

# THE CALORIMETRY OF COMBUSTIONS AND RELATED REACTIONS: ORGANIC COMPOUNDS

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## INTRODUCTION

My task in this lecture is to survey recent work on the combustion calorimetry of organic compounds, with particular reference to advances described in papers submitted to this Symposium.

It would be well to start the survey by considering why physical chemists are interested in the combustion calorimetry of organic substances. The motive in most cases is that they wish to obtain values for the standard heats of formation of the substances, since combustion calorimetry generally provides the best means of obtaining such values, albeit indirectly. This motive is related to the over-all aim of the science of thermochemistry which was succinctly stated<sup>1</sup> by Professor Rossini in 1935 in the following terms: "To provide the experimental data for compiling a table of values from which may be calculated the heat of every possible chemical reaction". The present lecture affords an opportunity to reflect on how near thermochemists now are to achieving this object. The short answer is that we are not very near, notwithstanding the large amount of good calorimetric data that has been obtained since 1935, and at the end of the lecture I will offer some suggestions as to how research in *organic* thermochemistry might best be directed towards achieving the stated object.

In his 1935 lecture<sup>1</sup>, Professor Rossini referred to a "renaissance" which had taken place in thermochemistry during the 1920's. He was referring to the increase in accuracy by about one order which thermochemists were called upon to make in their experiments, and did make, in order to yield enthalpies of formation which were comparable in accuracy with entropies of formation then being obtained for the first time. It is clear that progress has continued through the years since 1935, and accurate heats of formation for many organic compounds, especially hydrocarbons, have now been obtained. It is also clear that a new advance is now under way, following the development of rotating-bomb calorimetry and its recognition as the preferred method for determining the energies of combustion of "difficult" organic compounds (*e.g.* those containing the elements S, Si or F)—this advance began here in Lund, with the work of Stig Sunner.

I now propose to consider recent developments in the combustion calorimetry of organic compounds in more detail. I shall consider as "recent" any work published during the last four years, that is, since the memorable Symposium on Thermodynamics held in Fritzens-Wattens, Austria, in August 1959.

## THE LITERATURE OF ORGANIC THERMOCHEMISTRY

The outstanding event of the last four years was the publication of *Experimental Thermochemistry*, Vol. 2<sup>2</sup>. This book, like its predecessor *Experimental Thermochemistry*<sup>3</sup>, resulted from a remarkable piece of international co-operation, organized by the former Subcommission on Experimental Thermochemistry of I.U.P.A.C. Taken together, the two volumes of *Experimental Thermochemistry* provide a broad, up-to-date, introduction to the techniques of thermochemistry, and there are doubtless many participants in this Symposium who have had cause to be grateful for the timely appearance of these books.

Other noteworthy additions to the literature of organic thermochemistry are Mortimer's monograph<sup>4</sup> on *Reaction Heats and Bond Strengths*, and a volume of the 6th edition of *Landolt-Börnstein* that is devoted entirely to thermal data<sup>5</sup>. The comprehensive coverage of the literature by the latter should make a search through abstracts unnecessary whenever a thermochemist wishes to find out whether a certain thermal property of a given compound has been measured (before 1960). Useful though it is in this respect, *Landolt-Börnstein* suffers in my opinion from two defects: firstly, it is not a critical compilation, so that a thermochemist will have to seek guidance from other sources<sup>6-9</sup> if he requires a *selected* value for a heat of formation, and secondly it is not capable of being brought up to date frequently, which is really a necessary requirement in the conditions of rapid expansion which prevail in thermochemistry today. In fact the problem of compiling a comprehensive, yet critical, collection of heats of formation of organic compounds, which is capable of being frequently revised, is one that remains to be solved.

## APPARATUS AND TECHNIQUE

Several recently described bomb calorimeters require smaller samples than do most bomb calorimeters at present in use. For example, the aneroid silver bomb first referred to by Meetham<sup>10</sup> at the Fritzens-Wattens Symposium and now described fully<sup>11</sup> requires only about 150 mg of organic substance. Meetham and Nicholls<sup>11</sup> carried out a series of combustions of benzoic acid and by measuring the energy equivalent of the calorimeter electrically they were able to give the first value of  $\Delta U_c^\circ$  for benzoic acid to be determined in other than a water-immersed bomb. Still further reduction in sample size is possible by use of the bombs described by Ponomarev and Alekseeva<sup>12</sup>, by Mackle and O'Hare and by Calvet and Tachoire<sup>13, 14</sup>. Bomb calorimeters which require only centigrams or even milligrams of sample will obviously be of value for studying compounds which are difficult to synthesize or isolate from natural sources in quantity.

