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Heats of Combustion and Formation of the 1-Bromoalkanes from C_4 through C_8

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The heats of combustion of highly purified samples of five 1-bromoalkanes have been determined with a moving-bomb calorimetric method.

The purification of samples of the following compounds is described: 1-bromobutane, 1-bromopentane, 1-bromohexane, 1-bromoheptane and 1-bromooctane. Data on density and refractive index for the spectral lines D, Hα and Hβ, at 20 and 25°C, of the purified samples are given and compared with corresponding data from previous investigations.

The following values, in kcal/mole, are reported for the heat of combustion, $-\Delta Hc°$, at 25°C, of the liquid sample in gaseous oxygen to form gaseous carbon dioxide, liquid water and liquid bromine, with reactants and products in their thermodynamic standard states: 1-bromobutane 649.17 ± 0.30, 1-bromopentane 805.30 ± 0.34, 1-bromohexane Sample I 962.82 ± 0.36, 1-bromohexane Sample II 961.91 ± 0.38, 1-bromoheptane 1118.52 ± 0.38, 1-bromooctane 1274.52 ± 0.54.

Combination of these values with the known standard heats of formation of carbon dioxide and water and with values for the heats of vaporization of the various bromine compounds yields the following values, in kcal/mole, for the heat of formation, $-\Delta Hf°$, at 25°C, of the gaseous compound from carbon(graphite), gaseous hydrogen and liquid bromine, with reactants and products in their thermodynamic standard states: 1-bromobutane 25.67 ± 0.40, 1-bromopentane 31.02 ± 0.46, 1-bromohexane 34.97 ± 0.48 (Sample I) and 35.88 ± 0.49 (Sample II), 1-bromoheptane 40.69 ± 0.52, 1-bromooctane 46.26 ± 0.65.

The derived heat of formation data are discussed and found to be internally consistent with the possible exception of the heat of formation value derived from the heat of combustion of Sample I of 1-bromohexane.

Modern experimental data from which heats of formation for monobromoalkanes can be calculated, are available only for ethyl bromide [1], the two propyl bromides [2–5] and *sec.*-butyl bromide [5,6]. Experimental data on other members of this class of compounds are therefore needed and, as a first step in this direction, heats of combustion have been determined, with the moving-bomb method, for carefully purified samples of the C_4—C_8 1-bromoalkanes. The observed bomb-calorimetric data have been reduced to standard heats of combustion and the latter then combined with heats of formation for carbon dioxide and water to yield standard heats of formation for the given compounds.

This paper describes the purification of the samples and the heat of combustion experiments and presents the observed and derived heat of combustion and formation data.

MATERIALS

Benzoic acid. The benzoic acid samples used in the calibration experiments with the calorimeters A and B were National Bureau of Standards standard sample 39g[7] and 39f[8], respectively.

Paraffin oils. The paraffin oil samples used as auxiliary material in the combustion experiments with the bromine compounds were the same as those described in Ref.[5]

Bromine compounds. The bromine compound samples were all obtained by careful purification of commercial products. The latter were first treated chemically and then purified by successive fractional distillations at two or more different pressures, using the same apparatus and technique as described in Ref.[5] Details of the purification of the various samples follow.

1-Bromobutane. The commercial sample (Columbia Organic Chemicals) was treated with phosphorus pentoxide. The resulting 180 g were purified by two successive fractional distillations at pressures 750 and 340 mm, respectively. In the final distillation 80 % (53 g) of the distillate was collected over a density range of 0.0003 g/ml. The second half (27 g) of this distillate, all of which was collected at constant density, was treated with calcium sulfate and subjected to simple distillation at atmospheric pressure. The middle fraction from this distillation was used in the heat of combustion experiments.

1-Bromopentane. The commercial sample (Columbia Organic Chemicals) was treated with phosphorus pentoxide. The resulting 83 g were purified by two fractional distillations at pressures 760 and 41 mm, respectively. In the final distillation 80 % (23 g) of the distillate was collected at constant density. This product was treated with calcium sulfate and distilled at 64 mm. A middle fraction from this distillation was used in the heat of combustion experiments.

