

was expected since, as Sworski has pointed out, when insufficient bromide is present to protect the H_2 which is formed from water decomposition, this H_2 will partly be drawn into the reaction by free OH radicals and thereby add to the yield of H_2O_2 . The observed yield in pure water is therefore higher than the value found by extrapolating the yields in bromide solution to zero bromide concentration. The extrapolated values, shown as intercepts in Fig. 4, should however give the true value of $F + E$ in water. This value is seen to be higher in 0.01 *N* sulfuric acid than in air-saturated water by about 0.085. Increasing the H_2SO_4 concentration to 0.8 *N* increases $F + E$, according to Sworski, by an additional 0.03.

Schwarz¹⁰ has derived the variation of $F + E$ with bromide concentration on the basis of a simple radical diffusion model. No explanation is evident at present for the variation of $F + E$ with acid concentration.

(10) H. A. Schwarz, *THIS JOURNAL*, **77**, 4960 (1955).

CHEMISTRY DEPARTMENT
BROOKHAVEN NATIONAL LABORATORY
UPTON, N. Y.

Thiophene: Heat of Combustion and Chemical Thermodynamic Properties¹

BY W. N. HUBBARD, D. W. SCOTT, F. R. FROW AND G. WADDINGTON

RECEIVED JULY 5, 1955

As part of a study in this Laboratory,² of the thermodynamic properties of thiophene the heat of combustion was determined by the Huffman-Ellis method³ in a conventional type of bomb calorimeter. The value of the heat of formation thereby obtained was published as a preliminary value only, because it was realized that the Huffman-Ellis method for sulfur compounds was inadequate for combustion calorimetry of the accuracy desired. The preliminary datum was not deemed reliable enough for use in calculating the heat and free energy of formation of thiophene as a function of temperature. Since publication of this earlier work, a rotating-bomb method⁴ has been developed for the combustion calorimetry of sulfur compounds and has been shown to give more reliable results than the Huffman-Ellis method. The heats of combustion and formation of thiophene have now been re-determined by the rotating-bomb method. This note reports the more reliable results obtained with the improved method and gives values for the heat and free energy of formation of thiophene as a function of temperature calculated by use of these results.

Combustion Calorimetry.—Part of the same highly purified sample of thiophene used in the

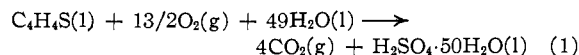
(1) This investigation was part of American Petroleum Institute Research Project 48A on "The Production, Isolation and Purification of Sulfur Compounds and Measurement of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

(2) G. Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith and H. M. Huffman, *THIS JOURNAL*, **71**, 797 (1949).

(3) H. M. Huffman and E. L. Ellis, *ibid.*, **57**, 41 (1935).

(4) W. N. Hubbard, C. Katz and G. Waddington, *J. Phys. Chem.*, **58**, 142 (1954).

earlier study² was also used for the study reported here. The apparatus and method have been described elsewhere.⁴ A summary of the calorimetric results is given in Table I. The last column of the table gives the experimentally determined values of $\Delta U_c^\circ/M$, the change in internal energy at 25° per gram mass of thiophene, for the idealized combustion reaction (eq. 1)



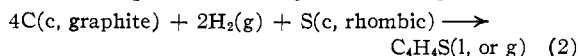
in which each reactant and product is in its appropriate standard state.⁵

The combustions were carried out in the platinum-lined bomb, Pt-4.⁴ The samples were contained in Pyrex ampoules. Ten grams of water was initially added to the bomb. The air originally present in the bomb was not removed when the bomb was charged with oxygen. Each combustion was initiated at 23.00°, and the quantities of thiophene and auxiliary oil (Sample USBM-P3_a) were chosen to produce a 2° temperature rise in the calorimeter. When 60% of the expected rise in temperature had been reached, rotation of the bomb was started. The bomb was rotated for 90 seconds.

The energy equivalent of the calorimetric system, C_{ex} (calor.), was determined by six combustions of benzoic acid (National Bureau of Standards Sample 39g). The precision of the energy equivalent determinations was unusually good—standard deviation of the mean, 0.002%.

