

THE STUDY AND PREPARATION OF
IODINE MONOCHLORIDE
WITH VARIOUS
AMINES

A SENIOR THESIS

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BY

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VITA

Cecil William Hickam, Jr. was born in Pulaski, Virginia, on August 3, 1939, the son of Nancy Lindsay Hickam and Cecil William Hickam. He attended high school at Pulaski High School in Pulaski, Virginia, before entering Washington and Lee University in September of 1956.

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IODINE MONOCHLORIDE COMPOUNDS

Work has previously been done with iodine, bromine, iodine monochloride, and iodine monobromide, which act as Lewis acids, toward benzene, pyridine, and bipyridine. We began a study of reactions of iodine monochloride with amines which are not aromatic. We used ethylenediamine, piperidine, triethylamine, tripropylamine, and aniline. Therefore this thesis deals with the study and preparation of iodine monochloride derivatives with various amines. The overall purpose was: first, to determine if iodine monochloride addition compounds involving the above amines could be prepared and second, if they could be prepared to investigate their stability. My report on iodine monochloride complexes for Physical Chemistry 267 gives a literature report on the work already done on iodine monochloride complexes.

The method used in preparing the iodine monochloride compounds with various amines is as follows: A definite amount of the liquid amine, which had been purified by drying over potassium hydroxide and then distilling in a separation column, was dissolved in carbon tetrachloride, which had been dried over calcium chloride and distilled. Solutions of the order of 0.1M to 0.4M in concentration were prepared usually, about 100 mls. were used in a run. Likewise, an iodine monochloride solution in carbon tetrachloride

of the same concentration was prepared. The iodine monochloride was purified by heating until the crystals melted (ICl has a m.p. of 26°C), and then letting it slowly cool until about $3/4$ th of the iodine monochloride was solidified, at which time the liquid was poured off. This repeated. The compounds were prepared by slowly adding the iodine monochloride solution from a burette to the solution of the amine in a flask, which was manually stirred. The process usually took fifteen minutes. The solution was then filtered on a Buchner funnel. Since carbon tetrachloride was the solvent, the product was usually dry after filtering for twenty minutes.

Here follows an account of each compound prepared and the observations.

I. PYRIDINE-IODINE MONOCHLORIDE- This compound is reported in the literature as having a melting point of 132°C (Y. A. Fialkov and I. P. Muzyka in Zhur. Obsheei Khim, 18, 1205, (1948)), and a melting point of 128.5°C (C. A., 43, 1949^b, (1949)). For further preparations, I made a study on the yield obtained upon using different concentrations. The preparation of pyridine iodine monochloride by using 100 mls. of 0.1M pyridine in CCl_4 and 100 mls. of 0.1M ICl in CCl_4 gave an 81% yield. With 0.2M concentrations a yield of 86% was obtained, and with a 0.3M concentrations a 90% yield was obtained, and with a 0.4M concentrations a 96% yield was obtained. Therefore in conclusion of my work a 0.4M concentration will get

better yields. The observations during the adding of the ICl to the amine by means of a burette were: (1.) At first the solution turned green. (2.) With additional ICl the solution turns yellow. (3.) Finally a fine, white precipitate is noticed. (4.) Near the end of the addition of ICl the solution turns red, which indicates that there is an excess of ICl.

It was noticed if the product was dried in the oven at 80°C, the compound would slowly decompose and also that the melting point of the product made from 0.1M changed from 126-129°C to 120-130°C. Therefore, with further work, the oven was not used to dry the products.

Observations were:

Conc.	M.P.	Yield	Color
0.1M	126-129°C	81%	very pale yellow
0.2M	127-128°C	86%	very pale yellow
0.3M	126-128°C	90%	very pale yellow
0.4M	-	96%	very pale yellow

II. gamma-PICOLINE-IODINE MONOCHLORIDE - The observations were the same as for the pyridine case during the process of reaction. Using 0.4M solutions a 94% yield was obtained. The gamma-picoline iodine monochloride had a very sharp melting point of 112°C; in fact, it instantly turned to a very dark red liquid. The product was very pale yellow.

III. PIPERIDINE-IODINE MONOCHLORIDE- During the reaction the first precipitate appeared as small balls, but at the end, the precipitate was fine as was the case with pyridine ICl and gamma-picoline ICl. On filtering, the precipitate was white and gummy, but after twenty minutes filtering the product was white (abit brown), fine, and hard. It gave a sharp decomposition point at 92°C and a yield of 95%. But after the product was put in a sample bottle and allowed to stand for a week, the product turned to a dark, very very hard, "chocolate" compound. A melting point of the hard, "chocolate" piperidine ICl was taken; it began decomposing at 52°C , but it turned to a definite liquid between 59 and 60°C . Dr. Robert Whitaker on running a chloride analysis by the Volhard method found that the chlorine content of freshly prepared piperidine ICl was 13.8% and of the "chocolate bar" was 13.6%. The calculated chlorine content is 14.3% for a one to one complex.

