Most of these compounds were examined for antiviral activity by Dr. D. J. Bauer of The Wellcome Laboratories of Tropical Medicine, Euston Road, London, England. Although several of the compounds showed some activity against one of the viruses used, that of Rift Valley Fever, on repetition of the experiments most of these proved to be inactive. Only one compound, N-(2,5-dimethoxy-4-nitrophenethyl)-dichloroacetamide (XIII of Table IB), gave a consistently positive result against Rift Valley Fever.

Acknowledgment.—The author is indebted to Samuel W. Blackman for the microanalyses included.

Experimental

A number of typical preparative procedures are outlined below.

N-(2,5-Dimethoxyphenethyl)-dichloroacetamide (VIII).—A mixture of 18 g. (0.1 mole) of 2,5-dimethoxyphenethylamine and 17 g. (0.12 mole) of methyl dichloroacetate was heated for two hours at 100°. The reaction mixture was cooled, 100 cc. of ether was added, and after scratching and chilling there was obtained 27 g. (93%) of white crystals. After recrystallization from benzene–hexane these melted at 83–84°.

N-(2,5-Dimethoxy-4-nitrophenethyl)-dichloroacetamide (XIII).—To 29 g. (0.1 mole) of the above amide (VIII) in 300 cc. of glacial acetic acid was added bit by bit with cooling and good stirring 15 cc. of concentrated nitric acid over a period of one hour. Yellow prisms start to precipitate near the end of the acid addition. After all acid had been added the mixture was left for two hours at room temperature, and then was diluted with 3 liters of cold water. The yellow crystalline product was collected and washed with water; yield 29 g. (87%); after recrystallization from methanol it melted at 155–156°.

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Spectrophotometric Study of the Tetrachloroiodide Complex in Acetonitrile

BY ALEXANDER I. POPOV AND JOHN N. JESSUP

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In conjunction with a detailed investigation of the behavior of polyhalogen ions in solutions, it was found necessary to study the absorption spectrum of trimethylsulfonium tetrachloroiodide. While a large number of metallic salts of the tetrachlorohydroiodic acid have been reported in the literature,[1] these compounds were found unsuitable for this investigation since they are only soluble in water or aqueous alcohol, solvents which rapidly hydrolyze the polyhalogen complexes. In order to obtain compounds soluble in organic solvents, it was necessary to resort to the salts of large organic cations. Trialkyl sulfonium salts were chosen because of the ease with which they can be prepared.

Following the method given by Werner,[2] 2 g. of trimethylsulfonium iodide was dissolved in 200 ml. of glacial acetic acid containing about 8% of carbon tetrachloride, and a slow stream of dry chlorine was passed through the solution for several minutes. The solution was cooled to 0° and yellow crystals of the complex crystallized out. The product was filtered, washed with chloroform to remove excess chlorine, and dried in an oven at 50°. About 1.7 g. (50% yield) of the complex was obtained. The melting point of the final product was 180° which does not agree with the m.p. of 155° given by Werner. Analysis for chlorine gave 40.2% Cl, calculated for $(CH_3)_3SICl_4$, 41% Cl. The compound was quite stable when kept stoppered and out of contact with moisture. Odor of chlorine was noticeable, however, if it was exposed to humid air.

It was found impossible to recrystallize this compound even if the solvents were previously saturated with chlorine. Invariably a mixture of the tetrachloride and the dichloride complexes was obtained.

For comparison purposes it was necessary to prepare the analogous dichloroiodide complex. Method of preparation suggested by Dobbin and Mason[3] was used with some modifications. Dry trimethylsulfonium iodide was placed in an erlenmeyer flask and a current of chlorine was passed over it. A dark brown residue appeared in the first step of the reaction, being probably the iodine chloride formed: $(CH_3)_3SI + Cl_2 \rightarrow (CH_3)_3SCl + ICl$. After several minutes the dark color disappeared and a yellow crystalline product was obtained. Since in all cases the analysis showed an excess of chlorine present (due to the formation of some tetrachloroiodide complex), the complex was recrystallized from alcohol, dried in an oven at 50°, and analyzed. The amount of chlorine found was 25.2%, calculated for $(CH_3)_3SICl_2$, 25.8% Cl. The melting point was 103° which agreed with that given by Dobbin and Mason. The yield was 60%.

It was necessary to cool the erlenmeyer during the reaction, and to pass the chlorine only at a very slow rate; otherwise, iodine chloride formed in the first step of the reaction would be carried off with resulting poor yields.

Since the ultraviolet spectrum of these complexes was of particular interest, the choice of a suitable solvent was somewhat restricted. Alcohols could not be used for reasons already given, and the saturated aliphatic hydrocarbons did not possess sufficient polarity to dissolve appreciable amounts of the complex.

Acetonitrile solutions were found to be relatively stable for short periods of time and the solvent did possess the required transmittancy in the ultraviolet region. As in all previous work with the polyhalogen complexes,[4] the purity of the solvent was quite critical.

Acetonitrile was purified by shaking it for several hours with a concentrated solution of potassium hydroxide, drying over anhydrous sodium carbonate and then distilling from phosphorus pentoxide through a three-foot column. The b.p. was 81.0° at 760 mm. of pressure.

Solutions were prepared by dissolving the required amount of the complex in acetonitrile, just before the absorption measurements. Usually,

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(1) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, New York, N. Y., 1950, p. 1198 ff.

(2) E. A. Werner, *J. Chem. Soc.*, **89**, 1625 (1906).

(3) L. Dobbin and O. Mason, *ibid.*, **47**, 67 (1885).