1-Bromohexane Sample I. After treatment of the commercial sample (Columbia Organic Chemicals) with phosphorus pentoxide the product (100 g) was fractionally distilled at 160 mm, and 90 % (85 g) of the distillate was collected over a density range of 0.0004 g/ml. Several fractions were discolored. Therefore, all fractions of the 85 g of distillate collected were combined and treated first with 10 % sodium bicarbonate solution and then with water, and then dried with calcium chloride and finally with phosphorus pentoxide. The dry sample was purified by successive fractionations at pressures 20 and 60 mm, respectively. All the distillate (16 g) in the final distillation was collected over a density range of 0.0002 g/ml. This product was treated with calcium sulfate and subjected to simple distillation at 8 mm. A middle fraction from this distillation was used in the heat of combustion experiments.

1-Bromohexane Sample II. The commercial sample (Kebo) was treated successively with 48 % hydrobromic acid, water, 10 % sodium carbonate solution and water. The product was dried with calcium chloride and with calcium sulfate and the resulting 1 000 g were fractionated by successive distillations at pressures 200, 100, and 50 mm. In the final distillation 77 % (240 g) of the distillate was collected over a density range of 0.0002 g/ml (the whole distillate was collected over a density range of 0.0005 g/ml). The fractions making in all 240 g were combined into one sample. A vapor phase chromatographic test on the sample did not indicate the presence of any impurities. Part of this sample, after treatment with calcium sulfate and simple distillation, was used in the heat of combustion experiments.

1-Bromoheptane. The commercial sample (Columbia Organic Chemicals) was treated in order with conc. hydrochloric acid, water, 10 % sodium bicarbonate solution and water,

Table 1. Comparison with earlier data of density and refractive index data for the samples prepared in the present investigation.

Compound and reference	Density g/ml		Refractive index					
			D		Hα		Hβ	
	20°	25°	20°	25°	20°	25°	20°	25°
1-BROMOBUTANE								
Present investigation	1.2758	1.2686	1.4398	1.4374	1.4371	1.4347	1.4463	1.4438
Tschamler, Richter and Wettig [9]		1.2694	1.43981					
Skau and McCullough [10]		1.2686						
Lucas, Dillon and Young [11]	1.2756	1.2686	1.4403					
Timmermans and Martin [12]	1.27568	1.26844	1.43975	1.43725	1.43690	1.43440	1.44615	1.44355
1-BROMOPENTANE								
Present investigation	1.2186	1.2123	1.4444	1.4420	1.4418	1.4394	1.4509	1.4485
Skau and McCullough [10]		1.2121						
1-BROMOHEXANE								
Present investigation Sample I	1.1745	1.1688	1.4475	1.4452	1.4449	1.4426	1.4539	1.4516
Present investigation Sample II	1.1745	1.1686	1.4475	1.4454	1.4446	1.4425	1.4537	1.4513
Tschamler, Richter and Wettig [9]		1.1690						
1-BROMOHEPTANE								
Present investigation	1.1402	1.1348	1.4503	1.4481	1.4477	1.4456	1.4566	1.4544
Deffet [13]	1.1399	1.1345			1.4477	1.4456	1.4568	1.4546
1-BROMOOCTANE								
Present investigation	1.1129	1.1077	1.4526	1.4505	1.4499	1.4478	1.4588	1.4567
Deffet [13]	1.1129	1.1078			1.4501	1.4481	1.4592	1.4572

and then dried first with calcium chloride and finally with phosphorus pentoxide. The resulting 83 g were purified by successive fractional distillations at pressures 105 and 45 mm, respectively. In the final distillation all the distillate was collected over a density range of 0.0001 g/ml. Part of this distillate was used in the heat of combustion experiments without further treatment.