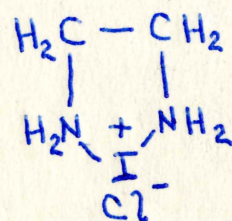
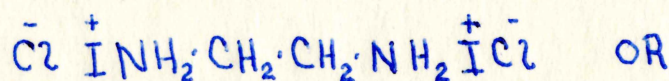
IV. TRIETHYLAMINE-IODINE MONOCHLORIDE- On making this compound with 0.4M concentrations, the solution after adding 50 mls. of ICl was an ugly brown, and the flask became warm. Upon filtering a small brown precipitate was obtained and also an oily layer, which passed through the filter paper. No definite melting point obtained. Therefore I decreased the concentrations to 0.1M, and

I also put the reaction flask in an ice bath during the process to avoid any redox side reaction. I got better results in this experiment in that I obtained about half a gram of a light yellowish product which sublimed at high temperatures and turned to a definite dark red liquid around 220°C.

V. TRIPROPYLAMINE-IODINE MONOCHLORIDE- No precipitate was obtained - just two liquid layers in the reaction flask. No further work was done with tripropylamine. It is believed that steric hindrance interfered with this reaction, for it must be remembered that the iodine atom is very large, and three n-propyl groups offer considerable steric hindrance.

VI. ETHYLENEDIAMINE-IODINE MONOCHLORIDE- On adding a drop of ICl to the ethylenediamine solution a definite precipitate was obtained, which was yellow, gummy, and spherical. On further addition of ICl, the precipitate formed began to be fine. There was still one big gummy ball, like a golf ball. On filtering there seemed to be two products: (1.) a fine orange-tan powder and (2.) a dark, gummy product. After drying the gummy product by suction of the Buchner funnel, it could be pulverized easily. It was observed that some decomposition occurred between 60 and 70°C, but most of the compound remained solid and melted in the vicinity of 220°C. Dr. Whitaker

on running a chloride analysis by the Volhard method got a chlorine content of 17.17%, but the calculated chlorine content for a one to one ratio is 16.0% and for a two to one ratio is 18.4%. It was noticed by Dr. Whitaker that by ether extraction some I_2 (it is believed) was extracted; so after extracting the product five times with ether, he got a chloride analysis of 18.58%. This shows a two to one ratio. Extraction of this product with ether in a Soxhlet apparatus for four days gave a product which had a much lighter tan color. Some decomposition occurred between 241 to 252°C, and this substance melted between 257 and 262°C. Therefore, I postulate that probably both the one to one and the two to one compounds were formed, but that the two to one compound predominates and is purified by ether extraction. Another interesting point is that the precipitate formed was a ball, and this seems to indicate chelation. However, spectroscopic studies, freezing point depression, or other determinations would be needed to prove if the two to one compound was linear or chelated. We were unable to do this. That the original compound seems to decompose to a certain extent between 60 and 70°C maybe explained by the presence of some of the one to one ratio compound. We believe the predominate complex of iodine monochloride with ethylenediamine to be:



VII. ANILINE-IODINE MONOCHLORIDE- On adding one drop of iodine monochloride to the aniline solution there was a purple precipitate, which immediately turned green. On adding ICl the solution turns to a dark blue-green. When filtered the precipitate was blue, but within a few hours, it had turned green. It decomposed between 166 and 167°C. When Dr. Whitaker ran a Volhard chloride analysis and I ran a Sodium fusion test, we found no chloride in the compound. In Sidgwick's Organic Chemistry of Nitrogen on page 53, he states that one type of oxidation of aniline is called polymolecular products. I quote, "These consist of a large number of compounds some of quite high molecular weight; important examples are emeraldine, nigraniline, and the aniline blacks of which there are two main classes, the so called 'greenable' blacks which are not stable and turn green on keeping and the stable 'ungreenable' black." Since our compound did not contain chloride and was green, we postulate the ICl caused the aniline to undergo mild oxidation, and that we got a 'greenable' aniline black compound.

Chart showing my observations and some facts about the amines.

Amine	dielectric constant	K_b at 25°	M.P.	Exper. % of Cl ⁻	Calc. % of Cl ⁻	Color
Pyridine	12.5 at 25°C	2.4×10^{-9}	126° to 128°	14.88	14.68	very pale yellow
gamma-Picoline	10.0 at 20°C	1.1×10^{-8}	dec. at 112°	14.8	13.9	pale yellow
Piperidine	5.9 at 20°C	1.58×10^{-3}	dec. at 92°	13.8 fresh & 13.6 chocolate	14.3	white (abit of brown)
Triethylamine	3.15 at 21°C	5.65×10^{-4}	dec. about 220°C	23.4	27.0 for 1 to 1 & 13.5 for 2 to 1	light yellow
Tripropylamine	-	4.43×10^{-4}	oil			oil
Ethylene-diamine	16.0 at 18°C	8.5×10^{-5}	dec. 241° to 252° melts 257° to 262°	18.58	16.0 for 1 to 1 & 18.4 for 2 to 1	m ed. tan
Aniline	7.21 at 20°C	4.6×10^{-10}	dec. 166° to 167°	0.0	14.1	green

In summary I believe I showed that there is a relationship between the basicity of the amine and the stability of the amine's iodine monochloride derivative. It was observed with the aromatic amines that their melting points are in the range of 100°C , and they are stable. The stability of these compounds may be explained by two factors. First, there are six electrons forming a pi cloud in the benzene nucleus. Second, there are empty orbitals of low energy on the iodine atom. Therefore, it is a possibility that double bonding occurs. The non aromatic compounds except for piperidine ICl are tan and have decomposition points over 200°C ; also the amines of these compounds have higher K_b values than do the aromatic amines. These facts indicate that the ICl derivatives of these non-aromatic amines are more ionic in nature than are the ICl derivatives of the aromatic amines.

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