On the Accuracy of Heat of Combustion Data Obtained with a Precision Moving-Bomb Calorimetric Method for Organic Bromine Compounds

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The purpose of the investigation has been to establish the accuracy of results obtainable with a recent high-precision moving-bomb method for measuring heats of combustion at 25°C of solid and liquid organic bromine compounds. The approach has been to compare, for five selected bromine compounds, heats of formation calculated from heat of combustion data obtained by the given method, with those derived from calorimetric data on heats of reactions other than combustion. The purification of samples of the following compounds is described: 1,2-dibromobutane, 1,2-dibromo*cyclo*hexane,1-bromo-propane, 2-bromopropane and 2-bromobutane. 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: 1,2-dibromobutane 614.26 ± 0.52, 1,2-dibromo*cyclo*hexane 867.54 ± 0.60, 1-bromopropane 491.54 ± 0.34, 2-bromopropane 490.42 ± 0.42, 2-bromobutane 646.52 ± 0.30. Standard heats of formation at 25°C calculated from the heat of combustion data are compared with values calculated from reaction-calorimetric data on heats of addition of bromine (in three cases) and hydrogen bromide (in six cases) to unsaturated hydrocarbons, and from data on the heat of hydrogenation of 1-bromopropane to propane. In the first three cases the heat of formation values from combustion data were found to disagree with those from reaction-calorimetric data by as much as two to three kcal/mole, but in all other cases the values obtained from the two types of calorimetric data were virtually the same. The results of the comparison are discussed and it is concluded that the combustion calorimetric method for organic bromine compounds can give heats of combustion accurate within error limits of approximately 0.01 %.

Two previous papers [1,2] described a moving-bomb method for combustion calorimetry of organic bromine compounds and the method of reducing the observed heats of combustion to standard conditions. It was found that

results were of an immediate precision [3 (p. 430)] slightly better than 0.01 %. Although this precision was satisfactorily high, undetected systematic errors might render the accuracy [3] of obtained heat of combustion data much lower than this. It has been necessary, therefore, to determine the absolute accuracy of the method, and the results of the investigation are reported here.

METHOD

There are several possible ways of investigating the accuracy of the results obtainable by the application of a given method for the determination of the heats of combustion of organic compounds [4 (p. 216)]. One is to compare results of combustion experiments with other appropriate calorimetrically determined heats of reaction. Since the principal use for heat of combustion data is to derive corresponding heats of formation, the approach made here is to compare, for certain selected bromine compounds, heats of formation calculated both from heat of combustion data and from calorimetric data on heats of reactions other than combustion.

The selection of compounds for this comparison was governed by various considerations. One was that comparison should be based on heats of formation calculated from data obtained in as many different high-precision calorimetric investigations on heats of reaction as are available. Suitable investigations have already been reported on the heats of: (i) gas-phase addition of bromine to certain alkenes [6], (ii) liquid-phase addition of bromine to certain *cyclo*alkenes and alkenes [7], (iii) gas-phase addition of hydrogen bromide to *cyclo*propane and certain alkenes [8–10], and (iv) gas-phase reduction of 1-bromopropane to propane [11]. Secondly, since it was originally intended to apply the present bomb-calorimetric technique to some lower mono- and dibromoalkanes, it was clearly advantageous to choose the substances for comparison from this class of compounds. Accordingly, the following compounds were chosen: 1,2-dibromobutane, 1,2-dibromo*cyclo*hexane, 1-bromopropane, 2-bromopropane and 2-bromobutane. The purification of samples of these compounds and the determination of their heats of combustion is described in the following section.

HEAT OF COMBUSTION MEASUREMENTS

Apparatus and Procedure

Two different calorimetric systems, A and B, were used in the heat of combustion measurements. Calorimeter A has been described in detail in Ref.[1] and calorimeter B, which was an earlier model of calorimeter A, has been described briefly in Refs. [4,12] Calorimeter A was used for the measurements on the samples of 1,2-dibromobutane and 1,2-dibromo*cyclo*hexane and calorimeter B for 1-bromopropane and 2-bromobutane. Measurements on the 2-bromopropane sample were made with both calorimeters.

The experimental procedures used in experiments with calorimeters A and B have been described in Ref.[1] and Refs.[4,12], respectively. In both cases, volatile liquid combustion samples were sealed in soft-glass ampoules [13(p. 45)] and a baffle (top) [13(p. 48), 14(p. 145)] was used when required.

Possible systematic errors in results obtained with calorimeters A and B have been discussed in Ref.[1] and Refs.[15,16], respectively.

Materials

Benzoic acid. The benzoic acid samples used in the calibration experiments with calorimeters A and B were National Bureau of Standards standard sample 39g[17] and 39f[18], respectively.

Paraffin oil. The two paraffin oil samples used as auxiliary material in the combustion experiments with the bromine compounds were both redistilled mineral oils. The sample used in experiments with calorimeter A, Paraffin oil USBM-P3a, has been described previously [1(p. 1531)]. The sample used in experiments with calorimeter B, Paraffin oil L, was found to have a percentage composition corresponding to the empirical formula $CH_{1.97}$ and a density of 0.8838 g/ml at 20.00°C.

Bromine compounds. The bromine compound samples were all obtained by careful purification of commercial products except for the 1,2-dibromo*cyclo*hexane, the original sample of which was synthesized as described below. The various original samples were first treated chemically and then purified by successive fractional distillations at two or more different pressures. The all-glass, packed distilling column was equipped with controlled heating element jacket and a total condensation — variable takeoff head [19]. The material in the still pot was heated with a near infrared heat lamp, which gave a very smooth boiling even at rather low distillation pressures. The efficiency of the column, as determined with a carbon tetrachloride — benzene mixture [20], was found to be equivalent to 24 theoretical plates for total reflux at a distillation rate of about 6 ml/min. The progress of each distillation was followed by measuring the density of the successive fractions of the distillate. The density measurements were made with a standard Ostwald-Sprengel pycnometer to an accuracy estimated at $\pm$ 0.0001 g/ml. The fractionation was continued until more than 75 % of the distillate in a distillation was collected at a constant density, and until two distillations at different pressures gave distillates having the same density within the uncertainty of the density measurements. This last precaution precluded the presence of azeotropic mixtures. Details on the purification of the various samples follow.

1,2-Dibromobutane. A 500 g sample (Eastman Organic Chemicals) with the density $d_4^{20} = 1.7926$, $d_4^{25} = 1.7844$ was treated in order with conc. sulfuric acid, water, 10 % sodium carbonate solution and water, and was finally dried with calcium chloride. The product was purified by six successive fractional distillations at the following pressures: 100, 45, 20, 50, 20 and 25 mm. In the final distillation 80 % (77 g) of the distillate was collected over a density range of 0.0002 g/ml.

1,2-Dibromocyclohexane. This substance was prepared from *cyclo*hexene by the addition of bromine in carbon tetrachloride containing a little ethyl alcohol [21]. The product, 640 g, was treated with ethyl alcoholic potassium hydroxide *etc.*, as described in Note 7 of Ref.[21], and dried first with calcium chloride and then with phosphorus pentoxide. The dry sample was purified by successive fractionations at pressures 50, 20, 8, 7, and 20 mm. In the final distillation 80 % (82 g) of the distillate was collected over a density range of 0.0002 g/ml.

1-Bromopropane. A commercial sample (Columbia Organic Chemicals) was treated with phosphorus pentoxide. The resulting 168 g were purified by three successive fractional distillations at pressures 755, 360, and 755 mm, respectively. All the distillate (25 g) in the final distillation was, except for the first few grams, collected over a boiling temperature range of 0.02°C and a corresponding density range of 0.0003 g/ml.

