# Thermochemical Investigations on Organic Sulfur Compounds

## III.  On the possible use of thianthrene as a secondary standard in bomb calorimetry for sulfur compounds *

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In the determination of heats of combustion of organic compounds in a bomb calorimeter, the presence of sulfur in the molecule may cause several systematic errors. In 1934 the IUPAC Standing Commission for Thermochemistry pointed out the importance of calibrating the calorimetric system with a standard substance containing the same element as the substance being studied.[1] Thus, many errors of a systematic character will tend to be minimized. Two years later the Standing Commission proposed sym-diphenylthiourea or thioglycolic acid as sulfur-containing test-substances [2].

From the following discussion concerning the requirements which a suitable secondary standard substance should fulfil, it is concluded that neither sym-diphenylthiourea nor thioglycolic acid can be accepted as a satisfactory secondary standard.

## REQUIREMENTS FOR A SECONDARY STANDARD

Huffman has summarized the requirements which a standard substance for bomb calorimetry should fulfil [3]:

1. *It should be readily obtainable in a pure state.*
2. *It should be easy to dry and should remain so without special precautions.*
3. *It should be completely stable at elevated temperatures.*
4. *It should not be volatile.*
5. *It should pellet readily.*
6. *It should be readily inflammable.*
7. *It must burn completely.*

However, further requirements are necessary for a standard substance containing sulfur. It is obvious that the common practice of burning sulfur

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* Paper I and II in this series:  References 4 and 5.

compounds together with an auxiliary substance such as paraffin oil should be avoided in the case of the secondary standard.

8. *It should be burned without use of an auxiliary substance.*

The last requirement follows from the attempt to minimize the influence from possible (unknown) systematic errors due to the presence of sulfur. Some of these errors may vary significantly if widely varying amounts of sulfur are burned either as elemental sulfur or as an organo-sulfur compound *. It is impossible in practice to maintain constant the amount of sulfur present in combustions of various substances.

The energy equivalent of the calorimeter restricts the quantity burned for substances with low sulfur content. For example, a reasonable amount of octadecylmercaptane for a combustion in an ordinary bomb calorimeter would be 0.5 g, a quantity which contains less than 2 milliatoms of sulfur.

The upper limit for the amount of sulfur in a single combustion is set partly by the increasing risk of incomplete oxidation to sulfuric acid with increasing amounts of sulfur and partly by the necessity of avoiding sulfuric acid in high concentrations in the final state. It was found in this laboratory that 8 milliatoms of sulfur in each combustion experiment were oxidized completely to hexavalent sulfur (*cf.* below). Waddington and co-workers burned by "The Huffman-Ellis Method" [6] an amount of thiophene corresponding to 10 milliatoms of sulfur without observing any sulfur dioxide [7]. In this case, if 10 ml of water is used in the bomb, the sulfuric acid obtained will be 2 $N$ which, at the present, is a reasonable upper limit for the concentration of the acid, considering the approximations made in correcting the actual to the idealized bomb process [4]. It is not advisable to increase the amount of water in the bomb as the errors in the calculation of the heat of solution of carbon dioxide then no longer may become significant [4].

Therefore, when burning a substance with a high percentage of sulfur, the quantity used is limited and thus the heat evolved from the combustion of the compound is rather small. In the use of the method of comparative measurements the total heat evolved should be kept constant, and the use of an auxiliary substance is required. This decreases the accuracy with which the heat of combustion of the sulfur compound can be determined. In such cases it is desirable to burn as large a quantity of the compound as possible.

From what has been said it is evident that the amount of sulfur used in a combustion must be varied from one compound to another — in practice between approximately 2—3 and 8—10 milliatoms of sulfur. Thus, it is not possible to standardize the calorimeter by burning a standard substance "under conditions identical with those which will characterize later on the combustion of the substance investigated"[1]. The choice of a standard substance must therefore be the result of a compromise, the amount of substance burned should correspond to 5—7 milliatoms of sulfur. This is the basis for the statement of the next requirement.

9. *The quantity of standard substance burned should contain a sufficient amount of the element in question (sulfur) to give a final state comparable to that*

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* For small variations in the amount of sulfur present in a combustion, such errors are negligible; *cf.* communication IV (to be published).