In addition to the experiments shown in the table, three others were carried out. After the first experiment, a significant amount of carbon was found occluded in the partially fused remnant of the stem of the Pyrex ampoule. After the fourth experiment, SO_2 was found in the discharge gases of the bomb. It is probable that in charging the bomb for this experiment some of the air (necessary for complete oxidation of the sulfur to its +6 valence state) was inadvertently removed. After the fifth experiment, the presence of shattered glass and a large amount of carbon in the bomb indicated a violent rupture of the ampoule when the charge in the bomb was fired, accompanied probably by loss of sample from the crucible.

Table II gives the values for (a) the change in internal energy, ΔU_c° , of the idealized combustion reaction (eq. 1); (b) the enthalpy change, ΔH_c° , of the same reaction; (c) the standard heat of vaporization, ΔH_{vap}° (data of ref. 2 extrapolated to 25° and corrected for gas imperfection); and (d) the standard heat of formation, ΔH_f° , of thiophene in both the liquid and ideal gas states (eq. 2).



The table also includes values of ΔH_f° of the liquid obtained by Sunner and Lundin,⁶ Moore, Renquist and Parks⁷ and Franklin and Lumpkin,⁸ and the value obtained previously in this Laboratory.² The

(5) W. N. Hubbard, D. W. Scott and G. Waddington, *ibid.*, **58**, 152 (1954).

(6) S. Sunner and B. Lundin, University of Lund, Lund Sweden, unpublished measurement.

(7) G. E. Moore, M. L. Renquist and G. S. Parks, *THIS JOURNAL*, **62**, 1505 (1940).

(8) J. L. Franklin and H. E. Lumpkin, *ibid.*, **74**, 1023 (1952).

TABLE I^{a,b}
 SUMMARY OF THIOPHENE COMBUSTION EXPERIMENTS

Comb. no.	$C_{\text{eff.}}^{\text{I}}$ (cont.) cal. deg. ⁻¹	$C_{\text{eff.}}^{\text{II}}$ (cont.) cal. deg. ⁻¹	m' , g.	ΔT_c , deg.	q_{fuse}	q_{oil}	q_{CO_2}	q_{N}	$q_{\text{dila.}}$	$q_{\text{cor.}}$	$\Delta U_c^\circ/M$, cal. g. ⁻¹
2	13.77	13.78	0.93769	2.00259	15.46	316.88	3.23	5.43	+0.05	+0.54	-8012.0
3	13.77	13.77	.94130	1.99970	15.03	281.08	3.22	3.39	+ .04	+ .55	-8009.9
6	13.77	13.77	.93212	2.00044	15.50	349.07	3.24	13.91	+ .07	+ .45	-8007.2
7	13.77	13.78	.93120	2.00258	16.40	359.28	3.23	10.34	+ .07	+ .49	-8016.0
8	13.82	13.83	.92515	1.99954	16.16	403.43	3.23	6.85	+ .09	+ .53	-8011.9
9	13.81	13.82	1.03135	2.20066	16.20	340.39	3.50	8.33	- .19	+ .59	-8011.4
Av. -8011.4 ± 1.18 ^c											

^a Auxiliary data: $C_{\text{eff.}}$ (calor.) = 3909.0 cal. deg.⁻¹; volume of bomb = 0.3471 l.; initial total pressure = 30 atm.; electrical ignition energy = 1.35 cal.; ρ , density of thiophene at 25° = 1.05887 g. ml.⁻¹ [W. E. Haines, R. V. Helm, C. W. Bailey and J. S. Ball, *J. Phys. Chem.*, **58**, 270 (1954)]. ^b The column headings of this table correspond to the following computation item numbers of ref. 5: $C_{\text{eff.}}^{\text{I}}$ (cont.), item 75; $C_{\text{eff.}}^{\text{II}}$ (cont.), item 76; m' , mass of compound, item 2; ΔT_c , items 79-78-80, q_{fuse} , item 97; q_{oil} , item 96; q_{CO_2} , item 87; q_{N} , item 92; $q_{\text{dila.}}$, items 90 + 91; $q_{\text{cor.}}$, items 81 + 82 + 83 + 84 + 85 + 88 + 89 + 93 + 94; and $\Delta U_c^\circ/M$, item 99. ^c The uncertainty given is the standard deviation of the mean.