2-Bromopropane. A commercial sample (Columbia Organic Chemicals) was treated in order with conc. hydrochloric acid, 10 % sodium bicarbonate solution and water. The product was dried with calcium chloride and with phosphorus pentoxide and the resulting 155 g were fractionated by successive distillations at pressures 740, 750, and 760 mm. In the final distillation 80 % (19 g) of the distillate was collected over a boiling range of 0.01°C corresponding to a density range of 0.0004 g/ml.

2-Bromobutane. A 100 g sample (Columbia Organic Chemicals) was purified by successive fractional distillations at 750 and 170 mm pressure, respectively. In the final distillation 75 % (39 g) of the distillate was collected over a density range of 0.0001 g/ml. This product was dried with calcium sulfate and subjected to simple distillation at 290 mm. The middle fraction from this distillation was used in the heat of combustion experiments.

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°
1,2-Dibromobutane								
Present investigation	1.7954	1.7870	1.5149	1.5125	1.5113	1.5089	1.5238	1.5213
Dillon, Young and Lucas [23]	1.7951	1.7870	1.5150	1.5125				
1,2-Dibromocyclohexane								
Present investigation	1.7903	1.7833	1.5529	1.5506	1.5492	1.5469	1.5620	1.5598
Goering and Sims [24]		1.784		1.5507				
Winstein [25]		1.7826		1.5507				
1-Bromopropane								
Present investigation	1.3550	1.3465	1.4346	1.4320	1.4318	1.4292	1.4412	1.4385
Tschamler, Richter and Wettig [26]		1.3467	1.43419					
Skau and McCullough [27]		1.3455						
Timmermans and Martin [28]	1.35135	1.34305	1.43435	1.43175	1.43180	1.42920	1.44119	1.43854
2-Bromopropane								
Present investigation	1.3142	1.3055	1.4255	1.4226	1.4228	1.4200	1.4321	1.4293
Skau and McCullough [27]		1.3063						
Timmermans and Martin [29]	1.31389	1.30554	1.43562	1.42277	1.42286	1.42006	1.43230	1.42940
2-Bromobutane								
Present investigation	1.2607	1.2533	1.4370	1.4345	1.4342	1.4318	1.4435	1.4410
Skau and McCullough [27]		1.2530						
Timmermans and Delcourt [30]	1.26086	1.25365			1.43434	1.43204	1.44369	1.44124
Lucas, Dillon and Young [31]	1.2607	1.2534	1.4374					

Table 1 gives the results of density measurements, 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 densities were determined as described above and the refractive indices were measured with a calibrated Pulfrich refractometer, giving refractive index values within error limits of $\pm$ 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 (*cf.* Ref.[22]) previous investigations [23–31] are also listed in Table 1.

RESULTS

The results of the calibration experiments with benzoic acid are presented in Tables 2 and 3, those of the combustion experiments with the paraffin oils in Tables 4 and 5, and those with the various bromine compounds in Tables 6 and 7. The symbols have the same significance as in corresponding Tables of Ref.[1] The additional symbols denote:

Table 2. Results of calibration experiments on calorimeter A.

$t_h = 25.0°C$	$V(Bomb) = 0.2670$ liter; $m^i(Cont.) = 20.745$ g; $\varepsilon^i(Cont.) = 3.198$ cal/deg
$t_i = 24.1°C$	$V^i(H_2O \text{ tot.}) = 0.810$ ml; $-\Delta Ec/M$(Benzoic acid NBS 39g) $= \dfrac{6\ 317.83}{\pm\ 0.62}$ cal/g[a]

$P^i(gas.) = 30.0$ atm; $m(Pt) = 8.528$ g

$$-\Delta Ec/M\text{(Fuse)} = 3\ 971 \pm 4 \text{ cal/g}$$

m' g	m''' g	Δt deg	$-\Delta E(HNO_3)$ cal	$-\Delta E_{\text{I.B.P.}}/\Delta t$ cal/deg
0.80083	0.00551	0.87575	1.50	5 804.04
0.80130	0.00554	0.87649	0.60	5 801.64
0.80069	0.00548	0.87560	2.10	5 804.57
0.80132	0.00551	0.87608	0.65	5 804.41
0.80065	0.00564	0.87577	1.35	5 803.03
0.80141	0.00550	0.87610	0.45	5 804.66
0.80173	0.00568	0.87667	0.60	5 804.18
0.80149	0.00539	0.87659	0.35	5 801.38
			Mean	5 803.49
		Standard deviation of mean		$\pm$ 0.47
			$\varepsilon°(Calor.) = 5\ 821.01 \pm 0.47$ cal/deg

[a] At 25°C under the actual bomb conditions.

$\varepsilon^f(Cont.)$	the energy equivalent of the final contents of the bomb
$-\Delta E_{\text{oxid.}}(As_2O_3)$	the heat evolved per mole of the reaction $As_2O_3(aq) + O_2(g) \rightarrow As_2O_5(aq)$, *cf.* Refs.[1](p. 1525-26), [2](p. 621).
$m(glass)$	the mass of the glass ampoule containing the combustion sample.

It should be noted that, (i) the results listed in Tables 2, 4, and 6 were all obtained in experiments with calorimeter A and those in Tables 3, 5, and 7 in experiments with calorimeter B; (ii) the reference temperature, t_h, was 25.0°C in experiments with calorimeter A and 20.0°C in experiments with calorimeter B; and (iii) 0.810 ml of water was introduced into the bomb in the calibration as well as the combustion experiments on paraffin oil with calorimeter A, while in the corresponding experiments with calorimeter B 30 ml of arsenious oxide solution were placed in the bomb.

Calculation of results. The results of the calibration experiments given in Table 2 were calculated as described in Ref.[1] For the calibration experiments given in Table 3, however, this method of calculation had to be modified as follows. Firstly, since all experiments with calorimeter B were so arranged that $t_h = t_i$, eqn. 14 of Ref.[1] changed to:

$$\varepsilon°(Calor.) = -\Delta E_{\text{I.B.P.}} / \Delta t + C_P(H_2O)m^i(Cont.) - \varepsilon^f(Cont.) \tag{1}$$

Secondly, the computation of the heat of combustion of the standard benzoic acid under the actual bomb conditions of the calibration experiments,

Table 3. Results of calibration experiments on calorimeter B.

$t_h = 20.0°C$	V(Bomb)$=0.2750$ liter	m(Pt)$=4.722$ g; m^i(Cont.)$=45.69$ g	ε^f(Cont.) $=$
$t_i = 20.0°C$	V^i(soln.)$=0.03001$ liter	$-\varDelta Ec°/M$(Benzoic acid NBS 39f)	32.17 cal/deg
P^i(gas.)$=$	C^i(soln.)$=0.0625_5$	$=6\ 314.12 \pm 0.62$ cal/g at 20°C	
30 atm	mole As_2O_3/liter	$-\varDelta Ec°/M$(Fuse) $= 3\ 971 \pm 4$ cal/g	

m' g	m''' g	$\varDelta t$ deg	$-\varDelta E(CO_2)$ cal	$-\varDelta E(HNO_3)$ cal	$-\varDelta E_{\Sigma}$ cal	$-\varDelta E_{\text{I.B.P.}}/\varDelta t$ cal/deg
0.73458	0.00491	0.99413	15.31	1.45	−1.91	4 704.01
0.73404	0.00469	0.99289	15.30	0.80	−1.91	4 704.90
0.73319	0.00494	0.99202	15.28	0.75	−1.91	4 704.55
0.73340	0.00420	0.99144	15.28	1.30	−1.91	4 706.24
0.73508	0.00503	0.99438	15.32	0.85	−1.91	4 705.88
0.73450	0.00497	0.99384	15.31	1.50	−1.91	4 705.16
					Mean	4 705.12
				Standard deviation of mean		± 0.34
				$\varepsilon°$(Calor.) $= 4\ 718.62 \pm 0.34$ cal/deg		

$-\varDelta Ec/M$(Benzoic acid), from the certified value under certificate conditions [18] could not be made using the factor given in the certificate [18] since the actual bomb conditions differed too radically from the certificate conditions. Therefore, eqn. 15 of Ref.[1] could not be used in its original form for computation of $-\varDelta E_{\text{I.B.P.}}$. Instead the standard heat of combustion per gram of the benzoic acid sample, $-\varDelta Ec°/M$(Benzoic acid), was calculated from the certificate value using the Washburn reduction as given in Ref.[2] For the individual cali-

Table 4. Results of combustion experiments on paraffin oil USBM-P3a.

