Reduction to Standard Heat of Combustion of Bomb Calorimetric Data for Organic Bromine Compounds

LARS BJELLERUP

Department of Organic Chemistry, University of Lund, Lund, Sweden

The rigorous Washburn reduction of combustion calorimetric data for organic bromine compounds is discussed and applied to a recent high-precision moving-bomb method.

The general scheme for the reduction is treated in two respects: (i) The accuracy of the reduction is improved by presentation of experimental data for the auxiliary numerical quantities entering some of the more important corrections. For \( \text{S}_2\text{O}_3 - \text{S}_2\text{O}_4 - \text{HBr} \) solutions of various composition, data are thus given for, (a) the density at 20 and 25°C, (b) the heat capacity at 25°C, and (c) the solubility of carbon dioxide at 20 and 25°C. (ii) The general scheme is modified to apply specifically to the above-mentioned bomb calorimetric method.

A combustion-bomb calorimetric method for organic bromine compounds has recently been described \(^1\) by which results of an immediate precision \(^2\) slightly better than 0.01% can be obtained. To take full advantage of this high precision in order to obtain high-accuracy standard heats of combustion for organic bromine compounds, the application of rigorous Washburn corrections \(^3\) to the calorimetric data obtained is required. The original Washburn reduction \(^3\) treated data obtained on compounds containing only carbon, hydrogen and oxygen. Later, the Washburn reduction was extended to apply to nitrogen compounds of the formula \( \text{C}_n\text{H}_m\text{O}_c\text{N}_d \) \(^4\) and to sulfur compounds of the formula \( \text{C}_n\text{H}_m\text{O}_c\text{S}_d \) \(^7\). In Ref. \(^9\) a complete and rigorous treatment was given not only of those corrections usually described as the "Washburn corrections", but of all other corrections that must be applied to the original calorimetric data from combustion experiments with organic sulfur compounds in order to obtain the energy of the idealized combustion reaction, i.e. the standard heat of combustion of the compound investigated. The corrections were treated separately and presented in a systematic computation form in which the various terms were kept separate. This mode of presentation had several advantages. One was that many of the terms, either unchanged or modified, enter into reductions to standard heat of combustion of calorimetric data obtained on organic compounds containing other elements instead of sulfur. This was illustrated by discussion of the modifications to the general computation form for sulfur compounds that had to be made to apply it to
organic nitrogen, chlorine, bromine and iodine compounds, respectively. For chlorine and bromine compounds, however, no critical selection could be made of the numerical quantities that enter into some of the more important corrections, because reliable experimental data were not available for these quantities cf. Refs. 9 (p. 126–127), 10 (p. 217–218) Through recent work in this laboratory, data have been obtained for the more important of these auxiliary quantities. Part of this work has been reported elsewhere 11 and the remainder is given here.

More specifically, the aim of this paper is to describe the modifications and additions that have to be made to the treatment, given in Ref. 9 (p. 114–119), of the reduction to standard heat of combustion of bomb calorimetric data for bromine compounds, to make the reduction applicable to and commensurate in accuracy with the experimental method described in Ref. 1.

MODE OF PRESENTATION. NOTATION

For convenience the same presentation and notation as in Ref. 9 is used in this paper. On only a few points, which are clearly indicated in the text, is the treatment and the notation of this paper different from those of Ref. 9.

ACTUAL BOMB PROCESS AND IDEALIZED COMBUSTION REACTION

The actual process occurring in the bomb in combustion experiments with organic bromine compounds, using the method given in Ref. 1, was discussed in detail in the cited paper.

The idealized combustion reaction, to which the standard heat of combustion of the compound is referred, is defined by eqn. 1, where reactants and products are in their thermodynamic standard states 12.

\[ C_xH_yO_zBr_a(c \text{ or liq}) + (a + b/4 - c/2) O_2(g) \longrightarrow \]
\[ \longrightarrow a \ CO_2(g) + b/2 \ H_2O(liq) + c/2 \ Br_2(liq) \] (1)

It should be noted that this idealized combustion reaction is the same as that given in Refs. 9 (p. 118), 10 (p. 211, eqs. 2)

CALCULATION OF THE CORRECTIONS

The calculation of the standard heat of combustion from the original calorimetric data was described in Ref. 1. Some of the corrections were treated in detail and the rest, mainly those usually described as the Washburn corrections, are discussed here. These are presented as modifications to the various items of the computation formula for bromine compounds given in Ref. 9 (p. 114–119) and make the reduction applicable to data obtained with the experimental method described in Ref. 1.