 TABLE II
 DERIVED DATA AT 25°; COMPARISON WITH RESULTS OF OTHER INVESTIGATIONS, KCAL. MOLE⁻¹

	ΔU_c°	ΔH_c°	ΔH_f° , liquid	ΔH° vap., liquid to ideal gas	ΔH_f° , ideal gas
This investigation	-674.06 ± 0.216	-675.55 ± 0.216	+19.20 ± 0.239		+27.49 ± 0.239
Sunner and Lundin ⁸			+19.13 ± 0.10		
Moore, Renquist and Parks ⁷			+19.62 ± 0.23		
Waddington, <i>et al.</i> ²			+19.52 ± 0.25	÷8.29 ± 0.008	
Franklin and Lumpkin ⁸			+19.2 ± 1.3		

 TABLE III
 THE MOLAL THERMODYNAMIC PROPERTIES OF THIOPHENE^a

T , °K.	$-(F^\circ - H_0^\circ)/T$ cal. deg. ⁻¹	$H^\circ - H_0^\circ/T$ cal. deg. ⁻¹	$H^\circ - H_0^\circ$, kcal.	S° , cal. deg. ⁻¹	C_p° , cal. deg. ⁻¹	$\Delta H_f^\circ{}^b$, kcal.	$\Delta F_f^\circ{}^b$, kcal.	$\log_{10} K_f{}^b$
0	0	0	0	0	0	15.02	15.02	-∞
273.16	55.09	10.10	2.760	65.19	15.82	12.28	19.86	-15.89
298.16	55.99	10.65	3.176	66.65	17.42	12.07	20.56	-15.07
300	56.05	10.70	3.208	66.74	17.52	12.06	20.62	-15.02
400	59.46	13.11	5.246	72.57	23.02	11.31	23.58	-12.89
500	62.65	15.56	7.780	78.21	27.47	10.77	26.72	-11.68
600	65.69	17.84	10.71	83.54	30.95	10.36	29.95	-10.91
700	68.60	19.92	13.94	88.52	33.74	10.07	33.24	-10.38
800	71.39	21.79	17.44	93.18	36.01	9.87	36.56	-9.99
900	74.06	23.48	21.14	97.54	37.91	9.76	39.90	-9.69
1000	76.61	25.01	25.01	101.62	39.54	9.74	43.26	-9.45

^a To form an internally consistent set of values of the thermodynamic properties and to retain the higher accuracy of increments with temperature of a given property, some values in this table are given to more decimal places than are justified by the absolute accuracy. ^b The standard heat, standard free energy and common logarithm of the equilibrium constant for the formation of thiophene by the reaction: $4C(\text{graphite}) + 2H_2(g) + \frac{1}{2}S_2(g) = C_4H_4S(g)$.

value of Sunner and Lundin was determined with a rotating-bomb calorimetric system⁹ and is comparable in reliability to that of this investigation. The remaining values were obtained by the less reliable stationary-bomb method. The uncertainties given in Table II are "uncertainty intervals" (equal to twice the "over-all" standard deviations) for the results of this investigation and are estimates for the data of other investigators.

The Chemical Thermodynamic Properties.—The value obtained for ΔH_f° was used to compute the standard heat, standard free energy and common logarithm of the equilibrium constant for the formation of thiophene at selected temperatures from 0 to 1000°K. Diatomic sulfur gas, $S_2(g)$, was used

(9) The calorimetric system and method used by Sunner and Lundin is described in a thesis, "Studies in Combustion Calorimetry Applied to Organo-Sulfur Compounds," by S. Sunner; Carl Bloms Boktryckeri, Lund, Sweden, 1949.

as the reference state for elemental sulfur. The thermodynamic functions for thiophene given in ref. 2¹⁰ were revised by the inclusion of empirical corrections for anharmonicity, as described in an earlier publication from this Laboratory.¹¹ The empirical parameters, $Z = 0.48$ cal. deg.⁻¹ mole⁻¹ and $\nu = 650$ cm.⁻¹, were selected to fit the calorimetric vapor heat capacity data of ref. 2. The revised thermodynamic functions for thiophene are listed in columns 2-6 of Table III. Thermodynamic func-

(10) The vibrational assignment of ref. 2 has been revised by interchange of four frequencies among symmetry classes, but this revision does not change the calculated thermodynamic functions. See J. P. McCullough, S. Sunner, H. L. Finke, W. N. Hubbard, M. E. Gross, R. E. Pennington, J. F. Messerly, W. D. Good and G. Waddington, *THIS JOURNAL*, **75**, 5075 (1953), Table VIII.

