

THERMOCHEMISTRY OF ORGANIC FLUORINE COMPOUNDS AND CARBON COMPOUNDS OF METALS BY ROTATING-BOMB CALORIMETRY*

W. D. GOOD and D. W. SCOTT

*Petroleum Experiment Station, Bureau of Mines, U.S. Department
of the Interior, Bartlesville, Oklahoma, U.S.A.*

Rotating-bomb calorimetry was first applied to organic compounds that contain chlorine, bromine, or sulphur. Techniques developed for these classes of compounds, mostly at the University of Lund and at the Bureau of Mines in Bartlesville, have been described in the book *Experimental Thermochemistry*¹. The development of rotating-bomb methods made accurate combustion calorimetry feasible for other classes of compounds besides those of chlorine, bromine, or sulphur. Two of these other classes of compounds have received attention in the Bureau of Mines laboratory in recent years, namely: (a) organic fluorine compounds and (b) organo-metallic compounds and other carbon compounds of metals. Techniques developed for rotating-bomb calorimetry of these two classes of compounds are reviewed in this paper.

ORGANIC FLUORINE COMPOUNDS

Chemistry of the bomb process

In combustion calorimetry of an organic fluorine compound, $C_aH_bO_cN_dF_e$, the sample reacts with oxygen in a calorimetric bomb containing some water. The products are some or all of the following: CO_2 , H_2O , N_2 , HNO_3 , HF, and CF_4 . Traces of HNO_3 are formed from nitrogen impurity in the oxygen with which the bomb is charged, even if the compound itself does not contain nitrogen. If the compound is not highly fluorinated, all of the fluorine appears in the products as HF. However, if the compound is highly fluorinated, 80 per cent or more of the fluorine may appear in the products as CF_4 . Examination of combustion products for fluorine-containing compounds other than hydrogen fluoride and tetra-fluoromethane has always given negative results.

Rotating-bomb calorimeter, bomb, and fittings

The calorimeter² used for organic fluorine compounds embodies several improvements over earlier models, the most noteworthy of which is provision for continuous rotation of the bomb to the end of the calorimetric experiment. Continuous rotation assures homogeneity and equilibrium of the final contents of the bomb and simplifies the correction for energy generated by rotation of the bomb.

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Owing to the corrosive nature of the hydrofluoric acid in the combustion products, a platinum-lined bomb was used. The bomb was placed in the calorimeter in the inverted position. The crucible and all other internal fittings of the bomb were made of platinum. Slight attack of the platinum crucible occurred during combustion of highly fluorinated samples, but the amount of attack was scarcely significant thermochemically.

Containers for volatile samples

Glass ampoules could not be used as containers for volatile fluorine compounds, because the glass would react with the hydrogen fluoride in the combustion products. In early work, fused-silica ampoules were used, and thermochemical corrections were applied for reaction between the silica and hydrogen fluoride. In later work, volatile samples were sealed in polyester film bags³. These containers are impervious to compounds of all degrees of fluorination, and they undergo complete combustion along with the samples they contain.

Experimental procedures

In general, the calorimetric procedures were similar to those of rotating-bomb methods for other classes of compounds. The bomb initially contained water, usually 10 ml. Carbon dioxide having been expelled from the solution, the total acidity of the final bomb contents was determined by acid-base titration, loss of hydrogen fluoride being prevented by converting it to non-volatile HF_2^- ion. Nitric acid was determined by Devarda's method. Hydrogen fluoride was determined as the total acidity (corrected for nitric acid), and tetrafluoromethane was then determined by difference.

Comparison experiments

Reduction of the calorimetric results to standard states could not be made rigorously because certain data, particularly values of the solubility and heat of solution of carbon dioxide in aqueous hydrofluoric acid as functions of concentration, were lacking. Errors from inexact reduction to standard states were minimized by use of comparison experiments. In these experiments, the sample was benzoic acid and either succinic acid or a hydrocarbon oil, and the bomb initially contained a solution of hydrofluoric acid. The amounts were selected so that the evolution of energy, the amount of carbon dioxide formed, and the amount and concentration of the final bomb solution all were nearly the same as in the combustion experiment with the fluorine compound. The comparison experiments were used to determine an *apparent* energy equivalent of the calorimetric system. The value of the *apparent* energy equivalent was used to compute the heat of combustion of the fluorine compound. In the result so obtained, errors from inexact reduction to standard states were eliminated or made much smaller by cancellation.

