to be 1,2-isopropylidene-L-iduronolactone. Further investigation of this by-product is planned.

D-Glucuronolactone from Monoacetone-D-glucuronic Acid*.[15]—A solution containing 100 mg. of monoacetone-D-glucuronic acid, m.p. 144–145°, in a few ml. of water was heated on the steam-bath for two hours, and then evaporated to dryness on the steam-bath. Seeding of the residual sirup and the addition of a few drops of ethanol then produced 75 mg. (quantitative) of D-glucuronolactone, m.p. 168–172°, $[\alpha]_D$ 20°, in water.

6-C^{14}-D-Glucose.—A suspension of 535 mg. of 6-C^{14}-monoacetone-D-glucuronic acid, m.p. 143–144°, in 25 ml. of toluene was heated under reflux for three hours. The resulting clear solution was cooled and diluted with 15 ml. of petroleum ether (Skellysolve F). The ensuing crystallization was completed by gradual dilution with an additional 35 ml. of petroleum ether. The acetonated lactone separated as well-formed needles adhering to the surface of the flask. The product was isolated by decantation of the solvents and washed in place, by decantation, with petroleum ether; yield, 485 mg. (98%), m.p.* 119–120°.

The acetonated lactone was dissolved in 40 ml. of water containing 150 mg. of sodium borohydride. One-half hour later, an additional 100 mg. of sodium borohydride was rinsed in with 5 ml. of water. After standing four hours at room temperature, the solution was acidified by the dropwise addition of 2 ml. of 6 N sulfuric acid and then heated for one hour on the steam-bath. The cooled solution then was passed through a column containing in successive bands 15 ml. of Duolite A-4,[17] 15 ml. of Amberlite IR-100-H, and 15 ml. of Duolite A-4. The combined effluent and washings were concentrated at reduced pressure to a colorless sirup. Crystallization from 3–4 ml. of 95% ethanol yielded 185 mg. of 6-C^{14}-D-glucose, m.p. 145–146°, $[\alpha]_D$ 52.5°, equil. in water*.

The crystallization filtrate and washings (ethanol) were diluted with water and then used to dissolve 500 mg. of non-radioactive D-glucose. Concentration and crystallization then yielded 500 mg. of 6-C^{14}-D-glucose showing 10% of the specific radioactivity shown by the undiluted radioactive sugar. The yield of 6-C^{14}-D-glucose from 6-C^{14}-monoacetone-D-glucuronolactone is thus approximately 60%.

Acetonation of D-Glucuronolactone*.[9]—D-Glucuronolactone (240 mg.) was stirred in a closed flask (magnetic stirrer) for 2.5 hours with 15 ml. of acetone containing 0.1 ml. of sulfuric acid. The resulting clear solution then was passed through a column containing 8 ml. of Duolite A-4 moistened with acetone. Concentration of the effluent left a residue of crystalline monoacetone-D-glucuronolactone. Recrystallization from ether–petroleum ether gave 190 mg. (64%) of the product, m.p. 119–120°.

Radioactivity of Products.—The undiluted 6-C^{14}-D-glucuronolactone and 6-C^{14}-D-glucose described above were calculated from the original dilution of $NaC^{14}N$ to give approximately 10^6 dis./min./mg. When counted as thin layers (*ca.* 1 µg./sq. cm.) in the Nucleometer,[18] each product showed approximately 5 × 10^5 ct./min./mg.

---

[17] Product of Chemical Process Co., Redwood City, Cal. After regeneration and washing, this resin, prior to use, was treated with several volumes of 5% sodium chloride solution and then washed free of chloride ion.

[18] Manufactured by Radiation Counter Laboratories, Chicago, Ill.

