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COMPLEXES OF 2-AMINOPYRIDINE AND ITS SUBSTITUTED DERIVATIVES WITH IODINE

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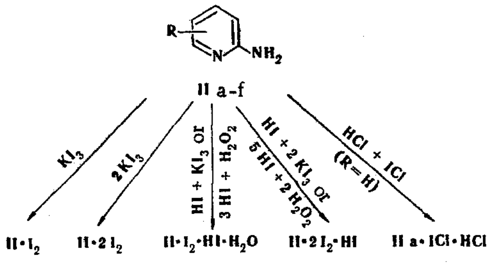
Depending on the amount of halogen used, 2-aminopyridine and its ring-substituted derivatives form complexes with 1 or 2 moles of iodine. In the presence of hydriodic acid, one equivalent of acid is included in the complex. 2-Amino-3,5-dibromopyridine forms a complex with 1 mole of iodine even in the presence of excess iodine or in the presence of HI. According to the IR spectra, the iodine in the complexes is coordinated with the ring nitrogen atom.

A large amount of research has been devoted to the study of complexes of pyridine and its alkyl-substituted derivatives (I) with iodine; however, information on complexes of 2-aminopyridine (IIa) is extremely limited. According to [1], base IIa forms a complex of the IIa $\cdot I_2$ type on reaction with a solution of KI_3 or of hydrogen peroxide in a solution of hydriodic acid. The UV spectrum of this complex is presented in [2]. Complexes of base IIa with ICl [3] and Pt^{2+} [4.6], Ag^+, and Cu^{2+} [7] salts have also been described.

We have found that IIa and its ring-substituted derivatives (IIb-f) react with iodine to give complexes of several types, which are shown in the scheme in Table 1. The complexes were obtained by the action of KI_3 on base II in water (method A) or in hydriodic acid (method B) and also by the action of hydrogen peroxide on solutions of the bases in hydriodic acid (method C).

The composition of the complex depends on the amount of iodine used in the reaction, the ring substituents, and the character of the medium. Complexes of the general type II $\cdot I_2$ are formed in all cases in the reaction of an equimolar amount of iodine by method A, whereas excess iodine leads to II $\cdot 2I_2$ complexes. However, in the case of 2-amino-3,5-dibromopyridine (IIe) the IIe $\cdot I_2$ complex is obtained even when 3 moles of iodine are used.

In hydriodic or hydrochloric acid solutions base IIa reacts with KI_3 solution to give IIa $\cdot I_2 \cdot HI \cdot H_2O$ or IIa $\cdot 2I_2 \cdot HI$ complexes depending on the amount of iodine used, monohalo-substituted IIc and IId form complexes only of the II $\cdot I_2 \cdot HI \cdot H_2O$ type even in the presence of excess iodine, and dibromo substituted IIe forms a IIe $\cdot I_2$ complex.



II a R=H; b R=3-CH$_3$; c R=5-I; d R=5-Cl; e R=3,5-Br$_2$; f R=6-NH$_2$

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TABLE 1. Complexes of 2-Aminopyridine and Its Substituted Derivatives with Iodine

