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A SPECTROSCOPIC INVESTIGATION OF THE REACTION BETWEEN IODINE AND CYCLOPROPYLAMINE

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The formation of charge-transfer complexes between iodine and several aliphatic amines has been the subject of many investigations (1-4). However, there seems to have been no mention of studies with cyclopropylamine even though it has long been recognized that the cyclopropyl ring displays some characteristics of unsaturated substances (5), and the interaction between iodine and cyclopropylamine may differ from that observed with aliphatic amines.

We have studied spectroscopically the reaction between iodine and cyclopropylamine in n-heptane solution. Preliminary results suggest that a 1:1 charge-transfer complex between iodine and cyclopropylamine was formed first; subsequently precipitation of white crystals of a 2:1 cyclopropylamine-iodine complex, $(\overset{\frown}{C}_3H_5NH_2)_2I_2$ [A], occured.

Spectroscopic grade of n-heptane and resublimed iodine were used in the experiments. The cyclopropylamine was supplied by Aldrich Chemical and was dried over solid potassium hydroxide and distilled before use. Visible and ultraviolet absorption spectra were determined with a Cary model 14 spectrophotometer using a 10 mm. path length quartz cell. Special care was taken to exclude moisture in the procedure of preparing and mixing solution.

When cyclopropylamine was added to a n-heptane solution of iodine, an absorption spectrum was obtained immediately which showed the same spectroscopic features as the 1:1 triethylamine-iodine complex (4). The maximum at 440 mμ is assigned to the "blue-shifted" visible band of iodine which ordinarily appears at 520 mμ in n-heptane. The peak at 290 mμ is assigned to the charge-transfer band characteristic of amine-iodine systems. However, upon standing, the period of time depending on reactants concentrations, the solution gradually became colorless with a precipitation of some fine white crystals and both the absorption peaks of the solution at 440 and 290 mμ disappeared.

The isolated solid product, [A], was thoroughly washed with n-heptane and dried at 100°C. It was readily soluble in water but not in alcohol and some other common organic solvents. It melted at 235 °C and its aqueous solution gave an absorption spectrum with maxima at 320 and 260 mμ. Treatment of [A] with an aqueous solution of silver nitrate gave a precipitate of silver iodide. Anal. Found: C, 20.17; H, 3.79; N, 7.74; I, 68.01%. Calc. for $(\hat{C}_3H_5NH_2)_2I_2$: C, 19.56; H, 3.80; N, 7.60; I, 69.02%.

When the solid product [A] was dispersed in KBr and pressed into a pellet, it gave an infrared spectrum with strong bands at 3030, 2940 and 2970 cm^{-1} as well as others characteristic of the cyclopropyl ring. However, the strong band of a primary amine at about 1600 cm^{-1} was not observed. The n.m.r. spectrum of [A] in an aqueous solution has resonances centered at 65 cps (8 H of the cyclopropyl rings) and at 175 cps (2 H of the rings adjacent to the N atoms) with integrated areas of the two signals in the ratio of 4:1. The N-H protons were, however, not observed due to the rapid exchange with the OH protons from the water solvent. This n.m.r. spectrum is, in general, similar to that of an acidified aqueous solution of cyclopropylamine, in which the cyclopropylammonium ion gave resonance signals centered at 55 cps (4 H) and at 160 cps (one H).

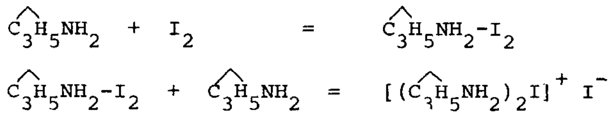
These results suggest that the solid product [A] has probably an ionic structure $[(\hat{C}_3H_5NH_2)_2I]^+\ I^-$. The presence of the iodine atom attached to the nitrogen could account for the low field shifts of the resonance signals observed.

The formation of cyclopropylammonium iodide, $\hat{C}_3H_5NH_3^+ \ I^-$ [B], was considered as possible reaction product in the presence of moisture (6):

$$3\ (\hat{C}_3H_5NH_2)_2I_2 + 3\ H_2O \rightleftharpoons 5\ \hat{C}_3H_5NH_3^+I^- + \hat{C}_3H_5NH_3^+IO_3^-$$

To this end, cyclopropylammonium iodide was prepared by the reaction of ammonium iodide with cyclopropylamine in an aqueous medium. A pale yellow solid [B] was obtained upon slow evaporation of the solution to dryness. After recrystallization in alcohol, the solid melted at 250 °C. It was readily soluble in alcohol and other common organic solvents and its identity was confirmed by chemical analysis, infrared and n.m.r. spectroscopy. The aqueous solution of [B] gave an absorption spectrum which displayed a continuum with an absorption onset at about 260 mμ, distinctly different from that of [A]. Comparison of this and other spectra indicates that compound [B] was not the solid product precipitated from the iodine-cyclopropylamine solution.

Thus, it seems that the reaction between iodine and cyclopropylamine proceeds via an intermediate of a 1:1 charge-transfer complex which then leads to the formation of a molecular addition complex:



$$\hat{C}_3H_5NH_2 + I_2 = \hat{C}_3H_5NH_2\text{-}I_2$$

$$\hat{C}_3H_5NH_2\text{-}I_2 + \hat{C}_3H_5NH_2 = [(\hat{C}_3H_5NH_2)_2I]^+ I^-$$

The cyclopropyl ring apparently facilitates the developing ammonium ion structure. Other evidence which points to the existence of [A] was that the reacting solution did not decolorize and precipitate until a certain period of time after mixing, whereas the formation of a 1:1 charge-transfer complex was observed immediately.

It is interesting to note that the only other 2:1 amine-iodine complex which has been isolated, was the picoline_2I_2 (7). Recently Schmulbach and Hart (8) have also presented evidence for the existence of a 2:1 triethylamine-iodine complex but failed to isolate the compound. In the case of picoline, the stability of the 2:1 complex is assumed to be due to the delocalization of the positive charge of the iodinium ion throughout the ring. Such an explanation also seems to be valid in this case of cyclopropylamine, since the cyclopropyl ring possesses similar properties typical of delocalized bonding. However, further investigation including X-ray analysis is necessary before any definite conclusion can be made.

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