terest to determine whether alkylboron compounds would perform as well. Long and Norrish[1] have already investigated the combustion of trimethylboron. However, they included no evidence to substantiate the completeness of combustion other than the observation that, at the end of there action, relatively small quantities of dark material were present in the bomb.

In this research, tri-*n*-butylboron has been burned in a calorimeter and the carbon dioxide and residual boric oxide measured. The heat of combustion has been measured, and from this value the heat of formation and the B–C bond energy have been calculated.

Experimental

Tri-*n*-butylboron.—Tri-*n*-butylboron was synthesized by the method reported by Johnson, *et al.*[4] The material was carefully fractionated and the center fraction, with a boiling point of 89.5° at 9 mm. pressure, was used for this study.

Apparatus and Procedure.—A Parr Adiabatic Calorimeter with an Illium constant volume bomb[5] was used for the measurements. The bomb was calibrated using standard benzoic acid supplied by Parr Instrument Co. The details of the procedure and analysis for carbon dioxide have already been reported.[3] For this compound, 30 atmospheres proved to be a proper oxygen pressure. The boric acid present at the end of the reaction was titrated with sodium hydroxide using a mixed indicator.[6]

Results and Discussion

After several preliminary experiments, the proper conditions for good combustion were obtained and the data for the last four consecutive runs are shown in Table I.

TABLE I

Sample wt., g.	$\Delta E_{\text{comb.}}$, kcal./g.	Carbon, %	Boron, %
0.5649	11.62	78.51	5.97
.4340	11.57	78.41	5.85
.4069	11.60	78.12	5.87
.4384	11.62	[a]	5.90
Average	11.60	78.37	5.90
Theor. anal.		79.12	5.94

[a] Gas leak occurred during analysis.

In all cases, traces of dark material were found indicating that the reaction was not absolutely complete; however, the analytical data show clearly that good combustion was attained. Although only 99.1% of the expected carbon dioxide and 99.3% of the boric oxide were recovered, the heat of combustion measured might well be closer to the correct value and is considered to be within ±0.5% of this value. This is based on the fact that there are inevitable mechanical losses in the analysis and also that some heat release occurs even for the material which is not completely oxidized to B_2O_3 and CO_2. It is quite likely that the experimental value is somewhat lower than the actual value since the combustion is not absolutely complete.

The value for the heat of combustion was converted from a constant volume to a constant pressure process and in addition a correction was made for the amount of boric acid which formed.[1] No correction was made for incompleteness of combustion nor were the Washburn corrections applied.[7]

The heat of the reaction ($\Delta H_{\text{comb.}}$ 25° ref. temp.)

$$B(C_4H_9)_3(l) + 19{}^1/{}_2O_2(g) \longrightarrow 12CO_2(g) + {}^1/{}_2B_2O_3(s) + 13{}^1/{}_2H_2O(l)$$

then becomes −2110 ± 10 kcal./mole.

The heat of formation of $B(C_4H_9)_3(l)$ was calculated from the above reaction assuming that the heat of formation for $B_2O_3(s)$ is −306 kcal./mole,[8] for $CO_2(g)$ is −94.1 kcal./mole,[9] and for $H_2O(l)$ is −68.3 kcal./mole.[9] The value arrived at is −94 kcal./mole; by adding the heat of vaporization of 13 kcal./mole,[10] the heat of formation of $B(C_4H_9)_3(g)$ becomes −81 kcal./mole. From this value, a recent compilation of bond energies and heats of atomization,[11] and a value of 97 kcal./mole for the heat of atomization of boron,[9] the B–C bond energy was found to be 70 kcal./mole. This value is in good agreement with the value for the B–C bond energy 74 kcal./mole calculated from the heat of combustion of trimethylboron listed by the National Bureau of Standards.[9]

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[4] J. R. Johnson, H. R. Snyder and M. G. Van Campen, Jr., THIS JOURNAL, **60**, 115 (1938).

[5] "Oxygen Bomb Calorimetry and Oxygen Bomb Combustion Methods," Parr Manual #120, Parr Instrument Co., Moline, Ill.

[6] H. Blumenthal, *Anal. Chem.*, **23**, 992 (1951).

[7] E. W. Washburn, *J. Research Natl. Bur. Standards*, **10**, 525 (1933).

[8] E. J. Prosen, W. H. Johnson and F. Y. Pergiel, Natl. Bur. Standards Report #1552, March 26, 1952.

[9] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Circular No. 500, Natl. Bur. Standards, Feb. 1, 1952.