1-Bromooctane. The commercial sample (Kebo) was treated in order with conc. sulfuric acid, water, 10 % sodium carbonate solution and water. The product was dried with calcium chloride and the resulting 515 g were fractionated by successive distillations at pressures 100 and 40 mm. In the final distillation 89 % (318 g) of the distillate were collected over a density range of 0.0002 g/ml. Part of this distillate was dried with calcium sulfate and distilled at 2 mm. A middle fraction was taken for the combustion experiments.

Table 1 gives the densities, at 20 and 25°C, and refractive indices for the spectral lines D, Hα and Hβ, at 20 and 25°C, of the samples used in the heat of combustion experiments. The density measurements were made with a standard Ostwald-Sprengel pycnometer to an accuracy estimated at ± 0.0001 g/ml and the refractive indices were measured with a calibrated Pulfrich refractometer, giving refractive index values within estimated error limits of ± 0.0001.

For comparison with earlier data on density and refractive index of highly purified samples of the various compounds, the results from certain selected previous investigations [9-13] are also listed in Table 1.

Table 2. **Results of combustion experiments on 1-bromobutane, 1-bromopentane, 1-bromohexane Sample I, and 1-bromoheptane.**

Calorimeter B

t_h = 20.0°C; t_i = 20.0°C; P^i(gas.) = 30.0 atm

V(Bomb) = 0.2750 liter; V^i(soln.) = 0.03001 liter; C^i(soln.) = 0.0625_5 mole As_2O_3/liter

$\varepsilon°$(Calor.) = 4 718.62 ± 0.34 cal/deg; $-\Delta Ec°/M$(Oil) = 10 972.1 ± 0.7 cal/g; $-\Delta Ec°/M$(Fuse) = 3 971 ± 4 cal/g

m(Pt) = 5.764 g; $-\Delta E_{oxid.}(As_2O_3)$ = (77.4 ± 0.1) × 10^3 cal/mole

m′ g	m″ g	m‴ g	m(glass) g	ε(Calor.) cal/deg	ε^f(Cont.) cal/deg	Δt deg	$n^f(As_2O_5)$ mole	$-\Delta E(CO_2)$ cal	$-\Delta E(HNO_3)$ cal	$-\Delta E$(Au) cal	$-\Delta E$(Pt) cal	$-\Delta E$(HBr) cal	$-\Delta E_\Sigma$ cal	$-\Delta Ec°/M$ cal/g
1-BROMOBUTANE														
0.60492	0.15996	0.00455	0.111	4 671.77	32.19	0.99982	0.001057	10.86	1.75	0.03	0.08	24.08	0.40	4 727.7
0.61800	0.16166	0.00479	0.112	4 671.76	32.19	1.01765	0.001087	11.04	1.05	0.03	0.08	24.60	0.40	4 729.6
0.62208	0.14750	0.00438	0.110	4 671.77	32.19	0.98858	0.001085	10.71	1.75	0.03	0.08	24.76	0.40	4 731.0
													Mean	4 729.4
										Standard deviation of mean				± 0.7_6[a]
1-BROMOPENTANE														
0.60170	0.12956	0.00451	0.139	4 671.78	32.23	1.00033	0.000945	10.87	1.80	0.03	0.06	21.69	0.38	5 322.0
0.59458	0.13210	0.00477	0.094	4 671.83	32.23	0.99816	0.000944	10.85	0.90	0.03	0.06	21.44	0.38	5 321.4
0.57889	0.14080	0.00460	0.136	4 671.80	32.23	1.00054	0.000919	10.88	1.10	0.03	0.06	20.87	0.38	5 323.1
													Mean	5 322.2
										Standard deviation of mean				± 0.7_9[a]
1-BROMOHEXANE Sample I														
0.66101	0.06811	0.00480	0.123	4 671.79	32.24	0.99492	0.000954	10.76	1.50	0.02	0.04	21.81	0.38	5 824.1
0.64126	0.08200	0.00459	0.110	4 671.81	32.25	1.00187	0.000926	10.86	1.15	0.02	0.04	21.16	0.36	5 820.8
0.62659	0.09517	0.00477	0.096	4 671.83	32.26	1.01468	0.000898	11.01	1.50	0.02	0.04	20.67	0.34	5 823.5
													Mean	5 822.8
										Standard deviation of mean				± 0.7_3[a]
1-BROMOHEPTANE														
0.63811	0.05940	0.00492	0.105	4 671.84	32.27	1.00078	0.000858	10.87	1.20	0.02	0.06	19.38	0.36	6 233.5
0.59224	0.08533	0.00476	0.104	4 671.86	32.27	0.99951	0.000792	10.89	1.20	0.02	0.06	17.99	0.34	6 233.2
0.60950	0 06559	0 00487	0.094	4 671.87	32.27	0.97711	0.000821	10.62	1.30	0.02	0.06	18.51	0.35	6 235.9
0.63266	0.06649	0.00472	0.109	4 671.84	32.27	1.01014	0.000849	10.97	0.95	0.02	0.06	19.22	0.36	6 236.1
													Mean	6 234.7
										Standard deviation of mean				± 0.6_5[a]

