Apparatus. Chromatographic tank about 3 inches in diameter and 6 inches high provided with an air-tight cover. Micropipets, 1 μl., 5 μl. Whatman No. 20 paper strips $1^1/_2$ inches wide and 6 inches in length.

Procedure. The mixture to be examined is prepared as a 5% solution in acetone. A sample of 1 to 5 μl. is applied to a spot on the paper strip about 10 mm. from the bottom. The strip is hung in the chromatographic tank so that the lower portion is inserted to a depth of about 1 to 3 mm. in mineral spirits previously saturated with water. The tank is then covered and the liquid is allowed to ascend about 100 mm. up the paper. The paper is removed from the tank and air-dried for a few minutes. The paper is coated with the ceric ammonium nitrate solution by applying with a paint brush. The paper is washed with water to remove excess reagent and then air-dried leaving colored spots to indicate the location of the phenols. The R_f' values are calculated as the distance to the top of the spot divided by the distance of the solvent front (*2*).

RESULTS AND DISCUSSION

The paper strip after drying can be examined to determine the presence and position of the three isomers. The *ortho* isomer has an R_f' value of 0.94 and the spot is rust-red colored. The *meta* isomer has an R_f' value of 0.70 and the spot is a light tan color. The *para* isomer has an R_f' value of 0.02 with a light green colored spot. The spots are permanent although the colors tend to fade slightly after a few days.

It is necessary to use mineral spirits previously saturated with water. The use of anhydrous mineral spirits results in an overlapping of the spots of the *ortho* and *meta* isomers. It has also been determined that for best results no isomer should be present in amounts less than 15% in the original mixture.

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The Use of Iodine Cyanide in the Determination of Iodide Ion

SIR: During a study of the reaction of iodine cyanide with thioethers, it was noticed that iodine appeared on acidification of a solution containing both iodide ion and iodine cyanide. The reaction is very rapid even at 0° C., and

$$H^+ + I^- + ICN \rightleftharpoons HCN + I_2 \quad (1)$$

can be made stoichiometric for the limiting reactant in the presence of an excess of the other. The iodine may be determined spectrophotometrically either directly in the aqueous solution or after extraction into carbon tetrachloride. Iodine cyanide provides half of the iodine formed and thus doubles the color produced when other oxidizing agents, such as ferric salts, nitrous acid, or hydrogen peroxide are used under similar conditions.

A procedure for the spectrophotometric determination of microquantities of iodine has been described by Custer and Natelson (*4*). The initial step involved oxidation by alkaline permanganate. Collins and Watkins (*2*) oxidized iodides to iodine with an acidified nitrite solution and extracted the iodine with carbon tetrachloride. Crouch (*3*) described a multistep process employing bromine oxidation and eventual measurement of a starch iodine complex. Where applicable, the procedures described below appear to be much simpler than any of these.

EXPERIMENTAL

Reagents and Apparatus. Iodine cyanide was synthesized according to the procedure of Bak and Hillebert (*1*). The product obtained after washing with ice water and air drying was used. The contaminating iodine or iodide ion (less than 0.002 mole/mole) was easily corrected for by control analyses. The compound was stored in a refrigerator. The initially colorless crystals discolored slowly on aging. Pure samples could be obtained by washing with ice-cold chloroform or petroleum ether (b.p. 30° to 60° C.). The iodine cyanide was used as a 0.10 to 0.15*M* aqueous solution, and could be kept in a refrigerator without crystallization at this concentration. Carbon tetrachloride was distilled before use. All other reagents were analytical grade and were used without purification.

A Beckman model DU spectrophotometer was used for the absorption determinations. The instrument was fitted with a narrow entrance slit to permit measurements on 0.4-ml. samples in the standard 1.5-ml. cuvettes with a 1-cm. path length. Slit widths of 0.2 to 0.3 mm. were employed.

