THE SPECTRAL PROPERTIES OF IODINE - TRICHLORIDE IN CARBON TETRACHLORIDE SOLUTION

A THESIS

presented to the faculty of the Chemistry Department of Washington and Lee University as a completion of work for a Bachelor of Science degree in Chemistry.

By

George Broward Fozzard

May, 29, 1962

VITA

The author was born in Jacksonville, Florida on April 13, 1939, the son of Elise Allen and Harry Broward Fozzard. He attended Robert E. Lee Senior High School in Jacksonville and was graduated in the June of 1957. He entered Auburn University in the fall of that year and transfered to Washington and Lee University two years later, where he is a condidate for a Bachelor of Science degree in Chemistry.

Introduction

The investigation of iodine trichloride as an electron acceptor system for strong donors by R. D. Whitaker, J. R. Ambrose, and C. W. Hickam has proven very fruitful. In order to complete the investigation of the iodine trichloride acceptor system, an investigation with weak donors was undertaken. This study was to be attempted through a spectrophotometric investigation of carbon tetrachloride solution of iodine trichloride and aromatic hydrocarbons. The experimental procedure for this investigation was divided into two parts, first a systematic quantitative investigation of the spectrophotometric properties of iodine trichloride in carbon tetrachloride solution and second the determination of formation constants for the iodine trichloride donor system.

Procedure

The investigation of the spectrophotometric properties of iodine trichloride was undertaken by the following procedure:

Pure iodine trichloride was prepared by standard methods and stored in a glass stoppered bottle under chlorine in a desicator in a refrigerator. The storage period was from one to three weeks; there was no noticeable decomposition during this time. A typical series would procede as follows. A twenty five milliliter volumetric flask is dried for 20

minutes at 110 c, removed from the oven and allowed to cool to room temperature. The iodine trichloride is removed from the refrigerator and placed in the balance room. The volumetric flask is weighed to the nearest tenth of a milliliter on a Metler electric balance. The falsk is removed from the balance pan, and using a Nicrome spatula, approximately 0.0500 g of iodine trichloride is placed in the flask. The flask is replaced on the balance and the flask with iodine trichloride is weighed to the nearest tenth of a milligram. The flask is immediately removed and filled to the mark with spectro-grade carbon tetrachloride. The weighing procedure takes approximately ten minutes.

The iodine trichloride takes approximately twenty minutes to go into solution. Four more solutions were prepare by quantitative dilution as follows: fifteen milliliters of the solution described above (solution A) is placed in a twenty five milliliter volumetric flask and diluted to the mark with spectro-grade carbon-tetrachloride to give solution B. Fifteen milliliters of solution B is placed in a twenty five milliliter volumetric flask and diluted to to the mark to yield solution C. The procedure outlined above is followed to prepare solutions D and E. Two matched ground glass stoppered, one centimeter, absorption cells are rinsed with carbon tetrachloride filled with spectro-grade carbon tetra-chloride. The Beckman Double-beam spectro-

photometer is them adjusted for one hundred percent transmission with both cells filled with spectro-grade carbon tetrachloride. The sample cell is then removed, emptied, rinsed with solution E, filled with solution E and the absorption spectra from 500 to 270 m taken.

The absorption cell is removed, emptied, rinsed with solution D, filled with solution D, and absorption spectra taken. This procedure is repeated for solutions C, B, and A. At all times druing this procedure, the volumetric flask and absorption cell are kept tightly stoppered with ground glass stoppers. The entire procedure from the beginning of weighing to the end of the last absorption spectra takes approximately two and one half hours.

Discussion

The equilibrium $ICl_3 \rightleftharpoons ICl + Cl_2$ had been suggested, but there appeared to be no quantitative data on this system. A preliminary investigation seemed to indicate that the system was displaced considerably to the right. It was decided that a complete investigation of this system would be profitable and, in fact, necessary before any significant studies of formation constants of weak donor systems could be undertaken.

It was found that the absorption spectra curve of iodine trichloride in carbon tatrachloride was a composite curve composed of a peak coinciding with a chlorines peak and a peak which coincides with iodine trichloride peak. The data from several solution-groups as outlined is analyzed by a method designed to yield both the equilibrium constant and the molar extinction coefficient with some indication of the precision of the data. A graph is plotted of the eqation

$$K = \frac{[ICl_3]_o^2 (\alpha_{ICl_3} - \alpha_{ICl})}{A - \alpha_{ICl}[ICl_3]_o} - 2[ICl_3]_o + \frac{A - \alpha_{ICl}[ICl_3]_o}{\alpha_{ICl_3} - \alpha_{ICl}}$$

ICl_3 is the initial concentration of iodine trichloride, A is observed absorbance, α_{ICl_3} is the molar absorbance of iodine trichloride, α_{ICl} is molar absorbance of iodine monochloride and K is the equilibrium constant. When analyzed this data yields

$$K = 2.8 \times 10^{-3} \pm 0.7 \times 10^{-3}$$

and

$$\alpha_{ICl_3} = 171 \pm 2$$

These results will be obtained only if extreme care is

exercised to aviod the loss of chlorine from the test solution. Any loss of chlorine will result in a shift in the line down and to the right as exemplified by the line (fig. 2). If the test solution is allowed to stand open to the atmosphere as in an open type cell, the small peak at 330 m (fig. 1-2) will disappear in approximately one hour. The Large peak at 460 m (fig. 1-3) will drop slightly to yield the peak for iodine trichloride. No work was attempted with the iodine trichloride donor systems.