*found after combustions of compounds containing an average amount of the same element.*

Neither of the two substances proposed by the Standing Commission for Thermochemistry fulfils the last two requirements. The heat of combustion of the sym-diphenylthiourea is calculated to be approximately 1 680 kcal per mole. In a calorimeter of conventional design in which the total heat evolved is between 5 000 and 8 000 calories only about 3 to 5 millimoles of this substance may be burned. On the other hand, it is necessary to use about 15 to 20 millimoles of thioglycolic acid to obtain the same amount of heat. Thus the sulfur content of diphenylthiourea is too low and that of thioglycolic acid too high to make the substances desirable as standards.

In searching for a suitable standard substance for bomb calorimetry of sulfur compounds, the behaviour of thianthrene was investigated.

### SYNTHESIS AND PURIFICATION OF THIANTHRENE

Thianthrene was synthesized from pure benzene, freshly distilled sulfur monochloride and aluminum chloride (Fries and Vogt [8]). The crude thianthrene was recrystallized from benzene, distilled at 0.2 mm Hg in an all-glass apparatus without standard joints, twice recrystallized from benzene and subjected to sublimation at $10^{-3}$ mm Hg and 100° C. The products from three different syntheses, all showing the same m.p. 155.9° C, were combined (sample A, 750 g). Two sulfur analyses both showed 29.8 % S (calculated value 29.64 %). Sample A was subjected to a slow freezing-out process whereby 75 % of the substance crystallized (sample B) and the rest was discarded. The purity of samples A and B was checked by observation of melting point curves * in an apparatus described by Smit [9]. From the result it was evident that one freezing-out operation greatly improved the purity. The melting interval decreased from 0.25° C to 0.18° C ($\pm$ 0.02°). At the same time both the initial and the final melting temperatures increased, from 155.70 to 155.90° and from 155.95 to 156.08° C. For sample A premelting began at 155.25 and for sample B at 155.70° C. On the basis of certain assumptions the amount of impurity may be roughly estimated from the melting point curve [9,10]. By this method the depression of the melting point of sample B due to the presence of impurities was calculated to be 0.02° C. Determination of the cryoscopic constant of thianthrene gave a mean value of 24.5° C per mole of impurity per 100 g of solvent. Thus a depression of 0.02° corresponds to 0.8 millimole of impurity per 100 g of thianthrene (0.18 mole-%). The purity of sample B was hence estimated to be 99.8 mole-%.

### SUITABILITY OF THIANTHRENE AS A SECONDARY STANDARD

A preliminary investigation concerning the fulfilment of requirements 1 to 9 gave the following results:

1. Thianthrene is readily synthesized in large quantities. It has the advantage that it can be purified according to a variety of methods: recrystallization, distillation, sublimation and freezing-out. It is expected that by a carefully controlled freezing-out operation the purity could be increased considerably beyond the purity of sample B.

2. The high temperature conditions encountered in the purification process warrant a completely dry product. The hygroscopicity of thianthrene was investigated as follows. A finely pulverized sample (2 g) of thianthrene was kept

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* These curves were obtained during a visit with Prof. J. Coops, Vrije Universiteit, Amsterdam; we wish to express our thanks to Dr. Coops and his co-workers for their experienced advice and helpfulness.

at 21.3° C and 98 % relative humidity in a small dish. Table 1 gives the weight of the dish plus substance at different time intervals. No absorption of moisture could be detected within the accuracy of the balance.

*Table 1. Hygroscopicity of thianthrene.*

| Day | 1 | 2 | 3 | 6 | 8 | 10 | 13 | 15 | 23 |
|---|---|---|---|---|---|---|---|---|---|
| Weight (grams) | 15.11869 | 69 | 66 | 66 | 69 | 68 | 64 | 69 | 69 |

3. The thianthrene was distilled at 200° C and then frozen out at 156° C over a period of several hours, yet the purity increased. However, the thermal stability should be investigated further.

4. The volatility of a 2 g sample of powdered thianthrene in an even layer of 10 cm² surface was examined at 21.3° C in the open air (Table 2). On the average the volatility was found to be 0.01 mg per 24 hours.

*Table 2. Volatility of thianthrene.*

| Hours | 3 | 23 | 47 | 119 | 167 | 216 | 288 | 336 |
|---|---|---|---|---|---|---|---|---|
| Weight (grams) | 19.71775 | 75 | 73 | 70 | 69 | 69 | 60 | 53 |

5. Thianthrene is easy to pellet.

6—7. No difficulties have been encountered in igniting thianthrene and under the conditions employed it burns completely.