Procedure. The sample should contain no more than 1.0 μmole of iodide ion in a total volume of 0.4 ml. or less. Up to 0.1 ml. of the stock iodine cyanide solution is added and the total volume made up to 0.5 ml. with water. One of two procedures is then followed:

(a) Add 0.25 ml. of 37% hydrochloric acid to the 0.5-ml. sample containing the iodine cyanide. Iodine is produced immediately. A fixed volume of carbon tetrachloride is then added (0.57 ml.), and extraction effected by gentle inversion of the small test tube. The absorbance of an aliquot of the CCl_4 solution (0.4 to 0.5 ml.) is then measured at 524 mμ against a water reference.

(b) Add 0.05 ml. of 37% hydrochloric acid to the 0.5-ml. sample, and measure the absorbance of the solution at 440 mμ against a water reference. The foregoing operations may be carried out at either 2° C. or at room temperature.

RESULTS AND DISCUSSION

When tested with standard solutions of potassium iodide, both procedures gave linear relationships between the number of μmoles of iodide ion and the measured absorbance. Procedure (a) was normally carried out at 2° C., procedure (b) at room temperature. The data were treated by linear regression.

Procedure (a)

$$A_{524} = (1.374 \pm 0.010)\,x + (0.002 \pm 0.012) \quad (2)$$

Procedure (b)

$$A_{440} = (1.529 \pm 0.015)\,x + (0.005 \pm 0.008) \quad (3)$$

where x is the number of μmoles of iodide ion in the sample. The intercept figures reflect the small contamination with iodide in the particular sample of iodine cyanide reagent.

In procedure (a) it was sufficient to have only a slight excess of iodine cyanide in accordance with Equation 1. More than 2 μmoles of reagent did not increase the slope of the line summarized by Equation 2. In procedure (*b*) a minimum of a 15-fold molar excess was required to give the data in Equation 3. (A 25-fold molar excess was used when the sample contained sodium dodecyl sulfate.) Under these conditions and within the limits of error of the determination, the results were not affected by the presence in the sample of 0.2*M* sodium chloride or 0.05*M* sodium dodecyl sulfate.

As well as ensuring the conversion of iodide ion to iodine, an increasing hydrochloric acid concentration was found

to increase the absorptivity of the aqueous iodine solution (Figure 1). However, since the concentration could be conveniently increased only by increasing the total volume, an optimum concentration was found to be given by the addition of 0.1 ml. of 37% HCl to the 0.5-ml. samples.

The distribution coefficient of iodine between water and carbon tetrachloride at 25° C. is 0.0118 (*5*). In approximately 4*N* hydrochloric acid and at 2° C., the value was found to be 0.111. Within the range of interest this value was independent of concentration. As long as this condition holds, the carbon tetrachloride aliquot will contain an amount of iodine linearly related to the total amount, in spite of incomplete extraction, provided that the volumes of both phases are accurately controlled.

When a thioether was present in the sample to be analyzed, the instantaneous appearance of iodine on acidification was accompanied by a much slower but continuing production of iodine. For analytical purposes this difficulty can be overcome in one of two ways. If the thioether is soluble in an immiscible organic solvent, for example carbon tetrachloride, it can be removed from the assay aliquot by a preliminary extraction before acidification. Iodide ion is not extracted, and most of the iodine cyanide stays in the aqueous phase [solubility ratio 4.8 between water and carbon tetrachloride at 25° C. (*6*)]. If a very water soluble thioether is involved, the assay is carried out at 2° C. to slow the secondary reaction as much as possible. The solution is then extracted twice with carbon tetrachloride at accurately timed intervals after acidification. The release of iodine is sufficiently slow that a very small extent of reaction is actually involved and a simple correction to zero time can be made.