* There are two obvious misprints in eqn. 29 of Ref. 1. The equation should read:

\[ -\Delta E_{\text{corr}}M(\text{compound}) = \frac{1}{m} \left\{ -\Delta E_{\text{I.B.P.}} - \left[ -\Delta E(\text{As}) - \Delta E(\text{Oil}) - \Delta E(\text{Fuse}) - \Delta E(\text{CO}_2) - \right. \right. \]
\[ \left. - \Delta E(\text{HNO}_3) - \Delta E(\text{Au}) - \Delta E(\text{Pt}) \right] - \Delta E(\text{HBr}) - \Delta ES \} \]

Initial and final states

(1) \( C_4H_8O_3Br_4 \); (2) \(-\) (6) unchanged; (7) \( C_5H_12O_3Br_4 \); (8) \(-\) (12) unchanged; (13) \( C_5H_14O_3Br_4 \); (14) \(-\) (23) unchanged; (24) \(-\) (25) these two items are entirely formal. They can be deleted and the following treatment accordingly modified; (26) \(-\) (29b) unchanged;

(29c) \( g^i \), the ratio of the vapor pressure of \( H_2O \) over the initial solution to that over pure water. Experimental data are not available for the lowering of the vapor pressure by arsenious oxide. From data on comparable compounds (boric acid) however, \( g^i \) for the 0.0625 M \( As_2O_3 \) solution, used in Ref.\(^1\), can be estimated at 0.998;

(29d) \( K^{*}i(O_2) \) the solubility of \( O_2 \) in the initial bomb solution in moles per liter of solution per atm \( O_2 \) pressure. Since no data on the solubility of \( O_2 \) in aqueous \( As_2O_3 \) solutions are available the values of the solubility in pure water, given in the table on p. 84 in Ref.\(^9\), will be used as an approximation;

(30) \(-\) (34) unchanged;

(35) \( n^i(O_2 \text{ diss.}) = K^{*}i(O_2)V^i(\text{soln.})(P^i(\text{gas.}) - P^i(H_2O \text{ vap.})) \). Since, in combustion experiments with bromine compounds, \( N_2 \) is present only as a small impurity in the \( O_2 \) and since it can be treated as though it were \( O_2 \), except for the formation of \( HNO_3 \), the notation \( (O_2 + N_2) \) used in Ref.\(^9\) has been changed to \( O_2 \) in this paper;

(36) \( n^i(O_2 \text{ tot.}) = n^i(\text{gas.}) - n^i(H_2O \text{ vap.}) + n^i(O_2 \text{ diss.}) \).

The stoichiometry of the isothermal bomb process can be described by the following set of equations:

\[
\begin{align*}
C_4H_8O_3Br_4 + [a + (b-d)/4-c/2] O_2 & \rightarrow a CO_2 + (b-d)/2 H_2O + d HBr \\
As_2O_3 + O_2 & \rightarrow As_2O_5 \\
1/2 N_2 + 5/4O_2 + 1/2 H_2O & \rightarrow HNO_3 \\
Au + 1/4 O_2 + 2 HBr & \rightarrow HAuBr_2 + 1/2 H_2O \\
Pt + 1/2 O_2 + 4 HBr & \rightarrow H_2PtBr_4 + H_2O
\end{align*}
\]

The amounts of \( HNO_3 \), \( HAuBr_2 \) and \( H_2PtBr_4 \) present in the final bomb solution are listed in the items:

(37) \( n^i(HNO_3) \); (37a) \( n^i(HAuBr_2) \); (37b) \( n^i(H_2PtBr_4) \). Under the conditions of the experimental technique described in Ref.\(^1\) these quantities are small enough to permit decomposition, as outlined in Ref.\(^9\) (p. 123-132), of the corresponding substances under actual bomb conditions immediately after Step 12 without significant loss in accuracy. This means that all terms involving \( n^i(HNO_3) \), \( n^i(HAuBr_2) \) and \( n^i(H_2PtBr_4) \), except in items 86a, 86b and 86c, can be left out from the subsequent discussion.