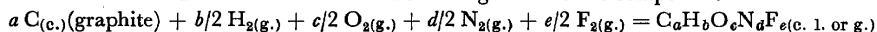
Results

Values of heat of formation for 15 organic fluorine compounds determined by rotating-bomb calorimetry are listed in *Table 1*. These derived results were obtained from the experimental values of the heat of combustion by

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use of presently accepted values for the heat of formation of $\text{CO}_2(\text{g.})$, $\text{H}_2\text{O}(\text{l.})$ and HF (in aqueous solution)⁵ and the value⁶, $\Delta H_{298.15}^\circ = -218.3$ kcal mole⁻¹ for CF_4 . If the heat of vaporization has been determined, the heat of formation is given for the vapour state as well as for the condensed state.

Table 1. Heat of formation of organic fluorine compounds



Compound	$\Delta H_{298.15}^\circ$ (kcal mole ⁻¹)			Ref.
	Crystals	Liquid	Gas	
<i>o</i> -Fluorobenzoic acid	- 134.3 ₃			2
<i>m</i> -Fluorobenzoic acid	- 137.8 ₄			2
<i>p</i> -Fluorobenzoic acid	- 138.9 ₅			2
4-Fluorotoluene		- 43.4 ₃	- 34.0	4
Fluorobenzene		- 34.7 ₅	- 26.4 ₃	2
1,2-Difluorobenzene		- 76.2 ₉	- 67.6 ₅	4
1,3-Difluorobenzene		- 79.6 ₃	- 71.3 ₇	4
1,4-Difluorobenzene		- 79.2 ₃	- 70.7 ₀	4
Benzotrifluoride		- 147.8 ₅	- 138.8 ₇	2
<i>m</i> -Fluorobenzotrifluoride		- 193.2 ₄	- 184.1 ₇	3
Perfluoropiperidine		- 482.9	- 475.8	4
Perfluoromethylcyclohexane		- 683.4	- 675.3	3
Perfluoroethylcyclohexane		- 778.9	- 769.7	3
Poly(tetrafluoroethylene)	- 193.5*			2
Perfluoro- <i>n</i> -heptane		- 797.7	- 789.0	3

* kcal monomole⁻¹ for material that had received no heat treatment.

ORGANO-METALLIC AND RELATED COMPOUNDS

Chemistry of the bomb process

Four carbon compounds of metals were studied by rotating-bomb calorimetry: tetramethyl-lead⁷, tetraethyl-lead⁸, lead oxalate⁸, and dimanganese decacarbonyl⁹. Solid products from combustion of these compounds were dissolved by a solution in the bomb. For lead compounds, the solution contained nitric acid and a little arsenious acid. This solution, in the presence of oxygen under pressure, dissolved all solid lead compounds to give Pb^{2+} in solution. For the manganese compound, the solution contained nitric acid and a little hydrogen peroxide; this solution dissolved all solid manganese compounds to give Mn^{2+} in solution. Rotation of the bomb after the combustion reaction was finished assured the rapid solution of the solid products wherever they might be in the bomb.

Lead oxalate alone would not sustain combustion, and use of an equal mass of hydrocarbon oil as promoter was necessary to obtain complete combustion. Tetramethyl lead, on the other hand, would detonate to produce "soot" and other incompletely oxidized products, and dilution with a hydrocarbon oil as moderator was necessary to obtain smooth combustion which went to completion. The heat of dilution was determined in separate experiments. Tetraethyl-lead had satisfactory combustion characteristics.

Two complications were encountered with the manganese compound. First, a lower-than-normal pressure of oxygen was needed to obtain the

solid products in a finely divided state suitable for solution; unfortunately, at the required lower oxygen pressure, a "carbon residue" was formed. Second, catalytic decomposition of the hydrogen peroxide in the bomb solution took place in the presence of manganous ion. However, appropriate thermochemical corrections were possible for both of these complicating effects.

Rotating-bomb calorimeter, bomb, and fittings

The same calorimeter was used for the organo-metallic and related compounds as was used for the organic fluorine compounds. The provision for continuous rotation of the bomb was particularly necessary because of the relatively long time required to dissolve the solid products.

