The Structure of the Cations from 2- and 4-Pyridones and Related Pyridines (1,2).

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An infrared spectral investigation of 2- and 4-pyridone hexachloroantimonates and hexachlorostannates is reported. Protonation of these pyridones occurs on oxygen to form the 2- and 4-hydroxypyridinium ions, as witnessed by the presence of both OH and NH stretching bands. Aromatic ring and skeletal frequencies in these cations correlated very well with those found in other 2- and 4-substituted pyridinium hexachloroantimonates included in this study.

Introduction.

The fine structure of many potentially tautomeric heteroaromatic systems has received the attention of a number of investigators. In this category fall 2- and 4-pyridones, **1** and **2** whose unsaturated lactam and keto-enamine forms **1a** and **2a**, are stabilized to a large degree by dipolar structures, **1b** and **2b**, respectively. The reported appearance of an OH stretching band in the infrared (IR) spectra of **1** or **2** in the solid state or in relatively concentrated solutions suggests the presence of the tautomeric 2- and 4-pyridinols, **1c** and **2c**, respectively, but is generally agreed that the resonance-stabilized carbonyl forms predominate in the unsubstituted species (3,7-12). The mode of protonation of 2- and 4-pyridone

became controversial when Spinner originally concluded that protonation took place on the ring nitrogen atom leading to cations **3** and **4** (12). Spinner later revised these structures and agreed that they are correctly represented by **5** and **6**, respectively (13,14,26,27).

This project set out to compare the IR spectra of a number of salts of 2- and 4-pyridones with those of closely related 2- and 4-substituted pyridinium salts in order to obtain additional evidence for structures **5** and **6**. Pyridinium hexachloroantimonates and hexachlorostannates were found to handle easier experimentally and, in general, their IR spectra were sharper than the corresponding hydrohalides, particularly in the region of associated OH and NH stretching bands. The bulky and less nucleophilic complex anions were less susceptible to hydrogen-bonding compared to the halide anions and this resulted in clearer OH and NH bands in the solid-state spectra of the hexachloroantimonates and hexachlorostannates. These salts crystallized readily from a solution of the pyridine or pyridone in concentrated hydrochloric acid containing either antimony pentachloride or stannic chloride and had relatively sharp melting points. Although full spectra of the salts are recorded (1), a limited number of bands pertinent to the arguments are listed in Table I-III.

Results and Discussion.

2- And 4-Pyridone and Their Cations.

Until recently, an analysis of the 1600-1700 cm^{-1} region of the solution spectra of 2-pyridone was complicated by the presence of di and polymeric species in solution, besides solvent shifts due to hydrogen-bonding effects. Isotopic labelling aided in assigning the high frequency bands in that region to C=O stretching motions, admittedly coupled with C=N (ring) stretching and N–H in-plane bending modes (8,9). Protonation of 2-pyridone by conversion to the hexachloroantimonate or stannate
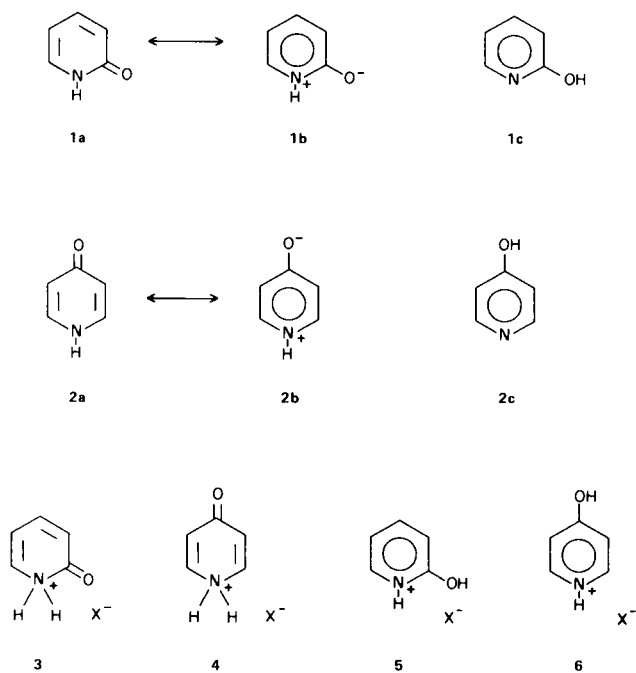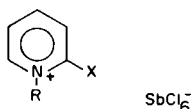
TABLE I

Partial Assignments of Infrared Absorption Bands (cm^{-1}) in 2-Substituted
Pyridinium Hexachloroantimonates (From Nujol and Fluorolube Mulls).