(38) \(-\) (38a) unchanged; (39) \( n^i(HBr) = d \); (40) \( n^i(H_2O \text{ liq.}) = n^i(H_2O \text{ tot.}) - (b-d)/2 - n^i(H_2O \text{ vap.}) \); (41) \( m^i(\text{soln.}) = 18.016n^i(H_2O \text{ liq.}) + \)

*Acta Chem. Scand. 14 (1960) No. 3*
+ 197.82n'(As₂O₃) + 229.82n'(As₂O₅) + 80.924n'(HBr); (42) wt.%/(As₂O₃) =
= 197.82n'(As₂O₃)/m'(sln.); (42a) wt.%/(As₂O₅) = 229.82n'(As₂O₅)/m'(sln.);
(42b) wt.%/(HBr) = 80.924n'(HBr)/m'(sln.). (43) delete;
(44) ρ'(sln.) = ρ(H₂O) + 0.00785 wt.%/(As₂O₃) + 0.00808 wt.%/(As₂O₅) +
+ 0.00710 wt.%/(HBr) g/ml. This equation has been found to represent,
within an uncertainty of ± 0.0001 g/ml, experimental data on the densities
at 20 and 25°C of seven aqueous As₂O₃—As₂O₅—HBr solutions of various
compositions within the concentration ranges 0—1.23 wt.% of As₂O₃, 0—1.28
wt.% of As₂O₅ and 0—1.79 wt.% of HBr, which are the ranges of interest
in the given method.¹
(45) unchanged; (46)—(47) delete; (48)—(49) unchanged;
(50) n'(CO₂ tot.) = a;
(51) K(CO₂) = 0.0383, and 0.0336 mole/liter atm at 20 and 25°C, respectively.
The solubility of CO₂ in aqueous As₂O₃—As₂O₅—HBr solutions, similar
in composition to those obtained in combustion experiments, has been mea-
sured * by use of the method given in Ref.⁷ (p. 86). It was found that the solubility
of CO₂ was the same in each of three investigated solutions, which had
the following compositions:
(A) 0.0633 M As₂O₃; (B) 0.0475 M As₂O₃—0.0158 M As₂O₅—0.0671 M HBr;
(C) 0.0317 M As₂O₃—0.0316 M As₂O₅—0.122 M HBr. Therefore the solubility
values given above can be used in all combustion experiments irrespective of the
HBr concentration in the final bomb solution.
(52)—(55) unchanged;
(56) n'(O₂ tot.) = n'(O₂ tot.) — [a + (b — d)/4 — c/2] — n'(As₂O₅);
(57) Kᵗ'(O₂), the solubility of O₂ in the final bomb solution in moles per
liter of solution at unit fugacity (in atm) of O₂ gas. Since no data on the
solubility of O₂ in As₂O₃—As₂O₅—HBr solutions are available the values of the
solubility in pure water, given in Ref.⁸ (p. 88), will be used as an approxima-
tion;
(58) unchanged; (59) Kᵗ'(O₂) = D(O₂)Kᵗ'(O₂);
(60) n'(O₂ diss.) = \[\frac{0.082054(tₐ + 273.2)Kᵗ'(O₂)V'(sln.)}{1 + 0.082054(tₑ + 273.2)Kᵗ'(O₂)V'(sln.)/V'(gas.)} \] n'(O₂
tot.);
(61) n'(O₂ gas.) = n'(O₂ tot.) — n'(O₂ diss.); (62) n'(gas.) = n'(O₂ gas.) +
+ n'(CO₂ gas.) + n'(H₂O vap.); (63)—(65) unchanged;
(66) gᵗ, the ratio of the vapor pressure of H₂O over the final solution to
that over pure H₂O. Experimental data are not available for the vapor
pressure lowering of water by the mixture of As₂O₃, As₂O₅ and HBr present
in the final bomb solution. As in item 29e, however, gᵗ for an average final
bomb solution, having the composition 0.02 M As₂O₃—0.04 M As₂O₅—0.16 M
HBr, was estimated at 0.993 from data¹³ (p. 293—294) on comparable
compounds;
(67) n'(H₂O vap.) =
gᵗ[C₀ + (a(O₂) — a(CO₂) — a(O₂)]x(CO₂)] V'(gas.)/18.016.

