene (50 ml) with a partial take-off condenser for 2 h. When the reaction was over, the solvent was removed under reduced pressure. The residue was extracted with fresh benzene (50 ml) and centrifuged to remove insoluble material. The compound was then crys-

230

tallized by concentration. The crystals were washed with hexane and dried in a vacuum at room temperature. The yellow solid weighed 3.46 g (85% of the theoretical yield). Analysis showed Hg 50.52%; $C_7H_5O_2HgC_6H_5$ requires Hg 50.31%. The molecular weight measured by vapour pressure osmometry in benzene was 405 (the calculated value is 399).

Other phenylmercury chelates were prepared in a similar way [11].

2.3. The insertion reaction

Sulphur dioxide gas from a cylinder, which had been dried using sulphuric acid, was condensed to a liquid on the sample (0.5 - 1 g) in a longnecked flask immersed in a mixture of ice and salt. Care was taken to prevent moisture entering the reaction flask. After 1 h, when about 10 ml liquid sulphur dioxide had collected over the sample, the flow rate of the gas was reduced. In several cases the reaction was accompanied by a rapid change in the colour and appearance of the compound. The mixture in the flask was shaken occasionally and was then allowed to remain in a slow stream of the gas for 2 h, after which the flask was taken out of the refrigerant and the liquid sulphur dioxide was allowed to evaporate. Finally the substance was kept under reduced pressure (0.5 mmHg) at room temperature for 1h. Samples were taken for analysis within 1 - 2 h of isolating the compound.

The sulphur dioxide insertion products of phenylmercury chelates were solids with sharp melting or decomposition temperatures and were insoluble in common solvents. They reacted quantitatively with aqueous iodine, a reaction which has been used by us for the volumetric estimation of the sulphur dioxide content of these compounds. The compounds prepared are listed in Table 1.

3. Results and discussion

The sulphur dioxide insertion products of chelated phenylmercury compounds are generally stable at room temperature. A few of them tended to decompose gradually in a day or two, but even these could be preserved indefinitely under liquid sulphur dioxide. The sulphur dioxide molecule appears to be held tenaciously by these insertion products at room temperature and is not released even under reduced pressure. However, on treatment with dilute hydrochloric acid, sulphur dioxide is evolved and phenylmercury chloride and the free ligand can be isolated from the products of decomposition.

Generally the insertion of sulphur dioxide into the M-C bond is accompanied by the formation of any one of the following five types of compounds [1].

Chelating ligand		Phenyl m	tercury	chelate	SO ₂ inse	tion produ	ıct		
	^P functional group	Colour	M.p.	^U functional group	Colour	M.p. or	^D functional	^v so ₂	
			0			dec. (d) temp. (°C)	dnoza	Asym - metric	Sym - metric
Salicylaldehyde	C=0 1667	Yellow	120	C=0 1640	White	260 (d)	C=0 1667	1035	815
8-Hydroxyquinoline	C=C, C=N 1587	Yellow	182	C=N 1575 C=C 1600	Yellow	250	C=N 1575 C=C 1600	1000	840
Benzoylphenyl hydroxylamine	C=0 1630 N-0 920	Yellow	112	C=0 1560 N-O 930, 945	White	205	C=0 1620 N-0 930	1025	825
o-Hydroxy-benzophenone	C=0 1640	Orange	183	C=0 1590	White	220	C=0 1640	1045	825
<i>p</i> -Methoxy-0-hydroxy- benzophenone	C=0 1620	Yellow	165	C=0 1560	White	210	C=0 1610	1045	805
Salicylidene aminophenol	C=N 1630	Brown	150	C=N 1620	Brown	06	C=N 1650	1050	825
Salicylaldazine	C=N 1630 N-N 905	Yellow	180	C=N 1630 N-N 910, 920	White	250	C=N 1630 N-N 920	1045	825
Sulphur dioxide gas		:						1360	1151

232

Properties of phenylmercury chelates and their SO_2 insertion products

TABLE 1



IR techniques have been employed to identify the various types of insertion compound. The S-sulphinates exhibit the (S–O) stretching frequencies ν_{asym} (S–O) and ν_{sym} (S–O) in the ranges 1250 - 1100 and 1100 - 1050 cm⁻¹. The structures (2), (3) and (4) show the above absorption bands at 1100 - 1050 and 1000 - 800 cm⁻¹ or lower. The O-alkyl S-sulphoxylates are rarely produced in the common insertion reactions. In the spectrum of the structure bridged through both oxygen atoms, the (S–O) frequency is observed in the range 1030 - 900 cm⁻¹. In another bridged structure (5) involving one sulphur and one oxygen, the (S–O) stretching bands are seen at 1200 and 950 cm⁻¹.

Any proposed structure for the sulphur dioxide insertion products of phenylmercury chelates should clarify the following points: (1) whether sulphur dioxide enters between mercury and the phenyl group or between mercury and the chelate; (2) whether the compounds so obtained are O-sulphinates (Hg-O-S) or S-sulphinates (Hg-S-R); and (3) whether there has been a change in the nature of the S-O bonds of sulphur dioxide in these compounds.