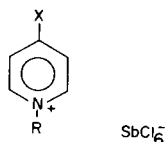| R	X	OH Stretch	NH Stretch	C–C and C–N Ring Modes	C–H in-plane bend	C–H out-of-plane bend
H	OCH₃	---	3275 m 3190 m	1638 s	1167 s	770 s
H	Cl	---	3236 m 3167 w	1611 m	1168 w	745 s
H	OH	3587 m-b	3300 s 3240 sh	1647 sh 1631 vs	1164 m	769 s
H	OH (a)	3548 m-b	3254 sh 3204 m	1634 vs	1164 m	786 vs
CH₃	OH	3625 m-b	----	1645 s	1165 m	771 s
CH₃	OH (a)	3522 m-b	----	1643 s	1164 m	782 s
CH₃	OCH₃	---	----	1641 s	1167 s	773 vs
OCH₃	OCH₃	---	----	1624 s	1168 m	775 s
OH	OCH₃	3605 m	----	1631 s	1165 m	769 s

(a) For the corresponding hexachlorostannate.

provide salts whose IR spectra (Table I) are compatible with the cation **5**. Such an assignment rests principally on the observation in these two products of an OH stretching band around 3400-3600 cm^{-1}. Such bands were visible not only in these two salts but also in the hexachloroantimonates of 1-methyl-2-pyridone, 4-pyridone, 1-methyl-4-pyridone and those from a number of pyridine 1-oxides (due to N^+–OH) and could hardly be attributed to any other vibration. The relatively high frequency mode in the OH, NH stretching frequency region suggests this absorption to be due to a free OH stretching mode, the bonded OH and NH vibrations being in an envelope of broad bands from 2400 to 3000 cm^{-1}. The (relatively) free NH stretching modes were clearly discernible at lower frequencies in all of the pyridinium hexachloroantimonates studied in which such a group should logically be present. It is absent in N-methyl and N-methoxy pyridinium salts.

Spinner and White have questioned our assignment of the OH stretching band at 3587 cm^{-1} for crystalline 2-pyridone hexachloroantimonate and have suggested that it was due to water attached to or incorporated in the

salt. They report that drying at 110° (0.05 mm) for 1 hour could dehydrate this salt with subsequent dramatic changes in the IR spectrum. We are fully aware of this phenomenon. As a matter of fact, this salt (and some others) had to be prepared and recrystallized from concentrated (and not mere dilute) hydrochloric acid. Exposure of this salt to dilute hydrochloric acid or water, or heat, produced a yellow product which could not be characterized with any sense of certainty. As a matter of fact, such a yellow product of indefinite melting point, variable elemental analysis and unpredictable IR spectrum was produced when 2-pyridone was exposed to antimony pentachloride in chloroform in the presence or absence of hydrogen chloride gas. Even when mulling 2-pyridone hexachloroantimonate in air (rather than in a dry-box) yellowing of this previously colorless material was noticed. At the completion of this work, the paper by Cook (14) appeared on the IR spectra of complexes of 2-pyridone and it became evident that the 2-pyridone antimony pentachloride complex possessed quite a different IR spectrum from that of the salt. On this basis, we feel that we are reporting on the IR spectrum of the 2-hydroxypyridinium

TABLE II

Partial Assignments of Infrared Absorption Bands (cm⁻¹) in 4-Substituted
Pyridinium Hexachloroantimonates (From Nujol or Fluorolube Mulls).

X
⬡
N⁺
R   SbCl₆⁻

R	X	OH Stretch	NH Stretch	C–C and C–N Ring Modes	C–H in-plane bend	C–H out-of-plane bend
H	OCH₃	----	3310 s	1645 s	1195 s	739 vs
H	Cl	----	3297 m	1636 m	1199 w	743 vs
H	OH	3624 sh 3428 m	3310 s	1652 s	1192 s	743 s
H	OH (a)	3404 m	3224 m	1643 s	1192 m	803 s
CH₃	OH	3423 m	----	1649 s	1195 s	850 s
CH₃	OH (a)	3569 w 3500 w	3284 w	1649 s	1189 m	852 s
CH₃	OCH₃		----	1651 s	1206 m	845 s
OCH₃	OCH₃	----	----	1631 s	1189 s	844 vs
OH	OCH₃	3572 w	----	1635 s	1198 m	847 s

(a) For the corresponding hexachlorostannate.