(4) (a) R. E. Buckles, A. I. Popov, W. F. Zelezny and R. J. Smith, THIS JOURNAL, **73**, 4525 (1951); (b) R. E. Buckles, J. Yuk and A. I. Popov, *ibid.*, **74**, 4379 (1952); (c) A. I. Popov and E. H. Schmorr, *ibid.*, **74** 4672 (1952).

the concentration was checked by an iodometric titration, and a good agreement was obtained with concentrations calculated from the weight of the sample. Every precaution was taken not to expose the solution to atmospheric moisture more than it was absolutely necessary. Two concentration ranges were used, depending on the region investigated. The solutions were approximately 10^{-3} M for measurements in the 380–260 mμ range, and 10^{-5} M in the 260–210 mμ range.

Absorption measurements were made on a Beckman model DU spectrophotometer and the final runs were on a Cary recording spectrophotometer model 11. Matched silica cells of 1-cm. path length were used. The experiments were carried out at room temperature, which was approximately 25°.

Preliminary measurements showed that the absorption spectrum of the tetrachloroiodide complex did change with time. Fresh solutions of this complex gave two maxima, one at 214 mμ with a molar absorbancy index of 42000,[5] and a second at 340 mμ with a molar absorbancy index of 1280. In about 30 minutes it was noticed that the absorbancy of the first peak increased and the maximum was shifted toward longer wave lengths, while the second maximum remained at the same wave length, but decreased in absorbancy.

A time study of this change of absorption is illustrated in Fig. 1. After 24 hours the maxima were at 227 and 338 mμ with the molar absorbancy indices of 55000 and 410, respectively. No further change of the absorption spectrum with time was observed.

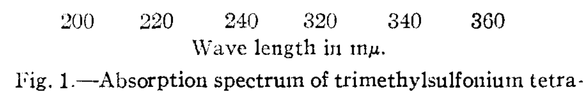

Fig. 1.—Absorption spectrum of trimethylsulfonium tetrachloroiodide in acetonitrile: curve 1, fresh solution; curve 2, after 2.5 hours; curve 3, after 24 hours.

The absorption curve of the dichloroiodide complex in acetonitrile is given in Fig. 2. The solution appeared to be stable and did not change the absorption spectrum with time. It is seen that this curve essentially coincides with the 24-hour old curve of the tetrachloroiodide complex. Presence of two isobestic points (Fig. 1) at 219 and 245 mμ shows that only two absorbing species were present in solution, and therefore the conclusion is warranted that the tetrachloroiodide ion dissociated in acetonitrile to the dichloroiodide and chlorine.

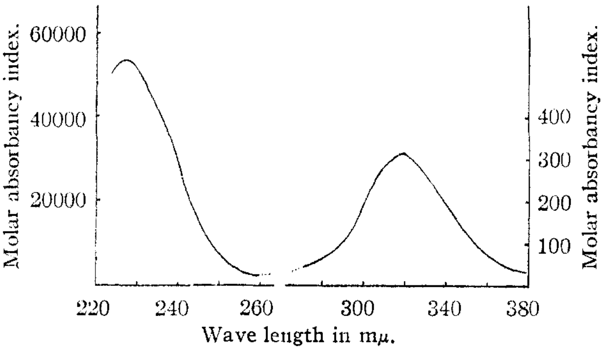

Fig. 2.—Absorption spectrum of trimethylsulfonium dichloroiodide in acetonitrile.

Undoubtedly, a fast equilibrium $(CH_3)_3SICl_4 \rightleftarrows (CH_3)_3SICl_2 + Cl_2$ is established, and curve 1, Fig. 1, illustrates the equilibrium conditions. The slow reaction observed is very probably due to the shift in equilibrium because of removal of chlorine by the chlorination of the solvent.

Since the tetrachloroiodide ion can be considered as a complex of iodine trichloride with Cl^-, it seems interesting to note that apparently this complex formation stabilizes iodine trichloride to some extent. It has been fairly well established that iodine trichloride molecule is stable only in the solid state[6] and dissociated in solution, immediately and completely, to iodine chloride and chlorine. If this was the case with the tetrachloroiodide complex, the initial absorption curve should be a composite curve of ICl_2^- and Cl_2. That this is not the case is easily seen from the fact that the absorbancy increases with time at 227 mμ. Attempts were made to obtain absorption curves of iodine trichloride and of chlorine in acetonitrile, but the results were unsatisfactory, because, in order to obtain sufficient amount of absorption, comparatively concentrated solutions ($\geqslant 10^{-2}$ M) had to be prepared and under these conditions the chlorination of the solvent was quite rapid.

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(5) Nomenclature used in this paper follows the recommendations of the National Bureau of Standards, Letter Circular, LC-857 (1947).

(6) A. E. Gillam and R. A. Morton, *Proc. Roy. Soc.* (*London*), **A124**, 604 (1929).

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A Polarographic Study of Thallium Pyrophosphate Complexes

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Polarographic studies of pyrophosphate complexes of various metals have been reported by Sartori,[2] Rogers and Reynolds,[3] Laitinen and Onstott[4] and Reynolds and Rogers.[5] In these investigations, no mention is made of the formation of thallium pyrophosphate complexes; and it is the purpose of the present paper to report a quantitative study of such compounds.

Experimental

Preliminary measurements were made with a Sargent model XI polarograph. Final waves were determined point

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(1) On leave from Faculdade de Filosofia, Ciencias e Letras da Universidade de Sao Paulo, Sao Paulo, Brazil.

(2) G. Sartori, *Gazz. chim. ital.*, **64**, 3 (1934).

(3) L. B. Rogers and C. A. Reynolds, THIS JOURNAL, **71**, 2081 (1949).

(4) H. A. Laitinen and E. I. Onstott, *ibid.*, **72**, 4729 (1950).

(5) C. A. Reynolds and L. B. Rogers, *Anal. Chem.*, **21**, 176 (1949).