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The Reaction of Aqueous Dibromoiodate(I) with Pyridine

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Reaction of pyridine with an Andrews solution prepared in hydrobromic acid, rather than in the usual hydrochloric acid, gives *N*-iodopyridinium bromide at low acid and pyridinium dibromoiodate(I) at high acid concentrations. The molecular weight values of *N*-iodopyridinium bromide in nitrobenzene as well as the ultraviolet and infrared spectra support ionization in polar solvents but discount the presence py_2I^+ ions. The cryoscopic and spectroscopic properties of pyridinium dibromoiodate(I) are consistent with a double charge-transfer complex, comprising pyridinium ions, pyH^+, and dibromoiodate(I) ions, IBr_2^-.

Pyridine reacts with an Andrews solution to give yellow crystalline *N*-iodopyridinium dichloroiodate(I) in good yield.[1] By analogy, addition of pyridine to an Andrews-type solution, prepared in hydrobromic acid,[2] instead of the usual hydrochloric acid, might be expected to give *N*-iodopyridinium dibromoiodate(I). This is not the case. Instead, two other products are obtained; one is a pale yellow crystalline material analyzing as C_5H_5NIBr from solutions of hydrobromic acid below 0.06 *M*, while the second is an orange crystalline material analyzing as $C_5H_5NHIBr_2$ from hydrobromic acid solutions exceeding 1 *M* concentration. A mixture of the two products is obtained between these two hydrobromic acid levels.

Experimental Section

Reagents.—Chemicals were of AR quality. Solvents were purified and dried by standard techniques.

Preparation.—*N*-Iodopyridinium bromide, C_5H_5NIBr, rapidly precipitated on adding excess pyridine (5 ml) to the solution resulting from mixing 0.1 *M* potassium iodide (25 ml) in 0.1 *M* hydrobromic acid (50 ml) with 0.05 *M* potassium iodate (25 ml). The pale yellow product recrystallized from absolute ethanol melted at 112° (lit.[3] mp 114°). *Anal.* Calcd for C_5H_5NIBr: C, 21.0; H, 1.75; N, 4.85; I, 44.0. Found: C, 21.3; H, 1.90; N, 4.70; I, 43.2.

Pyridinium dibromoiodate(I), $C_5H_5NHIBr_2$, crystallized slowly on adding excess pyridine (5 ml) to an ice-cold solution resulting from mixing 0.1 *M* potassium iodide (25 ml) in 6 *M* hydrobromic acid (50 ml) with 0.05 *M* potassium iodate (25 ml). The orange product recrystallized from 3 *M* hydrobromic acid melted at 173–175° (lit.[4] mp 173–175°). *Anal.* Calcd for $C_5H_5NHIBr_2$: C, 16.35; H, 1.64; N, 3.82; I, 34.6. Found: C, 16.35; H, 1.70; N, 3.80; I, 34.9.

Molecular weights were evaluated in naphthalene (Rast) and in nitrobenzene (Beckman). Rast's method gave 289 ± 20 and 360 ± 20, respectively, in reasonable agreement with the calculated values (C_5H_5NIBr, 286; $C_5H_5NHIBr_2$, 367). The results in nitrobenzene were 103 ± 5 for *N*-iodopyridinium bromide but for pyridinium dibromoiodate(I) approached half the theoretical value at infinite dilution.

Infrared spectra were run for both compounds using freshly prepared saturated solutions in pyridine and in nitrobenzene, as potassium bromide disks, and in Nujol mulls, using a Perkin-Elmer Model 521 instrument. No useful data resulted from scans between 2000 and 4000 cm^{-1}. Owing to very low solubility, scans in carbon tetrachloride, benzene, and cyclohexane provided little information; neither did a scan of pyridinium dibromoiodate(I) in carbon disulfide.

Visible and ultraviolet spectra were run on a Unicam SP800 spectrophotometer.

Results and Discussion

Popov and Rygg[3] have suggested that *N*-iodopyridinium bromide ionizes according to $2pyIBr \rightleftarrows (py)_2I^+ + IBr_2^-$. An attempt has been made to support this self-ionization process by relating certain infrared bands to dihaloiodate(I) and *N*-iododipyridinium ions,[5] although Yarwood[6] has expressed doubts over these assignments because little difference is apparent between the spectra of the *N*-iodopyridinium chloride complex, for example, in polar and nonpolar solvents.

The molecular weight obtained in nitrobenzene, 103 ± 5, is not consistent with the above ionization mechanism, indeed it would appear that at least three species are formed in nitrobenzene. Thus, an appropriate ionization could involve the solvent

$$pyIBr + 2C_6H_5NO_2 \rightleftharpoons C_6H_5NO_2I^+ + C_6H_5NO_2py + Br^-$$

since both $C_6H_5NO_2I^+$ and $C_6H_5NO_2py$ are known to be weak charge-transfer complexes.[7]

The cryoscopic molecular weight determination of pyridinium dibromoiodate(I) in nitrobenzene indicates incomplete ionization, and if the two ionic species are pyH^+ and IBr_2^- as suggested by spectroscopic evidence, the cryoscopic measurements give a value of about 10^{-9} for $[pyH^+][IBr_2^-]/[pyHIBr_2]$.