A bomb made of nickel-chromium alloys was used because the thin lining of a platinum-lined bomb might be damaged by spattering of molten metal or oxides. However, some interior fittings less liable to such damage were made of platinum. To prevent short circuiting of the ignition current through the conducting bomb solution, the insulated electrode was mounted on a post integral with the head of the bomb. When the bomb was in the calorimeter in the inverted position, the top of the post was above the surface of the bomb solution.

A platinum crucible was satisfactory for the manganese compound. However, platinum crucibles were not inert to the combustion products of the lead compounds, so fused-silica crucibles were used. The fused silica fluxed somewhat with the solid lead compounds, but the amounts of the products (lead silicate and aqueous silicic acid) could be determined and appropriate thermochemical corrections applied for the fluxing reaction.

Containers for volatile samples

Samples of tetraethyl-lead were enclosed in unsealed ampoules of fused silica. As the ampoules were of the same material as the crucibles, single thermochemical corrections could be made for fluxing with both the crucible and the fragments from the ampoules. Samples of tetramethyl-lead, diluted with hydrocarbon oil, were sealed in polyester film bags similar to those used for the organic fluorine compounds. No containers were needed for the non-volatile solids, lead oxalate and dimanganese decacarbonyl.

Experimental procedures

In general, the calorimetric procedures were similar to those of rotating-bomb methods for other classes of compounds. The bomb initially contained the solution (usually 50 ml) to dissolve the solid products. The reaction period was longer than normal because of the time required for the solid products to dissolve. When the calorimetry was complete, the final bomb contents were analysed chemically. The amount of reducing agent (arsenious acid or hydrogen peroxide) remaining was determined, and all other determinations necessary for application of thermochemical corrections or verifying the chemistry of the bomb process were made.

Comparison experiments

Use of comparison experiments for fluorine compounds has already been described. Comparison experiments for the organo-metallic and related compounds were even more important because of the greater volume of bomb solution and therefore larger corrections for dissolved carbon dioxide. In these comparison experiments, the sample was benzoic acid or hydrocarbon oil or both, in amounts selected so that the evolution of energy and the amount of carbon dioxide formed, or at least the latter, were the same as in the combustion experiment. An inorganic compound of the metal, solid $\text{Pb}(\text{NO}_3)_2$ or a concentrated solution of $\text{Mn}(\text{NO}_3)_2$, was placed in a second crucible in the bomb. (The hygroscopic $\text{Mn}(\text{NO}_3)_2$ solution was enclosed in a glass ampoule.) The amount and composition of the initial bomb solution was such that the final bomb solution duplicated the one in the combustion experiment. The comparison experiments, in addition to minimizing errors from inexact reduction to standard states, also allow the combustion reaction to be referred to the inorganic compound of the metal as product, with the latter in a physical state for which the heat of formation is well known. Possible errors because the calorimetry is not strictly a substitution method are also cancelled by use of comparison experiments.

Results

Values of the heat of formation of the four organo-metallic or related compounds, determined by rotating-bomb calorimetry, are listed in *Table 2*. These derived results were obtained from the experimental values

Table 2. Heat of formation of organo-metallic and related compounds
 $a \text{C}_{(c)} + b/2 \text{H}_{2(g)} + c/2 \text{O}_{2(g)} + d\text{M}_{(c)} = \text{C}_a\text{H}_b\text{O}_c\text{M}_d$ (c. l. or g.) M is Pb or Mn

Compounds	$\Delta H_{298.15}^\circ$ (kcal mole ⁻¹)			Ref.
	Crystals	Liquid	Gas	
Tetramethyl-lead		23.5	32.6	7
Tetraethyl-lead		12.8		8
Lead oxalate	- 203.2			8
Dimanganese decacarbonyl	- 400.9			9

of the heat of combustion by use of presently accepted values for the heat of formation of $\text{CO}_{2(g)}$, $\text{H}_2\text{O}_{(l)}$, HNO_3 (in aqueous solution), $\text{Pb}(\text{NO}_3)_2(c)$, and $\text{Mn}(\text{NO}_3)_2$ (in aqueous solution)⁵.

DISCUSSION

The rotating-bomb method can be used for accurate combustion calorimetry of most solid or liquid organic fluorine compounds. The rotating-bomb method also makes possible accurate combustion calorimetry of organo-metallic and related compounds, although special problems have to be solved for compounds of each particular metal and even for individual compounds of a given metal. The thermochemistry of both classes of compounds is now on a sound experimental basis.

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