Calorimeter A					
$t_h = 25.0°C$		V(Bomb) $= 0.2670$ liter	$\varepsilon°$(Calor.) $= 5\ 821.01$	ε(Calor.) $=$	
			± 0.47 cal/deg	5 800.63 cal/deg	
$t_i = 24.1°C$		$V^i(H_2O$ tot.$) = 0.810$ ml		ε^i(Cont.) $=$	
				3.21 cal/deg	
P^i(gas.) $= 30.0$ atm; m(Pt) $= 8.528$ g			$-\varDelta Ec°/M$(Fuse) $= 3\ 971 \pm 4$ cal/g		

m'' g	m''' g	$\varDelta t$ deg	$-\varDelta E(CO_2)$ cal	$-\varDelta E(HNO_3)$ cal	$-\varDelta E_{\Sigma}$ cal	$-\varDelta Ec°/M$ cal/g
0.44937	0.00529	0.85422	0.49	1.60	−1.07	10 978.9
0.45589	0.00534	0.86696	0.49	1.70	−1.07	10 983.5
0.45438	0.00596	0.86388	0.49	0.30	−1.07	10 978.2
0.45502	0.00592	0.86522	0.49	1.75	−1.07	10 977.1
0.45967	0.00598	0.87429	0.49	2.04	−1.07	10 979.4
0.45470	0.00526	0.86428	0.49	0.90	−1.07	10 980.4
					Mean	10 979.6
				Standard deviation of mean		± 0.9

Table 5. Results of combustion experiments on paraffin oil L.

Calorimeter B

$t_h = 20.0°C$ V(Bomb) = 0.2750 liter $\varepsilon°$(Calor.) = 4 718.62 ± 0.34 cal/deg

$t_i = 20.0°C$ V^i(soln.) = 0.03001 liter

P^i(gas.) = 30.0 atm C^i(soln.) = 0.0625$_5$ mole As_2O_3/liter $-\Delta Ec°/M$(Fuse) = 3 971 ± 4 cal/g

m'' g	m''' g	m(Pt) g	ε(Calor.) cal/deg	ε^f(Cont.) cal/deg	Δt deg	$-\Delta E(CO_2)$ cal	$-\Delta E(HNO_3)$ cal	$-\Delta E_\Sigma$ cal	$-\Delta Ec°/M$ cal/g
.42465	0.00444	4.722	4 673.25	32.30	0.99644	11.26	1.20	0.08	10 970.9
.42516	0.00497	4.722	4 673.25	32.30	0.99824	11.28	0.90	0.08	10.973.4
.42491	0.00410	4.722	4 673.25	32.30	0.99709	11.26	1.45	0.08	10 974.1
.42428	0.00468	7.002	4 670.97	32.37	0.99452	11.25	2.15	0.08	10 971.6
.42474	0.00475	4.90	4 673.07	32.30	0.99711	11.26	2.10	0.08	10 970.5

| | | | | | | | | Mean | 10 972.1 |
| | | | | | | | Standard deviation of mean | | ± 0.7 |

bration experiments the quantities $-\Delta E(CO_2)$ and $-\Delta E_\Sigma$ were then computed, as given in Ref.[2], and finally the $-\Delta E_{I.B.P.}$ values were calculated from the following modification of eqn. 15 of Ref.[1]:

$$-\Delta E_{I.B.P.} = -m'\Delta Ec°/M(\text{Benzoic acid}) - m'''\Delta Ec°/M(\text{Fuse}) - \Delta E(CO_2) - \Delta E(HNO_3) + \Delta E_\Sigma \quad (2)$$

The results of the combustion experiments listed in Tables 4—7 were calculated as given in Ref.[1] by use of the following main equations:

$$\varepsilon(\text{Calor.}) = \varepsilon°(\text{Calor.}) - C_P(H_2O)m^i(\text{Cont.}) \quad (3)$$

$$-\Delta E_{I.B.P.} = [\varepsilon(\text{Calor.}) + \varepsilon^i(\text{Cont.}) \text{ or } \varepsilon^f(\text{Cont.})]\Delta t \quad (4)$$

$$-\Delta Ec°/M = \frac{1}{m'}\left\{- \Delta E_{I.B.P.} - [-\Delta E(\text{As}) - \Delta E(\text{Oil}) - \Delta E(\text{Fuse}) - \Delta E(CO_2) - \Delta E(HNO_3) - \Delta E(\text{Au}) - \Delta E(\text{Pt})] - \Delta E(\text{HBr}) - \Delta E_\Sigma\right\} \quad (5)$$

The two last $-\Delta Ec°/M$ values given for 2-bromopropane in Table 7 were obtained by conversion from 25°C to 20°C of the two $-\Delta Ec°/M$ values given for 2-bromopropane in Table 6. In the calculations the following values were used for the heat capacity, $C_P°$, at 25°C of liquid 2-bromopropane, gaseous oxygen, gaseous carbon dioxide, liquid water and liquid bromine, respectively: 33 (estimated), 7.017 (Ref.[32]), 8.874 (Ref.[32]), 17.996 (Ref.[32]) and 17.00 (Ref.[33]) cal/deg mole.

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. 6, in which all reactants and products are in their thermodynamic standard states [32] at the temperature t_h:
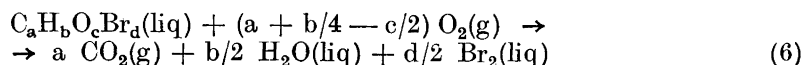
$$C_aH_bO_cBr_d(\text{liq}) + (a + b/4 - c/2) O_2(g) \rightarrow$$
$$\rightarrow a\ CO_2(g) + b/2\ H_2O(\text{liq}) + d/2\ Br_2(\text{liq}) \quad (6)$$

Table 6. Results of combustion experiments on bromine compounds.

Calorimeter A
t_h = 25.0°C
t_i = 24.1°C
P^i(gas.) = 30.0 atm

V(Bomb) = 0.2670 liter
V^i(soln.) = 0.03005 liter
C^i(soln.) = 0.06286 mole As_2O_3/liter

$\varepsilon°$(Calor.) = 5 821.01 ± 0.47 cal/deg
$-\Delta Ec°/M$(Oil) = 10 979.6 ± 0.9 cal/g
$-\Delta Ec°/M$(Fuse) = 3 971 ± 4 cal/g