Ultraviolet Spectra.—In hydrobromic acid (3 *M*), pyridine exhibits a peak at 257 nm (ϵ 4580) with inflections at 253 and 262 nm. This fine structure is similar to that noted in the corresponding absorption in 5 *M* hydrochloric acid.[1] Due to the very high background absorption of hydrobromic acid below 240 nm, it is not possible to establish an absorption for pyridine in 3 *M* hydrobromic acid corresponding to that observed at 212 nm in 5 *M* hydrochloric acid. This absorption can be related to the presence of pyH^+ (it is certainly sensitive to varying concentration of hydrochloric acid), but unfortunately this region cannot be used to

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confirm the existence of pyH^+ in hydrobromic acid media.

The modified Andrews solution containing dibromoiodate(I) ions[2] exhibits intense charge-transfer absorption (ϵ 50,000) at 254 nm and a weak absorption at 378 nm (ϵ 619). Popov and Swenson[8] observed similar absorptions for dibromoiodate(I) ions in acetonitrile, at 256 nm (ϵ 54,000) and 370 nm (ϵ 606). The 256-nm peak is probably due to an $n \rightarrow \nu$ charge-transfer transition.[9]

The spectra of *N*-iodopyridinium bromide and pyridinium dibromoiodate(I) in hydrobromic acid (3 *M*) are essentially identical. Both spectra show definite evidence of IBr_2^- (at 255 and 375–377 nm), but the high background absorption of hydrobromic acid again precludes any observations below 240 nm. The 255-nm peak shows no pyridine inflections because of the great intensity of the IBr_2^- absorption at this wavelength. In each case the 255-nm absorption is asymmetric, indicating that π electrons contribute to the $n \rightarrow \nu$ charge-transfer excitation[9] which is probably responsible for most of this absorption.

In water, methanol, and glacial acetic acid, *N*-iodopyridinium bromide exhibits an absorption at 257 nm with inflection points at 252 and 264 nm, similar to the spectrum of pyridine. Also, the 375-nm peak is not evident, suggesting that no dibromoiodate(I) ions are formed. It is, therefore, likely that in neutral or weakly acidic media, *N*-iodopyridinium bromide yields pyridine in dilute solutions, and not charge-transfer species such as pyI^+ or $(py)_2I^+$ ions. Of course, it must not be discounted that extremely rapid solvolysis which is so characteristic of active halogen compounds has obliterated some peaks, especially as the spectra now show an additional absorption near the iodine frequency at 450 nm.

Solutions of pyridinium dibromoiodate(I) in water and methanol show peaks at 203 nm as well as at 257 nm with the attendant inflections at 252 and 264 nm. Freshly made solutions in methanol show an additional absorption at 218 nm. In glacial acetic acid, only one peak is observed in the 256-nm region, but all three solvents show peaks at 383, 385, and 378 nm, respectively. Even though, as a result of decomposition an iodine absorption shows at 445 nm in water and methanol, the general features in these media support an initial ionization of pyridinium dibromoiodate(I) to IBr_2^- and pyH^+, although the ultraviolet evidence for pyH^+ is tenuous particularly as its existence necessarily involves its characteristic equilibrium with pyridine.

Infrared Spectra. *N*-Iodopyridinium Bromide.—The infrared spectrum of *N*-iodopyridinium bromide has been the subject of several investigations,[5,10–12] and a reasonable assignment of all bands between 80 and 4000 cm^{-1} has been made.[5] However, there are some discrepancies between the present work and previously reported spectra,[5] particularly with regard to the $(py)_2I^+$ species and its absorption around 434 cm^{-1}.

In the present work, absorptions at 625 and/or 630 cm^{-1} appear in potassium bromide disk, Nujol mull, and carbon disulfide, as well as in the polar solvents pyridine and nitrobenzene. This parallels Yarwood's observations of the ν_3 band for pyICl which occurred at 632 ± 1 cm^{-1} in eight out of eleven solvents.[6] The absence in this study of a $(py)_2I^+$ band (noted by Haque and Wood[5]) around 434 cm^{-1} is consistent with Yarwood's study[6] on pyICl. Although the $(py)_2I^+$ ion exists in solid $py \cdot 2I_2$, and presumably in complexes of the stoichiometric type $((py)_2I)B$, where B = ClO_4, NO_3, BF_4, or PF_6, there is no crystallographic evidence for this ion in any solid 1:1 pyIX complex.[13] Self-ionizations of 1:1 complexes, $2pyIX \rightleftharpoons (py)_2I^+ + IX_2^-$, occur in polar solvents but the infrared evidence presented[5] in support of such processes is unsatisfactory.

Pyridinium Dibromoiodate(I).—There are differences between the infrared spectra of pyridinium dibromoiodate(I) and *N*-iodopyridinium bromide, particularly regarding the comparative dearth of absorptions below 700 cm^{-1} for pyridinium dibromoiodate(I).

Taking vibrations at about 630, 1000, and 1240 cm^{-1} which are supposedly sensitive to halogen electronegativity changes,[5,11,12] it is only in pyridine that pyridinium dibromoiodate(I) gives absorptions at each vibration frequency, although the nearest to 1240 cm^{-1} is the strong absorption at 1257 cm^{-1}. Probably of greater significance and perhaps supporting the presence of pyH^+ is the lack of the 630-cm^{-1} absorption in Nujol mull and potassium bromide disk.

The frequency of infrared absorptions should be similar[14] for the two $n \rightarrow \sigma$ charge-transfer complexes since they involve the same base. Little difference in the infrared spectra is thus expected in the 400–2000-cm^{-1} range. However, a comparison of the β(C–H) bands at 1030 and 1240 cm^{-1} in *N*-iodopyridinium compounds and at 1040 and 1250 cm^{-1} in pyridinium dibromoiodate(I) supports increased charge transfer in the pyridinium compound compared with the *N*-iodopyridinium compound.

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