[a] This value has been estimated as given in text.

Table 3. Results of combustion experiments on 1-bromohexane Sample II.

Calorimeter A

t_h = 25.0°C V(Bomb) = 0.2670 liter ε°(Calor.) = 5 822.45 ± 0.33 cal/deg m(Pt) = 8.854 g in expt. no. 1-6; 18.424 g in expt. no. 7-10

t_i = 24.1°C V^i(soln.) = 0.03015 liter in expt. no. 1–3; 0.03005 liter in expt. no. 4–10 $-\Delta Ec^\circ$/M(Oil) = 10 971.6 ± 0.6 cal/g in expt. no. 1–6; 10 984.4 ± 1.2 cal/g in expt. no. 7–10

P^i(gas.) = 30.0 atm C^i(soln.) = 0.0629$_1$ mole As_2O_3/liter $-\Delta Ec^\circ$/M(Fuse) = 3 971 ± 4 cal/g $-\Delta E_{oxid.}(As_2O_3)$ = (77.4 ± 0.1) × 10[3] cal/mole

Expt. No.	m′ g	m″ g	m‴ g	m(glass) g	ε(Calor.) cal/deg	ε^i(Cont.) cal/deg	Δt deg	$n^f(As_2O_5)$ mole	$-\Delta E(CO_2)$ cal	$-\Delta E(HNO_3)$ cal	$-\Delta E$(Au) cal	$-\Delta E$(Pt) cal	$-\Delta E$(HBr) cal	$-\Delta E_\Sigma$ cal	$-\Delta Ec^\circ/M$ cal/g
1	0.653639	0.116178	0.005679	0.0832	5772.98	32.22	0.88903	0.000917	10.62	2.40	0.01	0.03	20.77	0.31	5 814.9
2	0.595775	0.149650	0.005203	0.1040	5772.98	32.22	0.89298	0.000858	10.72	1.00	0.03	0.02	18.92	0.29	5 811.6
3	0.631233	0.131386	0.005126	0.0875	5772.98	32.22	0.89433	0.000913	10.71	0.90	0.02	0.03	20.06	0.32	5 810.8
4	0.606192	0.143907	0.005543	0.0901	5773.09	32.12	0.89349	0.000853	10.67	2.10	0.01	0.05	19.25	0.33	5 817.8
5	0.662344	0.112724	0.005433	0.0932	5773.06	32.12	0.89143	0.000949	10.61	1.15	0.02	0.03	21.06	0.32	5 816.8
6	0.649002	0.122353	0.005368	0.1039	5773.05	32.13	0.89604	0.000925	10.67	1.20	0.01	0.03	20.63	0.31	5 817.2
7	0.703072	0.090822	0.005107	0.0799	5763.50	32.43	0.89231	0.001018	10.60	1.30	0.02	0.03	22.36	0.32	5 811.4
8	0.661589	0.112691	0.004821	0.0818	5763.52	32.42	0.89196	0.000948	10.62	0.95	0.02	0.04	21.03	0.32	5 818.0
9	0.688238	0.105649	0.005043	0.0824	5763.50	32.42	0.90595	0.000993	10.80	1.40	0.03	0.04	21.88	0.27	5 816.8
10	0.685332	0.098890	0.005264	0.0786	5763.51	32.42	0.89000	0.000981	10.58	1.25	0.04	0.04	21.79	0.32	5 815.4
														Mean	5 815.1
														Standard deviation of mean	± 0.8$_8$