A considerable change in the sulphur dioxide IR spectra is to be expected in these compounds and such a change has indeed been observed. The original sulphur dioxide absorption bands are absent from the IR spectra of these insertion compounds; instead, well-defined new peaks are observed in the regions 1050 - 995 and 840 - 810 cm⁻¹ (Table 1). In gaseous sulphur dioxide these bands are observed at 1360 and 1151 cm⁻¹. The downward shift of the bands of sulphur dioxide in these complexes from those of gaseous sulphur dioxide may be attributed to the lengthening of the S-O bond owing to the insertion reaction. The observed values of the new peaks

are consistent with the values reported in the literature for other metal Osulphinates [4, 6]. There are only two possible positions in which sulphur dioxide can be inserted in the phenylmercury chelate molecule. These are: (a) between mercury and the phenyl group; and (b) between mercury and the chelating ligand. To find out the site of sulphur dioxide insertion in the above compounds, the spectra of the sulphur dioxide insertion products were compared with the spectra of the parent phenylmercury chelates. In some cases the coordination ligand frequencies were little affected by the insertion of sulphur dioxide; in other cases they were affected owing to weakening of coordination (Table 1). The former phenomenon suggests that the insertion has taken place in the phenyl-mercury bond. However, in cases where the IR absorption values of the chelates are affected by the insertion reaction, the inference is that the influence of sulphur dioxide insertion at a nearby site was sufficient to weaken or break the coordination. Moreover, insertion between mercury and the chelating ligand would give rise to a sulphite structure and organic sulphites are known to absorb at 1200 cm^{-1} .

The phenylmercury chelate with sulphur dioxide inserted gave, when decomposed with warm dilute hydrochloric acid, phenylmercury chloride, sulphur dioxide and the free chelating ligand. This behaviour has been confirmed by observations made in the cases of mercury and bismuth benzene sulphinates [7, 12]. Mercury benzene sulphinate decomposed when heated in a vacuum, giving sulphur dioxide and a high yield of diphenylmercury. Felder and Deacon have used this method to prepare diarylmercury compounds [7]. An interesting reaction reported by Deacon and Cookson is the formation of diarylmercury from mercury acetate and sodium arylsulphinate in water [10].

$$\begin{array}{l} \text{Hg(OAc)}_2 + 2\text{NaO}_2\text{SR} \xrightarrow{\text{water, 80 °C}} \text{RHg(SO}_2\text{R}) + 2\text{NaOAc} + \text{SO}_2 \\ \\ \text{Hg(OAc)}_2 + 2\text{NaO}_2\text{SR} \xrightarrow{\text{boiling water}} \text{R}_2\text{Hg} + 2\text{NaOAc} + 2\text{SO}_2 \end{array}$$

The formation of triphenylbismuth from bismuth tribenzene sulphinate in boiling water has been reported by Deacon and Fallow [13].

$$Bi(O_2SR)_3 \longrightarrow BiR_3 + 3SO_2$$

Similar reactions should be possible in the case of the sulphur dioxide insertion products of chelated phenylmercury compounds when they are treated with dilute hydrochloric acid. In this respect these compounds resemble similar products obtained from organotin chelates [14].

The IR spectra suggest that the sulphur dioxide insertion products of phenylmercury chelates are O-sulphinates and that the sulphur dioxide insertion is between mercury and the phenyl group rather than between mercury and the chelating ligand. For a monomeric chelate (*e.g.* the 8hydroxyquinolino complex) the following structure can be suggested:



PHENYL MERCURY QUINOLINATE

INTERMEDIATE

SO, - INSERTION PRODUCT

References

- 1 A. Wojcicki, Adv. Organomet. Chem., 12 (1974) 31.
- 2 W. Kitching and C. W. Fong, J. Organomet. Chem., 59 (1973) 213.
- 3 W. Kitching, B. Hegarty, S. Winstein and W. G. Young, J. Organomet. Chem., 20 (1969) 253.
- 4 W. Kitching and C. W. Fong, Organomet. Chem. Rev., Sect. A, 5 (1970) 281.
- 5 R. J. Otto, J. Prakt. Chem., 1 (1870) 179.
- 6 A. Wojcicki, P. J. Pollick and J. P. Bibler, J. Organomet. Chem., 16 (1969) 201.
- 7 G. B. Deacon and P. W. Felder, Aust. J. Chem., 22 (1969) 549.
- 8 N. A. D. Carey and H. C. Clark, Can. J. Chem., 46 (1968) 649.
- 9 G. B. Deacon and P. W. Felder, J. Am. Chem. Soc., 90 (1968) 493, 6895.
- 10 A. J. Bloodworth, J. Organomet. Chem., 23 (1970) 27.
- 11 S. K. Pandit, Sarada Gopinathan and C. Gopinathan, J. Less-Common Met., 65 (1979) 191
- 12 P. G. Cookson and G. B. Deacon, Aust. J. Chem., 24 (1971) 1599.
- 13 G. B. Deacon and G. D. Fallow, Aust. J. Chem., 25 (1972) 2107.
- 14 S. Gopinathan, C. Gopinathan, C. I. Jose and J. Gupta, Indian J. Chem., 13 (1975) 78.