was obtained 0.48 g. (100%) of methyl phenyl sulfone, m.p. 87–88°; the melting point of a mixture with authentic methyl phenyl sulfone (m.p. 88°) was undepressed.

Similar results were obtained with bis-(trimethylsilylmethyl) sulfone and heptamethyl-(methanesulfonylmethyl)-cyclotetrasiloxane.

Three grams (0.018 mole) of trimethyl-(methanesulfonylmethyl)-silane was placed in a tube with a narrow graduated top. Ten milliliters of 5% sodium hydroxide solution was added. The mixture became very hot. It was shaken for 30 seconds and quickly cooled to room temperature under running water. The upper phase (2.0 ml., 100%) had $n^{20}D$ 1.3774; hexamethyldisiloxane has $n^{20}D$ 1.3772.[15]

Cleavage of Sulfones by Acids.—Three grams of trimethyl-(methanesulfonylmethyl)-silane was heated under reflux for 24 hours with 15 ml. of 5% hydrochloric acid. The sulfone was completely soluble in the hot solution. On cooling there was obtained 2.05 g. (68%) of trimethyl-(methanesulfonylmethyl)-silane of unchanged melting point. No hexamethyldisiloxane was observed.

Six grams (0.016 mole) of heptamethyl-(methanesulfonylmethyl)-cyclotetrasiloxane was heated under reflux for 24 hours with 100 ml. of 5% hydrochloric acid. The product was a soft gel. The gel was separated, washed thoroughly with boiling water, and dried for three days at room temperature and a pressure of 10 μ. It contained 2.2% sulfur and 35.3% silicon; the starting material contained 8.6% sulfur and 30% silicon.

The filtrate was evaporated to dryness under reduced pressure and the residue was recrystallized from benzene, yielding 0.56 g. (38%) of dimethyl sulfone, m.p. and m.m.p. 87–88°.

Three and two-tenths grams (0.0086 mole) of heptamethyl-(methanesulfonylmethyl)-cyclotetrasiloxane was heated under reflux for 20 hours with 20 ml. of water. The mixture was filtered and the filtrate was extracted several times with pentane. The aqueous phase was evaporated to dryness, yielding 0.72 g. (90%) of dimethyl sulfone, m.p. and m.m.p. 87–88°.

Four grams (0.024 mole) of trimethyl-(methanesulfonylmethyl)-silane was dissolved in 15 ml. of 96% sulfuric acid. The solution was stirred and heated at 85–90° for 30 minutes. The evolved gas was collected in a gas buret; it measured 560 ml. (94%) at 24° and 750 mm. and was shown to be pure methane by mass spectrometric analysis.

The sulfuric acid solution was poured over ice and neutralized with barium carbonate. The mixture was filtered and the filtrate was evaporated to dryness. The residue was extracted with chloroform and the chloroform solution was evaporated to dryness. Recrystallization of the residue from benzene yielded 1.2 g. (52%) of dimethyl sulfone, m.p. and m.m.p. 87–88°.

Preparation of Silicone Oils Containing the $-CH_2SCH_3$ Group.—Thirty-four and two-tenths grams (0.1 mole) of heptamethyl-(methanethiomethyl)-cyclotetrasiloxane, 0.65 g. (0.004 mole) of hexamethyldisiloxane and 1.3 ml. of 96% sulfuric acid were shaken together for 23 hours. Ten milliliters of water was added and the mixture was shaken for another hour. The oil was drawn off, shaken with anhydrous calcium chloride and precipitated calcium carbonate and filtered. It was devolatilized by heating for one hour at 100° and 0.5 mm. The resulting oil contained 9.2% sulfur (calculated 9.4% sulfur) and had a viscosity of 111 centistokes at 100°F.

Attempted Equilibration of Heptamethyl-(methanesulfonylmethyl)-cyclotetrasiloxane with Octamethylcyclotetrasiloxane and Hexamethyldisiloxane.—A mixture of 11.2 g. (0.03 mole) of heptamethyl-(methanesulfonylmethyl)-cyclotetrasiloxane, 8.88 g. (0.03 mole) of octamethylcyclotetrasiloxane and 1.62 g. (0.01 mole) of hexamethyldisiloxane was shaken with 1.0 ml. of 96% sulfuric acid for 40 hours. The product consisted of two phases, a slightly yellow, extremely viscous lower layer and a colorless, less viscous, upper layer. The phases were separated and washed and dried as described above. The upper layer, 15.3 g., contained 0.5% sulfur; the lower layer, 4.5 g., contained 14.4% sulfur. Similar results were obtained when heptamethyl-(methanesulfonylmethyl)-cyclotetrasiloxane was equilibrated with hexamethyldisiloxane alone, using sulfuric acid as the catalyst.