Complex	Preparative method	Molar ratios of the base to I_2 (or H_2O_2)	Dec. temp., °C	Empirical formula	Found, %				Calculated, %				Yield, %
					C	H	free I	N	C	H	free I	N	
$IIa \cdot I_2 \cdot H_2O$	A	1 : 1	65—66	$C_5H_6N_2 \cdot I_2 \cdot H_2O$	15,8	2,1	70,0	7,1	15,7	2,1	69,5	7,3	70
$IIa \cdot 2I_2$	A	1 : 2	62—64	$C_5H_6N_2 \cdot 2I_2$	9,9	1,0	83,0	4,5	10,0	1,0	84,3	4,6	83
$IIa \cdot I_2 \cdot HI \cdot H_2O$	B, C	1 : 1	67—69	$C_5H_6N_2 \cdot I_2 \cdot HI \cdot H_2O$	11,9	1,4	52,0	5,5	12,1	1,7	51,5	5,7	86 (B), 60 (C)
$IIa \cdot 2I_2 \cdot HI$	B, C	1 : 3	65—67	$C_5H_6N_2 \cdot 2I_2 \cdot HI$	8,3	1,0	70,3	3,8	8,2	1,0	69,5	3,8	80 (B), 83 (C)
$IIb \cdot 2I_2$	A	1 : 2	85—87	$C_6H_8N_2 \cdot 2I_2$	11,7	1,4	—	4,5	11,7	1,3	—	4,6	81
$IIc \cdot I_2$	A	1 : 1	82—84	$C_5H_5IN_2 \cdot I_2$	13,5	1,1	53,0	6,0	12,9	1,1	53,0	6,0	73
$IIc \cdot 2I_2$	A	1 : 2	54—55	$C_5H_5IN_2 \cdot 2I_2$	8,6	0,9	67,0	3,9	8,3	1,0	69,3	3,9	58
$IIc \cdot I_2 \cdot HI \cdot H_2O$	B, C	1 : 2	68—70	$C_5H_5IN_2 \cdot I_2 \cdot HI \cdot H_2O$	9,5	1,0	40,5	4,3	9,7	1,3	41,0	4,5	85 (B), 87 (C)
$IId\ I_2 \cdot HI \cdot H_2O$	B	1 : 2	60—66	$C_5H_5ClN_2 \cdot I_2 \cdot HI \cdot H_2O$	11,3	1,2	47,6	4,9	11,3	1,5	48,0	5,3	90
$IIe \cdot I_2$	A, B	1 : 2	61—64	$C_5H_4Br_2N_2 \cdot I_2$	11,7	1,1	49,0	5,6	11,8	0,8	50,2	5,5	95
$IIf \cdot 2I_2 \cdot HI$	B	1 : 4	56—59	$C_5H_7N_3 \cdot 2I_2 \cdot HI$	8,1	1,1	67,0	5,6	8,1	1,1	68,0	6,0	44

TABLE 2. IR Spectra of 2-Aminopyridine and Its Substituted Derivatives and Their Complexes (frequencies in cm^{-1})

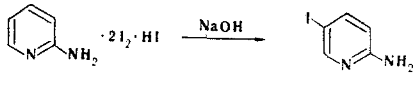
IIa	$IIa \cdot I_2$	$IIa \cdot 2I_2$	IIc	$IIc \cdot I_2$	IIe	$IIe \cdot I_2$	$IIe \cdot Br_2$
3460	3460	3460	3410	3490	3468	3480	3435
3325	3330	3340	3320	3380	3305	3300	3340
1635	1630	1630	1640	1645, 1618	1630	1630	1655
1600	1590	1600	1590	1585	1590	1570	1610
1565	1560	1570	1550	1550	1550	—	1530
1490	1490	1500	1485	1485	1485	1465	—
1340	—	—	—	—	1390	1390	1380
1325	1325	1320	1315	1315	1315	1330	1330
1280	1265	1265	1260	1265	1265	1240	1220
—	—	1160	1140	1150	1145	1110	1115
—	—	—	1090	1080, 1050	1095	—	—
990	1010	1010	997	1005	1005	1020	—
—	—	—	—	—	930	930	915
840	840	850	825	840	830	890, 875	880
775	765	768	775	765	775	—	790
745	725	730	750, 725	720	750, 725	747	745, 730
675	—	...	645	650	680	700	700
635	650	...	625	620	635	645	645
532	525	...	540	540	519	545, 505	540
440	432	...	450	430	450	420	435

Similarly, in hydriodic acid with excess bromine the latter base gives a IIe · Br_2 complex. The reaction of base IIa with an equimolar amount of iodine monochloride in hydrochloric acid gives the IIa · ICl · HCl complex.