[10] H. A. Skinner and T. F. S. Tees, *J. Chem. Soc.*, 3378 (1953).

[11] H. Gilman and G. E. Dunn, *Chem. Revs.*, **52**, 77 (1953).

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Structures of Some Thorium-dye Compounds Exhibiting Selective Ion-exchange Properties

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The use of the insoluble thorium–Amaranth dye compound as a selective ion exchanger in the colorimetric determination of fluoride ion[1] suggested the desirability of a study of the chemical structures and ion-exchange characteristics of other thorium–dye compounds. The chelate structure proposed[1] for the bonding of thorium ion through the hydroxy and azo groups on the Amaranth (2-hydroxy-1,1′-azonaphthalene-3,4′,6-trisulfonate ion) was not consistent with the 3:1 thorium–dye ratio subsequently found by spectrophotometric titration. This investigation was undertaken to elucidate the structures of other thorium–dye compounds which might undergo selective ion exchange.

Experimental

Spectrophotometric titrations of thorium ion with sulfonic acid dyes consisted of the reaction of a constant amount of one reactant with varying amounts of the other. The reaction mixture was filtered through a freshly precipitated and well washed barium sulfate mat in a confined spot filtration apparatus.[2] The porosity of the mat was such that it quantitatively filtered out any insoluble thorium–dye compound formed but allowed unreacted thorium ion or dye to pass through. By spectrophotometric determination of the unreacted dye in the filtrate, data were obtained from which the amount of dye which reacted with the

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[1] J. L. Lambert, *Anal. Chem.*, **26**, 558 (1954).

[2] J. L. Lambert, T. E. Moore and Paul Arthur, *ibid.*, **23**, 1193 (1951).

TABLE I

REACTIONS OF VARIOUS DYES WITH THORIUM ION

Dye	CI No.	Abs. max., mμ	No. functional groups					Free Th complex	Ratio Th:Dye
			$-SO_3^-$	$-COO^-$	$-OH$	$-N=$[c]	$>CO$		
Azo dyes									
Amaranth[a]	184	521	3	0	1	0	0	Insol.	3:1
Diamond black F[b,d]	299	..	2	1	2	0	0	Insol.	...
Acid alizarin red B[b]	..	500	2	1	1	0	0	Insol.	2:1
Ponceaux SX[a]	..	..	2	0	1	0	0	Sl. sol.	...
Erio chrome black T[b,d]	203	..	1	0	2	0	0	Sl. sol.	...
Orange I[a]	150	..	1	0	1	0	0	Sl. sol.	...
Orange II[b]	151	482	1	0	1	0	0	Sl. sol.	1:1
Orange IV[b]	143	..	1	0	0	1	0	Sl. sol.	...
Alizarin yellow R[b]	40	..	0	1	1	0	0	(Sol.)	...
Anthraquinone dyes									
Alizarin cyanine green G[b]	..	602	2	0	0	2	2	Insol.	2:1
Alizarin blue black B[b]	1085	..	1	0	1	2	2	Sl. sol.	...
Indigoid dyes									
Sodium indigo disulfonate[a]	1180	609	2	0	0	2	2	Insol.	1:1, 2:1
Nitro dyes									
Naphthol yellow S[a,b]	10	..	1	0	1	0	0	Sl. sol.	...
Thiazine dyes									
Methylene blue[b]	922	..	0	0	0	3	0	(Sol.)	...
Triphenylmethane dyes									
Guinea green B[a]	666	..	2	0	0	2	0	Sl. sol.	...
Soluble blue[b]	705	..	3	0	0	3	0	Sl. sol.	...
Crystal violet[b]	681	..	0	0	0	3	0	(Sol.)	...
Pararosaniline[b]	..	..	0	0	0	3	0	(Sol.)	...

[a] Certified Food, Drug and Cosmetic colors. Structural formulas may be found in M. B. Jacobs, "The Chemical Analysis of Food and Food Products," D. Van Nostrand Co., Inc., New York, N. Y., 1938, pp. 79–83. [b] Structural formulas may be found in K. Venkataraman, "The Chemistry of Synthetic Dyes," Vols. I and II, Academic Press, Inc., New York. N. Y., 1952. The syntheses of Acid Alizarin Red B and Alizarin Yellow R from intermediates are described but no structural formulas are given. Acid Alizarin Red B was assumed to be the trisodium salt, as the *p*H of 8.8 determined for a 1% solution was consistent with neutralized sulfonate ion groups and slight hydrolysis of the neutralized carboxylate ion group. [c] Basic nitrogens other than azo nitrogens. [d] These dyes bind very strongly to cellulose and do not wash off readily.

thorium ion could be obtained by graphical methods. The mat was prepared by mixing 10 ml. each of 0.02 *F* barium chloride and 0.02 *F* sodium sulfate solutions and filtering with suction through Whatman No. 50 filter paper.