Reaction of Pentamethyl-(methanesulfonylmethyl)-disiloxane with Sulfuric Acid.—Twenty-one and seventenths grams (0.09 mole) of pentamethyl-(methanesulfonylmethyl)-disiloxane was shaken for 24 hours with 1.0 ml. of 96% sulfuric acid. The mixture was distilled at room temperature and a pressure of one mm. The volatile material consisted of 5.7 g. (0.035 mole) of hexamethyldisiloxane, $n^{20}D$ 1.3771.

The residue was extracted with pentane and the insoluble material was washed with water and dried, yielding 11.3 g. (0.035 mole) of 1,3-bis-(methanesulfonylmethyl)-tetramethyldisiloxane, m.p. 68–71°. Recrystallization from toluene–heptane raised the m.p. to 71–72°.

Acknowledgment.—The author wishes to thank Dr. J. R. Ladd for the preparation of the chloromethyl compounds, and Mr. E. M. Hadsell and Mrs. J. R. Ladd for fractional distillation of the sulfides.

SCHENECTADY, NEW YORK

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[15] R. O. Sauer, THIS JOURNAL, **66**, 1707 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Stability of Tetrabutylammonium Tetrachloroiodide[1]

BY ROBERT E. BUCKLES AND JACK F. MILLS

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Tetrabutylammonium tetrachloroiodide on illumination either in solution or as a solid lost hydrogen chloride and yielded (1-chlorobutyl)-tributylammonium ion which was isolated as the tetrachloroiodide. No analogous reaction was observed with tetramethylammonium tetrachloroiodide. The dissociation of tetrabutylammonium tetrachloroiodide into the dichloroiodide and chlorine was measured spectrophotometrically. At 25° in acetonitrile the pK of dissociation was 3.8 and in ethylene chloride 3.7. Dissociation in trifluoroacetic acid was quantitative. The absorption spectra of the tetrachloroiodides in either acetonitrile or ethylene chloride were found to change appreciably when the dissociation was suppressed since the absorption characteristic of the dichloroiodide was no longer observed.

Earlier preparative and analytical work on both metal and substituted ammonium tetrachloroiodides has been well outlined by Sidgwick.[2] In most cases the compounds were found to decompose slowly to give the more stable dichloroiodide and molecular chlorine. This instability in the case of trimethylsulfonium tetrachloroiodide has been recently investigated spectrophotometrically in acetonitrile.[3] The equilibrium between the tetrachloroiodide and the dichloroiodide and chlorine was presumably set up, but the extent of dissocia-

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[1] Work carried out under Contract No. AT(11-1)-72, Project No. 7 with the U. S. Atomic Energy Commission. Abstracted from the Ph.D. Thesis of Jack F. Mills. Presented before the Division of Organic Chemistry of the American Chemical Society, Kansas City, Mo., March, 1954.

[2] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, London, 1950, pp. 1198–1200.

[3] A. I. Popov and J. N. Jessup, THIS JOURNAL, **74**, 6127 (1952).

tion could not be measured because the chlorine was lost either by chlorination or volatilization.

In the present investigation the extent of dissociation of tetrabutylammonium tetrachloroiodide was measured spectrophotometrically in acetonitrile and in ethylene chloride. Dissociation constants were calculated[4] from the absorption spectra of the dissociated and the undissociated tetrachloroiodide. The latter spectrum in each case was obtained by suppression of the dissociation with excess chlorine. Excess dichloroiodide ion produced a similar suppression but quantitative measurements were not satisfactory because of the intense absorption of the dichloroiodide ion[5] in the region of the spectrum where the tetrachloroiodide has suitable absorption. For calculation of the dissociation constants, corrections were made for the absorption caused by the dichloroiodide ion and the chlorine formed in the dissociation and for the dissociation of the dichloroiodide ion, itself, especially in ethylene chloride where it is appreciable.[5] The dissociation constant at 25° in acetonitrile was $(1.43 \pm 0.19) \times 10^{-4}$ and that in ethylene chloride $(1.85 \pm 0.11) \times 10^{-4}$ where the measure of the precision sets the 95% confidence limits of the averages. Measurements were made throughout the region 300–400 mμ and in several different solutions with concentrations of the order of 10^{-3} *M*. Equilibrium was reached in these solutions in an hour or two. Unless subjected to strong illumination the solutions then underwent no appreciable change for several hours. More dilute solutions with concentrations of the order of 10^{-5} *M* showed changes which were much more erratic even when kept in complete darkness. Consequently no quantitative measurements of the extent of dissociation could be made.