ST. LOUIS, MISSOURI

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

The Stability of the Tetramethylammonium Polyiodides in Ethylene Chloride[1]

BY ROBERT E. BUCKLES, JAMES P. YUK AND ALEXANDER I. POPOV

RECEIVED FEBRUARY 14, 1952

The three known tetramethylammonium polyiodides, $(CH_3)_4NI_3$, $(CH_3)_4NI_5$ and $(CH_3)_4NI_9$, have been studied spectrophotometrically in ethylene chloride. The pentaiodide and the enneaiodide were shown to have absorption spectra consistent with the view that in dilute solutions they are virtually completely dissociated into the triiodide and iodine. The method of continuous variation applied to mixtures of iodine and tetramethylammonium monoiodide gave evidence that the only stable polyiodide in very dilute solutions in ethylene chloride is the triiodide. The dissociation of the triiodide into the monoiodide and iodine was calculated to have a pK value of 7.0 ± 0.2 at 25°.

A fairly large number of quaternary ammonium polyiodides including triiodides, pentaiodides, heptaiodides and enneaiodides have been reported.[2]

The stability and identity of each of these solid polyiodides has been studied to some extent as a part of its preparation and isolation. In some cases there have been more detailed studies such as that of the system: tetramethylammonium iodide–iodine, which has been reported[3] to show the tri-, penta- and enneaiodides with congruent m.p.'s whereas the m.p. of the heptaiodide was incongruent. Attempts to isolate the tetramethylammonium heptaiodide have not been successful.[2a] X-Ray diffraction studies of the crystals of tetraethylammonium triiodide[4] and tetramethylammonium pentaiodide[5] have led to the determination of the crystal structure in each case.

From an early study[6] of the solubilities of mixtures of iodine and tetramethylammonium iodide in nitrobenzene it was concluded that the enneaiodide was the highest polyiodide which existed in solution. These results, however, merely point up the fact that the enneaiodide was insoluble enough to precipitate under certain conditions and do not give any information as to the relative concentrations of the various polyiodides in solution.

The ultraviolet absorption spectrum of p-bromophenyltrimethylammonium triiodide has been measured.[7] Also the spectra of mixtures of quaternary ammonium iodides with iodine in aqueous alcohol have been reported.[8] In neither case was any study of the identity of the absorbing species carried out. It has been suggested on the basis of some electrical conductivity measurements

---

[1] Part of this work was carried out under Contract No. At(11-1)-72, Project No. 7, with the Atomic Energy Commission. Presented before the Organic Division of the American Chemical Society, Milwaukee, Wisconsin, April 1, 1952.

[2] (a) F. D. Chattaway and G. Hoyle, *J. Chem. Soc.*, **123**, 654 (1923); (b) H. McCombie and T. H. Reade, *ibid.*, **123**, 141 (1923); (c) D. Strömholm, *J. prakt. Chem.*, **67**, 345 (1903); (d) A. Geuther, *Ann.*, **240**, 66 (1887); (e) R. Muller, *ibid.*, **108**, 1 (1858); (f) Weltzien, *ibid.*, **91**, 33 (1854).

[3] F. Olivari, *Atti. accad. Lincei*, **17**, II, 717 (1908).

[4] R. C. L. Mooney, *Phys. Rev.*, **53**, 851 (1938).

[5] R. J. Hach and R. E. Rundle, THIS JOURNAL, **73**, 4321 (1951).

[6] H. M. Dawson and E. C. Goodson, *J. Chem. Soc.*, **85**, 796 (1904).

[7] F. L. Gilbert, R. R. Goldstein and T. M. Lowry, *ibid.*, 1092 (1931).

[8] C. K. Tinkler, *ibid.*, **93**, 1611 (1908).

of the tetramethylammonium polyiodides in molten iodine that the enneaiodide is partially dimerized in this solution.[9]

Except for a recent investigation[10] of the stability of tetrabutylammonium tribromide in bromotrichloromethane no study of the stability of quaternary ammonium polyhalides in relatively non-polar solvents has been carried out. The present investigation is concerned with the identity of species in ethylene chloride solutions of tetramethylammonium triiodide tetramethylammonium pentaiodide and tetramethylammonium enneaiodide.