The free thorium–Amaranth compound tended to peptize readily and could be used as an analytical reagent only when supported on cellulose. The thorium–dye compounds found to be insoluble or nearly insoluble in the free state were formed on cellulose in two ways: (I) by placing the filter paper in a 0.2% solution of the dye, blotting, drying, and immersing in 1% thorium nitrate tetrahydrate solution; and (II) by placing the paper in the thorium nitrate solution, blotting, drying and immersing in the dye solution. After washing thoroughly and blotting free of excess water, the cellulose-supported compounds were tested for insolubility by swirling eight minutes in 20 ml. of distilled water, and for ion-exchange properties by swirling eight minutes in 20 ml. of 10 p.p.m. fluoride ion solution.

Thorium ion solutions were prepared from reagent grade thorium nitrate tetrahydrate. Whatman No. 42 ("ashless," retentive grade, 5.5-cm. diameter) filter paper was chosen as the cellulose support for the thorium–dye compounds because of its purity and uniform porosity. All spectrophotometric measurements were made with a Beckman Model DU spectrophotometer using 10-mm. cells.

Results

The relative solubilities of the free thorium-dye compounds were determined by observing the residue left on the barium sulfate mat. Those residues which were markedly insoluble on washing with distilled water are classed as insoluble in Table I. Those which showed a pronounced tendency to "bleed" when washed are said to be slightly soluble, while the solutions which formed no filterable compound are listed as soluble, meaning that the compound either is soluble or does not form under these conditions. No significant color changes were observed when any of the dyes studied reacted with thorium ion, although Acid Alizarin Red B changed from orange to pinkish orange, and Amaranth changed to a slightly more purplish hue.

Spectrophotometric titrations were run on all the insoluble compounds except that of Diamond Black F, which stains cellulose irreversibly. The ratios of thorium ion to dye were determined graphically from Fig. 1, and are listed in Table I along with the wave lengths of the maximum absorbancies of the dyes. Table I also lists the type and number of functional groups per dye molecule which might possibly react with thorium ion.

Amaranth, Acid Alizarin Red B and Alizarin Cyanine Green G formed very insoluble thorium compounds, and their titration curves in Fig. 1 show sharply defined equivalence points. Orange II formed no insoluble compound when both titrating solutions were 0.0001 *F* (curve E′) but did form an insoluble compound when both were 0.001 *F* (curve E). The thorium–Orange II compound is more soluble than the four other thorium-dye compounds, and tended to give erratic values below the equivalence point. Curve E is the result of two sets of determinations at 0.001 *F*. The slope of the line past the equivalence point is unequivocal, but the slope of the line before the equivalence point had to be calculated by the method of least squares. The portions of curves D and E past