Ponomarev's and Alekseeva's bomb<sup>12</sup> is a massive nickel cylinder with a spherical combustion chamber in the middle of the cylinder; the bomb fits into a compartment in a copper sphere which contains an imbedded platinum resistance thermometer. Since the energy equivalent of this aneroid bomb calorimeter is not much less than that of an orthodox water-containing bomb calorimeter, the *ca.* 20 mg charge that is burned in it produces only a small temperature rise, which requires sensitive instrumentation for its measurement. Mackle and O'Hare's bomb calorimeter (described in paper I: 8), on the other

hand, has a very low energy equivalent—indeed a temperature rise of *ca.* 1° is produced by the combustion of only 10 mg of organic compound. A low energy equivalent is obtained by making the bomb its own calorimeter, with the resistance thermometer wound onto the bomb body, and by having the wall of the bomb (copper) much thinner than in conventional equipment. So thin in fact is the wall that it is necessary to equalize the pressure of oxygen within the bomb with the pressure in the interspace between the bomb and its isothermal jacket; an inevitable consequence of this arrangement is that the correction for heat transfer is somewhat higher than the corresponding correction in an orthodox isothermal calorimeter. The steel micro-bomb of Calvet and co-workers<sup>13</sup>, which is capable of containing a high oxygen pressure, fits into a standard Calvet micro-calorimeter; to date, benzoic acid is the only organic substance for which combustions have been reported. Calvet and Tachoire<sup>14</sup> have also described a glass bomb, again for use in a Calvet micro-calorimeter; it has been employed for combustion reactions with an oxygen pressure of *ca.* 1 atmosphere, but could in principle be used for measurement of the heats of many other types of chemical reaction.

There has been a welcome re-awakening of interest in flame calorimetry as a means of providing precise values of  $\Delta H_c^\circ$  for volatile organic compounds. Thus Pilcher and co-workers<sup>15</sup> have recently described a flame calorimeter with which they have determined the heats of combustion of certain ethers; results for three more ethers are presented in paper I: 10. In Pilcher's calorimeter an organic vapour is carried into the glass combustion vessel in a stream of argon, where it mixes at a jet with primary oxygen and burns at a second jet (quartz) in a supply of secondary oxygen. Ignition is effected by high-voltage discharges across a 4 mm gap between two platinum points. The combustion gases leave the vessel *via* a heat exchanger and are then analysed for their content of carbon dioxide and water, from which the amount of reaction is calculated.

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It is not feasible to review the numerous minor developments in bomb calorimetric technique which have taken place in the last four years. There is, however, one major development that should be mentioned, namely the rapidly increasing use of plastic containers for enclosing materials for combustion. These containers, principally polyester or polyethylene, find use where the material for combustion is volatile or sensitive to water or oxygen. A detailed description of methods of making and using bags of polyester film has been given<sup>16</sup>, and in paper I: 1, Good, Månsson and McCullough describe a technique for preparing a mixture of two accurately-weighed components, using one bag inside another. In paper I: 5, Gundry, Head and the present author present an equation which gives  $\Delta U_c^\circ$  of Melinex brand polyester film as a function of the humidity of the air with which the film was equilibrated. The parameters of the equation are similar to those of an equation given by Good and Scott<sup>16</sup> for Mylar brand polyester film. Also, the value of  $\Delta U_c^\circ$  for zero humidity agrees with Skinner and Snelson's determination<sup>17</sup> of this quantity for Melinex. Undoubtedly, plastic materials are a boon to combustion-calorimetrists who have to deal with volatile or air-sensitive substances, but I think it should

be pointed out to intending users of these plastics that they are not without their disadvantages. Thus polyethylene film is pervious to many organic liquids, whilst polyester film also has minor drawbacks as the following quotation from paper I: 1 shows: "Recognition of the hygroscopicity of the polyester, and of its tendency to become statically charged must be emphasized. Recent experiments have shown that several compounds, including water, permeate the polyester film very slowly, and appropriate precautions in its use must be taken."

## HEAT OF COMBUSTION MEASUREMENTS

There follows a survey of recent measurements of heats of combustion, arranged according to the basic method of the measurement: (i) static-bomb calorimetry, (ii) rotating-bomb calorimetry, (iii) flame calorimetry.

