

Interaction of Sulphuryl Chloride with Tertiary Amines

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Sulphuryl chloride reacts with pyridine, β - and γ -picolines, quinoline, isoquinoline and piperidine forming addition compounds having 1 : 2 stoichiometry. Infrared spectra of the adducts reveal the coordination of the tertiary amine through its nitrogen atom to the sulphur atom of sulphuryl chloride.

In earlier communications¹⁻⁴ concerning the interaction of tertiary amines with a variety of oxyhalides, it has been established that bases act as donors to the central atom of oxyhalide molecule. In common with other second row elements, sulphur has six orbitals available for bond formation and thus a maximum of six bonds can be formed by it. Work on sulphuryl chloride as a polar solvent⁵ has indicated that solutions of acceptors or donors are inonic in nature. An adduct of pyridine with sulphuryl chloride is also known⁶. In the present study sulphuryl chloride has been shown to react with tertiary amines forming 1 : 2 adducts with them. The infrared spectra of these adducts have been interpreted to indicate the mode of interaction of the reacting species.

EXPERIMENTAL

Solvents and tertiary amines were purified as already reported^{1,2}. Sulphuryl chloride was refluxed over mercury and then purified by repeated distillation in an all glass apparatus. All precautions necessary to avoid the contact of materials with moisture or damp atmosphere were taken.

Preparation of complexes: Pyridine-sulphuryl chloride: Cold solution of pyridine (8 g., 0.1 mole) in 15 ml. of dry carbon tetrachloride was added to the ice cold solution of sulphuryl chloride (13.5 g., 0.1 mole) in carbon tetrachloride (25 ml). The precipitate formed on their mixing was filtered, repeatedly washed with carbon tetrachloride and petroleum ether to free it from unreacted components and finally dried under vacuum. The variation in the molar ratio of the reactants and change of solvent had no effect on the composition of the compound. Complexes of sulphuryl chloride with other bases were prepared by a similar procedure.

Chlorine content of the complexes was estimated by Volhard's method⁷ and nitrogen was estimated by micro-analytical techniques. The solid complexes were examined for their I.R. spectra as thin paste in paraffin oil while liquid samples were examined as thin films in NaCl plates using Perkin Elmer-337 infrared spectrophotometer. Conductance of the complexes was measured in nitrobenzene solution.

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RESULTS AND DISCUSSION

Sulphuryl chloride and tertiary bases react to form addition compounds of the composition $\text{SO}_2\text{Cl}_2 \cdot 2\text{B}$ where B is a base (Table I). There is no effect of change in relative quantities of the reactants on the stoichiometry of the complexes. The complexes of β -picoline and quinoline are semi-solids while all others are solids. The complexes have been found to be insoluble in most of the solvents except in nitrobenzene in which they have a slight solubility. Molar conductance of millimolar solutions of these complexes in nitrobenzene has been determined and the values of $3.4\text{--}9.3 \text{ cm}^2 \text{ ohm}^{-1} \text{ mole}^{-1}$ indicate that these complexes are nearly non-ionic in nitrobenzene⁸.

TABLE I

State, melting points, molar conductance in nitrobenzene and analyses of 1 : 2-complexes of SO_2Cl_2 with tertiary bases.

Base	Colour and state	m.p. °C	Molar conductance* ($\text{cm}^2\text{-ohm}^{-1}$ mole^{-1})	Found %		Required %	
				X	N	X	N
Pyridine	Yellow semi solid	—	3.4	24.4	9.3	24.2	9.55
β -Picoline	Yellow	—	1.28	21.5	7.8	21.8	8.70
γ -Picoline	Yellow solid	51	9.3	20.8	9.0	21.8	8.70
Quinoline	Deep yellow semi-solid	—	2.3	18.2	7.3	18.1	7.42
Isoquinoline	White solid	58	2.5	17.9	7.2	18.1	7.42
Piperidine	„	86	4.6	23.1	6.5	28.4	6.45

* $10^{-3}M$ solution in nitrobenzene.

Infrared spectra of the complexes have been examined and the major frequencies of the bases which have undergone significant perturbation on coordination are recorded in Table II. The changes in the frequencies of the bands are due to the coordination of tertiary amines through their nitrogen atoms. For example, the bands of pyridine at 3055 cm^{-1} for $\nu(\text{C-H})$; and at $1583, 1572, 1483, 1439 \text{ cm}^{-1}$ for $[\nu(\text{C} \equiv \text{C}) + \nu(\text{C} \equiv \text{N})]$ shift to 2800 and $1630, 1600, 1530, 1480 \text{ cm}^{-1}$ respectively in its complex with sulphuryl chloride. Similar trend in the shift of these bands of pyridine has been observed on coordination with metal halides⁹ and oxyhalides¹⁻⁴. The ring vibrations of pyridine (Table II) also show a marked shift to the higher spectral region of coordination which is in fair agreement with the results reported by Gill *et al.*¹⁰. The bands due to the stretching frequency of ($\text{S} = \text{O}$) in sulphuryl chloride¹¹ are at 1400 and 1100 cm^{-1} . The spectrum of pyridine complex shows a lowering of these bands which is in line with the changes which occur in the spectra of adducts of acetic anhydride with tertiary amines¹². Since no Lewis acid is used for coordination with SO_2Cl_2 , this marked shift indicates the polarization of $\text{S} = \text{O}$ bond and subsequent