(11) J. P. McCullough, H. L. Finke, W. N. Hubbard, W. D. Good, R. E. Pennington, J. F. Messerly and Guy Waddington, *ibid.*, **76**, 2661 (1954). See also R. E. Pennington and K. A. Kobe, *J. Chem. Phys.*, **22**, 1442 (1954).

tions for C(graphite) and H₂(g) given by Wagman *et al.*,¹² and thermodynamic functions for S₂(g) and the value $\Delta H_{298.16}^{\circ} = 30.84$ kcal. for 2 S(rhombic) = S₂(g), given by Evans and Wagman¹³ were used. The calculated values of ΔH_f° , ΔF_f° , and $\log_{10} K_f$ for thiophene are listed in the last three columns of Table III.

Acknowledgment.—The authors wish to thank S. Sunner and B. Lundin⁶ for making available an unpublished value of the heat of formation of thiophene.

(12) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

(13) W. H. Evans and D. D. Wagman, *ibid.*, **59**, 141 (1952).

CONTRIBUTION NO. 50 FROM
THERMODYNAMICS LABORATORY
PETROLEUM EXPERIMENT STATION
BUREAU OF MINES
BARTLESVILLE, OKLAHOMA

The Preparation and Reactions of Dihalotetraalkylditin Compounds¹

BY OTTO H. JOHNSON, HENRY E. FRITZ, DAVID O. HALVORSON AND ROGER L. EVANS

RECEIVED JUNE 20, 1955

Johnson and Fritz recently reported the preparation of a dihalotetraalkylditin.² They obtained dichlorotetra-*n*-butylditin through a coupling of dichlorodi-*n*-butyltin using sodium ethoxide in ethanol.

Further studies of this reaction have revealed that certain organic bases can replace the sodium ethoxide in this coupling. Several amines were used to prepare 1,2-dichlorotetra-*n*-butylditin by mixing equimolar quantities of dichlorodi-*n*-butyltin and the organic base, followed by the addition of a small quantity of alcohol. Immediately following the addition of the ethanol, the crystalline amine hydrochloride separated. Table I lists the amines tested and the yields of the ditin compounds obtained. The evidence suggests that a strong base is necessary to make the reaction proceed.

Several other dihalotetraalkylditin compounds have been synthesized using various amines as condensing agents. Besides 1,2-dichlorotetra-*n*-butylditin which has been previously reported, 1,2-dichlorotetraethyliditin, 1,2-dichlorotetra-*n*-propyliditin, 1,2-dichlorotetra-*n*-amyliditin, 1,2-dichlorotetraphenylditin and 1,2-dibromotetra-*n*-butylditin have been prepared.

The greater reactivity of bromine over chlorine in this coupling reaction was demonstrated by coupling bromochlorodibutyltin. A 92% yield of 1,2-dichlorotetra-*n*-butylditin was isolated. The bromine was cleaved and was isolated in high yield as the amine hydrobromide.

Experimental

Synthesis of Dichlorotetra-*n*-butylditin, Using Various Organic Bases.—In general, 0.025 mole of dichlorodibutyltin was mixed with 0.025 mole of the selected base in 50 ml. of anhydrous ether, and 20 ml. of anhydrous ethanol added immediately with stirring. When triethylamine was used,

(1) This research was supported by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command.

(2) O. H. Johnson and H. E. Fritz, *J. Org. Chem.*, **19**, 74 (1954).

the solution turned slightly yellow on mixing dichlorodibutyltin and the base, and a white precipitate formed which dissolved on stirring. On adding the ethanol a permanent white precipitate of triethylamine hydrochloride (m.p. 254°) was formed in about 98% yield. Evaporation of the slightly yellow filtrate and recrystallization from acetone gave white crystals of dichlorotetra-*n*-butylditin, m.p. 110–112°.