### Static-bomb calorimetry

Table 1 lists recent work on hydrocarbons. Papers by Rossini and co-workers<sup>18-20</sup> contain precise values of  $\Delta H_c^\circ$  for certain olefins which provide a basis for calculating the heats of combustion, formation, hydrogenation or

Table 1. Recent static-bomb combustions of hydrocarbons

Investigators	Substances	Remarks
Bartolo and Rossini <sup>18</sup> Rockenfeller and Rossini <sup>19</sup>	Hexenes Heptenes, octenes, nonenes	Heats of hydrogenation and isomerization of olefins discussed in terms of structure
Labbauf and Rossini <sup>20</sup>	Olefinic derivatives of cyclohexane and cyclopentane	
Loeffler and Rossini <sup>21</sup>	Derivatives of n-decane	Mean CH <sub>2</sub> increment for $-\Delta H_c^\circ$ (liq. state) found to be 156.29 kcal mole <sup>-1</sup>
Dauben <i>et al.</i> <sup>23</sup>	<i>Cis</i> and <i>trans</i> 9-methyl-decalin	<i>Trans</i> 1.39 ± 0.64 kcal mole <sup>-1</sup> (liq. state) more stable than <i>cis</i>
Speros and Rossini <sup>24</sup>	<i>Cis</i> and <i>trans</i> decalin, and naphthalene derivatives	<i>Trans</i> 2.69 ± 0.31 kcal mole <sup>-1</sup> (liq. state) more stable than <i>cis</i>
Browne and Rossini <sup>25</sup>	<i>Cis</i> and <i>trans</i> hydrindan	<i>Trans</i> 1.04 ± 0.53 kcal mole <sup>-1</sup> (liq. state) more stable than <i>cis</i>
Margrave <i>et al.</i> <sup>26</sup>	<i>Trans-syn-trans</i> and <i>trans-anti-trans</i> perhydro-anthracene	<i>Syn</i> 5.39 ± 0.86 kcal mole <sup>-1</sup> (gas state) more stable than <i>anti</i>
Coops <i>et al.</i> <sup>27</sup> Kozina <i>et al.</i> <sup>28</sup> Fierens and Nasielski <sup>29</sup>	Cyclanes C <sub>10</sub> to C <sub>17</sub> Cyclopropane derivatives Cyclopropane derivatives	Combustions done at the National Bureau of Standards
Bedford <i>et al.</i> <sup>30</sup>	Biphenylene	Strain energy estimated

isomerization for other olefins. Loeffler and Rossini<sup>21</sup> gave a precise value for the increment in  $\Delta H_c^\circ$  per CH<sub>2</sub> group, for the liquid state; the value agreed with that given by Fraser and Prosen<sup>22</sup>. Rossini *et al.*<sup>23-25</sup> also studied hydrocarbons with two fused alicyclic rings and obtained information on the energy

difference between *cis*-fused and *trans*-fused isomers. Margrave *et al.*<sup>26</sup> measured the heats of combustion of two isomeric perhydro-anthracenes (I and II). The *trans-syn-trans* compound (I) was found to be thermochemically more stable than the *trans-anti-trans* compound (II), and from this result the chair form of cyclohexane was calculated to be thermochemically 4.8 kcal mole<sup>-1</sup> more stable than the skew-boat form (gas state). This finding was in accord with that of an earlier study<sup>31</sup> from the same laboratories of the heats of combustion of the isomeric lactones (III) and (IV).



(I)



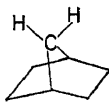
(II)



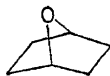
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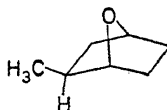
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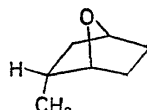
(V)



(VI)



(VII)



(VIII)

There is considerable interest in the problem of strain in carbocyclic compounds, and Coops and his colleagues<sup>27</sup> have now extended their earlier studies of cyclanes to include the C<sub>10</sub> to C<sub>17</sub> members of this series. Two groups<sup>28, 29</sup> have reported measurements on cyclopropane derivatives, whilst measurements on the highly-strained compound biphenylene have been published from Keele University<sup>30</sup>. In paper I: 7 these workers give values of  $\Delta H_c^\circ$  for bicyclo-[2,2,1]-heptane (V), its 7-oxa-derivative (VI) and its *exo*-2-methyl-7-oxa- (VII) and *endo*-2-methyl-7-oxa-derivative (VIII). They conclude that the strain energy in (V) is *ca.* 18.5 kcal mole<sup>-1</sup>, made up of both angular strain and torsional strain (the hydrogen atoms are almost completely eclipsed), but the strain in the oxa-compound (VI) is much less, *ca.* 6.5 kcal mole<sup>-1</sup>. Their conclusion with regard to the other compounds is that the *endo*-isomer is slightly more strained than the *exo*-isomer. (All values apply to the liquid state.)

Recent combustion studies on C,H,O compounds are summarized in Table 2. It is a welcome sign that precise values for simple alcohols, aldehydes, ethers, carboxylic acids *etc.* are now being obtained, because the older literature values are often unreliable, due largely to the use of impure specimens.

