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Bomb calorimetry—contributions of the 1960s from East Germany[1]

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Abstract

In the 1960s in East Germany, scientific and technological concerns led to investigations by two independent teams into the improvement of bomb calorimetry techniques, the results of which are not widely known. The procedures are described in detail in the publications referred to in this survey.

INTRODUCTION

The worldwide problems with raw materials that became obvious during the 1950s led to extensive scientific research which, in chemistry, had the following objectives: to optimize procedures for the maximum use of time and space; to develop relationships between molecular structure and energy content; and to understand the safety aspects of chemical plants in order to minimize losses (in the workforce as well as material losses).

Thermochemical research requires exact caloric data, primarily combustion enthalpies, which alone or in conjunction with phase change enthalpies, provide the necessary basis for that research.

The experimental determination of combustion enthalpies is based on the work of Berthelot. The uncertainty of this classical method was, however, too great to be adequate for these purposes. The even higher uncertainties that occur with less readily inflammable samples or samples containing heteroatoms posed additional experimental problems. Thus improvements in techniques were imperative.

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EXPERIMENTAL

Two independent teams of physical chemists in East Germany, with differing objectives, therefore attempted to improve experimental conditions.

Geiseler and Quitzsch and their team at the University of Leipzig developed rotating-bomb calorimeters of varying bomb volumes [1-6]. They used sample masses of about 250 mg or less and achieved reliable results even if heteroatoms were present in the samples.

The team of Peters and Tappe at the German Academy of Sciences in Berlin carried out systematic investigations on a static bomb in order to determine the details of the combustion process necessary to further improve it. They used a windowed bomb for their experiments, which they monitored photographically as well as cinematographically, using various materials, sample quantities, crucible geometries, atmospheres and pressures. Flame temperatures were measured pyrometrically.

RESULTS AND DISCUSSION

From the numerous techniques developed by the Leipzig team, only the semi-micro rotating-bomb combustion calorimeter will be mentioned here; for a detailed description, see ref. 6. It was mainly used for investigating small amounts of heterocyclic ketones, the so-called thiacyclo-alkanones. Figure 1 shows the apparatus. During each measurement, the bomb rotated 60 times around the horizontal axis and once around the vertical. This double rotation was controlled by a special mechanism. The heat equivalent of this calorimeter was 3.6 kJ K^{-1}; the sample masses used for the experiments were 100 mg maximum and the uncertainty was within the range of less than 0.001%.

This type of calorimeter had been preceded by others of varying sizes. What they all had in common was the use of a metal block as the body of the bomb calorimeter, the measurement of temperatures by means of the thermistor inside the metal block (see Fig. 1), the evacuation of the block environment to about 1.3×10^{-7} bar and the tempering of the calorimeter jacket according to the multi-jacket principle.

The experiments carried out in such apparatus yielded valuable data, as well as major contributions to theoretical organic chemistry. By determining standard molar enthalpies of formation and bond energies it was possible to calculate the energy contributing to mesomeric stabilization in cyclic compounds containing sulphur. The experiments were carried out on trithiones, isotrithiones, 1,2-dithiins, dithiocarbonates and cyclic trithiocarbonates. It was also possible to determine energy differences between isomeric compounds, e.g. between *cis*- and *trans*-dibenzyl-dithio-enthene and for the three octanones.

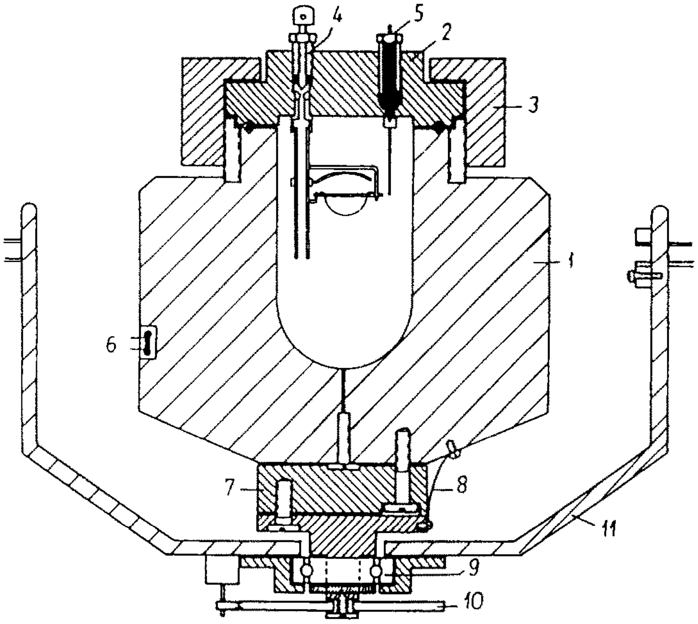

Fig. 1. Cross-section of the combustion bomb: 1, shell of bomb; 2, cap; 3, cap screw; 4, needle valve; 5, ignition electrode; 6, thermistor; 7, plastic block; 8, power cable; 9, ball bearing; 10, cog wheel; 11, U-shaped suspension device.