Table 4. Results of combustion experiments on 1-bromooctane.

Calorimeter A

$t_h = 25.0°C$	V(Bomb) = 0.2670 liter	$\varepsilon°$(Calor.) = 5 821.01 ± 0.47 cal/deg	m(Pt) = 17.994 g
			ε(Calor.) = 5 762.57 cal/deg
$t_i = 24.1°C$	V^i(soln.) = 0.03005 liter	$-\Delta Ec°$/M(Oil) = 10 979.6 ± 0.9 cal/g	ε^i(Cont.) = 32.41 cal/deg
P^i(gas.) = 30.0 atm	C^i(soln.) = 0.0628_5 mole As_2O_3/liter	$-\Delta Ec°$/M(Fuse) = 3 971 ± 4 cal/g	$-\Delta E_{oxid.}(As_2O_3)$ = (77.4 ± 0.1) × 10^3 cal/mole

m′ g	m″ g	m‴ g	m(glass) g	Δt deg	$n^f(As_2O_5)$ mole	$-\Delta E(CO_2)$ cal	$-\Delta E(HNO_3)$ cal	$-\Delta E$(Au) cal	$-\Delta E$(Pt) cal	$-\Delta E$(HBr) cal	$-\Delta E_\Sigma$ cal	$-\Delta Ec°/M$ cal/g
0.651095	0.066860	0.005858	0.0548	0.88031	0.000788	10.49	0.30	0.05	0.02	17.67	0.30	6 589.1
0.648572	0.086604	0.005344	0.0491	0.91399	0.000796	10.91	0.65	0.04	0.02	17.60	0.31	6 582.4
0.674744	0.068958	0.005302	0.0409	0.91130	0.000834	10.85	0.65	0.03	0.01	18.31	0.31	6 588.1
0.654363	0.079064	0.005559	0.0422	0.90671	0.000810	10.81	0.30	0.03	0.02	17.76	0.31	6 584.2
0.647449	0.070521	0.005679	0.0623	0.88248	0.000791	10.52	0.65	0.02	0.03	17.57	0.31	6 583.6
0.651145	0.072602	0.005523	0.0610	0.89100	0.000772	10.62	1.15	0.03	0.03	17.67	0.31	6 589.4
0.653175	0.069570	0.005142	0.0649	0.88707	0.000811	10.57	0.15	0.02	0.01	17.73	0.31	6 584.4
											Mean	6 585.9
											Standard deviation of mean	± 1.0_9

HEAT OF COMBUSTION MEASUREMENTS

Apparatus and procedure

The same calorimetric systems, A and B, and the same experimental procedures used in the work reported in Ref.[5] were used in the present heat of combustion measurements. Calorimeter A was used for the measurements on the samples of 1-bromohexane Sample II and 1-bromooctane and calorimeter B for 1-bromobutane, 1-bromopentane, 1-bromohexane Sample I and 1-bromoheptane.

Results

The results of the combustion experiments are presented in Tables 2—4. The symbols have the same significance as in corresponding tables of Refs.[5,14]. It should be noted that, (i) the results listed in Table 2 were obtained in experiments with calorimeter B and those in Tables 3 and 4 in experiments with calorimeter A; and (ii) the reference temperature, t_h, was 20.0°C in experiments with calorimeter B and 25.0°C in experiments with calorimeter A.