* The author's thanks are due to Dr. S. Sunner, Thermochemistry Laboratory, University
  of Lund, for making these measurements in connection with the work reported in Ref.⁷

Energy factors and calorimetric data

(68)—(69) unchanged. For the 0.0625 M As₂O₅ solution, used as initial bomb solution in Ref.¹, a value for (δV/δT)p of 2.57 × 10⁻⁷ liter/g deg was obtained from experimental density data. In the same way (δV/δT)p values were obtained for various As₂O₅—HBr solutions having compositions corresponding to combustion experiments with samples containing from 4 to 7 mgatoms of bromine. In all cases the value of (δV/δT)p was found to be virtually the same and equal to 2.35 × 10⁻⁷ liter/g deg. Therefore the following values can be used at 25°C for all combustion experiments with the method of Ref.¹: (δE/δP)ₛₜ(soln.) = −0.00186 cal/g atm and (δE/δP)ₛₜ(soln.) = −0.00170 cal/g atm;

(70) delete;

(71) ΔEₚₜ(soln.(O₂) and (71a) ΔEₚₜ(soln.(O₂), the change of internal energy in cal/mole at tₕ for the solution of O₂ in the initial and final bomb solution, respectively. Since no data are available for the heat of solution of O₂ in aqueous As₂O₅ and As₂O₅—HBr solutions, the corresponding values for pure water, given in Ref.⁹ (p. 100), will be used as an approximation;

(71b) ΔEₚₜ(soln.(CO₂), the change of internal energy in cal/mole at tₕ for the solution of CO₂ in the final bomb solution. From the solubility data given above in item 51 a value for ΔEₚₜ(soln.(CO₂) of −4 000 cal/mole at 22.5°C was obtained for the pertinent final bomb solutions. By the use of a temperature coefficient of + 44 cal/mole deg ⁹ (p. 99),¹ the following values were obtained for ΔEₚₜ(soln.(CO₂)): −4 110 and −3 890 cal/mole at 20 and 25°C;

(71c) ΔEₒₚₜ(HBr), the change of internal energy in cal/mole at tₕ for the oxidation of HBr in Soln. I (under a pressure of 1 atm) with O₂ (in its standard state) to water and bromine (both in their standard states) according to the equation d(HBr·nH₂O)(in Soln. I) + d/4 O₂(g) → d(n + 1/2) H₂O(liq) + + d/2 Br₂(liq). No experimental values have been obtained for the energy of this reaction and since no data are available for the energy of formation of HBr in aqueous As₂O₅—As₂O₅ solutions, it is not possible to calculate values for ΔEₒₚₜ(HBr). However, the values of ΔEₒₚₜ(HBr), given in Ref.⁹ (p. 119) can be used as a satisfactory approximation since the error introduced thereby is almost entirely cancelled by the introduction of the same error, but with opposite sign, in the ΔEₒₚₜ(As₂O₅) value given in the following item;

(71d) unchanged. From experimental data reported ¹¹ for the heat of the reaction [As₂O₅ + 2 H₂O](aq) + 2 Br₂(liq) → [As₂O₅ + 4 HBr](aq) a value of −(77.4 ± 0.1) × 10³ cal/mole was calculated for the change of internal energy, ΔEₒₚₜ(As₂O₅(aq)), for the reaction As₂O₅(aq) + O₂(g) → As₂O₅(aq). In this calculation, it was assumed that the energy of formation of HBr in aqueous As₂O₅—As₂O₅ solution is the same as that in pure water.¹² Thus, by using ΔEₒₚₜ(As₂O₅(aq)) for −ΔEₒₚₜ(As₂O₅), the error introduced by the approximation is almost entirely cancelled by an analogous error introduced in item 71c. The value 77.4 × 10³ cal/mole will therefore be used for ΔEₒₚₜ(As₂O₅) at 25°C;

