heavy organic layer separated and steam distilled. The product was distilled through a Lecky–Ewell column 72 cm. long and of 20 mm. diameter.

The distillation curve had plateaus at three temperatures at 5 mm.: 20 g. of unreacted *m*-aminobenzotrifluoride was obtained at 60–65°; 79 g. of 3-amino-4-bromobenzotrifluoride at 80–85°; 23.5 g. of 5-amino-2-bromobenzotrifluoride at 104–108°. A considerable amount of residue was left which was undoubtedly identical with the 5-amino-2,4-dibromo- or 3-amino-2,4-dibromobenzotrifluoride found in later experiments. The formation of the dibromide could be prevented by doubling the quantity of *m*-aminobenzotrifluoride.

In some cases the crude brominated mixture was deaminated. The relative amounts of the various products under these conditions are given in Table I.

3-Amino-4-bromobenzotrifluoride.—A center fraction of the 80–85° fraction had the following properties: b.p. 81–82° at 5 mm., n^{25}D 1.5197, d^{25}_4 1.694.

Anal. Calcd. for $C_7H_5BrF_3N$: Br, 33.29; N, 5.83. Found: Br, 33.28; N, 5.61.

The structure of the compound was established by deamination followed by hydrolysis of the $-CF_3$ group according to the method employed by Le Fave.[7] The melting point of 254–256° for the resulting *p*-bromobenzoic acid agrees with the reported value.[8]

5-Amino-2-bromobenzotrifluoride.[6]—Although this compound was formed in the experiment described above, larger amounts were obtained when two moles of *m*-aminobenzotrifluoride was treated with one mole of bromine. The properties of this substance are as follows: b.p. 104–108° at 5 mm., 81–84° at 0.5 mm., m.p. 55–56°.

Anal. Calcd. for $C_7H_5BrF_3N$: Br, 33.29; N, 5.83. Found: Br, 33.06; N, 5.78.

Deamination of this material gave *o*-bromobenzotrifluoride. Final identification was made by converting the amine by the Sandmeyer reaction to a bromochlorobenzotrifluoride which had the following physical properties: b.p. 198°, n^{25}D 1.5056, m.p. 14.9–16.2°. The values compare with those reported for 2-bromo-5-chlorobenzotrifluoride.[6]

5-Amino-2,4-dibromo- or 3-Amino-2,4-dibromobenzotrifluoride.—Bromination of *m*-aminobenzotrifluoride at 50° in the presence of iron filings gave a relatively large amount (13% conversion) of aminodibromobenzotrifluoride, b.p. 113–115° at 3 mm., m.p. 45–47°.

Anal. Calcd. for $C_7H_4Br_2F_3N$: Br, 50.11; N, 4.39. Found: Br, 50.08; N, 4.35.

The compound was deaminated and hydrolyzed to 2,4-dibromobenzoic acid.[9]

Deamination Reactions with Ethanol.—The procedure was adapted from that of Clarke and Taylor.[10] To 300 ml. of 95% ethanol in a one-liter flask equipped with a stirrer, thermometer and addition funnel were added 0.5 mole of the amine and 55 ml. of 96% sulfuric acid. The solution was cooled to −5° and 0.58 mole of sodium nitrite dissolved in the minimum amount of water slowly added. The temperature was maintained between 0 and 5° during the reaction and for one hour afterwards. The addition funnel was replaced by a reflux condenser and the temperature of the solution slowly raised to 30° where it was maintained for an hour, finally being raised slowly until reflux began and the evolution of nitrogen ceased. The reaction mixture was then distilled through a 12-inch column packed with Berl saddles until the temperature reached 80°. The distillate was added to 1500 ml. of water and the lower layer separated. The residue from the fractionation was steam distilled and the oil obtained added to the water-insoluble layer. The combined products were dried and distilled through an 18-inch column packed with $^1/_8$ inch glass helices.

Deamination Reactions with Hypophosphorus Acid.—The procedure was adapted from that of Kornblum.[11] About 125 ml. of concentrated hydrochloric acid was added to a 500-ml. flask equipped as for the ethanol deaminations. One-quarter mole of the amine was added slowly, the mixture cooled to −5° and 0.36 mole of sodium nitrite dissolved in a small amount of water added while the temperature was held below 10°. The resulting solution was stirred for half an hour and a precooled 50% solution containing one mole of hypophosphorus acid slowly added. Stirring was continued for two hours after all the acid had been added and the flask stored at 10° for 18 hours. The heavy, red liquid which separated was dried and distilled.