Calculation of results. The results were calculated as given in Ref.[14] by use of eqns. 3—5 of Ref.[5]

Unit of energy. Auxiliary quantities. The results are given in terms of the defined thermochemical calorie equal to 4.1840 abs. joules. The $-\Delta Ec°/M$ values refer to the reaction represented by eqn. 1, in which all reactants and products are in their thermodynamic standard states [15] at the temperature t_h:

$$C_nH_{2n+1}Br(liq) + (6n+1)/4\ O_2(g) \rightarrow n\ CO_2(g) + (2n+1)/2\ H_2O(liq) + + \tfrac{1}{2}Br_2\ (liq) \qquad (1)$$

For both samples of benzoic acid used in calibration experiments with the two calorimeters the certified value [7,8] for the heat of combustion under certificate conditions is 26.4338 ± 0.0026 abs. kj/g mass which is equal to 6 317.83 ± 0.62 cal/g mass. This value is recalculated, as given in Refs.[5,16], to give the values 6 312.92 ± 0.62 and 6 314.12 ± 0.62 cal/g mass for the standard heat of combustion per gram mass of the sample, $-\Delta Ec°/M$, at 25°C and 20°C, respectively.

In addition to the numerical quantities given in Ref.[5 (Table 8)] the values listed in Table 5 were used in the calculation of the results. The symbols in Table 5 denote: ϱ the density, c_P the specific heat, and $(\partial E/\partial P)_T$ the energy of compression of the substance. The density values are from the present paper. The specific heat values for 1-bromobutane, 1-bromopentane and 1-bromohexane were obtained from data given in Ref.[17] by plotting and extrapolation, and the specific heat values for 1-bromoheptane and 1-bromooctane were estimated by analogy with the three lower homologues. The $(\partial E/\partial P)_T$ values were calculated from the corresponding density data using the approximate relation $(\partial E/\partial P)_T = -T(\partial V/\partial T)_P$ as discussed in Ref.[18 (p. 542—43)]

Uncertainties. The standard deviations of mean given in Tables 3 and 4 were calculated in the conventional way [19 (p. 433)]. Because of the small number of experiments on each of the compounds listed in Table 2 the standard deviations of mean in this table were calculated by the method given in Ref.[20 (p. 73—74)] utilizing all 13 individual experiments of the table.

Table 5. Auxiliary quantities for calculation of results [a].

Compound (liq)	ϱ g/ml		c_p cal/g deg 25°C	$(\partial E/\partial P)_T$ cal/g atm 20 – 25°C
	20°C	25°C		
1-Bromobutane	1.2758	1.2686	0.27	–0.0064
1-Bromopentane	1.2186	1.2123	0.28	–0.0061
1-Bromohexane	1.1745	1.1687	0.30	–0.0060
1-Bromoheptane	1.1402	1.1348	0.31	–0.0060
1-Bromooctane	1.1129	1.1077	0.32	–0.0060

[a] See text for comments.

The final over-all standard deviations [19 (p. 432)] given in Table 6 were calculated by the method described in Ref.[5 (p. 130)] using the following values for the ratios s_i/q_i:

$s_1/q_1 = 0.5 \times 10^{-4}$; $s_2/q_2 = 0.7 \times 10^{-4}$ (Table 2), 0.6×10^{-4} (Table 3) and 0.8×10^{-4} (Table 4); $s_3/q_3 = 0.6 \times 10^{-4}$ (Table 2), 1.0×10^{-4} (Table 3) and 0.8×10^{-4} (Table 4); $s_4/q_4 = 350 \times 10^{-4}$; $s_5/q_5 = 13 \times 10^{-4}$.