TABLE III

C–H Out-of-Plane Bending Frequencies (cm⁻¹)
of Pyridone Hexachlorostannates

⬡—X
N⁺
R   SnCl₆⁻
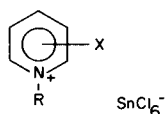
R	X	ν	$\Delta\nu$ (a)
H	4-OH	803 s	----
D	4-OD	861 vs	58
CH₃	4-OH	852 s	49
H	2-OH	786 vs	----
D	2-OD	792 vs	6
CH₃	2-OH	782 s	-4

(a) $\Delta\nu$ is the frequency difference between the pyridinium cation
(R = H) and its deuterio- and methyl- analogs, respectively.

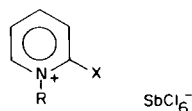cation formed by the O-protonation of 2-pyridone by
hexachloroantimonic acid.

One manifestation of this result is the fact that the
high-frequency band at about 1640 cm⁻¹ in the salts of
2-pyridone must be a ring mode and cannot be a vibration
involving a C=O stretching vibration. Such an assignment
is corroborated by the fact that other 2-substituted pyri-
dines (Table I) possess a strong band in the 1610-1650
cm⁻¹ region. On this basis, the data in Tables I and II
suggest that 2- and 4-pyridones protonate on oxygen to
form the 2- and 4-hydroxypyridinium cations, respectively.
It should be mentioned that O-protonation of several
4-pyridones was recognized by Cook (15).

In- and Out-of-Plane C–H Bending Frequencies.

One C–H in-plane mode is remarkably consistent for
2-substituted pyridinium hexachloroantimonates listed in
Table I, and is observed at 1166 ± 2 cm⁻¹. A C–H out-
of-plane mode occurs at about 770 cm⁻¹ in these 2-sub-
stituted pyridinium ions, with the exception of the 2-
chloro derivative where it is found at 745 cm⁻¹ (Tables I

TABLE IV

Elemental Analyses and Physical Constants of 2-Pyridinium Hexachloroantimonates

R	X	M.p., °C	Molecular Formula		Analyses C, %	H, %	N, %
H	OCH$_3$	252-254(a)	C$_6$H$_8$Cl$_6$NOSb	Calcd.	16.21	1.81	3.15
				Found	16.01	1.90	2.98
H	Cl	233-236	C$_5$H$_5$Cl$_7$NSb	Calcd.	13.37	1.12	3.12
				Found	13.56	1.35	2.87
H	OH	126-129(a)	C$_5$H$_6$Cl$_6$NOSb	Calcd.	13.96	1.41	3.27
				Found	14.05	1.55	3.07
CH$_3$	OH	195-200(b)	C$_6$H$_8$Cl$_6$NOSb	Calcd.	16.21	1.81	3.15
				Found	16.40	2.13	2.98
CH$_3$	OCH3	249-250(c)	C$_7$H$_{10}$Cl$_6$NOSb	Calcd.	18.33	2.20	3.05
				Found	18.34	2.03	2.99
OCH$_3$	OCH$_3$	244-245(c)	C$_7$H$_{10}$Cl$_6$NO$_2$Sb	Calcd.	17.71	2.12	2.95
				Found	17.40	2.15	3.03
OH	OCH3	162-165	C$_6$H$_8$Cl$_6$NO$_2$Sb	Calcd.	15.64	1.75	3.04
				Found	15.65	2.04	3.01

(a) Prepared by Spinner (Ref. 13) but no m.p. is recorded. (b) Cook (Ref. 14) reports m.p. 186-189°. (c) This salt was recrystallized from ethanol:acetone, 9:1.

and III). In contrast, in 4-substituted pyridinium hexachloroantimonates one C–H in-plane mode appears at 1189 ± 9 cm^{-1} while the out-of-plane bending vibration varied considerably. This was particularly noticeable when the group on the quaternized ring nitrogen was changed from H to OH, CH$_3$, or OCH$_3$ (Table II and III), changing by some 50-60 cm^{-1}.

A reasonable explanation for this behavior is advanced by the following arguments. For correlation purposes, infrared vibrations of pyridines and pyridinium ions have been compared with substituted benzenes (16,17). For example, the unsubstituted pyridinium cation may be considered as a monosubstituted benzene, a 2-substituted cation as an ortho-disubstituted benzene, etc. These analogies hold only if the group, $\geq$N$^+$–R, behaves as a substituent on the aromatic ring and its vibrations do not couple significantly with those of the ring C–H modes. With 2-substituted pyridinium cations, it seems that these modes do not couple and it is reasonable to consider these salts analogs of ortho-disubstituted benzenes. In 4-substituted pyridinium cations, if the substituent on nitrogen is

a proton, then the N–H vibration couples with the C–H modes and the out-of-plane mode exhibits behavior expected of mono-substituted benzenes. However, if the proton is replaced by a methyl, methoxyl or hydroxyl group, or a deuteron, then interaction with the ring is disrupted and the cations behave as para-disubstituted benzenes.

