COMBUSTION CALORIMETRY OF ORGANIC BROMINE COMPOUNDS: THE ACCURACY OF DATA OBTAINED WITH A MOVING-BOMB TECHNIQUE

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A moving-bomb calorimetric method for measuring heats of combustion at 25°C of solid and liquid organic bromine compounds has recently been developed[1]. The calorimetric system is calibrated by combustion of standard benzoic acid under certified bomb-calibrating conditions. In order to obtain well-defined equilibrium final states in the bomb in combustion experiments with bromine compounds, however, the bomb liquid must differ both in nature and amount from that specified for calibration experiments with benzoic acid. Thus, 3 g of water per litre of bomb volume are used in the calibration experiments, whereas 112 g of 0·06 M arsenious oxide solution per litre of bomb volume are used in the combustion experiments with bromine compounds. Calibration experiments with benzoic acid and combustion experiments, with paraffin oil and with *p*-bromobenzoic acid have all given results of a precision slightly better than 0·01 per cent. This demonstrates that the various additional complications introduced into the procedure by the presence of a reasonable percentage of bromine in the sample do not affect the precision obtainable with the given apparatus and procedure. Although the precision of the method has thus been found to be satisfactorily high, the difference in conditions of combustion and calibration experiments may give rise to non-cancelling systematic errors. Therefore the accuracy of the heat of combustion data obtained has to be investigated. Since the principal use for heat of combustion data is to derive corresponding heats of formation, a suitable approach would be 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. Such a comparison has been made and the results will be briefly reported here.

HEAT OF COMBUSTION DATA

Samples of the compounds listed in *Table 1* were carefully purified. The products obtained were found to have the density and refractive indices given in the same table. From heat of combustion experiments with the pure samples the standard heats of combustion at 25°C given in *Table 2* were obtained. In the same table are also listed heat of vaporization data calculated from published information[2–4].

Table 1. Density and refractive indices for the samples used in the heat of combustion experiments

Compound	*d* (g/ml)		n_D	
	20°C	25°C	20°C	25°C
1,2-Dibromobutane	1·7954	1·7870	1·5149	1·5125
1,2-Dibromocyclohexane	1·7903	1·7833	1·5529	1·5506
1-Bromopropane	1·3550	1·3465	1·4346	1·4320
2-Bromopropane	1·3142	1·3055	1·4255	1·4226
2-Bromobutane	1·2607	1·2533	1·4370	1·4345

Table 2. The heats of combustion and vaporization at 25°C

Compound (liq.)	$-\Delta H_c^\circ$ (kcal/mole)*	ΔH_v (kcal/mole)†
1,2-Dibromobutane	614·15 ± 0·54	10·80 ± 0·20
1,2-Dibromocyclohexane	867·45 ± 0·60	
1-Bromopropane	491·50 ± 0·34	7·75 ± 0·20
2-Bromopropane	490·37 ± 0·42	7·30 ± 0·20
2-Bromobutane	646·50 ± 0·30	8·45 ± 0·25

* The uncertainties given in this column are equal to twice the final " over-all " standard deviation.

† The values given in this column refer to the process $C_aH_bBr_{d(l.)} \longrightarrow C_aH_bBr_{d(g.)}$, at saturation pressure at 25°C. The uncertainties given are estimated.

COMPARISON OF HEAT OF FORMATION DATA FROM DIFFERENT METHODS

The standard heats of formation calculated from the heat of combustion data of *Table 2* are compared in *Table 3* with heats of formation calculated from heat of reaction data for the following reactions: addition of bromine to but-1-ene[5,6] and to cyclohexene[6]; addition of hydrogen bromide to

Table 3. Comparison of heats of formation from several methods

Substance	*Standard heat of formation at* 25°C (kcal/mole)		
	From heat of combustion data	*From other heat of reaction data*	*Difference*
1,2-Dibromobutane (g)	− 24·54 ± 0·58	− 22·47 ± 0·44[a]	− 2·07 ± 0·70
		− 21·58 ± 0·63[b]	− 2·96 ± 0·78[h]
1,2-Dibromocyclohexane (liq.)	− 38·46 ± 0·60	− 40·15 ± 0·46[c]	+ 1·69 ± 0·76
1-Bromopropane (g)	− 22·02 ± 0·40	− 21·77 ± 0·34[d]	− 0·25 ± 0·52
		− 21·13 ± 0·40[e]	− 0·89 ± 0·57
2-Bromopropane (g)	− 23·60 ± 0·46	− 24·07 ± 0·24[f]	+ 0·47 ± 0·52
2-Bromobutane (g)	− 28·69 ± 0·40	− 28·55 ± 0·30[g]	− 0·14 ± 0·50

[a] From[5]: but-1-ene (g) + bromine (g) ⟶ 1,2-dibromobutane (g).

[b] From[6]: but-1-ene (in CCl_4) + bromine (liq.) ⟶ 1,2-dibromobutane (in CCl_4).

[c] From[6]: cyclohexene (in CCl_4) + bromine (liq.) ⟶ 1,2-dibromocyclohexane (in CCl_4).

[d] From[7]: cyclopropane (g) + hydrogen bromide (g) ⟶ 1-bromopropane (g).

[e] From[10]: 1-bromopropane (g) + hydrogen (g) ⟶ propane (g) + hydrogen bromide (g).

[f] From[7,8]: propene (g) + hydrogen bromide (g) ⟶ 2-bromopropane (g).

[g] From[9]: butene (g) + hydrogen bromide (g) ⟶ 2-bromobutane (g). The value given is the mean of the three values calculated from the heats of hydrobromination of the three different normal butenes.

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

cyclopropane[7], propene[7,8], but-1-ene[9], *cis*-but-2-ene[9], and *trans*-but-2-ene[9], respectively; hydrogenation of 1-bromopropane to propane[10].

It is seen from *Table 3* that for 1,2-dibromobutane and 1,2-dibromocyclohexane the differences in the heats of formation obtained from different methods are significantly greater than the estimated uncertainties of the differences. It is to be noted that for the two comparisons with results from the work of Lister, the differences obtained are of opposite sign.

The accord of the heats of formation calculated from heat of combustion data with the heats of formation calculated from heats of reaction given by Lacher and co-workers is very good.

Note added in proof

A full account of this work will be presented in: L. Bjellerup. *Acta Chem. Scand.*, **15** (1961), in press.

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