Table 2. Recent static-bomb combustions of organic oxygen compounds

Investigators	Substances	Remarks
Skinner and Snelson <sup>17</sup> Snelson and Skinner <sup>32</sup>	Isomeric butanols	} Polyester bags used
	Isomeric propanols and cyclic ethers	
Gundry <i>et al.</i> <sup>33</sup>	n-Butyl alcohol	} Agreement with Skinner's value
Tjebbes <sup>34, 35</sup>	Alcohols and aldehydes	} Corrections necessary for water in the samples
Nicholson <sup>36, 37</sup>	Alcohols and aldehydes	
Andon <i>et al.</i> <sup>38</sup>	Phenols	} Strain energies estimated
Sellers and Sunner <sup>39</sup>	Cyclopentan-ol and -one cyclohexan-ol and -one	
Smutny and Bondi <sup>40</sup>	Aliphatic ethers	} Agreement with value from equilibrium studies
Sinke and Hildenbrand <sup>41</sup>	Propylene oxide	
Colomina <i>et al.</i> <sup>42</sup>	Alkyl phenyl ketones	
Sinke <sup>43</sup>	Formic acid	
Saville and Gundry <sup>44</sup>	Lactic acid	
Schwabe and Wagner <sup>45</sup>	Isomeric phthalic acids	
Silvestro and Lenchitz <sup>46</sup>	Ethylene carbonate	
Colomina <i>et al.</i> <sup>47, 48</sup>	Alkyl benzoic acids	

Traces of water are particularly hard to remove from some of these compounds and in the work of Tjebbes<sup>34</sup>, for example, a correction for residual water in the samples was necessary. Colomina and co-workers<sup>47, 48</sup> have published values of the heats of combustion of the three methylbenzoic acids and the six dimethylbenzoic acids. In paper I: 12 they complete the series with values for the remaining ten methyl-substituted benzoic acids; heats of combustion of other alkylbenzoic acids and of polymethylbenzenes and some heats of sublimation are also reported by this group.

Table 3 lists some of the C<sub>2</sub>H<sub>5</sub>N compounds studied recently; many contain unsaturated nitrogen. A range of amino-acids and their derivatives has been studied by Russian workers<sup>57, 58</sup>, whilst Gardner and Grigger<sup>60</sup> performed an

Table 3. Recent static-bomb combustions of organic nitrogen compounds

Investigators	Substances	Remarks
Hatton <i>et al.</i> <sup>49</sup> Bedford <i>et al.</i> <sup>50</sup>	Aniline	} Polyester bags used
	Aliphatic imine and amine, pyrazole and imidazole	
Bedford <i>et al.</i> <sup>51</sup>	Tetrahydropyridine piperidine and piperazine	} Polyester bags and glass ampoules used
	Pyrrolidine	
McCullough <i>et al.</i> <sup>52</sup> Scott <i>et al.</i> <sup>53, 54</sup> Hubbard <i>et al.</i> <sup>55</sup>	2- and 3-methylpyridine Pyridine and hippuric acid	} The acid is a suggested reference substance
Tjebbes <sup>56</sup> Ponomarev <sup>57</sup> Ponomarev <i>et al.</i> <sup>58</sup>	Isomeric diazines Amino-acids Amino-acid anhydrides and peptides	} Summarizing paper
Armstrong and Marantz <sup>59</sup> Gardner and Grigger <sup>60</sup> Donovan <i>et al.</i> <sup>61</sup>	Dicyano-acetylene Tetranitromethane 1,1-Dimethylhydrazine and tetramethyltetrazine	} Burned in carbon monoxide

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unusual combustion experiment when they burned tetranitromethane in an atmosphere of carbon monoxide. Hubbard, Frow and Waddington<sup>55</sup> studied hippuric acid as a possible reference substance for C,H,O,N-containing compounds. Their value for  $\Delta U_c^\circ$  agreed almost exactly with two previous measurements<sup>62, 63</sup>, but they suggested that the agreement may have been fortuitous, since it is difficult to prepare a really pure, dry sample of hippuric acid.

It is now well established that if an organic compound contains elements other than C,H,O or N, the rotating-bomb calorimeter is the preferred instrument for obtaining the heat of combustion. Nevertheless, some compounds containing the "difficult" elements can be successfully studied by means of the static-bomb, provided that thermal effects associated with the formation of solid by-products or of incomplete mixing in the liquid products are shown to be small. Examples of "difficult" compounds which have been successfully burned in a static-bomb are given in *Table 4*, refs. 64-73 (certain of these com-