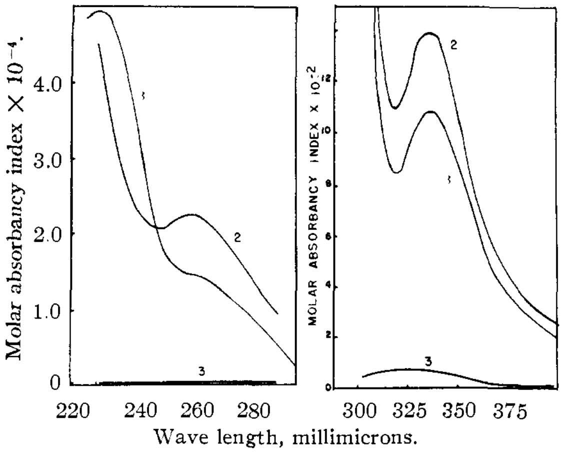

Fig. 1.—Absorption spectra in acetonitrile: 1, tetrabutylammonium tetrachloroiodide (solutions at equilibrium), 1.30×10^{-3} *M* for near ultraviolet and 6.0×10^{-5} *M* for far ultraviolet; 2, tetrabutylammonium tetrachloroiodide with dissociation suppressed (spectra corrected for absorption by chlorine), 7.2×10^{-4} *M* tetrachloroiodide and 9.9×10^{-3} *M* chlorine for near ultraviolet and 2.90×10^{-5} *M* tetrachloroiodide and 3.94×10^{-4} *M* chlorine for far ultraviolet; 3, 9.86×10^{-3} *M* chlorine in both regions.

The differences between the spectrum of dissociated tetrabutylammonium tetrachloroiodide and that of the undissociated salt corrected for the presence of excess chlorine are illustrated in Fig. 1. In acetonitrile the molar absorbancy index (molar extinction coefficient) for the peak at 336 mμ was 1.10×10^3 when dissociated and 1.39×10^3 when undissociated. The absorption spectra of the more dilute solutions were qualitative at best because of the instability of the solutions. In ethylene chloride a peak of molar absorbancy index 1.20×10^3 was observed at 338 mμ for the dissociated salt in 1.8×10^{-3} *M* solution. This value was increased to 1.55×10^{-3} when dissociation was suppressed. Also a new peak of molar absorbancy index 1.9×10^4 appeared at 259 mμ. Tetramethylammonium tetrachloroiodide gave qualitatively the same spectra as the tetrabutylammonium salt in the two solvents.

As was the case with the dichloroiodides[5] both tetrabutylammonium and tetramethylammonium tetrachloroiodides were completely dissociated in trifluoroacetic acid. This dissociation is illustrated in Fig. 2 where the absorption spectrum of tetrabutylammonium tetrachloroiodide is shown to be essentially identical with that of an equimolar mixture of chlorine and iodine chloride or that of iodine trichloride.

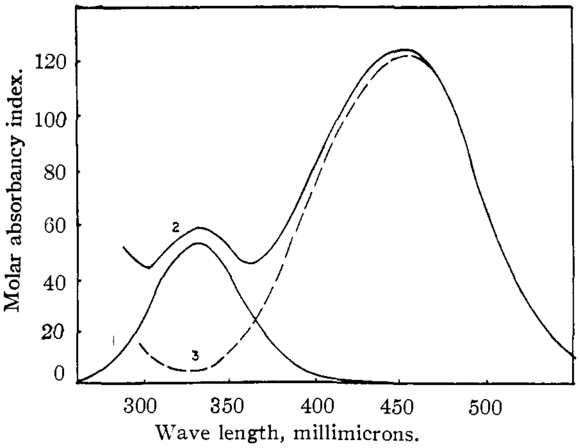

Fig. 2.—Absorption spectra in trifluoroacetic acid: 1, 3.0×10^{-2} *M* chlorine; 2, 9.3×10^{-3} *M* tetrabutylammonium tetrachloroiodide or 5.4×10^{-3} *M* iodine trichloride; 3, 2.34×10^{-2} *M* iodine chloride.