$-\Delta E_{oxid.}(As_2O_3)$ = (77.4 ± 0.1) × 10³ cal/mole

m' g	m'' g	m''' g	m(glass) g	ε(Calor.) cal/deg	ε^i(Cont.) cal/deg	Δt deg	$n^i(As_2O_3)$ 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
1,2-Dibromobutane m(Pt) = 17.996 g														
0.642508	0.256444	0.005881	0.0519	5 762.40	32.51	0.82059	0.001431	10.02	1.60	0.08	0.04	31.36	0.16	2 840.8
0.622896	0.293647	0.005703	0.0654	5 762.37	32.45	0.88110	0.001383	10.76	1.20	0.04	0.07	30.40	0.02	2 842.1
0.626494	0.299904	0.005083	0.0676	5 762.36	32.45	0.89452	0.001405	10.93	1.65	0.10	0.05	30.58	0.02	2 840.7
0.627561	0.299733	0.005228	0.0607	5 762.36	32.45	0.89433	0.001394	10.93	1.55	0.09	0.07	30.63	0.02	2 837.8
0.624233	0.296261	0.005153	0.0649	5 762.37	32.45	0.88572	0.001400	10.83	0.75	0.08	0.04	30.47	0.02	2 835.0
0.606059	0.308427	0.005378	0.0621	5 762.37	32.45	0.90001	0.001357	11.01	1.10	0.09	0.06	29.58	0.03	2 837.9
0.609773	0.304134	0.005177	0.0610	5 762.38	32.45	0.89377	0.001373	10.93	0.65	0.09	0.05	29.76	0.03	2 839.1
													Mean	2 839.1
												Standard deviation of mean		± 0.9₀
1,2-Dibromocyclohexane m(Pt) = 17.673 g														
0.633191	0.242096	0.005299	0.0393	5 762.76	32.38	0.86786	0.001280	10.90	0.35	0.07	0.04	27.53	0.00	3 580.8
0.613328	0.249100	0.005608	0.0439	5 762.77	32.38	0.86858	0.001243	10.95	0.50	0.06	0.03	26.67	0.00	3 579.1
0.619436	0.264593	0.005484	0.0489	5 762.74	32.40	0.90134	0.001242	11.32	1.00	0.08	0.02	26.94	0.01	3 575.6
0.626006	0.263931	0.005447	0.0574	5 762.73	32.40	0.90458	0.001249	11.36	1.00	0.04	0.06	27.22	0.01	3 579.4
0.622097	0.257557	0.005821	0.0411	5 762.75	32.40	0.89044	0.001254	11.18	0.60	0.04	0.05	27.05	0.01	3 580.4
													Mean	3 579.1
												Standard deviation of mean		± 0.9₂
2-Bromopropane m(Pt) = 17.673 g														
0.48086	0.309334	0.005420	0.0524	5 762.83	32.44	0.93053	0.000916	11.25	1.75	0.03	0.03	20.52	0.25	3 975.3
0.47680	0.284761	0.005933	0.0601	5 762.85	32.43	0.88164	0.000913	10.61	1.25	0.03	0.02	20.35	0.29	3 979.2
													Mean:	See Table 7 and text

Table 7. Results of combustion experiments on bromine compounds (Continued).

Calorimeter B
$t_h = 20.0°C$
$t_i = 20.0°C$
$P^i(\text{gas.}) = 30.0$ atm

$V(\text{Bomb}) = 0.2750$ liter
$V^i(\text{soln.}) = 0.0300_1$ liter
$C^i(\text{soln.}) = 0.0625_5$ mole As_2O_3/liter

$\varepsilon°(\text{Calor.}) = 4\,718.62 \pm 0.34$ cal/deg
$-\Delta E_c°/M(\text{Oil}) = 10\,972.1 \pm 0.7$ cal/g
$-\Delta E_c°/M(\text{Fuse}) = 3\,971 \pm 4$ cal/g

$-\Delta E_{\text{oxid.}}(As_2O_3) = (77.4 \pm 0.1) \times 10^3$ cal/mole

m' g	m'' g	m''' g	$m(\text{Glass})$ g	$\varepsilon(\text{Calor.})$ cal/deg	$\varepsilon^f(\text{Cont.})$ 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	$-\Delta E_c°/M$ cal/g
1-Bromopropane $m(Pt) = 6.580$ g in the first two experiments and 15.740 g in the following														
0.56036	0.21550	0.00466	0.074	4 670.98	32.28	0.99741	0.001095	10.83	2.75	0.04	0.10	24.83	0.41	3 988.2
0.55444	0.21451	0.00444	0.083	4 670.97	32.28	0.99012	0.001094	10.75	1.10	0.04	0.10	24.56	0.41	3 993.0
0.53588	0.22392	0.00507	0.085	4 661.82	32.55	0.99743	0.001049	10.84	0.80	0.04	0.10	23.74	0.40	3 986.8
0.53311	0.22257	0.00495	0.084	4 661.83	32.55	0.99182	0.001041	10.78	0.35	0.04	0.10	23.62	0.40	3 988.7
0.55786	0.21257	0.00476	0.087	4 661.81	32.57	0.98990	0.001086	10.74	0.60	0.04	0.10	24.72	0.41	3 989.0
													Mean	3 989.1
													Standard deviation of mean	± 1.0$_4$
2-Bromopropane $m(Pt) = 15.740$ g														
0.53496	0.22100	0.00451	0.090	4 661.83	32.54	0.98825	0.001042	10.74	0.90	0.05	0.10	23.70	0.42	3 978.1
0.51190	0.23375	0.00465	0.090	4 661.84	32.54	0.99814	0.000994	10.88	0.45	0.05	0.10	22.68	0.39	3 979.6
0.54035	0.22111	0.00496	0.092	4 661.82	32.54	0.99427	0.001051	10.80	0.55	0.05	0.10	23.94	0.41	3 984.9
														3 976.7^a
														3 980.6^a
													Mean	3 980.0
													Standard deviation of mean	± 1.4$_0$
2-Bromobutane $m(Pt) = 5.764$ g														
0.63617	0.14915	0.00457	0.119	4 671.74	32.20	1.00450	0.001106	10.90	2.40	0.03	0.08	25.32	0.42	4 711.2
0.62907	0.15489	0.00452	0.122	4 671.74	32.19	1.01008	0.001109	10.98	1.10	0.03	0.08	25.04	0.42	4 707.5
0.62596	0.14437	0.00443	0.120	4 671.76	32.18	0.98261	0.001095	10.65	1.60	0.03	0.08	24.92	0.43	4 710.8
0.63471	0.14290	0.00478	0.098	4 671.77	32.20	0.98840	0.001114	10.71	1.15	0.03	0.08	25.27	0.43	4 710.9
													Mean	4 710.1
													Standard deviation of mean	± 0.8$_7$

^{a} These values were obtained by reduction from 25°C to 20°C of the two $-\Delta E_c°/M$ values given in Table 6 (see text).

For both samples of benzoic acid the certified value [17],[18] for the heat of combustion under certificate conditions is 26.4338 ± 0.0026 abs. kj/g mass which is equal to 6317.83 ± 0.62 cal/g mass. This value was recalculated, by the method given in Ref.[2], to give the value 6312.92 ± 0.62 cal/g mass for the standard heat of combustion per gram mass of the sample, $-\Delta Ec^\circ/M$, at 25°C. This was converted to apply to 20°C by use of the following values at 25°C for the heat capacity, C_P°, of crystalline benzoic acid, gaseous oxygen, gaseous carbon dioxide and liquid water, respectively: 35.088 (Ref.[34]), 7.017 (Ref.[32]), 8.874 (Ref.[32]) and 17.996 (Ref.[32]) cal/deg mole. The value thus obtained for the standard heat of combustion at 20°C of the benzoic acid samples was 6314.12 ± 0.62 cal/g mass. In addition to the numerical quantities given above and in Ref.[2] the values listed in Table 8 were used in the calculation of the results. The symbols in Table 8 denote: ϱ the density, c_P the specific heat, and $(\partial E/\partial P)_T$ the energy of compression of the substance. The $(\partial E/\partial P)_T$ values were calculated, unless otherwise stated, from the corresponding density data using the approximate relation $(\partial E/\partial P)_T = -T(\partial V/\partial T)_P$ as discussed in Ref.[36](p. 542-43).