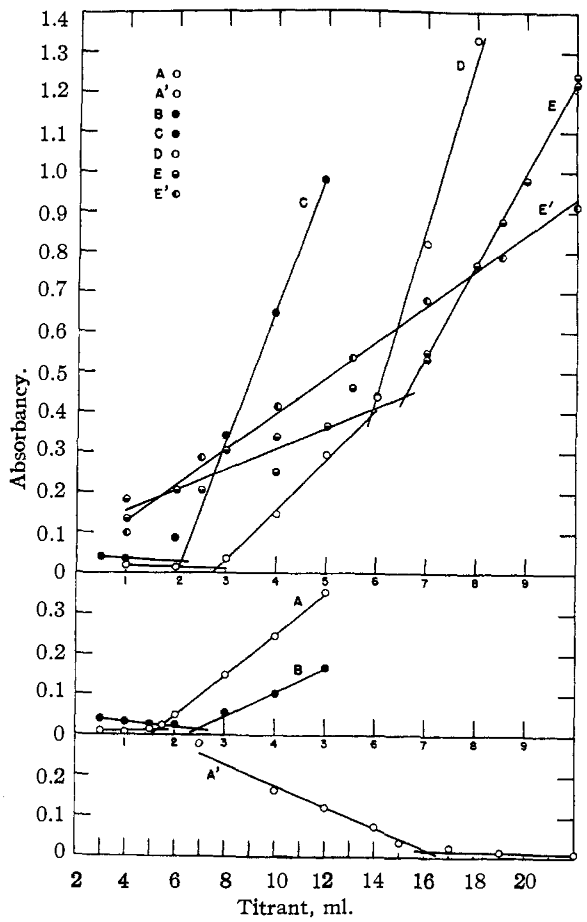

Fig. 1.—Spectrometric titration curves of thorium ion with various sulfonic acid dyes, and Amaranth dye with thorium ion. The reaction mixtures were brought up to the indicated volumes with distilled water before filtering: (A) five ml. of 0.0001 *F* thorium nitrate solution titrated with 0.0001 *F* Amaranth solution; total volume 20.0 ml.; (A') five ml. of 0.0001 *F* Amaranth solution titrated with 0.0001 *F* thorium nitrate solution; total volume 25.0 ml.; (B) five ml. of 0.0001 *F* thorium nitrate solution titrated with 0.0001 *F* Acid Alizarin Red B solution; total volume 10.0 ml.; (C) five ml. of 0.0005 *F* thorium nitrate solution titrated with 0.0005 *F* Alizarin Cyanine Green G solution; total volume 10.0 ml.; (D) five ml. of 0.001 *F* thorium nitrate solution titrated with 0.001 *F* sodium indigo disulfonate solution; total volume 15.0 ml.; (E) five ml. of 0.001 *F* thorium nitrate solution titrated with 0.001 *F* Orange II solution; total volume 15.0 ml.; (E') five ml. of 0.0001 *F* thorium nitrate solution titrated with 0.0001 *F* Orange II solution; total volume 15.0 ml.

the equivalence points can both be extrapolated back to the abscissa to indicate the 5:5 ratio for the thorium–Orange II compound and the second thorium–Indigo Disulfonate compound, if both compounds were highly insoluble.

The five insoluble thorium–dye compounds supported on cellulose all underwent ion exchange with 10 p.p.m. fluoride ion solution to release dye into the solution. Those formed by procedure (I) showed little or no bleeding in distilled water, while those formed by procedure (II) were spotty in appearance and tended to bleed considerably. Orange II showed the greatest tendency to bleed and bled an equal amount regardless of the method of preparation.

Discussion

The data appear to indicate that thorium ion reacts in neutral to slightly acid solution with dyes to form insoluble compounds only through sulfonate ion groups. The maximum number of thorium ions reacting with a dye molecule is equal to the number of sulfonate ion groups per dye molecule. Apparently both the 1:1 and the 2:1 compounds are formed under the conditions of the titration of thorium ion with Sodium Indigo Disulfonate, where both solutions are 0.001 *F*, with the 2:1 compound being the less soluble. Thorium ion in dilute aqueous solution under approximately neutral conditions binds strongly to cellulose, possibly through hydrogen bonding or a condensation reaction with hydroxy groups on the cellulose. It would be expected to have a reduced positive charge due to substitution of hydroxide ions for coördinated water molecules in the hydrated ion, and might well act as a monovalent cation in forming salt-like compounds of the general type

$$\text{Cellulose–O–Th(OH}_2)^+_n{}^-\text{O}_3\text{S–Ar(Dye)}$$

The proposed chelate ring structure[1] is not substantiated. The speed of fluoride ion–dye exchange, and the similarity of color of the free dye and the corresponding insoluble thorium compound indicate that the thorium–dye bond is predominantly ionic in nature.

The greater solubility of the thorium–dye compounds formed by procedure II is probably due to the solubilizing effect of sulfonate ion groups which have not reacted with thorium–cellulose. When formed by procedure I, with an excess of thorium ion present, all sulfonate ion groups presumably react with thorium–cellulose and the compound is much less soluble. Thorium–Orange II compound shows the same solubility when made by either I or II, as only one compound would be predicted with its lone sulfonate ion group.

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Photoinitiated Oxidation of Benzoic Acid by Ferric Ions in Aqueous Solution[1]

BY JEROME SALDICK AND AUGUSTINE O. ALLEN

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Evans and co-workers[2-4] have proposed that the photochemical action of Fe(OH)$^{+2}$ ions on organic substrates proceeds *via* free OH radicals in solution.

Bates and Uri[4] studied the photosensitized oxida-

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] M. G. Evans and N. Uri, *Nature*, **164**, 404 (1949).

[3] M. G. Evans, M. Santappa and N. Uri, *J. Polymer Sci.*, **7**, 243 (1951).

[4] H. G. C. Bates and N. Uri, THIS JOURNAL, **75**, 2754 (1953).