Solutions of tetrabutylammonium tetrachloroiodide in either acetonitrile or ethylene chloride which were illuminated with ultraviolet radiation underwent more extensive changes than those observed during dissociation. Eventually the tetrachloroiodide ion was destroyed and all of the iodine could be accounted for as a quantitative yield of triiodide ion which was measured spectrophotometrically.[6] In the presence of excess chloride ion in acetonitrile a quantitative yield of dichloroiodide ion was observed spectrophotometrically.[5] In either case no appreciable amount of iodine could have been used up in iodination.

In solution in ethylene chloride as well as in the crystalline state the tetrabutylammonium tetra-

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[4] A. I. Popov, K. C. Brinker, L. Campanaro and R. W. Rinehart, THIS JOURNAL, **73**, 514 (1951).

[5] R. E. Buckles and J. F. Mills, *ibid.*, **76**, in press (1954).

[6] R. E. Buckles, J. P. Yuk and A. I. Popov, *ibid.*, **74**, 4379 (1952).

chloroiodide reacted when illuminated to yield the (1-chlorobutyl)-tributylammonium ion which was isolated as the tetrachloroiodide. The same ion was formed when a solution of tetrabutylammonium chloride in ethylene chloride was treated with chlorine under illumination. Further chlorination was observed when (1-chlorobutyl)-tributylammonium tetrachloroiodide was illuminated in ethylene chloride.

The position of the chlorine on the monochlorotetrabutylammonium ion was established by treatment with silver oxide in hot water followed by a distillation of the product from the acidified solution. The formation of butyraldehyde was demonstrated by a Tollens test on the distillate and the formation of the 2,4-dinitrophenylhydrazone. Only with chlorine on the 1-carbon atom of the butyl group could butyraldehyde be the product of the degradation. The more highly chlorinated tetrabutylammonium ion also gave the same degradation product, but this result did not prove the position of the second chlorine was also the 1-position on a second butyl group although this would be the product expected.

Experimental Part

Tetrabutylammonium Tetrachloroiodide.—An excess of dry chlorine gas was passed into a solution of 20.0 g. (0.054 mole) of tetrabutylammonium iodide[6] in 150 ml. of chloroform. The solution was heated on a steam-bath for ten minutes and then cooled to yield 24.8–26.2 g. (90–95%) of the yellow crystalline product, m.p. 137–139°.[7] The product was prepared and stored in the dark because of its sensitivity to light. The crystalline salt gave no evidence of chlorine evolution on standing, but did evolve hydrogen chloride on illumination.

Anal. Calcd. for $C_{16}H_{36}Cl_4IN$: C, 37.6; H, 7.10; N, 2.74; ICl_3, 45.6. Found: C, 37.2; H, 7.15; N, 2.78; ICl_3, 44.9 (iodometric).

Tetramethylammonium Tetrachloroiodide.—Nearly quantitative yields (25 g.) of tetramethylammonium tetrachloroiodide were obtained when dry chlorine was passed into a solution of 20.0 g. (0.074 mole) of tetramethylammonium dichloroiodide[5] in 80 ml. of glacial acetic acid and 20 ml. of 6 *N* hydrochloric acid. The product after it was washed with carbon tetrachloride had m.p. 287–289°.

The same salt was obtained by the reaction of 20.0 g. (0.074 mole) of tetramethylammonium dichloroiodide with 19.0 g. (0.082 mole) of iodine trichloride (from chlorine and iodine chloride) in 200 ml. of glacial acetic acid on a steam-bath. Cooling gave 27.8 g. (99%) of the tetramethylammonium tetrachloroiodide, m.p. 288–289°. This salt had been prepared before,[8] but no m.p. was recorded. As in these earlier preparations the halogen analysis was low, indicating some decomposition of the tetrachloroiodide.

Anal. Calcd. for $C_4H_{12}Cl_4IN$: ICl_3, 68.0. Found: ICl_3, 66.3 (iodometric).

The crystalline salt decomposed slowly with evolution of chlorine, but it could be stored several weeks at 0° with little decomposition. Illumination of the solid salt failed to produce detectable amounts of hydrogen chloride.