*Table 4.* Recent static-bomb combustions of miscellaneous compounds

<i>Investigators</i>	<i>Substances</i>	<i>Remarks</i>
Johnson <i>et al.</i> <sup>64</sup>	Tri-alkyl borons	Boric acid and some amorphous boron produced
Kilday <i>et al.</i> <sup>65</sup> Birr <i>et al.</i> <sup>66-68</sup>	Borazine Tetraphenyl-silane -germane and -stannane Tetrastryryl-silane and -germane	} Single oxide apparently produced
Coughlin and Warren <sup>69</sup>	"Viton A" (C <sub>5</sub> H <sub>3.5</sub> F <sub>6.5</sub> ) <sub>n</sub>	
Bedford <i>et al.</i> <sup>70, 71</sup>	Organo-phosphorus compounds	} Orthophosphoric acid was the sole phosphorus-containing product
Bedford <i>et al.</i> <sup>72</sup>	Organic derivatives of cyclic phosphazenes (PNCl <sub>2</sub> ) <sub>3</sub> and (PNCl <sub>2</sub> ) <sub>4</sub>	
Hartley <i>et al.</i> <sup>73</sup>		Burned in a dry bomb; P <sub>4</sub> O <sub>10</sub> , N <sub>2</sub> + Cl <sub>2</sub> produced
Birr <sup>74, 75</sup>	Triphenyl-phosphorus, -arsenic, -antimony and -bismuth	Mixture of products formed except for the Bi compound which gave Bi <sub>2</sub> O <sub>3</sub> only
Tanaka <sup>76</sup> Jones <i>et al.</i> <sup>77</sup>	Siloxanes Acetylacetone derivatives of Fe(III), Cr(III), Co(III), Th(IV), Cu(II), Mg(II), VO <sup>2+</sup> , UO <sub>2</sub> <sup>2+</sup>	SiO <sub>2</sub> , C + SiC produced
Jones <i>et al.</i> <sup>77</sup>	Amino-acid complexes of copper	Single metal oxide apparently produced
		Cu, Cu <sub>2</sub> O + CuO produced

pounds, borazine and the phosphonitrilic chlorides, are not strictly organic, but have been included here because their structural relationship to true organic compounds is close). A further example of the successful application of the static-bomb to the combustion calorimetry of a "difficult" compound is provided by the work of Davies, Pope and Skinner, described in paper I: 2. These workers studied the combustion of tetra-alkyl tin compounds contained in polyester bags. They found that provided their initial oxygen pressure was 40 atmospheres the compounds burned well, as shown by analyses for carbon dioxide. The solid product was shown to contain stannic oxide and a little metallic tin, but no stannous oxide; the metallic tin was determined by igniting

the solid product in air to constant weight. Similar combustion experiments on organic derivatives of Group IV elements have been reported by Birr<sup>66-68</sup>, but there is insufficient experimental detail in his papers to judge whether the combustions went cleanly. The work of Coughlin and Warren<sup>69</sup>, who burned a fluorine-containing polymer in a platinum-lined static-bomb, is of interest. By using a very large excess of hydrocarbon as combustion aid they were able to convert all the combined fluorine to hydrofluoric acid; the drawback of this procedure was of course that only a small part of the measured heat came from combustion of the fluorine compound.

The lower part of *Table 4* contains references to static-bomb combustion studies that were clearly unsatisfactory<sup>74-77</sup>. Thus in the work on siloxanes, on triphenyl derivatives of phosphorus, arsenic and antimony, and on copper complexes, highly mixed combustion products were obtained. Obviously these compounds should be studied by rotating-bomb calorimetry.

### Rotating-bomb calorimetry

The three leading schools (Lund, Bartlesville and Belfast) in the application of rotating-bomb calorimetry to sulphur compounds have continued to publish good data (see *Table 5*). One of the compounds studied<sup>81</sup>, thia-adamantane,

*Table 5.* Recent rotating-bomb combustions

<i>Investigators</i>	<i>Substances</i>	<i>Remarks</i>
McCullough and Good <sup>78</sup>	Mercaptans, sulphides and disulphides	Correlation of $\Delta H_f^\circ$ values with structure
Good <i>et al.</i> <sup>79</sup>	Carbon disulphide	Burned with excess hydrocarbon
Good <i>et al.</i> <sup>80</sup>	Tetramethyl thiuram sulphide and disulphide	Bond energy term for S-S link estimated
Lacina <i>et al.</i> <sup>81</sup>	Thia-adamantane	
Månsson and Sunner <sup>82</sup>	Dimercaptans	
Davies and Sunner <sup>83</sup>	Dihydro- and tetrahydrothiophene	Strain energies estimated
Mackle and Mayrick <sup>84</sup>	Sulphides	} Liquid samples burned in polyethylene capsules under <i>ca.</i> 40 atm O <sub>2</sub> + N <sub>2</sub>
Mackle and McClean <sup>85</sup>	Benzyl mercaptan	
Mackle and O'Hare <sup>86</sup>	Sulphoxides	
Mackle and O'Hare <sup>87</sup>	Sulphones	
Bjellerup <sup>88</sup>	<i>p</i> -Bromobenzoic acid	A possible reference substance
Bjellerup <sup>89</sup>	Mono- and di-bromo alkanes	
Bjellerup <sup>90</sup>	1-Bromo-alkanes C <sub>4</sub> -C <sub>8</sub>	
Good <i>et al.</i> <sup>91</sup>	Difluorobenzenes, <i>p</i> -fluorotoluene and <i>m</i> -trifluorotoluene acid	The acid is a possible reference substance
Good <i>et al.</i> <sup>92</sup>	1,2-Bis-difluoroamino-4-methyl-pentane	
Good <i>et al.</i> <sup>93</sup>	Perfluoropiperidine	