Experimental

Tetramethylammonium Polyiodides.—A hot solution of the required amount of tetramethylammonium iodide and 3.3 g. (0.013 mole) of iodine in 30 ml. of methanol was cooled to yield the product. From 2.0 g. (0.010 mole) of monoiodide was obtained 3.5 g. (77%) of the triiodide, m.p. 117.0–117.2°; reported[2a] as 118°.[11] One gram (0.0050 mole) of the monoiodide yielded 3.4 g. (96%) of the pentaiodide, m.p. 129–130°; reported[2a] as 132°. The reaction of 0.50 g. (0.0025 mole) of the monoiodide gave 1.8 g. (75%) of the enneaiodide, m.p. 110°, which is that reported.[2a] The triiodide was the most difficult of the three to obtain pure. With other solvents or with different proportions of reagents either the monoiodide or the pentaiodide crystallized with the triiodide or even in place of it. Attempts to prepare the heptaiodide yielded only impure pentaiodide or enneaiodide. All of the crystalline polyiodides gave satisfactory iodometric equivalent weights when subjected to the method described[10] for tetrabutylammonium tribromide.

Ethylene Chloride.—Commercial ethylene chloride was shaken with concentrated sulfuric acid followed by two or three portions of water. The material was dried over calcium chloride and then heated with barium oxide under reflux. Distillation through a two-foot column packed with glass helices gave a product of b.p. 83.0–83.1° (740 mm.).

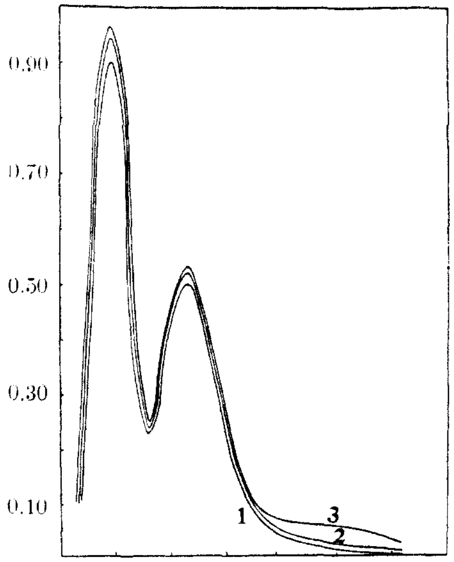


Fig. 1.—Absorption spectra in ethylene chloride: 1, tetramethylammonium triiodide; 2, tetramethylammonium pentaiodide; 3, tetramethylammonium enneaiodide. The solutions were 2×10^{-5} M. For the triiodide the absorption peaks were at 295 mμ ($a_M = 4.51 \times 10^4$) and 365 mμ ($a_M = 2.53 \times 10^4$). For the enneaiodide they were at 295 mμ ($a_M = 4.83 \times 10^4$) and 365 mμ ($a_M = 2.61 \times 10^4$).

Absorption Spectra.—Solutions of the polyiodides were prepared from weighed samples. Those of iodine were standardized by iodometry. Fresh stock solutions were prepared for each series of experiments. The absorbancies of the solutions were measured at 25° in calibrated silica cells of path length 1.000 ± 0.001 cm. with a Beckman DU spectrophotometer. The symbols and nomenclature suggested by the National Bureau of Standards[12] have been used throughout this article.

Results and Discussion

The absorption spectra of the three tetramethylammonium polyiodides in ethylene chloride are

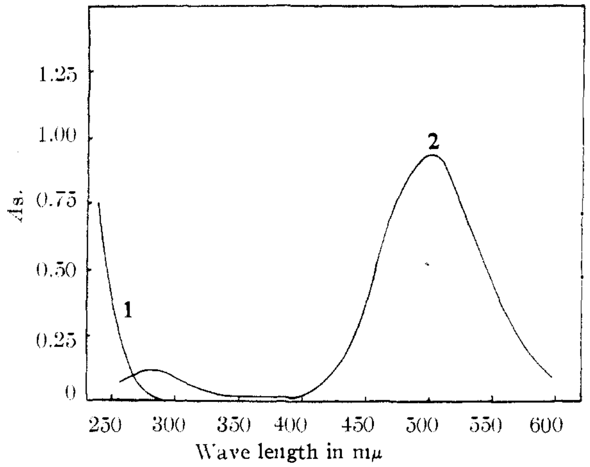


Fig. 2.—Absorption spectra in ethylene chloride: 1, 1.16×10^{-4} M tetramethylammonium monoiodide; 2, 1.06×10^{-3} M iodine.