    Final over-all precision. The standard deviations of the means given in Tables 2—7 are measures of the immediate precision [3](p. 430) of the various results. The over-all precision [3](p. 430) of the $-\Delta Ec^\circ/M$ mean value obtained for each bromine compound was estimated by calculation of the corresponding final over-all standard deviation [3](p. 432) as recommended in Ref.[3] The method of calculation given in Ref.[3], however, needs modification in order to be applicable to results from combustion experiments in which a considerable part of the total amount of heat evolved is associated with the combustion of an auxiliary material, the heat of combustion of which has been determined separately. The final over-all standard deviations given in Table 9 were obtained as follows.

Table 8. Auxiliary quantities for calculation of results.

Substance	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		
Benzoic acid	1.323 [a]	1.320 [b]	0.287 [c]	—0.0029 [d]
Paraffin oil USBM-P3a	0.8755 [e]	0.8724 [e]	0.53 [f]	—0.0060
Paraffin oil L	0.8838 [g]		0.53 [h]	—0.0060 [h]
Fuse		1.5 [i]	0.4 [j]	—0.007 [k]
1,2-Dibromobutane	1.7954 [g]	1.7870 [g]	0.20 [l]	—0.0038
1,2-Dibromo*cyclo*hexane	1.7903 [g]	1.7833 [g]	0.16 [l]	—0.0032
1-Bromopropane	1.3550 [g]	1.3465 [g]	0.269 [m]	—0.0066
2-Bromopropane	1.3142 [g]	1.3055 [g]	0.27 [l]	—0.0072
2-Bromobutane	1.2607 [g]	1.2533 [g]	0.27 [l]	—0.0066

    [a] Calculated from the value for the density at 25°C and the average of the two values for the coefficient of cubical expansion, γ, given in Ref.[35]; [b] Ref.[35]; [c] Ref.[34]; [d] Calculated from the aforementioned average value of the coefficient of cubical expansion, $\gamma = 0.00054$ deg⁻¹; [e] Ref.[1](p.1531); [f] Ref.[37](p. 93); [g] This work; [h] Taken as the same as that for Paraffin oil USBM-P3a; [i] Ref.[37](p. 81); [j] Ref.[37](p. 93); [k] Ref.[37](p. 90); [l] Estimated; [m] Ref.[38].

If the "second-order" quantities in eqns. 14 and 15 of Ref.[1] are neglected, the mean values of the energy equivalent of the calorimeter, $\varepsilon°$(Calor.), and the heat of combustion of the auxiliary oil, $-\Delta Ec°/M$(Oil), can be obtained from the following approximation equations:

$$\varepsilon°(\text{Calor.}) = -\Delta Ec/M(\text{Benzoic acid})(m/\Delta t)_{\text{b.a.}} \tag{7}$$

$$-\Delta Ec°/M(\text{Oil}) = \varepsilon°(\text{Calor.})(\Delta t/m)_{\text{oil}} =$$

$$-\Delta Ec/M(\text{Benzoic acid})(m/\Delta t)_{\text{b.a.}}.(\Delta t/m)_{\text{oil}} \tag{8}$$

in which $-\Delta Ec/M$(Benzoic acid) is the "accepted" value for the heat of combustion of the benzoic acid used in the calibration experiments, $(m/\Delta t)_{\text{b.a.}}$ is the mean of the individual values obtained for the ratio of benzoic acid mass to temperature rise in the calibration experiments, and $(\Delta t/m)_{\text{oil}}$ is the mean of the individual values obtained for the ratio of temperature rise to paraffin oil mass in the experiments by which the heat of combustion of the paraffin oil sample was determined. All three values, $-\Delta Ec/M$(Benzoic acid), $(m/\Delta t)_{\text{b.a.}}$, and $(\Delta t/m)_{\text{oil}}$, carry with them standard deviations, s_1, s_2, and s_3, respectively, which are estimated according to the procedure described in Ref.[3] Further, if the uncertainties in the "second-order" quantities $-\Delta E$(Fuse), $-\Delta E$(HNO$_3$), $-\Delta E$(Au), $-\Delta E$(Pt), $-\Delta E$(HBr) and $-\Delta E_\Sigma$ in eqn. 29 of Ref.[1] are neglected and the same quantities removed from the equation, the following approximate equation is obtained for calculation of the results of the combustion experiments with bromine compounds:

$$-\Delta Ec°/M(\text{Compound}) = \frac{1}{m'}\left\{-\Delta E_{\text{I.B.P.}} - [-\Delta E(\text{As}) - \Delta E(\text{Oil}) -\right.$$

$$-\Delta E(\text{CO}_2)]\bigg\} = \frac{1}{m'}\left\{\varepsilon°(\text{Calor.})\,\Delta t - n^{\text{f}}(\text{As}_2\text{O}_5)\,[-\Delta E_{\text{oxid.}}(\text{As}_2\text{O}_3)] -\right.$$

$$m''[-\Delta Ec°/M(\text{Oil})] - n^{\text{f}}(\text{CO}_2\text{ diss.})[-\Delta E_{\text{soln.}}(\text{CO}_2)]\bigg\} \tag{9}$$

where $-\Delta E_{\text{oxid.}}(\text{As}_2\text{O}_3)$ and $-\Delta E_{\text{soln.}}(\text{CO}_2)$ denote the same quantities as do the symbols $-\Delta E$(reaction 21) and $-\Delta E$(reaction 24) in Ref.[1], and $n^{\text{f}}(\text{As}_2\text{O}_5)$ and $n^{\text{f}}(\text{CO}_2\text{ diss.})$ denote the number of moles of As$_2$O$_5$ and of CO$_2$ in the final bomb solution. Combination of eqn. 9 with eqns. 7 and 8 leads to the following equation:

$$-\Delta Ec°/M(\text{Compound}) = \frac{1}{m'}\left\{-\Delta Ec/M(\text{Benzoic acid})(m/\Delta t)_{\text{b.a.}}\Delta t -\right.$$

$$-n^{\text{f}}(\text{As}_2\text{O}_5)[-\Delta E_{\text{oxid.}}(\text{As}_2\text{O}_3)]-m''\Delta Ec/M(\text{Benzoic acid})(m/\Delta t)_{\text{b.a.}}.(\Delta t/m)_{\text{oil}} -$$

$$-n^{\text{f}}(\text{CO}_2\text{ diss.})\,[-\Delta E_{\text{soln.}}(\text{CO}_2)]\bigg\} \tag{10}$$

from which it can be deduced [3] to what extent the standard deviations in the values $-\Delta Ec/M$(Benzoic acid), $(m/\Delta t)_{\text{b.a.}}$, $(\Delta t/m)_{\text{oil}}$, $-\Delta E_{\text{oxid.}}(\text{As}_2\text{O}_3)$ and $-\Delta E_{\text{soln.}}(\text{CO}_2)$ are carried over into the value obtained for $-\Delta Ec°/M$(Compound). The final over-all standard deviation, $s_{\text{over-all}}$, to be assigned to the mean value obtained for $-\Delta Ec°/M$(Compound) can thus be obtained from the equation (cf. Ref.[13(p. 74)]):

$$\frac{s_{\text{over-all}}}{-\Delta Ec^\circ / M(\text{Compound})} = \sqrt{\sum_{1}^{6}\left(f_i \times \frac{s_i}{q_i}\right)^2} \qquad (11)$$

where the quantities s_i are the standard deviations of the mean values q_i obtained from the sets of observations leading to the following quantities:

$q_1 = -\Delta Ec/M(\text{Benzoic acid})$ the "accepted" heat of combustion of the benzoic acid standard sample

$q_2 = \varepsilon^\circ(\text{Calor.})$ the energy equivalent of the calorimetric system

$q_3 = -\Delta Ec^\circ / M(\text{Oil})$ the heat of combustion of the auxiliary oil