has an intriguing cage structure, and it is to be hoped that the heat of sublimation of this compound will be determined, so that a calculation of the strain energy in thia-adamantane can be made.

Bjellerup has given a detailed description<sup>88, 89</sup> of his methods for the



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combustion calorimetry of organo-bromine compounds, in which arsenious oxide is used to reduce elemental bromine in the combustion product to hydrobromic acid. Comparison of the heats of formation of some of the bromine compounds studied by Bjellerup<sup>89</sup> with values obtained by reaction calorimetry showed good agreement for mono-bromo compounds but poor agreement for dibromo-compounds.

The Bureau of Mines group in Bartlesville has published the heats of combustion of some aromatic fluorine compounds<sup>91</sup>, and of two compounds containing N-F bonds<sup>92, 93</sup> (*Table 5*). The combustion calorimetry of organo-fluorine compounds using a platinum-lined rotating-bomb calorimeter has also been studied at Teddington, and is described by Gundry, Head and the present author in paper I: 5. We studied on the one hand *p*-fluorobenzoic acid and pentafluorobenzoic acid, with regard to their suitability as reference substances, and on the other hand perfluorobenzene and perfluorocyclohexene, as part of a programme on the thermodynamic properties of highly-fluorinated compounds. Agreement was found between our value of  $\Delta U_c^\circ$  for *p*-fluorobenzoic acid and the one published by Good, Scott and Waddington<sup>94</sup> for their so-called "B" sample of the acid. In our work on highly-fluorinated compounds we burned a hydrogen-containing compound (hexadecane or benzoic acid) along with the fluorine-containing compound, in order to minimize the formation of carbon tetrafluoride, the heat of formation of which has not been established with certainty. We deduced from our measurements on perfluorobenzene that this compound is thermochemically much less stable than was to have been expected.

Once the problem of the extreme corrosiveness of hydrofluoric acid under combustion conditions had been overcome, the way was open for exploiting the high solvent-power of the acid in rotating-bomb combustions of "difficult" compounds. This approach was pioneered by the Bartlesville group who first used it in combustions of silicon in a rotating-bomb into which hydrofluoric acid had initially been placed<sup>95</sup>; a fluorine-containing polymer was burned along with the silicon to produce a final solution of fluosilicic acid in excess hydrofluoric acid. A similar technique has since been used with organic silicon compounds and elemental boron. The application of the method to a boron compound, trimethylamineborane, is described by Good, Månsson and McCullough in paper I: 1. An intimate mixture of this compound with polyvinylidene fluoride was burned in a bomb that contained hydrofluoric acid; the final solution contained nitric, hydrofluoric and fluoboric acids. By combination of their value of  $\Delta H_c^\circ$  with their value of  $\Delta H^\circ$  for the conversion of boron to fluoboric acid in hydrofluoric acid solution, Good, Månsson and McCullough are able to calculate  $\Delta H_f^\circ$  of trimethylamineborane. Combination of this value in turn with  $\Delta H_f^\circ$  of trimethylamine and  $\Delta H^\circ$  for the addition of diborane to trimethylamine leads to a value of  $\Delta H_f^\circ$  for diborane. The result does not agree too well with earlier values, possibly because crystalline boron is used as the reference state, instead of amorphous boron as hitherto.

The extraordinary versatility of the rotating-bomb calorimeter is demonstrated by Mortimer and Sellers in paper I: 6. They used their bomb not only to study a combustion reaction but also to study a hydrolytic reaction involving the evolution of gas. The combustion reaction studied was that of triphenylarsine which, when burned in the presence of sodium hydroxide solution, gave

a homogeneous solution of sodium carbonate, arsenite and arsenate. Such an end-product is obviously to be preferred to that (arsenious and arsenic oxides, partly in solution) obtained in an earlier static-bomb combustion of triphenyl-arsine<sup>73</sup>. The hydrolytic reaction studied by Mortimer and Sellers was that of trimethyl-aluminium with acetic acid, yielding aluminium triacetate and methane. The heat of formation of the tri-acetate was determined separately by solution calorimetry, so that it was possible to calculate  $\Delta H_f^\circ$  of liquid trimethyl-aluminium. By combination with other recent measurements<sup>96</sup>,  $\Delta H_f^\circ$  for trimethyl-aluminium (gas) may be obtained.