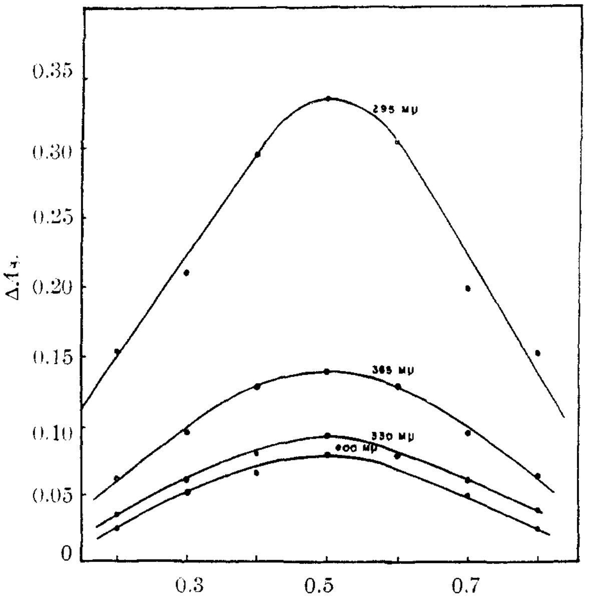


Fig. 3.—Method of continuous variation in ethylene chloride. The absorbancy of the solution less the calculated absorbancy of the iodine–tetramethylammonium iodide mixture is plotted against the mole fraction of iodine in the mixture. The total concentration of monoiodide plus iodine in each solution was 1.5×10^{-5} M.

---

(9) Ya. A. Fialkov and N. V. Aksel'rud, *J. Gen. Chem. (U.S.S.R.)*, **13**, 753 (1943).

(10) R. E. Buckles, A. I. Popov, W. F. Zelezny and R. J. Smith, This Journal, **73**, 4525 (1951).

(11) All m.ps. corrected.

(12) National Bureau of Standards, Letter-Circular, LC-857 (1947).

given in Fig. 1. That of the triiodide conforms fairly well with results reported[8,13] for the triiodide ion in water or ethanol. All three spectra are nearly identical except that the molar absorbancy index increases slightly as the mole ratio of iodine to monoiodide in the polyiodide increases. These results are consistent with the interpretation that the triiodide is the only polyiodide stable in dilute solutions and that its slight dissociation is suppressed in the solutions of the higher polyiodides by the iodine formed when the polyiodide dissociates to triiodide and iodine. In fact a solution with an excess of iodine greater than that to be found in a solution of the enneaiodide gave a spectrum identical with that of the enneaiodide except that the iodine peak at about 500 mμ was higher. For comparison the spectra of iodine and tetramethylammonium iodide in ethylene chloride are given in Fig. 2.

To verify the fact that the polyiodide existing in solution is the triiodide the method of continuous variation[14] was applied to mixtures of tetramethylammonium iodide and iodine varying in concentration from 1:9 to 9:1. Measurements were made at four wave lengths, and the difference between the absorbancy of the solution and the calculated absorbancy, assuming simple mixing of the monoiodide and the iodine, was plotted against the mole fraction. The results are given in Fig. 3. The peak for each wave length appears at a mole fraction of 0.5 which verifies the 1:1 compound, the triiodide, as the absorbing molecule. One must conclude from these results that the existence of the higher polyiodides in dilute solutions in appreciable concentrations is doubtful.