2-Bromo-5-chlorobenzotrifluoride.—A solution of 98 g. of 5-amino-2-bromobenzotrifluoride dissolved in 100 ml. of concentrated hydrochloric acid was treated at 0–5° with a solution containing 140 g. of sodium nitrite. After the diazotization was complete, 1.5 g. of copper powder was added and the solution heated gently. When the evolution of nitrogen had ceased, the mixture was steam distilled and the resulting oil dried and distilled. 2-Bromo-5-chlorobenzotrifluoride (45 g.), b.p. 197–202°, was obtained. A center fraction had a boiling point of 198°, m.p. 14.9–16.2° and n^{25}D 1.5056.

3,4-Dibromobenzotrifluoride.—By essentially the method described above, 0.2 mole of 3-amino-4-bromobenzotrifluoride was treated with 202 g. of 40% hydrobromic acid solution, 69 g. of sodium nitrite and, subsequently, copper powder to give a 71% yield of 3,4-dibromobenzotrifluoride, b.p. 101–102° at 25 mm., n^{25}D 1.5189, d^{25}_4 1.973, AR_F 1.19.

Anal. Calcd. for $C_7H_3Br_2F_3$: Br, 52.56. Found: Br, 52.54.

Hydrolysis with 100% sulfuric acid gave 3,4-dibromobenzoic acid, m.p. 235–236.5°. 3,4-Dibromobenzotrifluoride has previously been prepared by the direct bromination of benzotrifluoride.[2]

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[7] G. M. Le Fave, THIS JOURNAL, **71**, 4148 (1949).

[8] H. Hübner, J. Ohly and O. Philipp, *Ann.*, **143**, 247 (1867).

[9] R. H. C. Nevile and O. Winther, *Ber.*, **13**, 972 (1880).

[10] H. T. Clarke and E. R. Taylor, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 415.

[11] N. Kornblum, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 294.

Heat Capacities at Low Temperatures and Entropies at 298.16°K. of Hafnium Dioxide and Hafnium Tetrachloride

BY S. S. TODD

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Thermodynamic values of hafnium compounds have been lacking because of unavailability of adequately pure materials. Recently, substantially pure hafnium and some of its compounds have been produced in considerable amounts. This paper reports low-temperature heat capacity data and entropy values at 298.16°K. for hafnium dioxide and hafnium tetrachloride. No previous, similar data exist for either substance.

Materials.—The hafnium dioxide and hafnium tetrachloride were furnished by the Northwest Electrodevelopment Laboratory of the Bureau of Mines at Albany, Ore., along with the results of chemical and spectrographic analyses, which were reported in the recent paper of Orr,[1] who measured high-temperature heat contents of identical materials. The hafnium dioxide contained 1.66% zirconium dioxide and a 0.37% total of minor impurities. The hafnium tetrachloride contained 3.31% zirconium tetrachloride and 0.08% of minor impurities.

Heat Capacities.—The heat capacities were determined with previously described apparatus.[2] The results are expressed in defined calories (1 cal. = 4.1840 abs. joules), molecular weights accord with the 1951 International Atomic Weights,[3] and all weighings were reduced to vacuum. The measurements employed 339.96 g. of the dioxide and 277.65 g. of the tetrachloride.

The experimental heat capacity values are listed

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[1] R. L. Orr, THIS JOURNAL, **75**, 1231 (1953).

[2] K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

[3] E. Wichers, THIS JOURNAL, **74**, 2447 (1952).

in Table I. The results for hafnium dioxide were corrected for the zirconium dioxide content by means of data of Kelley,[4] and those for hafnium tetrachloride were corrected for the zirconium tetrachloride content by means of data of the author.[5] The corrections ranged from 0.09 to 0.99% for the dioxide and from 1.11 to 1.23% for the tetrachloride, depending upon the temperature.

The substances exhibit normal types of heat capacity curves over the temperature range 51–298°K., analogous in shape to those of the corresponding zirconium compounds.

TABLE I

HEAT CAPACITIES

T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole	T, °K.	C_p, cal./deg. mole
		HfO_2 (mol. wt., 210.60)			
52.47	2.216	114.60	6.507	216.37	11.82
56.55	2.499	124.63	7.153	226.34	12.21
60.70	2.818	136.02	7.843	236.13	12.53
65.29	3.177	146.13	8.435	245.94	12.89
70.13	3.525	156.02	9.000	256.36	13.21
74.90	3.853	166.07	9.523	266.38	13.51
80.36	4.237	176.11	10.04	276.25	13.81
85.12	4.562	187.91	10.61	286.50	14.11
94.99	5.220	196.35	10.98	296.34	14.33
104.57	5.845	206.35	11.42	(298.16)	(14.40)
		$HfCl_4$ (mol. wt., 320.43)			
52.26	11.48	114.45	20.54	216.53	26.81
56.24	12.17	124.48	21.54	226.22	27.18
60.51	13.00	135.90	22.55	236.15	27.47
64.93	13.85	146.16	23.34	245.86	27.71
69.42	14.63	155.96	23.98	256.37	27.93
73.99	15.34	166.15	24.60	266.41	28.16
79.91	16.25	176.19	25.15	276.27	28.40
84.01	16.86	186.15	25.64	286.53	28.62
94.88	18.30	196.10	26.07	296.55	28.73
104.44	19.42	206.33	26.42	(298.16)	28.80