8—9. In the calorimetric system used, the amount of thianthrene burned corresponded to 6 milliatoms of sulfur which is a suitable amount according to the preceding discussion. However, the amount of thianthrene which should be used for different calorimetric systems is variable and depends ultimately on the volume of the bomb used. The generally accepted procedure for the determination of the energy equivalent of a bomb calorimeter is to burn a standard sample of benzoic acid under standardized conditions. According to the recommendations of the Standing Commission for Thermochemistry [2] three grams of benzoic acid should be used per litre of bomb volume. Thus, the bomb volume determines the amount of heat that should be evolved in the standardizing experiments and also in all subsequent combustions of other substances carried out under equal conditions. In practice, the amount of thianthrene which should be burned in different bomb calorimeters can be expected to correspond to amounts of sulfur varying between 5 and 10 milliatoms.

CALORIMETRIC APPARATUS AND METHOD

The calorimeter and accessory apparatus, experimental procedure and methods of calculation have been described in detail [4]. However, a new method has been adopted for the determination of nitric acid. A systematic study of different methods showed that more reproducible results could be obtained in the estimation of the nitric and nitrous acids by using a direct method rather

than the earlier indirect one [11]. The nitrogen acids were reduced to ammonia with Devarda's alloy and the ammonia formed was distilled and titrated with 0.1 $N$ hydrochloric acid [7]. As previously, the amount of nitrous acid was determined colorimetrically using the method of Griess.

*Energy equivalent of the calorimeter.* The energy equivalent of the calorimeter was determined by burning National Bureau of Standards benzoic acid lots 39f and 39g with identical certified heats of combustion of 26.4294 ± 0.0026 int. kj or 6317.8 ± 0.6 cal per gram mass when burned under specified conditions at 25° C. This corresponds to $-\Delta Ec(p = 1; 293.16)$ * $= 6314.2 \pm$ 0.6 cal per gram mass for the reaction $C_7H_6O_2$ (s, 1 atm) $+ 7.5\ O_2$ (g, 1 atm) $=$ 7 $CO_2$ (g, 1 atm) $+ 3\ H_2O$ (liq, 1 atm). Table 3 shows a series of determinations of the net energy equivalent, $S_B$, of the calorimeter, which includes the 10 ml of water in the bomb and also the 30 atm of oxygen, but excludes the charge of substance(s) burned and the combustion products. These are included in $S_F$[4]. $S_B$ and $S_F$ are given in cal per temperature unit, which is, as in previous publications the temperature difference between two fixed points on the Beckmann thermometer, the lower corresponds to 20.00° C and the upper to 21.35° C (the difference between these two temperatures is the Interval Unit, I.U.). The first column of Table 3 gives the mass of benzoic acid, the second column the increase in temperature in interval units and the third column the sum of the heats evolved from the formation of the nitrogen acids (13.8 cal per millimole nitric and $-6.9$ cal per millimole nitrous acid formed from nitrogen, oxygen and water). The fourth column gives the heat of combustion of the cotton thread and the last column the net energy equivalent of the calorimeter.

*Table 3. Benzoic acid. $S_F = 0.6$ cal per I. U. Correction for dissolved carbon dioxide ($CO_2$-corr) $= 6.9$ cal. Washburn corrections ($W_c$) $= 3.3$ cal.*

| Benzoic acid<br>mg mass | $\Delta T_{corr}$<br>I. U. | $HNO_3 + HNO_2$<br>cal | Cotton<br>thread cal | $S_B$<br>cal/I. U. |
|---|---|---|---|---|
| 820.54 | 0.99263 | 8.4 | 13.9 | 5 251.5 |
| 821.42 | 0.99384 | 8.4 | 14.4 | 5 251.3 |
| 822.08 | 0.99453 | 8.4 | 14.3 | 5 251.8 |
| 821.08 | 0.99367 | 8.4 | 14.8 | 5 250.5 |
| 822.04 | 0.99468 | 8.4 | 15.4 | 5 251.8 |
| 822.06 | 0.99435 | 8.4 | 13.1 | 5 251.4 |
| 822.76 | 0.99547 | 8.4 | 13.9 | 5 250.6 |

Mean: $S_B = 5\ 251.3 \pm 0.4$ (average deviation) cal per I. U. at 20.00° C.