### Flame calorimetry

The heat of combustion of cyclopropene has been recorded in a recent note<sup>97</sup>. The derived value for  $\Delta H_f^\circ$  (g), +66.2 kcal mole<sup>-1</sup>, indicates a strain energy of no less than 53.3 kcal mole<sup>-1</sup>, as calculated by the method of ref. 98. Accurate values for the heats of combustion of the lower ethers are being determined at Manchester University by means of the flame calorimeter that was briefly described earlier in this survey. Thus Pilcher and co-workers<sup>15</sup> have already reported on diethyl ether, divinyl ether and ethyl vinyl ether, and in paper I: 10 they report on dimethyl ether, methyl n-propyl ether and methyl isopropyl ether. They compare their derived values of  $\Delta H_f^\circ$  (g) for the saturated ethers with values predicted by Allen's bond-energy scheme. Good agreement is found for dimethyl ether, diethyl ether and methyl n-propyl ether, but methyl isopropyl ether is found to be 1.4 kcal mole<sup>-1</sup> less stable than predicted. This fact is ascribed to repulsion between hydrogen atoms in methyl groups on either side of the oxygen atom. In the hydrocarbon of analogous structure, destabilization is only 0.3 kcal mole<sup>-1</sup>, but calculation based on molecular dimensions shows that more non-bonded interaction between hydrogen atoms would be expected in the ether than in the hydrocarbon.

## PREDICTION OF HEATS OF FORMATION OF ORGANIC COMPOUNDS

Quite early in the development of thermochemistry it was found that heats of formation of organic compounds may reasonably be considered to be additive functions of the bonds, or groups, making up the molecule. Many tables of bond energy terms (based on heats of formation from atoms) and of bond contributions to molecular heats of formation have been given through the years, and there has recently been a revival of interest in this topic; the most recent bond energy schemes are compatible with modern ideas about chemical bonding and non-bonded interactions. Very accurate schemes, applicable to alkanes and a few of their derivatives, have been proposed by Allen<sup>99</sup> (and elaborated by Skinner<sup>100, 101</sup>, and McCullough and Good<sup>78</sup>) and by Tatevskii and co-workers<sup>102</sup>. A simple scheme that is applicable to both aliphatic and benzenoid compounds has also been proposed recently<sup>103</sup>.

An important application of a bond energy scheme is in the calculation of heats of formation of compounds for which no experimental values exist. This application is of course closely related to the aim of thermochemistry as given at the beginning of this survey. The following questions then pose themselves: (i) How near are we to being able to compile a table of values from

which may be calculated the heat of every possible organic chemical reaction? (ii) What form should the table of values take? The answer to question (ii) involves personal preference, and I will state my preference for a table of values of bond or group contributions to molecular heats of formation in the ideal gas state. With such values available, the heats of formation of the molecules taking part in a given reaction could be estimated, and hence, by appropriate summation, the heat of the reaction itself (in the ideal gas phase) could be estimated; conversion of this value to the heat of reaction of the real gases, or of condensed phases, would then require methods of predicting imperfect gas behaviour and latent heats.

With regard to question (i) the answer turns on how many reliable, experimentally-based values of  $\Delta H_f^\circ$  (g) are available, since many methods are available for calculating bond contributions from the experimental data. There now follows an assessment of the availability of  $\Delta H_f^\circ$  (g) values, based on a division of the commoner types of organic compound into five classes.

(1) For alkanes, cyclanes and alkenes good data exist.

(2) For compounds of the type R-X (where R = alkyl or alkenyl) good data exist for many substituents X, though some notable gaps remain to be filled e.g. X = Cl; R = vinyl.

(3) For compounds  $R_1R_2Y$  (and for the more general case where the valence of atom or group Y is more than 2), some data for Y = N, S, SO or SO<sub>2</sub> are available, and data for Y = O are accumulating.

(4) For di- and poly-substituted alkanes, cyclanes and alkenes there is a dearth of data. What data are available suggest that bond-bond interactions are large (several kcal mole<sup>-1</sup>) when substituents are attached to the same carbon atom, small when they are attached to adjacent carbon atoms, and negligible when they are attached to 1,3 carbon atoms. Perfluorinated compounds are extreme examples of compounds wherein bond-bond interactions are significant. Some interesting theories of bonding in fluoro-compounds have recently been proposed<sup>104-106</sup> and it is important that they should be tested by good thermochemical data.