Derived standard heats of combusticn

The $-\Delta Ec°/M$ mean values given in Tables 2—4, cn recalculation by conventional methods [21 (p. 103–4)], gave the values listed in Table 6 for the standard energies of combustion, $\Delta Ec°$, at 20°C and 25°C, and the standard enthalpies of combustion, $\Delta Hc°$, at 25°C for the various compounds. The data refer to the combustion reaction represented by eqn. 1, in which all reactants and products are in their standard states. The uncertainties were calculated as described in the preceding section.

Table 6. Derived standard heats of combustion.

Compound and state	Molecular weight [a]	$-\Delta Ec°$ at 20°C kcal/mole	$-\Delta Ec°$ at 25°C kcal/mole	$-\Delta Hc°$ at 25°C kcal/mole
1-Bromobutane(liq)	137.032	648.08±0.30[b]		649.17±0.30[b]
1-Bromopentane(liq)	151.059	803.97±0.34		805.30±0.34
1-Bromohexane(liq)				
Sample I	165.086	961.26±0.36		962.82±0.36
Sample II			959.99±0.38[b]	961.91±0.38
1-Bromoheptane(liq)	179.113	1 116.72±0.38		1 118.52±0.38
1-Bromooctane(liq)	193.140		1 272.00±0.54	1 274.52±0.54

[a] Computed from the 1957 table of atomic weights[23].
[b] The uncertainties in this column are equal to twice the final over-all standard deviation; see text for comments.

Table 7. Derived standard heats of formation.

Compound	ΔHf°(liq) at 25°C kcal/mole	ΔHv[a] at 25°C kcal/mole	ΔHf°(g)[b] at 25°C kcal/mole
1-Bromobutane	-34.47 ± 0.31[c]	8.80 ± 0.25[d]	-25.67 ± 0.40[e]
1-Bromopentane	-40.72 ± 0.35	9.70 ± 0.30	-31.02 ± 0.46
1-Bromohexane Sample I	-45.57 ± 0.37	10.60 ± 0.30	-34.97 ± 0.48
Sample II	-46.48 ± 0.39	10.60 ± 0.30	-35.88 ± 0.49
1-Bromoheptane	-52.24 ± 0.39	11.55 ± 0.35	-40.69 ± 0.52
1-Bromooctane	-58.61 ± 0.55	12.35 ± 0.35	-46.26 ± 0.65

[a] For the process $C_aH_bBr_d$(liq) → $C_aH_bBr_d$(g), at saturation pressure at 25°C.
[b] See text for comments.
[c] The uncertainties in this column are equal to twice the final over-all standard deviation[19].
[d] The uncertainties in this column are estimates.
[e] The uncertainties in this column are equal to twice the final over-all standard deviation (including the estimated unceıtainties assigned to the ΔHv values in column 3)[19].

HEATS OF FORMATION

Standard heats of formation, ΔHf°, at 25°C, referring to reaction 2,

$$n\ C(c,\ graphite) + (2n+1)/2\ H_2(g) + \tfrac{1}{2}\ Br_2(liq) \rightarrow C_nH_{2n+1}Br(liq) \qquad (2)$$

were calculated from the $-\Delta H$c° values given in Table 6 and the selected values [15] for the standard heats of formation of gaseous carbon dioxide [24], —94.0539 ± 0.0108 kcal/mole, and liquid water [25], 68.3174 ± 0.0096 kcal/mole. The value for carbon dioxide is corrected to the present atomic weight of 12.011 for carbon. The derived standard heats of formation for the liquid compounds are given in column 2 of Table 7. In column 3 are listed heats of vaporization, ΔHv, at 25°C for the various compounds, calculated from data in Refs.[26,27]. Resulting standard heats of formation, at 25°C, of the compounds in the gaseous state are listed in column 4. Actually, the values given in this column apply to the compounds at their saturation pressures at 25°C. It can, however, be estimated [27] that reduction of the values to apply to the compounds in a state of unit fugacity (1 atm) will change the values by less than a few hundredths of a kcal/mole. Therefore the given values have been listed as standard heats of formation.