Peters and Tappe, in their systematic investigations of the combustion process in a static bomb carried out numerous experiments using benzoic acid [7]. They differentiated, as they did subsequently with other materials, between three clearly separate phases of the combustion process: ignition, combustion of the body of the material and, finally, extinction of the flame. The formation of soot is often a sign of incomplete combustion. As they point out, it can largely be avoided if the crucible is sufficiently heated during the combustion process. To achieve this, the mass of sample and the duration of the combustion process must be adequate, and the heat capacity of the crucible must be sufficiently low that the initially precipitated carbon can later burn completely. The crucible should therefore be made of thin platinum. In exceptional cases, quartz glass crucibles should be used.

Figure 2 shows the dependence of the duration of combustion on the initial weight. If there is too much sample in the crucible (to the right of the dotted line), the duration of combustion will decrease because some of the molten material overflows and is thus better supplied with oxygen. The thickness of the crucible wall does not influence the combustion duration.

By adding argon to oxygen, both the flame temperature and the duration of the combustion were influenced. The functional dependence illustrated in Fig. 3 and eqn. (1) yields an exponent for the flame temperature near −4, as expected with predominantly heat radiation in accordance with the

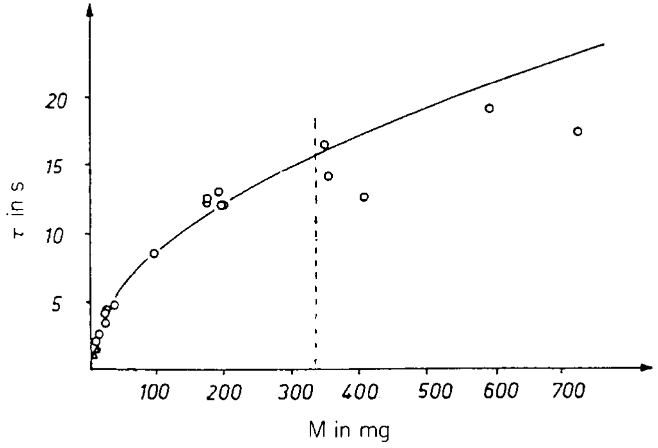

Fig. 2. Duration of combustion τ plotted against mass of benzoic acid M (diameter of crucible 14 mm).

Stefan–Boltzmann law

$$\tau_0 = BT^{-q} \tag{1}$$

where T is flame temperature (K) and q is 3.4 ± 0.8.

Finally, they developed a numeric flame model empirically for the combustion of benzoic acid in ball-cap-shaped platinum crucibles

$$\tau = C^{-1}(\pi R/d)^{-1/2}T^{-4}M^{1/2} \tag{2}$$

where R is the radius of curvature of the crucible, d is the density of the material, T is the flame temperature and M the mass of benzoic acid.

Further experiments using solid C–H–O compounds [8] yielded clearly differing ignition and combustion behaviour. Saccharose and succinic acid,

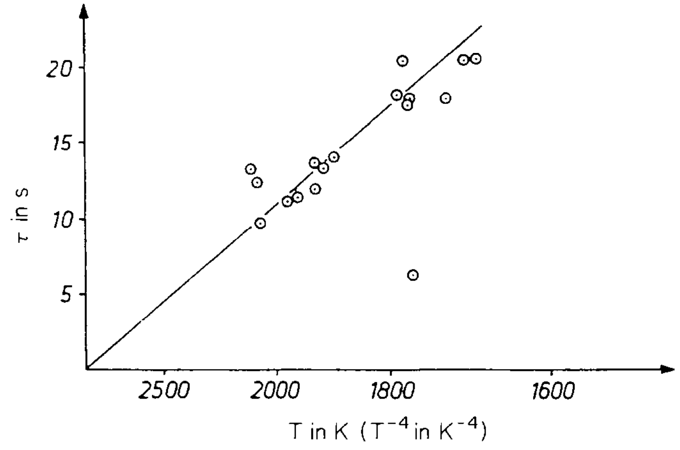

Fig. 3. Duration of combustion τ against flame temperature T (T is shown in K but scaled in T^{-4} in K^{-4}).

for example, formed CO-enriched gases of decomposition, which resulted in weak flames and low temperatures.

Investigations into the effect of oxygen pressure and NO formation during combustion [9] showed that pressures lower than 10 bar resulted in flames inadequate for calorimeter. It is recommended that the initial sample weight is kept below 3 g per litre of inner bomb volume in order to avoid passage of the gases through the flame.

These fundamental results were prerequisites and starting points for further thermochemical contributions. At the same time, they made possible the safe handling of combustion calorimetry in industrial laboratories.

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