(71e) unchanged. No heat of dilution data for As₂O₅·nH₂O are available and therefore the corresponding correction in item 92b has to be neglected.
Since C°(Solv.) is rather small and since the difference in concentration of As₂O₃ in Soln. III and in the initial bomb solution is also small, the error introduced by neglecting the correction in item 92b certainly will be barely significant;

(72)—(73) unchanged;

(74) ε°(Calor.), the energy equivalent of "the standard calorimetric system". As described in Ref.¹ the energy equivalent of the calorimetric system is divided in three parts: (i) ε°(Calor.), the energy equivalent of the whole system as assembled for a fictive experiment with no contents in the bomb ("the standard calorimetric system"), (ii) C_p(H₂O)m°(Cont.), the energy equivalent of an amount of water equal in mass to the contents of the bomb (cf. item 74a and 74b), and (iii) ε(Cont.), the energy equivalent of the contents of the bomb, by which is understood all removable matter in the interior of the bomb, including the platinum combustion crucible and its suspension ring (cf. item 75 and 76);

(74a) m°(Cont.), the mass of the contents of the bomb, is obtained from the relation m°(Cont.) = 32.00n°(O₂ tot.) + V°(soln.)ε°(soln.) + m(Sub.) + m(Pt) + m(glass);

(74b) ε(Cont.) = ε°(Calor.) — C_p(H₂O)m°(Cont.);

(75) ε(Cont.) = C_v(O₂)n°(O₂ tot.) + A_vV°(soln.)ε°(soln.) + B_v(H₂O vap.) + C_m° + C_m° + C_m° + C_m° + 0.0317m(Pt) + 0.17m(glass). For 0.0624 M As₂O₃ solution under a pressure of 1 atm the heat capacity, C_p, has been found¹¹ to be 0.988 cal/g deg at 25°C. This value will be used as an approximation for A°. For C_p(Pt) the value 0.0317 cal/g deg at 25°C is given in Ref.¹⁶

(76) ε(Cont.) = C_v(O₂)n°(O₂ tot.) + C_v(CO₂)n°(CO₂ tot.) + A_v[ε°(solv.) + 18V°(H₂O vap.)] + B_v(H₂O vap.) + 0.0317m(Pt) + 0.17 m(glass). As in the preceding item, C_p values for final bomb solutions under a pressure of 1 atm will be used as approximations for A°. For As₂O₃—As₂O₅—HBr solutions having compositions corresponding to combustion experiments with samples containing 5 and 6 mgatoms of bromine the heat capacities, C_p, at 1 atm and 25°C have been found* to be 0.969 and 0.964 cal/g deg, respectively;

(77) unchanged. With the method of Ref.¹ ΔE_ign is incorporated into the value of ε°(Calor.). Therefore it is formally put equal to zero in the calculations;

(78)—(79) unchanged;

(80) Δt_ex. This symbol was used in Ref.¹ for "the heat exchange correction" and it will be retained here. It represents the same quantity as does the symbol Δt_corr. in Ref.⁸

Changes in internal energy

(81)—(83) unchanged; (84) ΔE°_solv(O₂) = ΔE°_solv(O₂)n°(O₂ diss.); (85) unchanged; (86) ΔE_L.B.R. = ε(Cont.)Δt_ex. + ε(Cont.)Δt_h. + ΔE_ign;

* The author's thanks are due to Dr. I. Wadsö, Thermochmistry Laboratory, University of Lund, for making the heat capacity measurements.