EXPERIMENTAL

All melting and boiling points are uncorrected. Analyses for C, H and Cl were performed either by Dr. K. Eder, Geneva, Switzerland or Micro-Tech Laboratories, Skokie, Illinois. Nitrogen analyses were obtained by means of a Coleman Nitrogen Analyzer, Model 29. Infrared spectra were obtained on a Beckman IR-4 spectrophotometer (sodium chloride prism) and were calibrated by means of pertinent bands from the polystyrene spectrum. Some spectra were also recorded using a Perkin-Elmer 337 instrument. Spectra of solids were obtained as Nujol and Fluorolube mulls, those in solution in chloroform. Extremely hygroscopic samples were handled in the dry-box; they were recrystallized, filtered and transferred to a vacuum desiccator in the dry-box, and then also mulled in the dry atmosphere just prior to recording their spectra. The intensity of the IR bands are according to the following scale (in percent absorption): Less than 10, very weak

TABLE V

Elemental Analyses and Physical Constants of 4-Pyridinium Hexachloroantimonates
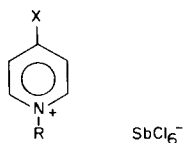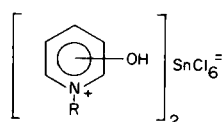

R	X	M.p., °C	Molecular Formula		Analyses		
---	---	---	---	---	C, %	H, %	N, %
H	OCH$_3$	135-138	C$_6$H$_8$Cl$_6$NOSb	Calcd.	16.21	1.81	3.15
				Found	16.26	1.94	3.23
H	Cl	238-240	C$_5$H$_5$Cl$_7$NSb	Calcd.	13.37	1.12	3.12
				Found	13.48	1.31	2.94
H	OH	169-175	C$_5$H$_6$Cl$_6$NOSb	Calcd.	13.96	1.41	3.27
				Found	13.94	1.69	3.08
CH$_3$	OH	155-159	C$_6$H$_8$Cl$_6$NOSb	Calcd.	16.21	1.81	3.15
				Found	16.34	2.10	3.08
CH$_3$	OCH$_3$	171-174(a)	C$_7$H$_{10}$Cl$_6$NOSb	Calcd.	18.33	2.20	3.05
				Found	18.42	2.41	2.92
OCH$_3$	OCH$_3$	230-232	C$_7$H$_{10}$Cl$_6$NO$_2$Sb	Calcd.	17.71	2.12	2.95
				Found	17.91	1.93	3.04
OH	OCH$_3$	243-246	C$_6$H$_8$Cl$_6$NO$_2$Sb	Calcd.	15.64	1.75	3.04
				Found	15.79	1.94	3.07

(a) Recrystallized from ethanol-acetone, 9:1.

TABLE VI

Elemental Analyses and Physical Constants of Pyridone Hexachlorostannates

Hexachlorostannate of	M.p., °C	Molecular Formula		Analyses		
---	---	---	---	C, %	H, %	N, %
2-Pyridone	100-110	C$_{10}$H$_{12}$Cl$_6$N$_2$O$_2$Sn	Calcd.	22.93	2.31	5.35
			Found	23.20	2.41	5.59
1-Methyl-2-pyridone	250-252 (a)	C$_{12}$H$_{16}$Cl$_6$N$_2$O$_2$Sn	Calcd.	26.12	2.92	5.00
			Found	26.07	3.13	4.74
4-Pyridone	247-249	C$_{10}$H$_{12}$Cl$_6$N$_2$O$_2$Sn	Calcd.	22.93	2.31	5.35
			Found	23.28	2.34	5.10
1-Methyl-4-pyridone	130-135	C$_{12}$H$_{16}$Cl$_6$N$_2$O$_2$Sn	Calcd.	26.12	2.92	5.00
			Found	25.82	3.28	4.68

(a) Ref. 14 reported m.p. 167-169°, but gave no elemental analysis.

(vw); 10-20, weak (w); 20-80, medium (m); 80-90, strong (s); above 90, very strong (vs). The terms shoulder (sh) and broad (b) are also used to describe the shape of the bands.

Starting Materials.

Commercial samples were distilled or recrystallized to constant m.p. 2- And 4-chloropyridine, 2-methoxypyridine, 2-pyridone, 1-methyl-2-pyridone and 4-nitropyridine 1-oxide were purchased from Aldrich Chemical Company, 4-pyridone from Winthrop Laboratories. Pyridine 1-oxide was kindly donated by Reilly Chemical Company. 2-Chloropyridine 1-oxide was prepared by the oxidation of 2-chloropyridine (18) and was converted to 2-methoxypyridine 1-oxide (20,21). Reduction of the N-oxide with iron powder and acetic acid yielded 2-methoxypyridine. Antimony pentachloride was purchased from Baker Chemicals (Reagent Grade).