(1-Chlorobutyl)-tributylammonium Tetrachloroiodide.—A solution of 30.0 g. (0.059 mole) of tetrabutylammonium tetrachloroiodide in 200 ml. of ethylene chloride was illuminated with an ultraviolet lamp for five days. The dark brown solution was evaporated to one-tenth of its original volume and added to 200 ml. of glacial acetic acid. An excess of dry chlorine gas was bubbled into this solution and yellow crystals precipitated immediately. Crystallization from a mixture of chloroform and glacial acetic acid gave 22.5 g. (70%) of (1-chlorobutyl)-tributylammonium tetrachloroiodide, m.p. 123–124°.

Anal. Calcd. for $C_{16}H_{35}Cl_5IN$: C, 35.2; H, 6.47; N, 2.57; ICl_3, 42.8. Found: C, 35.7; H, 6.43; N, 2.63; ICl_3, 42.8 (iodometric).

Illumination of 5.0 g. (0.0098 mole) of crystalline tetrabutylammonium tetrachloroiodide for several days yielded 2.1 g. (40%) of (1-chlorobutyl)-tributylammonium tetrachloroiodide, m.p. 123–124°, when the product was isolated as described above. Illumination for two days of 20 g. (0.072 mole) of tetrabutylammonium chloride[5] in 200 ml. of ethylene chloride saturated with chlorine gave rise to 3.0 g. (8%) of (1-chlorobutyl)-tributylammonium tetrachloroiodide, m.p. 123–124°, when the product was isolated as described above except that 9.5 g. (0.037 mole) of iodine was added before the acetic acid solution was treated with excess chlorine.

Dichlorotetrabutylammonium Tetrachloroiodide.—A solution of 20 g. (0.037 mole) of (1-chlorobutyl)-tributylammonium tetrachloroiodide in 200 ml. of ethylene chloride was illuminated and treated in the same way as described for tetrabutylammonium tetrachloroiodide. Several recrystallizations of the product from mixtures of chloroform and acetic acid gave 10.8 g. of a product, m.p. 101–103°. On the basis of its analyses this product was presumably a mixture of the starting material, (1-chlorobutyl)-tributylammonium tetrachloroiodide, and a dichloro salt, probably bis-(1-chlorobutyl)-dibutylammonium tetrachloroiodide.

Degradation of (1-Chlorobutyl)-tributylammonium Tetrachloroiodide.—A mixture of 10 g. (0.018 mole) of (1-chlorobutyl)-tributylammonium tetrachloroiodide and 30 g. (0.13 mole) of silver oxide in 200 ml. of hot water was stirred vigorously for 30 minutes. The solution was filtered, acidified with dilute sulfuric acid and distilled. The first 20 ml. was collected. A part of the distillate gave a strong Tollens test. A 10-ml. sample of the distillate was used to prepare the 2,4-dinitrophenylhydrazone of butyraldehyde, m.p. 119–121°. A small amount of the distillate on standing developed the characteristic odor of butyric acid.

The mixture of monochloro- and dichlorotetrabutylammonium tetrachloroiodides gave comparable results when treated as described above. No evidence of aldehyde formation was obtained when the procedure was carried out on tetrabutylammonium tetrachloroiodide.

Purification of Solvents.—Ethylene chloride,[9] trifluoroacetic acid[9] and acetonitrile[5] were purified as previously described.

Absorption Spectra Measurements.—Fresh stock solutions were prepared and standardized[5] for each series of measurements except when aging of solutions was investigated. Aging was carried out on some solutions in the dark, on some illuminated in the spectrophotometer, and on some illuminated by stronger ultraviolet lamps. Measurements were carried out at 25° in calibrated silica cells of path length 1.00 ± 0.01 cm. with a Cary model 11 recording spectrophotometer. The uniform nomenclature and symbology suggested by the National Bureau of Standards[10] has been used throughout this article. For each of the spectra given in the figures molar absorbancy index (molar extinction coefficient) has been plotted against wave length.

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[7] All m.p.'s corrected.

[8] W. N. Rae, THIS JOURNAL, **45**, 1725 (1923); C. Weltzien, *Ann.*, **99**, 1 (1856).

[9] R. E. Buckles and J. F. Mills, THIS JOURNAL, **75**, 552 (1953).

[10] National Bureau of Standards, Letter Circular LC 857 (1947).