Step 12a. The HNO₃, HAuBr₄ and H₂PtBr₄ are decomposed under final
bomb conditions according to the reactions HNO₃(aq) → 1/2 N₂(g) + 5/4
O₂(g) + 1/2 H₂O(liq), HAuBr₄(aq) + 1/2 H₂O(liq.) → Au(c) + 1/4 O₂(g) +
2HBr(aq) and H₂PtBr₄(aq) + H₂O(liq) → Pt(c) + 1/2 O₂(g) + 4 HBr(aq). As
discussed in Ref.¹ the following values of ΔE, at 25°C, can be used for these
reactions: ΔE_{decomp.}(HNO₃) = 14.18 × 10³, ΔE_{decomp.}(HAuBr₄) = 8 × 10³
and ΔE_{decomp.}(H₂PtBr₄) = 43.4 × 10³ cal/mole. The change of energy
associated with this step is the sum of the following three items:

(86a) ΔE_{decomp.}(HNO₃) = ΔE_{decomp.}(HNO₃)n(HNO₃);
(86b) ΔE_{decomp.}(HAuBr₄) = ΔE_{decomp.}(HAuBr₄)n(HAuBr₄);
(86c) ΔE_{decomp.}(H₂PtBr₄) = ΔE_{decomp.}(H₂PtBr₄)n(H₂PtBr₄);

(87) unchanged; (88) ΔE_{solv.}(O₂) = ΔE_{solv.}(O₂)n(O₂ diss.); (89) unchanged;
(90) — (91b) delete;

Step 19. The HBr is oxidized with O₂ in its standard state according
to the reaction d(HBr n H₂O)(in Soln.) + d/4 O₂(g) → d(n + 1/2) H₂O(liq) +
+ d/2 Br₂(liq). The water and the bromine are brought to their standard
states.

(92) ΔE_{oxid.}(HBr) = ΔE_{oxid.}(HBr)n(HBr);

Step 19a. The As₂O₅ in Soln. II is decomposed to As₂O₃ in Soln. III and
O₂ gas in its standard state.

(92a) ΔE_{decomp.}(As₂O₅) = ΔE_{decomp.}(As₂O₅)n(As₂O₅);

Step 19b. Water in its standard state is removed from Soln. III to bring
the concentration of As₂O₃ to C'(solvn.).

(92b) ΔE_{din.}(As₂O₃) = ΔE_{din.}(As₂O₃)n(As₂O₃);

(93) ΔE'(gas.) = (94) unchanged;

(99) ΔEₜ/Cₜ(M(Compound)) = nₜ ΔEₜ(C(Compound))/mₜ;

(100) ΔEₜ(C(Compound)) = Mₜ ΔEₜ/M(Compound)/1 000;

By definition of the quantities ΔEₜ/M(Compound) and ΔEₜ as follows:
ΔEₜ/M(Compound) = [items 86 + 86a + 86b + 86c + 87 + 92 + 92a - 96 - 97]/mₜ
ΔEₜ = items 81 + 82 + 83 + 84 + 85 + 88 + 89 + 92b + 93 + 94,
item 99 becomes

(99) ΔEₜ/Cₜ(M(Compound)) = ΔEₜ/M(Compound) + ΔEₜ/mₜ. The reason
for this operation is given in Ref.² (p. 102-103)

It is seen that the symbols ΔEₜ/Cₜ(M(Compound), ΔEₜ/L.B.P. and ΔEₜ denote the same quantities in this paper as in Ref.¹, and the symbols
ΔE_{decomp.}(HNO₃), ΔE_{decomp.}(HAuBr₄), ΔE_{decomp.}(H₂PtBr₄), ΔE_{solv.}(CO₂), ΔE_{oxid.}
(HBr), ΔE_{decomp.}(As₂O₅), nₜ ΔEₜ(Auxiliary material) and nₜ ΔEₜ(Fuse) of this
paper correspond with the symbols ΔE(HNO₃), ΔE(Au), ΔE(Pt),
-ΔE(CO₂), + ΔE(HBr), -ΔE(As), + ΔE(Oil) and + ΔE(Fuse), respectively, in Ref.¹

The numerical ΔEₜ values reported in Ref.¹ were calculated according
to the scheme given in this paper.

REFERENCES


Received December 7, 1959.