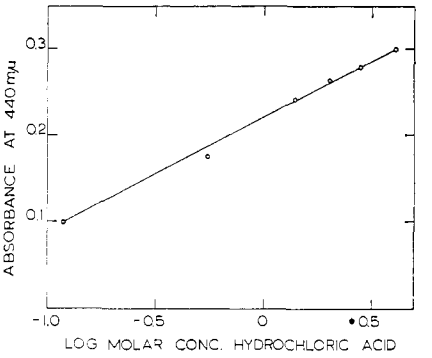

Figure 1. Absorbance in standard assay as function of hydrochloric acid concentration. In each case the sample was 0.203 μmoles of iodide ion and 1.58 μmoles of iodine cyanide in a volume of 0.5 ml. To these aqueous solutions varying amounts of HCl were added and the total volume made up to 0.75 ml.

Because of extensive hydrolysis of long chain alkyl sulfates by hydrochloric acid, forming viscous anisotropic solutions, procedure (a) was followed when the sample contained sodium dodecyl sulfate. Gentle inversions of the tubes were necessary to avoid the formation of fine emulsions when the iodine was being extracted. Phase separation was assisted by centrifugation. No satisfactory procedure has yet been worked out for solutions containing compounds such as cetyl trimethylammonium bromide due to specific complex formation between the latter and iodine.

The procedures may also be used to estimate iodine cyanide. For this purpose potassium iodide is used as the reagent and is added in the appropriate molar excess.

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Determination of Mercaptosilanes by Perchloric Acid–Catalyzed Acetylation and with Mercuric Acetate

SIR: A direct assay of the SiSC linkage in mercaptosilanes can be accomplished by the perchloric acid-catalyzed acetylation method of Fritz and Schenk (*1*). No direct assay of this linkage has previously been reported. The mechanism for the reaction of acetic anhydride with the SiSC linkage is presumably the same as that proposed for this method when employed for the direct determination of SiOC linkages (*5*). The acetylation method depends upon reaction of the mercaptosilane with excess acetic anhydride to give a thiolacetate and an acetoxysilane. The acetoxysilane and remaining anhydride are hydrolyzed and titrated with standard base.

The ease of hydrolysis of mercaptosilanes allows an indirect assay of the mercapto functional group by reaction with excess mercuric acetate in a methanol-toluene solvent. The excess mercuric acetate is titrated with standard hydrochloric acid in butanol to a thymol blue end point (*3*). Residual moisture in the solvents and hydrochloric acid–butanol titrant suffice for the hydrolysis of the mercaptosilane to the corresponding mercaptan.

EXPERIMENTAL

Perchloric Acid–Catalyzed Acetylation Method. Accurately weigh a sample containing about 5 meq. of the mercaptosilane into a 125-ml. glass-stoppered flask. Pipet into the flask 10 ml. of 1*M* acetic anhydride (0.04*M* perchloric acid) in ethyl acetate. Prepare this reagent as in (*1*) except for the changes in concentrations. Swirl the solution and let it stand for 5 minutes. Add 10 ml. of 3:1 pyridine-water and hydrolyze for more than 5 minutes. Add 4 drops of 0.1% 3:1 thymol blue–cresol red mixed indicator and titrate with alcoholic 0.5*N* potassium hydroxide to the blue end point. The reagent blank is run in the same manner, but without the sample. The mercapto content is calculated from the difference in volume between the sample and blank titrations.

Mercuric Acetate Method. Accurately weigh a sample containing about 4 meq. of mercaptosilane into a 250-ml. glass-stoppered flask containing 50 ml. of toluene. Pipet 50 ml. of 0.2*N* mercuric acetate in methanol (0.5 ml. acetic acid/liter) into the flask. Swirl the solution. Add three drops of 0.2% thymol blue indicator in ethanol. While stirring to promote reaction of the mercaptosilane with water in the titrant, titrate slowly with 0.2*N* hydrochloric acid in butanol to the red end point. The reagent blank is run in the same manner, but without the sample. The mercapto content is calculated from the difference in volume between the sample and blank titrations.