$q_4 = -\Delta E_{\text{soln.}}(CO_2)$ the heat of solution of carbon dioxide in final bomb solution

$q_5 = -\Delta E_{\text{oxid.}}(As_2O_3)$ the heat of oxidation of arsenious oxide in bomb solution

$q_6 = -\Delta Ec^\circ / M(\text{Compound})$ the heat of combustion of the compound under investigation,

and where the factors f_i are defined by the relations:

$$f_1 = f_2 = \left\{-\Delta E_{\text{I.B.P.}} - [-\Delta E(\text{Oil})]\right\} / -\Delta E(\text{Compound})$$
$$f_3 = -\Delta E(\text{Oil}) / -\Delta E(\text{Compound})$$
$$f_4 = -\Delta E(CO_2) / -\Delta E(\text{Compound})$$
$$f_5 = -\Delta E(\text{As}) / -\Delta E(\text{Compound})$$
$$f_6 = 1$$

in which $-\Delta E_{\text{I.B.P.}}$, $-\Delta E(\text{Compound})$, $-\Delta E(\text{Oil})$, $-\Delta E(CO_2)$ and $-\Delta E(\text{As})$, respectively, are rough means of the individual values, obtained in the various combustion experiments, for the heat effects associated with the actual amounts of the following reactions occurring in the bomb process: (i) the entire isothermal bomb process, (ii) the combustion of the bromine compound, (iii) the combustion of the auxiliary oil, (iv) the solution of carbon dioxide in the final bomb solution, and (v) the oxidation of arsenious oxide.

In the calculation of the final over-all standard deviations given in Table 9 the following values were used for the ratios s_i/q_i:

$s_1/q_1 = 0.5 \times 10^{-4}$, $s_2/q_2 = 0.8 \times 10^{-4}$ (Table 6) and 0.7×10^{-4} (Table 7), $s_3/q_3 = 0.8 \times 10^{-4}$ (Table 6) and 0.6×10^{-4} (Table 7), $s_4/q_4 = 350 \times 10^{-4}$, $s_5/q_5 = 13 \times 10^{-4}$. As is seen, the factors f_1 and f_2 were approximately equal to 1 for all the combustion experiments of the present investigation.

Derived data. Recalculation by conventional methods [37(p. 103-4)] of the $-\Delta Ec^\circ / M$ mean values given in Tables 6 and 7 yielded the values listed in Table 9 for the standard energies of combustion, ΔEc°, at 25°C and 20°C, and the standard enthalpies of combustion, ΔHc°, at 25°C for the various compounds. The data given in Table 9 refer to the combustion reaction represented by eqn. 6, in which all reactants and products are in their standard states [32].

HEATS OF FORMATION

For comparison of the results from the heat of combustion experiments with appropriate data from reaction-calorimetric studies, heat of formation values for the selected compounds were calculated from both sets of data.

Table 9. Derived standard heats of combustion.

Compound and state	Molecular weight [a]	$-\Delta Ec°$ at 25°C kcal/mole	$-\Delta Ec°$ at 20°C kcal/mole	$-\Delta Hc°$ at 25°C kcal/mole
1,2-Dibromobutane(liq)	215.940	613.08 ± 0.52[b]		614.26 ± 0.52[b]
1,2-Dibromo*cyclo*hexane(liq)	241.978	866.06 ± 0.60		867.54 ± 0.60
1-Bromopropane(liq)	123.005		490.68 ± 0.34[b]	491.54 ± 0.34
2-Bromopropane(liq)	123.005		489.56 ± 0.42	490.42 ± 0.42
2-Bromobutane(liq)	137.032		645.43 ± 0.30	646.52 ± 0.30

[a] Computed from the 1957 table of atomic weights [39].
[b] The uncertainties in this column are equal to twice the final over-all standard deviation; see text for comments.

Heats of formation from heat of combustion data.

For the compounds listed in Table 9 standard heats of formation, $\Delta Hf°$, at 25°C, referring to reaction 12, were calculated from the $-\Delta Hc°$ values

$$\text{a C(c, graphite)} + \text{b/2 H}_2\text{(g)} + \text{d/2 Br}_2\text{(liq)} \rightarrow \text{C}_a\text{H}_b\text{Br}_d\text{(liq)} \qquad (12)$$

given in Table 9 and the selected values [32] for the standard heats of formation of gaseous carbon dioxide [40] -94.0539 ± 0.0108 kcal/mole and liquid water [41] 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 10. In column 3 of the same table are listed heats of vaporization, ΔHv, at 25°C, for the various compounds, calculated from data given in Refs.[7,42–44]. In column 4 of Table 10 are given the resulting standard heats of formation, at 25°C, of the compounds in the gaseous state. Actually, the values given in this column apply to the bromine compounds at their saturation pressures at 25°C. It can, however, be estimated that reduction of the values to apply to the bromine compounds in a state of unit fugacity (1 atm) will change the values with

Table 10. Standard heats of formation from heat of combustion data.

Compound	$\Delta Hf°$(liq) at 25°C kcal/mole	ΔHv [a] at 25°C kcal/mole	$\Delta Hf°$(g) at 25°C [b] kcal/mole
1,2-Dibromobutane	-35.23 ± 0.52 [c]	10.80 ± 0.20 [d]	-24.43 ± 0.58 [e]
1,2-Dibromo*cyclo*hexane	-38.37 ± 0.60	12.10 ± 0.35	-26.27 ± 0.70
1-Bromopropane	-29.73 ± 0.34	7.75 ± 0.20	-21.98 ± 0.40
2-Bromopropane	-30.85 ± 0.42	7.30 ± 0.20	-23.55 ± 0.46
2-Bromobutane	-37.12 ± 0.31	8.45 ± 0.25	-28.66 ± 0.40

[a] For the process $C_aH_bBr_d$(liq) $\rightarrow$ $C_aH_bBr_d$(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 [3].
[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 uncertainties assigned to the ΔHv values in column 3) [3].

only a few hundredths of a kcal/mole. Only for 2-bromopropane will the reduction amount to the order of 0.10 kcal/mole. Therefore the given values have been listed as standard heats of formation.

Heats of formation from reaction-calorimetric data

1,2-Dibromobutane. The heat of formation of 1,2-dibromobutane can be calculated from two different sets of reaction-calorimetric data: (i) Conn, Kistiakowsky and Smith [6] found for the reaction butene-1(g) + bromine(g) → 1,2-dibromobutane(g), at 355°K and 1 atm total pressure, $\Delta H = -29.58 \pm 0.40*$ kcal/mole. This value corresponds to $\Delta H = -29.66 \pm 0.40$ kcal/mole for the reaction at 298°K, assuming the following heat capacity values, C_P°, in cal/mole deg, for the various compounds in the gaseous state: butene-1 [45] 20.57 at 300°K and 26.04 at 400°K; bromine [46] 8.62 at 300°K and 8.78 at 400°K; 1,2-dibromobutane [47] 30.35 at 300°K and 33.48 at 350°K. By combining this ΔH_{298} value with the standard heats of formation at 25°C of gaseous butene-1 [45,48,49], —0.03 ± 0.20 kcal/mole, and gaseous bromine [33], + 7.45 kcal/mole, a value of —22.24 ± 0.45 kcal/mole is derived for the standard heat of formation, ΔHf°, at 25°C of gaseous 1,2-dibromobutane. (ii) Lister [7] studied the reaction butene-1(in CCl$_4$ solution) + bromine(liq) → 1,2-dibromobutane(in CCl$_4$ solution) at 27°C and obtained $\Delta H = -26.921 \pm 0.276**$ kcal/mole. From this value and auxiliary data he calculated $\Delta H = -28.900 \pm 0.600$ kcal/mole for the reaction butene-1(g) + bromine(g) → 1,2-dibromobutane(g) at 27°C. Assuming this same value to apply at 25°C, and combining it with the standard heat of formation at 25°C of gaseous butene-1, given above, and with the enthalpy of vaporization of bromine, 7.466 kcal/mole, used by Lister in his calculations, the standard heat of formation, ΔHf°, at 25°C of gaseous 1,2-dibromobutane is calculated to be —21.46 ± 0.63 kcal/mole.