(5) For compounds with delocalized  $\pi$ -electron systems some reliable values of  $\Delta H_f^\circ$  (g) exist, and more values would become available if more latent heats were to be measured. Prediction of the heats of formation of compounds in this category is likely to prove difficult because the problem of allowing for conjugation energy will arise. A lesser, but not insignificant, problem is that of accounting for energy differences between isomers. In this connection, some values of  $\Delta H_f^\circ$  (g) for *o*-, *m*- and *p*-isomers in the benzene series have been collated in Table 6. Inspection of the table reveals that in general *o*-substituted compounds are thermochemically less stable than their *m*- and *p*-isomers, though the hydroxybenzoic acids constitute an exception to this rule—indeed, when it is remembered that the order of thermochemical stability may depend on the relative importance of inductive, mesomeric, steric and hydrogen-bonding effects in the compounds, no simple unexceptional rule is to be expected.

From what has just been said, it should be clear what remains to be done by the organic thermochemist. Little more work need be done on compounds in class (1). With regard to compounds in class (2) there is particular need for

Table 6. Heats of formation of *o*-, *m*- and *p*-isomers

Compounds	$\Delta H_f^\circ(\text{g})$ (kcal mole <sup>-1</sup> )	Compounds	$\Delta H_f^\circ(\text{g})$ (kcal mole <sup>-1</sup> )
<i>o</i> -Xylene <sup>7</sup>	+4.5	<i>o</i> -Methylphenol <sup>108</sup>	-30.7
<i>m</i> -Xylene <sup>7</sup>	+4.1	<i>m</i> -Methylphenol <sup>108</sup>	-31.6
<i>p</i> -Xylene <sup>7</sup>	+4.3	<i>p</i> -Methylphenol <sup>108</sup>	-30.0
<i>o</i> -Ethyltoluene <sup>7</sup>	+0.3	<i>o</i> -Ethylphenol <sup>108</sup>	-34.8
<i>m</i> -Ethyltoluene <sup>7</sup>	-0.5	<i>m</i> -Ethylphenol <sup>108</sup>	-34.9
<i>p</i> -Ethyltoluene <sup>7</sup>	-0.8	<i>p</i> -Ethylphenol <sup>108</sup>	-34.5
<i>o</i> -Difluorobenzene <sup>91</sup>	-67.7	<i>o</i> -Methylbenzoic acid <sup>109</sup>	-78.3
<i>m</i> -Difluorobenzene <sup>91</sup>	-71.4	<i>m</i> -Methylbenzoic acid <sup>109</sup>	-79.8
<i>p</i> -Difluorobenzene <sup>91</sup>	-70.7	<i>p</i> -Methylbenzoic acid <sup>109</sup>	-80.3
<i>o</i> -Dichlorobenzene <sup>107</sup>	+7.8	<i>o</i> -Hydroxybenzoic acid <sup>108</sup>	-116.3
<i>m</i> -Dichlorobenzene <sup>107</sup>	+6.7	<i>p</i> -Hydroxybenzoic acid <sup>108</sup>	-113.3
<i>p</i> -Dichlorobenzene <sup>107</sup>	+6.0		
<i>o</i> -Chloro-ethylbenzene <sup>107</sup>	-0.9		
<i>p</i> -Chloro-ethylbenzene <sup>107</sup>	-0.1		

more data on vinyl derivatives and alkyl halides (except bromides). It should be noted, however, that considerable economy of effort is possible in experimental work in this field. Thus, once  $\Delta H_f^\circ(\text{g})$  for *n*-butyl chloride has been well established, no great purpose will be served by attempts to determine  $\Delta H_f^\circ(\text{g})$  for higher 1-chloro-alkanes, because the values will almost certainly be predictable with the same accuracy as that with which they can be measured. For compounds in class (3), an encouraging amount of experimental work has recently been reported, as exemplified by four separate contributions to this Symposium on compounds wherein Y = O, Al, As and Sn. Saturated heterocyclics form a special case, and again an encouraging amount of work has recently been reported (see ref. 98 for a summary). For compounds in classes (4) and (5) it must be obvious that the scope for experimental work is enormous.

I would like to end the survey with a reminder that predictions of heats of formation can most satisfactorily be made for substances in the *ideal gas* state, and that the predictive methods rest on values of heats of formation in the *ideal gas* state of certain key compounds. Now I am well aware that many thermochemists require for their own purposes merely the heat of formation in the standard state, which for most organic compounds is the liquid or solid state. But I would urge that, wherever possible, the extra effort needed to obtain a latent heat of vaporization or sublimation should be made. Then, not only will the resulting data be of more value to the science of thermochemistry, but also deductions concerning conjugation energy, strain energy or structure will carry much greater weight.

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