1-Methyl-4-pyridone.

The synthesis followed the one for the conversion of 2-chloropyridine to 1-methyl-2-pyridone (22). A solution of 4-chloropyridine (11.4 g., 0.1 mole) in benzene (10 ml.) was added to an ice-cold solution of methyl sulfate in benzene (15.5 g., 0.125 mole in 24 ml.). (Note: Failure to cool one or both of these benzene solutions prior to mixing could result in a violent reaction). After 1 hour, a yellow precipitate (14.8 g.) was collected m.p. 105-108° (sealed tube) [lit. m.p. (23) for 1-methyl-4-chloropyridinium methosulfate is 93°]. Another crop (7.7 g.) was obtained by allowing the mother liquor to stand at room temperature. The total yield, 22.5 g., represents a 94% conversion.

The salt (22.5 g.) was added rapidly to cold 20% sodium hydroxide solution (50 ml.) and the resultant red solution warmed on the steam bath for 5 minutes. On cooling and adjusting the pH to 4 with acetic acid, the solution was evaporated in vacuo. Addition of chloroform and methanol (1:1) precipitated salts and the filtrate was concentrated once more. This process was repeated with chloroform-acetone (1:1) and the resultant organic layer distilled. 1-Methyl-4-pyridone was obtained as thick oil, b.p. 178° (4 mm) [lit. b.p. (24) 198° (5 mm)] and solidified to a hydroscopic solid, m.p. 97-99° (sealed tube) [lit. m.p. (25) is 92°].

Preparation of Hexachloroantimonates.

A solution of the base (0.01 mole) in concentrated hydrochloric acid (30-35 ml.) was treated with antimony pentachloride (1.5 ml., 0.012 mole). The salts were isolated usually in 90-100% yield. Their constants and analyses are recorded in Table IV-VI. Unless specified otherwise, they were recrystallized from hot concentrated hydrochloric acid. The salts were dried in vacuo at room temperature over phosphorus pentoxide.

The preparation of 4-hydroxypyridinium hexachloroantimonate differed from the general procedure: A solution of chloroantimonic acid was prepared by dissolving antimony pentachloride (0.75 ml., 0.066 mole) in chloroform (25 ml.) and saturating the solution with dry hydrogen chloride gas. 4-Pyridone (0.48 g., 0.0005 mole) was dissolved in boiling chloroform (50 ml.) and the saturated solution was filtered hot. On mixing the two chloroform solutions, cooling, and scratching, the salt was obtained. It was filtered onto a sintered glass funnel in a dry-box, and then transferred to a vacuum desiccator, with concentrated sulfuric acid and sodium hydroxide as desiccants. This salt was extremely hydroscopic and had to be mulled in the dry-box.

Hexachloroantimonates from N-oxides were prepared by the general method as outlined above. N-Methyl- and N-methoxypyridinium salts were made by first quaternizing the base, followed by precipitation of the pyridinium ion as the hexachloroanti-

monate. Two typical examples are described.

1-Methyl-2-methoxypyridinium Hexachloroantimonate.

Methyl sulfate (2.75 g., 0.022 mole) was added to 2-methoxypyridine (2.2 g., 0.02 mole) and a viscous mixture resulted. A portion of this syrup (2.75 g.) was dissolved in concentrated hydrochloric acid (30 ml.) and antimony pentachloride (1.5 ml., 0.012 mole) was added. The product (4.7 g.) melted at 238-239°. It was recrystallized from concentrated hydrochloric acid and the constants recorded in Table IV.

1,2-Dimethoxypyridinium Hexachloroantimonate.

2-Methoxypyridine 1-oxide (1.25 g., 0.01 mole) and methyl sulfate (1.4 g.) were warmed gently on a hot plate for a few minutes. The mixture was cooled, dissolved in concentrated hydrochloric acid (40 ml.) and antimony pentachloride (1.5 ml.) added. The salt formed was filtered and recrystallized from ethanol-acetone, 9:1 and its constants are in Table IV.

H-D Exchanges.

When a salt was stable, it was dissolved in deuterium oxide containing a few drops of concentrated deuterium chloride. Alternatively, the salt was suspended in concentrated deuterium chloride, warmed gently and recovered.

Pyridinium Hexachlorostannates.

The preparation was similar to that described for hexachloroantimonates except that stannic chloride (0.5 ml., 0.06 mole) was utilized.

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