The equilibrium constant for the dissociation of the triiodide in ethylene chloride at 25° was calculated by the method previously outlined.[15] The dissociation was suppressed by excess iodine as shown in the spectrum of the enneaiodide in Fig. 1. For a solution of concentration 2×10^{-5} M the degree of dissociation was found to be 0.068 ± 0.020 which corresponds to a pK value of 7.0 ± 0.2. This value can be compared with some of the reported values for the dissociation of triiodide ion in water: 2.90[16] at 16°, 2.87[17] at 25° and 2.68[13] at 39°. In alcohol a higher pK of 4.52 at 14° has been reported.[18] The still higher value in ethylene chloride is the result that would be expected in this relatively non-polar solvent.

---

[13] A. D. Awtrey and R. E. Connick, THIS JOURNAL, **73**, 1842 (1951).

[14] P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

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

[16] P. Job, *Compt. rend.*, **182**, 632 (1926).

[17] V. K. LaMer and M. H. Lewinsohn, *J. Phys. Chem.*, **38**, 171 (1934).

[18] P. Job, *Compt. rend.*, **182**, 1621 (1926).

IOWA CITY, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

The Thermal Decomposition of Deuterated Barium Butyrate

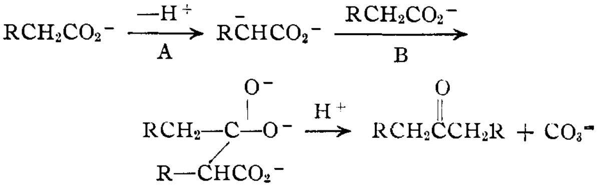
BY KENNETH B. WIBERG

RECEIVED FEBRUARY 28, 1952

The thermal decomposition of a mixture of deuterated and undeuterated barium butyrate has been effected. It is observed that deuterium exchange between the deuterated and undeuterated species is rapid with respect to the decomposition.

Although the thermal decomposition of barium salts of carboxylic acids has been known for many years, little is known about the details of the reaction. Among the few known facts are: (1) aliphatic acids lacking an α-hydrogen do not react,[1] (2) benzoic acid, however, does react,[2] (3) in the reaction of barium formate with barium acetate, the carbonyl group in the acetaldehyde formed is derived from the formate,[3] (4) there is no C^{13} isotope effect in the reaction,[4] and (5) cyclopentanone reacts with carbon dioxide and sodium acetate to give adipic acid.[1]

Two significantly different mechanisms have been proposed for this reaction. The first, that of Neunhoeffer and Paschke,[1] involves the initial formation of a β-ketoacid anion, followed by decarboxylation



The second, that of Bell and Reed,[3] suggests that in the reaction of barium acetate with barium formate, a methyl radical is first formed, which then reacts with the formate anion to give acetaldehyde or with acetate anion to give acetone.

It was hoped that some evidence concerning this reaction could be derived from a study of the thermal decomposition of a mixture of deuterated and undeuterated barium butyrate. If the ionic mechanism is correct, one would expect an isotope effect if step A (above) is rate controlling since it is known that the breaking of a carbon–deuterium bond is usually considerably slower than the

---

[1] O. Neunhoeffer and P. Paschke, *Ber.*, **72**, 919 (1939).

[2] E. Péligot, *Ann.*, **12**, 39 (1834). Other products of this reaction are: benzene, biphenyl (G. Chancel, *ibid.*, **72**, 279 (1849); **80**, 285 (1851)), anthraquinone (A. Kekule and A. Franchimont, *Ber.*, **5**, 909 (1872)), anthracene and 9-phenylfluorene (A. Behr, *ibid.*, **5**, 970 (1872)). Considering the variety of products formed, it is not unlikely that the mechanism of this reaction is different from that of the aliphatic acids.

[3] J. Bell and R. I. Reed, *Nature*, **165**, (1950).

[4] A. A. Bothner-By, L. Friedman and J. Bigeleisen, Brookhaven Conf. Rept., Chem. Conf. No. 4, 39 (Jan., 1950): *C. A.*, **45**, 3807 (1951).