Entropies.—The entropy increments between 51 and 298.16°K. (the measured range) were obtained by Simpson-rule integrations of C_p against log T plots. Extrapolations from 51 to 0°K. were made by means of the empirical Debye and Einstein function sums given below. The function sum for hafnium dioxide fits the measured data to within 1.0% up to 200°K. and to within 3.2% up to 298.16°K. Similarly, that for hafnium tetrachloride fits the measured data to within 1.0% up to 167°K. and to within 3.3% up to 298.16°K.

HfO_2: $D(266/T) + E(479/T) + E(794/T)$

$HfCl_4$: $D(69.0/T) + 2E(161/T) + 2E(402/T)$

The entropy results appear in Table II. They may be compared with values for zirconium dioxide and zirconium tetrachloride, which are, respectively, $S°_{298.16} = 12.12 \pm 0.08$[4b] and $S°_{298.16} = 44.5 \pm 0.5$.[5]

TABLE II

ENTROPIES AT 298.16°K. (CAL./DEG. MOLE)

	HfO_2	$HfCl_4$
0–51°K. (extrap.)	0.89	8.64
51–298.16°K (meas.)	13.29	36.93
$S°_{298.16}$	14.18 ± 0.10	45.6 ± 0.6

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[4] K. K. Kelley, (a) *Ind. Eng. Chem.*, **36**, 377 (1944); (b) U. S. Bur. Mines Bulletin 477 (1950).

[5] S. S. Todd, THIS JOURNAL, **72**, 2914 (1950).

Dehydration Products of 1,1,4,4-Tetraphenyl-1,4-butanediol[1]

BY WILLIAM J. WASSERMAN AND MILTON C. KLOETZEL

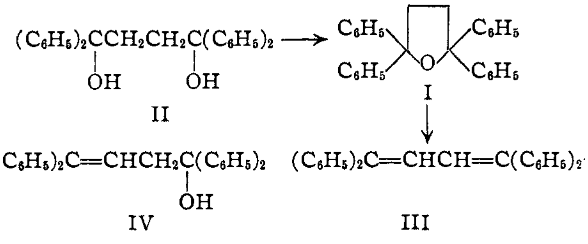
RECEIVED JANUARY 17, 1953

A compound melting at 182° and described as 2,2,5,5-tetraphenyltetrahydrofuran (I) was reported by Valeur[2] and again by Salkind and Teterin[3] to result from the dehydration of 1,1,4,4-tetraphenyl-1,4-butanediol (II) with boiling acetic acid. However, Acree[4] designated I as one of three possible structures for a substance, m.p. 163–165°, isolated from the reaction of phenylmagnesium bromide with diethyl succinate and also from the dehydration of the aforementioned diol.

In the course of certain investigations of the hydrogenated furan nucleus we had occasion to prepare I and therefore found it necessary to establish the identities of the materials melting at 182° and at 163–165°.

The reaction of phenylmagnesium bromide with methyl β-benzoylpropionate was found to yield diol II in 54% yield when effected at room temperature,[5] 49% at the temperature of refluxing ether, and 41% at 0°. In the latter instance there was also produced a 10% yield of 1,4-diphenyl-1,4-butanedione.

Dehydration of diol II with boiling acetic acid or with bromine yielded a compound melting at 180.5–181.5° as reported by Valeur[2] and by Salkind and Teterin.[3] This substance showed the proper analysis for a monodehydration product of diol II and did not react with cold permanganate solution. Zerewitinoff analysis indicated that the compound contained no active hydrogen. With anhydrous formic acid the compound was dehydrated to 1,1,-4,4-tetraphenyl-1,3-butadiene (III). This compound is therefore 2,2,5,5-tetraphenyltetrahydrofuran (I) as originally designated by Valeur.[2]



Valeur[6] and Dilthey and Last[7] have reported excellent yields of diol II from the slow addition of diethyl succinate to phenylmagnesium bromide at

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[1] Abstracted from the M.S. thesis of William J. Wasserman. Presented at the 123rd National Meeting of the American Chemical Society, Los Angeles, March, 1953.

[2] A. Valeur, *Compt. rend.*, **136**, 694 (1903).

[3] J. Salkind and V. Teterin, *Ber.*, **62**, 1746 (1929).

[4] S. F. Acree, *Am. Chem. J.*, **33**, 180 (1905).

[5] M. C. Kloetzel, THIS JOURNAL, **62**, 3405 (1940).

[6] A. Valeur, *Bull. soc. chim. France*, **29**, 683 (1903).

[7] W. Dilthey and E. Last, *Ber.*, **37**, 2639 (1904).