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TABLE II

Significant infrared bands (cm⁻¹) of tertiary amines and their complexes with sulphuryl chloride

Pyridine (Py)	Assignment	SO ₂ Cl ₂ .2Py	β -Picoline	(β)Assign.	SO ₂ Cl ₂ .2 β
3005 s	$\nu(\text{C—H})$	2950 bs	2975 s	C—H	2930 s
1583 s } 1572 s } 1483 s } 1439 s }	$\nu(\text{C} \cdots \text{C})$ + $\nu(\text{C} \cdots \text{N})$	1630 s } 1605 s } 1535 s } 1480 s }	1615 s } 1587 s } 1492 s }	$\nu(\text{C} \cdots \text{C})$ + $\nu(\text{C} \cdots \text{N})$	1535 s } 1605 s } 1550 s }
600 s } 405 s }	Ring vibrations	625 m 430 m	542 m 435 m	Ring vib.	565 m 450 w
— — — —	S = O* N \rightarrow S† S—Cl*	1390 s } 1135 s } 830 s 410 s	— — — —	S = O* N \rightarrow S* S—Cl*	1320 s } 1150 m } 790–810 s 405 w
γ -Picoline (γ)	Assignment	SO ₂ .Cl ₂ .2 γ	Quinoline (Q)	Assign.	SO ₂ Cl ₂ .2Q
2955 s	C—H	2900 s	3020 s	$\nu(\text{C—H})$	2920 s
1595 s } 1556 s } 1490 s }	$\nu(\text{C} \cdots \text{C})$ + $\nu(\text{C} \cdots \text{N})$	1630 s 1600 s 1520 m	1630 s } 1580 m } 1505 s }	$\nu(\text{C} \cdots \text{C})$ + $\nu(\text{C} \cdots \text{N})$	1650 s 1600 s 1555 s
513 s } 485 s }	Ring vibrations	530 m 495 m	— —	— —	— —
— — — —	S = O* N \rightarrow S† S—Cl*	1310 s } 1440 s } 840 s 405 m	— — — —	S = O* N \rightarrow S* S—Cl*	1380 s } 1130 m } 815 m 410 m
Piperidine (P)	Assignment	SO ₂ Cl ₂ .2P			
3290 s	$\nu(\text{N—H})$	3160 bs			
2925 s } 2840 m } 2755 m } 2722 m }	$\nu(\text{C—H})$	— — 2780 m 2750 m			
1470 s	H—C—H—bending	1460 s			
1330 s } 1320 s } 1280 s } 1260 s }	H—C—C—wagg	1390 s 1350 s 1305 m 1280 s			
1120 s } 940 s } 860 s }	Ring Vib.	1165 s 1030, s, 960 950			
822 s	H—N—C	865			
— — —	S = O† N \rightarrow S*	1370 s } 1080 s } 840 m			

† $\nu(\text{S} = \text{O})$ of SO₂Cl₂ are at 1415 s, 1180 s and $\nu(\text{S—Cl})$ at 410 cm⁻¹.

* New bands in the complexes.

strong bonding between the nitrogen atom of the base and the sulphur atom of sulphuryl chloride. Since the infrared spectrum of the complex of sulphuryl chloride with pyridine shows the S-Cl stretching band which is only slightly displaced as compared to that of pure sulphuryl chloride, the structure of complexes as $(\text{SO}_2\text{Cl}\cdot 2\text{Py})^+\cdot\text{Cl}^-$ or $(\text{SO}_2\cdot 2\text{Py})^{+2}\cdot 2\text{Cl}^-$ is not supported.

The spectral data for the complexes of β - and γ -picolines, quinoline and isoquinoline (Table II) reveal that the difference in the spectra of pure bases and their complexes with sulphuryl chloride is due to the coordination of former to the latter. The changes are of similar type as already discussed for analogous pyridine complex and the structure of the adducts, therefore, appears to be non-ionic.

The spectral bands of piperidine are displaced on coordination⁹. The direction and extent of displacement of important bands of piperidine in its complex with sulphuryl chloride is nearly the same as already reported for the complexes of piperidine with metal halides⁴ and other acceptors^{2-4,9}. For example, the N-H stretching frequency of piperidine at 3290 cm^{-1} (3350 cm^{-1} in CHCl_3) shifts to the lower spectral region by 130 cm^{-1} in its adduct with sulphuryl chloride. This is feasible if nitrogen atom of piperidine coordinates to sulphuryl chloride. The $\nu(\text{C-H})$, the H-C-C wagging, the amine ring vibrations and H-N-C deformation are the other significant bands of piperidine which shift to higher spectral region in its complex with sulphuryl chloride and other acceptors^{2-4,9}. The S=O stretching frequencies have been observed in the spectrum of this complex also. The lowering of S=O stretching frequency is larger as compared to that observed in the spectra of other complexes which in turn suggests the strongest donor features of piperidine towards sulphuryl chloride.

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