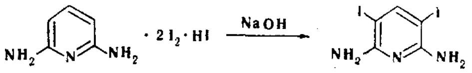
Depending on the amount of iodine liberated by the peroxide, IIa · I_2 · HI · H_2O and IIa · $2I_2$ · HI complexes are also obtained by the action of hydrogen peroxide on a solution of IIa in hydiodic acid. However, in the case of 2-amino-5-iodopyridine ((IIc), the IIc · I_2 · HI · H_2O complex is precipitated even when excess peroxide is present.

The hydriodide, diiodide, or tetraiodide structures of the complexes of IIa with iodine obtained in hydriodic or hydrochloric acid solutions by the action of KI_3 and also in hydriodic acid solution by the addition of peroxide are confirmed by the results of elementary analysis and also by their conversion, according to the results of thin-layer chromatography (TLC), on successive treatment with sodium thiosulfate solution and ammonium hydroxide to starting base IIa. Thus the 5 position is not iodinated by the action of iodine on base IIa in acidic media; this refutes the literature data [1].

Compound IIc is formed on treatment of the iodine complexes of IIa obtained in this research with aqueous solutions of alkali hydroxides, and the yield from the IIa · $2I_2$ · HI complex is 80%, while the yield from the IIa · I_2 complex, according to [1] and our observations, is only 50%



IIc



III

The 2,6-diaminopyridine complex (IIf) under similar conditions forms 2,6-diamino-3,5-diiodopyridine (III), whereas the complexes of the 5-iodo- and 3,5-dibromo-substituted derivatives of IIa (IId and IIe) are converted to the starting bases.

Data from the IR spectra of 2-aminopyridine (IIa) and its 5-iodo- (IIc) and 2,3-dibromo-substituted (IIe) derivatives and their complexes are presented in Table 2. The absence in the case of IIa of a substantial shift of the ν_{as} and ν_s bands of the amino group during complexing with iodine makes it possible, in analogy with [7, 8], to conclude that complexing occurs primarily at the ring nitrogen atom rather than at the amino group. The shift in the band at 990 cm^{-1} in the spectrum of IIa to 1010 cm^{-1} in the spectra of its complexes with 1 and 2 moles of iodine, which is similar to the shift observed during the formation of complexes of pyridine with iodine and iodine monochloride [9], also constitutes evidence that complexing occurs primarily at the ring nitrogen atom. Similar shifts in this region are also observed during the formation of complexes of IIc and IIe. Instead of the split band (1325-1340 cm^{-1}) that is present in the spectrum of amine IIa, the IR spectra of its complexes (IIa · I_2 · H_2O and IIa · $2I_2$), as in the case of complexes with divalent copper salts [7], contain a single band (1325 and 1320 cm^{-1}, respectively). The 400-800 cm^{-1} region, where a reduction in the number of bands and a shift to the low-frequency region are observed, proved to be important for the characterization of the complexes.

EXPERIMENTAL

The amount of complexed iodine and bromine was determined by the method in [10]. The melting points were measured with a Boetius microheater and were not corrected. The IR spectra of mineral oil suspensions (400-2000 cm^{-1}) and hexachlorobutadiene suspensions (2000-3600 and 1300-1500 cm^{-1}) of the compounds were recorded with a UR-20 spectrometer. Chromatography was accomplished with Silufol UV-254 in benzene–ethyl acetate (3 : 1), benzene–dioxane–glacial acetic acid (100 : 20 : 5), and chloroform–methanol–glacial acetic acid (75 : 20 : 5) systems.

Complexes. Method A. Ice was added to an aqueous solution or a fine suspension of 10 mmole of base II, after which a solution consisting of 2.54 g (10 mmole) of iodine, 4 g of potassium iodide, and 10 ml of water was added with stirring. After 0.5 h, the resulting precipitate was removed by filtration, washed with ice water, and dried successively in air and above sulfuric acid.