DISCUSSION OF RESULTS

The internal consistency of the derived heat of formation data in Table 7 can be checked in the following way.

It has been shown [28] that for several homologous series of hydrocarbons the standard heats of formation of the gaseous compounds can be expressed by the following relation:

$$\Delta H f^{\circ}_{298.15}\ [Y{-}(CH_2)_m{-}H,\ gas] = A + Bm + \delta \qquad (3)$$

Table 8. Values of δ in the relation $\Delta Hf°_{298.15}$ [$CH_2Br-(CH_2)_m-H$, gas] = A + B × m + δ for the standard heats of formation, in the gaseous state at 25°C, of the 1-bromoalkanes

m	A + B × m kcal/mole	$\Delta Hf°_{298.15}$ kcal/mole	$\delta = \Delta Hf°_{298.15} -$ (A + B × m) kcal/mole
	A = −11.164 kcal/mole, B = −4.926 kcal/mole		
4	−30.87	−31.02 ± 0.46	−0.15 ± 0.46
5 (Sample I)	−35.79	−34.97 ± 0.48	+ 0.82 ± 0.48
5 (Sample II)	−35.79	−35.88 ± 0.49	−0.09 ± 0.49
6	−40.72	−40.69 ± 0.52	+ 0.03 ± 0.52
7	−45.65	−46.26 ± 0.65	−0.61 ± 0.65
	A = −11.364 kcal/mole, B = −4.926 kcal/mole		
2	−21.22	−21.98 ± 0.40[a]	−0.76 ± 0.40
3	−26.14	−25.67 ± 0.40	+ 0.47 ± 0.40
4	−31.07	−31.02 ± 0.46	+ 0.05 ± 0.46
5	−35.99	−35.88 ± 0.49	+ 0.11 ± 0.49
6	−40.92	−40.69 ± 0.52	+ 0.23 ± 0.52
7	−45.85	−46.26 ± 0.65	−0.41 ± 0.65

[a] Ref.[5]

where $(CH_2)_m$—H is a *n*-alkyl group bonded to any end group Y (methyl, vinyl, phenyl, *cyclo*pentyl, *cyclo*hexyl), A is a constant characteristic of the end group, B is a constant for all *n*-alkyl series, independent of Y, and δ is a term which has a small finite value for the lower members of a series and becomes zero for the higher members, beginning near m = 4. Choosing the bromomethyl group as end group for the 1-bromoalkanes, CH_2Br—$(CH_2)_m$—H, and using the same relation 3 and the same numerical value of B, —4.926 kcal/mole, as for the various hydrocarbon series, a value for A can be calculated from the derived heat of formation values for 1-bromopentane, 1-bromohexane Samples I and II, 1-bromoheptane and 1-bromooctane, for which compounds $m \geq 4$ and for which δ in eqn. 3 therefore can be assumed to be zero. The value obtained for A is —11.164 kcal/mole. Using this figure the δ values given in the upper part of Table 8 are obtained. It is seen that only in the case of Sample I of 1-bromohexane does the value of δ differ significantly from zero. Preference may therefore be given to the heat of formation value obtained for Sample II of 1-bromohexane. Accordingly a different value for A can be calculated from the same heat of formation data as above with exclusion of that for Sample I of 1-bromohexane. The value —11.364 kcal/mole is thus obtained for A. Corresponding δ values are given in the lower part of Table 8.

The given discussion has thus shown that the heat of formation data derived from the heat of combustion values obtained in the present investigation are internally consistent when the heat of formation derived from the heat of combustion of Sample I of 1-bromohexane is excluded. It has also been shown that the standard heats of formation at 25°C of the C_5—C_8 1-bromoalkanes can be expressed by the relation:

$$\Delta Hf^{\circ}_{298.15}\ [CH_2Br—(CH_2)_m—H,\ gas] = —11.364 — 4.926 \times m\ kcal/mole$$
$$(m = 4, 5, 6, 7).$$

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