1,2-Dibromocyclohexane. Lister [7] investigated the reaction cyclohexene(in CCl$_4$ solution) + bromine(liq) → 1,2-dibromocyclohexane(in CCl$_4$ solution) at 27°C, and reported $\Delta H = -30448 \pm 124$ cal/mole (the error limits are the average deviation from the mean of six experiments), but considered the true uncertainty in the result to be ± 300 cal/mole. The heats of solution at 27°C of liquid cyclohexene and liquid 1,2-dibromocyclohexane in carbon tetrachloride were also measured in order to derive from the observed ΔH, the appropriate value for the reaction cyclohexene(liq) + bromine(liq) → 1,2-dibromocyclohexane(liq). The observed heats of solution were small and Lister therefore chose to take them as zero, allowing an extra uncertainty of ± 1 % from this cause. This leads to $\Delta H = -30.45 \pm 0.42$ kcal/mole for the reaction cyclohexene(liq) + Br$_2$(liq) → 1,2-dibromocyclohexane(liq) at 27°C. The same value can be applied to 25°C without appreciable error. Combining this value with the standard heat of formation, ΔHf°, at 25°C of liquid cyclohexene [50], —9.70 ± 0.19 kcal/mole, yields for the standard heat of formation, ΔHf°, at 25°C of liquid 1,2-dibromocyclohexane a value of —40.15 ± 0.46 kcal/mole.

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* The uncertainty is twice the "estimated total probable error" given in Ref.[6]
** The uncertainty is the average deviation from the mean of three experiments.

1-Bromopropane. Two independent heat of formation values can be calculated for 1-bromopropane from the following heat of reaction data: (i) Lacher, Kianpour and Park [10] measured for the reaction *cyclo*propane(g) + hydrogen bromide(g) → 1-bromopropane(g) at 401°K $\Delta H = -25\ 790 \pm 320$ cal/mole. This needed correction for the small amount of 2-bromopropane formed in the reaction *, yielding finally $\Delta H = -25\ 784 \pm 320$ cal/mole at 401°K. This value can be converted to apply to 298°K assuming the following values, in cal/mole deg, for the heat capacity, C_P°, of the various compounds in the gaseous state: for *cyclo*propane [51] 13.44 at 300°K and 18.33 at 400°K; for hydrogen bromide [46] 6.96 at 300°K and 6.98 at 400°K; for 1-bromopropane [47] 21.13 at 300°K and 25.93 at 400°K. The value obtained for the reaction at 298°K is $\Delta H = -25.854 \pm 0.320$ kcal/mole. Combination of this value with the standard heats of formation at 25°C of gaseous *cyclo*propane[52], $+12.74\pm0.14$ kcal/mole, and gaseous hydrogen bromide [32], -8.66 ± 0.20 ** kcal/mole, yields for the standard heat of formation, ΔHf°, at 25°C of gaseous 1-bromopropane a value of -21.77 ± 0.40 kcal/mole. (ii) Lacher *et al.*[11] measured for the reaction 1-bromopropane(g) + hydrogen(g) → propane(g) + hydrogen bromide(g) at 521°K $\Delta H = -13\ 100 \pm 376$ cal/mole. This value can be converted to give $\Delta H = -12\ 330 \pm 376$ cal/mole for the same reaction at 298°K, if the following values, in cal/mole deg, are used for the heat capacities, C_P°, of the various compounds in the gaseous state: for 1-bromopropane [47] 21.13 at 300°K and 25.93 at 400°K; for hydrogen [46] 6.97 at 400°K and 7.43 at 500°K; for propane [45] 22.54 at 400°K and 27.02 at 500°K; for hydrogen bromide [46] 6.98 at 400°K and 7.04 at 500°K. Combination of this ΔH_{298} value with the standard heats of formation at 25°C of gaseous propane [45,54], -24.820 ± 0.142 kcal/mole, and gaseous hydrogen bromide [32], yields for the standard heat of formation, ΔHf°, at 25° C of gaseous 1-bromopropane a value of -21.15 ± 0.45 kcal/mole.

2-Bromopropane. The enthalpy change for the reaction propene(g) + HBr(g) → 2-bromopropane(g) has been measured twice: Lacher, Walden, Lea and Park [8] obtained in 1950 at 367°K $\Delta H = -20\ 140 \pm 240$ cal/mole and Lacher, Kianpour and Park [10] obtained in 1957 at 401°K $\Delta H = -20\ 430 \pm 150$ cal/mole. After correction for the small amount of 1-bromopropane formed in the reactions (*cf.* footnote *), the two values become $\Delta H_{367} = -20\ 170 \pm 240$ cal/mole and $\Delta H_{401} = -20\ 460 \pm 150$ cal/mole. These values can be converted to apply to 298°K by use of the heat capacity values given above for hydrogen bromide and the following values, in cal/mole deg, for the heat capacity, C_P°, of propene [45] 15.34 at 300°K and 19.10 at 400°K; and of 2-bromopropane [47] 21.59 at 300°K and 26.41 at 400°K. The two values thus obtained for the reaction at 298°K are $\Delta H = -20.14 \pm 0.24$ kcal/mole and $\Delta H = -20.44 \pm 0.15$ kcal/mole. Combination of these values with the standard heats of formation at 25°C of gaseous propene [45,49], $+4.879 \pm 0.122$ kcal/mole, and gaseous hydrogen bromide [32], yields for the standard heat of formation, ΔHf°, at 25°C of gaseous 2-bromopropane -23.92 ± 0.33 and -24.22 ± 0.28 kcal/mole, respectively.

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* For the isomerization 2-bromopropane(g) → 1-bromopropane(g) at 401°K ΔH was taken as 2 000 cal/mole.

** This uncertainty is estimated, *cf.*, however, Ref.[53]

2-Bromobutane. Heat of formation values can be calculated for 2-bromo-butane from heat of reaction data obtained by Lacher, Billings, Campion, Lea and Park [9] for the following three reactions: (i) butene-1(g) + hydrogen bromide(g) → 2-bromobutane(g), $\Delta H_{367} = -20\ 150\ *\ \pm\ 180$ cal/mole; (ii) *cis*-butene-2(g) + hydrogen bromide(g) → 2-bromobutane(g), $\Delta H_{373} = 18\ 344\ \pm\ 157$ cal/mole; and (iii) *trans*-butene-2(g) + hydrogen bromide(g) → 2-bromobutane(g), $\Delta H_{383} = -17\ 340\ \pm\ 135$ cal/mole. These ΔH values can be converted to 298°K using the heat capacity values given above for hydrogen bromide and the following values, in cal/mole deg, for the heat capacity, C_P°, of butene-1 [45] 20.57 at 300°K and 26.04 at 400°K; of *cis*-butene-2 [45] 18.96 at 300°K and 24.33 at 400°K; of *trans*-butene-2 [45] 21.08 at 300°K and 26.02 at 400°K; and of 2-bromobutane [47] 26.75 at 300°K and 33.22 at 400°K. For the three reactions at 298°K the following ΔH values are obtained: —20.09 ± 0.18, —18.43 ± 0.16, —17.28 ± 0.14 kcal/mole, respectively. Combination of these values with the standard heats of formation at 25°C of gaseous butene-1 [45,48,49], —0.03 ± 0.19 kcal/mole, gaseous *cis*-butene-2 [45,48,49], —1.67 ± 0.30 kcal/mole, gaseous *trans*-butene-2 [45,48,49], —2.67 ± 0.24 kcal/mole, and gaseous hydrogen bromide [32], yields for the standard heat of formation, ΔHf°, at 25°C of gaseous 2-bromobutane the values (i) —28.75 ± 0.34, (ii) —28.76 ± 0.39 and (iii) —28.61 ± 0.34 kcal/mole, respectively.