Twofold or threefold quantities of iodine and potassium iodide were used for the preparation of the tetraiodides.

The complexes of the II · I_2 and II · $2I_2$ type were black (brown in the case of IIc) amorphous powders that were insoluble in water and quite soluble in organic solvents and incapable of prolonged storage. The complexes of base IIa were particularly unstable and decomposed to iodine, the starting base, and its 5-iodo-substituted derivative (IIc) after 3-4 days in air or in a desiccator over sulfuric acid. The IIb · $2I_2$ complex behaved similarly. The halogen-substituted bases (IIc, IId, and IIe) are relatively weak complexing agents. In contrast to the complexes of IIa, their complexes lost iodine even on treatment with 25% aqueous potassium iodide.

Method B. The reaction was carried out with 10 mmole of the base dissolved in 10 ml of 40% hydriodic acid or 36% hydrochloric acid as described above.

Method C. Ice was added to a solution of 6 g (6.3 mmole) of IIa in 38 ml of 40% HI, after which 5 mmole or, respectively, 12 or 18 mmole of 3% hydrogen peroxide was added, and the resulting precipitate was separated and washed with ice water.

The hydriodide complexes were obtained as dark crystals with a graphite luster in the case of complexes of the II · I_2 · HI · H_2O type or a yellow-greenish luster in the case of complexes of the II · $2I_2$ · HI type; they were quite soluble in organic solvents and only slightly soluble in water and could be stored satisfactorily. An iodine molecule was lost when the IIa · $2I_2$ · HI complex was washed with 25% potassium iodide solution.

2-Aminopyridineiodinium Chloride Hydrochloride (IIa · ICl · HCl). A 0.42-ml (10 mmole) sample of iodine monochloride was added to a solution of 0.94 g (10 mmole) of base IIa in 10 ml of concentrated HCl, after which the resulting shiny black precipitate was removed by filtration to give 1.6 g (54%) of a product with mp 122-124° (dec.). Found: C 20.8; H 2.5; N 9.3%. $C_5H_6N_2$ · ICl · HCl. Calculated: C 20.6; H 2.4; N 9.5%.

2-Amino-3,5-dibromopyridine Dibromide (IIe · Br_2). A 1.27-ml (25 mmole) sample of bromine was added to a solution of 2.52 g (10 mmole) of IIe in 10 ml of water and 3 ml of 40% hydrobromic acid. The initially formed resinous mass began to crystallize in the course of 2 h. The resulting yellow-brown crystals were removed by filtration and washed with water to give 3.79 g (92%) of a produce with mp 110-114° (dec.). Found: C 14.1; H 1.1; free Br 39.0; N 6.6%. $C_5H_4Br_2N_2$ · Br_2. Calculated: C 14.5; H 1.0; free Br 38.6; N 6.8%.

2-Amino-5-iodopyridine (IIc). A 37.6-g (50 mmole) sample of the IIa · $2I_2$ · HI complex was stirred with 400 ml of 10% aqueous sodium hydroxide solution until the black lumps disappeared. The brown precipitate was removed by filtration to give 8.8 g (80%) of a product with mp 128-129° (from benzene), in agreement with the data in [1]. Found: C 27.1; H 2.2; N 12.5%. $C_5H_5IN_2$. Calculated: C 27.3; H 2.3; N 12.7%.

2,6-Diamino-3,5-diiodopyridine (III). A 10-g (1.34 mmole) sample of 2,6-diaminopyridine tetraiodide hydroiodide was mixed with 30 ml of 20% aqueous sodium hydroxide solution, and the resulting precipitate was removed by filtration to give 4.6 g (95%) of cream-colored crystals with mp 218-220° (from dimethylformamide). Found: C 16.7; H 1.6; N 11.9%. $C_5H_5I_2N_3$. Calculated: C 16.6; H 1.5; N 11.6%.

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