Preparation of Individual Ditin Compounds. Preparation of the Et₂SnCl₂ Used as Starting Material.—Tetraethyltin (24.5 g., 0.1026 mole) was mixed with tin tetrachloride (26.6 g., 0.1026 mole) and the mixture warmed to 140°. The solution was then held at 220–230° for three hours and allowed to cool, forming a solid crystalline mass. Recrystallization from 60 ml. of petroleum ether (b.p. 60–68°) gave 8.7 g. of white needle-shaped crystals, m.p. 89°. Leaving the filtrate in a refrigerator for two days produced an additional 18.1 g.; total yield 52%.

Preparation of Dichlorotetraethyliditin.—Dichlorodiethyltin (8.7 g., 0.035 mole) was dissolved in 50 ml. of absolute ethanol and a solution of redistilled triethylamine (3.55 g., 0.035 mole) in 25 ml. of absolute ethanol was added within 15 seconds with vigorous stirring. The reaction was slightly exothermic and the temperature of the mixture rose to 35°. After about one minute of stirring a white solid began to separate. The stirring was continued for one hour, then the ethanol was distilled at room temperature under reduced pressure. Anhydrous ether (100 ml.) was added, dissolving part of the white solid. The residual solid was filtered off and the ether removed from the filtrate by distillation leaving 6.3 g. of white residue. The residue was crystallized from acetone, which dissolves any unreacted Et₂SnCl₂. The first crystallization gave 3.0 g. of white crystals. A second crystallization yielded 2.6 g.; total yield 77%.

Anal. Calcd. for (C₂H₅)₄Sn₂Cl₂: C, 22.63; H, 4.75; Cl, 16.70. Found: C, 22.45; H, 4.89; Cl, 16.48.

The white crystalline compound turned a slightly tan color when heated in air at 120° for several hours and sublimed at 160°. When a sample was sublimed at 0.1 mm. it decomposed giving (C₂H₅)₂SnCl₂ and a white residue melting at about 240°. The (C₂H₅)₄Sn₂Cl₂ decomposed and turned brown at about 175° when heated in a capillary melting point tube.

Dichlorotetra-*n*-propyliditin.—Dichlorodi-*n*-propyltin (13.8 g., 0.05 mole), prepared similarly to dichlorodiethyltin above, was dissolved in 100 ml. of ether, and a solution of hydrazine (1.52 g., 0.05 mole) in 40 ml. of anhydrous ethanol was added. A white precipitate formed immediately. The mixture was stirred for one hour and then filtered yielding 3.2 g. of a white solid which was washed with ether. The ether-ethanol filtrate was evaporated until the odor of ether was no longer discernible, leaving a final volume of about 35 ml. Cooling slowly gave large, soft, odorless white crystals of dichlorotetra-*n*-propyliditin, m.p. 120.5–121.5°; yield 11.2 g. (93%).

Anal. Calcd. for (C₃H₇)₄Sn₂Cl₂: C, 29.96; H, 5.86. Found: C, 29.80; H, 5.33.

The 3.2 g. of white solid obtained by the first filtration was probably a mixture of N₂H₄·HCl, m.p. 89°, N₂H₄·2HCl, m.p. 198°, and the ditin compound, m.p. 119–122°. It was partially water soluble, sintered at 90–95°, melted to a cloudy white liquid between 150–190° and cleared gradually to a clear liquid at 210–215°.

Dichlorotetraamyliditin.—0.93 g. (0.03 mole) of dichlorodi-*n*-amyltin in ether was treated with 0.96 g. (0.03 mole) of hydrazine in alcohol, and the reaction proceeded similarly to the synthesis of dichlorotetra-*n*-butylditin. The product was in the form of small white crystals, recrystallized from ethanol, mp. 96.5–97.5°, yield 92.8%.

Anal. Calcd. for (C₅H₁₁)₄Sn₂Cl₂: C, 40.52; H, 7.48. Found: C, 40.31; H, 7.43.

Dichlorotetraphenylditin.—Dichlorodiphenyltin (10.3 g., 0.03 mole), prepared similarly to dichlorodiethyltin, was dissolved in 60 ml. of ether and a solution of hydrazine (0.96 g., 0.03 mole in 25 ml. anhydrous ethanol) was added. A white precipitate formed immediately. The reaction was slightly exothermic, the temperature of the mixture rising to 35°. Stirring was continued for one hour, the mixture allowed to stand overnight and then filtered yielding 8.2 g. of white powder. The filtrate was evaporated down, and small white crystals were obtained from it.