Table 11. Comparison of standard heats of formation from various methods.

Compound and state	ΔHf° at 25°C kcal/mole		Difference between the heat of formation values from the two sets of data kcal/mole
	From heat of combustion data [a]	From reaction calorimetry data [b]	
1,2-Dibromobutane(g)	—24.43 ± 0.58 [c]	—22.24 ± 0.45 [c]	—2.19 ± 0.73 [c]
	—24.43 ± 0.58	—21.46 ± 0.63	—2.97 ± 0.78 [d]
1,2-Dibromo*cyclo*hexane(liq)	—38.37 ± 0.60	—40.15 ± 0.46	+1.78 ± 0.76
1-Bromopropane(g)	—21.98 ± 0.40	—21.77 ± 0.40	—0.21 ± 0.57
	—21.98 ± 0.40	—21.15 ± 0.45	—0.83 ± 0.60
2-Bromopropane(g)	—23.55 ± 0.46	—23.92 ± 0.33	+0.37 ± 0.57
	—23.55 ± 0.46	—24.22 ± 0.28	+0.67 ± 0.54
2-Bromobutane(g)	—28.66 ± 0.40	—28.75 ± 0.34	+0.09 ± 0.53
	—28.66 ± 0.40	—28.76 ± 0.39	+0.10 ± 0.56
	—28.66 ± 0.40	—28.61 ± 0.34	—0.05 ± 0.53

[a] This work.

[b] See text and Fig. 1 for references.

[c] The uncertainties in this column are equal to twice the final over-all standard deviation [3].

[d] This uncertainty is lower than the combined uncertainties of the two heat of formation values given in the preceding columns since the uncertainty in the heat of vaporization of 1,2-dibromobutane cancels in the difference.

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* This value has been corrected for the small amount of 1-bromobutane, formed in the reaction, by taking ΔH_{367} as 2 000 cal/mole for the isomerization 2-bromobutane(g) → 1-bromobutane(g).
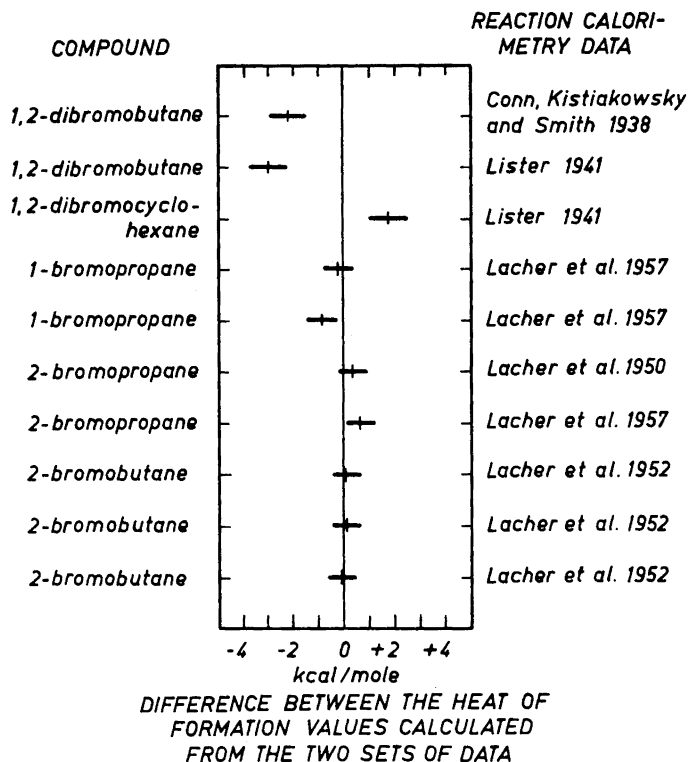
Fig. 1. Plot of the differences between the standard heats of formation calculated from heats of combustion from this work and those calculated from reaction calorimetry data from previous work. The lengths of the horizontal lines represent the uncertainties assigned to the observed differences.

The various heat of formation values obtained from the reaction-calorimetric data are listed in column 3 of Table 11.

COMPARISON OF HEATS OF FORMATION FROM THE VARIOUS METHODS AND DISCUSSION OF RESULTS

The standard heats of formation calculated from the heat of combustion data of the present investigation and from calorimetric data on heats of reactions other than combustion are compared in Table 11. The results of the comparison are shown graphically in Fig. 1. The references to the reaction calorimetry investigations are also listed in Fig. 1.

It is seen from Table 11 and Fig. 1 that the first three differences in column 4 of Table 11 are numerically greater than zero by amounts significantly greater than the uncertainties assigned to the various differences. The remain-

ing seven differences are, however, virtually equal to zero. This means that for the dibromides the heats of formation calculated from heats of combustion disagree with those obtained from the heats of *addition of bromine* to the corresponding unsaturated hydrocarbons, whereas for the monobromides the heats of formation obtained from heats of combustion are in good accord with those calculated from the heats of *addition of hydrogen bromide* to the corresponding unsaturated hydrocarbons, and from the heat of *reduction* of 1-bromopropane *with hydrogen*. It seems possible that although the precision in measurement of the heats of addition of bromine was good, the over-all accuracy was less than that obtained in the heats of addition of hydrogen bromide, because of the following facts: (i) The addition of hydrogen bromide to unsaturated compounds of the type considered here and under the given conditions is known to proceed chemically more cleanly than the addition of bromine; (ii) The main reaction product in the heat of addition of bromine experiments was identified only by measurement of its refractive index at a single temperature, whereas in the heat of addition of hydrogen bromide experiments the products, collected at the exit of the calorimeter, were quantitatively analyzed by infrared absorption spectrophotometry; (iii) As is seen from Fig. 1, the heat of formation obtained for 1,2-dibromobutane from the heat of combustion is numerically *greater*, by approximately 3 kcal/mole, than that obtained from the heat of addition of bromine to butene-1 as measured by Lister, whereas for 1,2-dibromo*cyclo*hexane the heat of formation obtained from the heat of combustion is numerically *less*, by approximately 2 kcal/mole, than that obtained from the heat of addition of bromine to *cyclo*hexene, which latter value was measured by Lister with the same apparatus and technique as for the addition of bromine to butene-1. This fact suggests that the discordance between the heats of formation from the two sets of data, for these two points of comparison is not due to a constant systematic error in one or both of the two experimental methods; (iv) As discussed by Lister [7(p. 148)] an inconsistency is found in the heats of hydrogenation [55,56] and addition of bromine [6,7] to *cis*-butene-2 and *cyclo*hexene. The heats of hydrogenation of the two compounds are, within the experimental errors, the same, whereas the heat of addition of bromine to *cyclo*hexene is numerically 3.3 kcal/mole *greater* than that to *cis*-butene-2. These results are definitely incompatible with one another.

For these reasons it seems justifiable to place more weight on the good accord of the heat of combustion data with the data on heats of addition of hydrogen bromide [8-11] than on the discord with the data on heats of addition of bromine [6,7]. It can therefore be concluded that, although the cause of certain discrepancies still has to be found, enough evidence has been obtained to prove that the moving-bomb method for combustion calorimetry of organic bromine compounds is capable of giving heats of combustion having an accuracy corresponding to the precision of the observed results. It has previously been found [1] that with the given method results of an immediate precision slightly better than 0.01 % can be obtained.

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