* Unfortunately, a list of symbols approved by the Standing Commission for Thermochemistry is lacking. The notations used are in conformity with those used by Rossini in his "Chemical Thermodynamics" [12]. In order to simplify the type-setting the standard reference state is indicated within brackets together with the temperature in degrees Kelvin. Thus $\Delta Ec$ ($p = 1$; 293.16) signifies the increase in internal energy of the combustion reaction at 293.16°K with both reactants and reaction products in given states (g = gaseous; liq = liquid; s = solid) and at unit pressure (1 atm). $\Delta Hf$ ($f = 1$; 298.16) signifies the standard heat of formation at 298.16° K with gaseous reactants and, if stated gaseous, the reaction product at unit fugacity; liquid and solid components are at unit pressure (1 atm). Thus, it has the same meaning as $\Delta Hf^{\circ}_{298.16}$. In each case it is specified if the energy quantities refer to one gram mass or to one mole.

## HEAT OF COMBUSTION OF THIANTHRENE

Two series of determinations of the heat of combustion of thianthrene are summarized in Table 4.
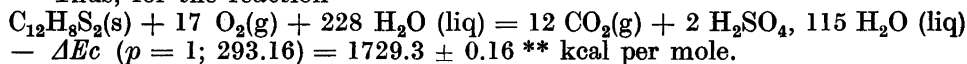
*Table 4. Thianthrene.*

Mol.wt 216.316                                      Density $d_4^{20} = 1.440$ *
$S_F = 0.2$ cal per I. U.   $CO_2$-corr $= 6.2$ cal.   $W_c = 1.2$ cal.
$S_B = 5\ 251.3$ cal per I. U. (next to last combustion 5 255.1). $- \Delta Ec$ $(p = 1;\ 293.16)$ given for formation of $CO_2$ and $H_2SO_4$, 115 $H_2O$.

| Thianthrene mg mass | $\Delta T_{corr}$ I. U. | $HNO_3 + HNO_2$ cal | Cotton thread cal | $- \Delta Ec$ $(p = 1;\ 293.16)$ cal per g mass |
|---|---|---|---|---|
| 644.76 | 0.98810 | 9.8 | 14.3 | 7 995.9 |
| 654.32 | 1.00222 | 9.8 | 14.0 | 7 992.5 |
| 653.49 | 1.00091 | 9.8 | 14.2 | 7 992.1 |
| 652.94 | 1.00100 | 9.1 | 17.8 | 7 995.1 |
| 652.48 | 0.99968 | 9.2 | 14.6 | 7 994.8 |
| 655.64 | 1.00408 | 9.4 | 15.6 | 7 992.4 |
| 651.61 | 0.99783 | 9.4 | 13.8 | 7 994.2 |
| 654.25 | 1.00196 | 9.4 | 13.7 | 7 995.3 |
| 653.34 | 0.99994 | 9.4 | 14.4 | 7 994.9 |
| 651.40 | 0.99758 | 9.4 | 13.3 | 7 995.6 |

Mean for the first series: 7 994.1 $\pm$ 1.4 cal per g mass
Mean for the second series: 7 994.5 $\pm$ 1.0 cal per g mass
Mean for both series: 7 994.3 $\pm$ 1.2 cal (average deviation) per g mass
                            $\pm$ 0.4$_5$ cal (standard deviation of the mean)

Thus, for the reaction
$$C_{12}H_8S_2(s) + 17\ O_2(g) + 228\ H_2O\ (liq) = 12\ CO_2(g) + 2\ H_2SO_4,\ 115\ H_2O\ (liq)$$
$- \Delta Ec$ $(p = 1;\ 293.16) = 1729.3 \pm 0.16$ ** kcal per mole.

## SUMMARY

The requirements for a substance considered suitable as a standard in bomb calorimetry for sulfur compounds are discussed. The amount of sulfur present in a combustion (as an organo-sulfur compound) cannot be kept constant and, in practice, it will vary between 2 and 10 milliatoms. It is therefore not possible to follow rigorously the recommendation of the IUPAC Standing Commission for Thermochemistry of the International Union of Pure and Applied Chemistry: to standardize the calorimeter by burning a standard substance "under conditions identical with those which will characterize later on the combustion of the substance investigated". The choice of a standard substance must be the result of a compromise, the amount of substance burned should correspond to an average amount of sulfur in the range between 5 and 7 milliatoms.

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* The density was determined on single crystals by a buoyancy method (Thomson's method). On two samples of crystals the values obtained were 1.440$_0$ and 1.439$_5$.
** The "overall" standard deviation [13,4].

Thianthrene was investigated as to its suitability as a standard substance and was found to be promising. However, further investigations, especially concerning the purification of thianthrene, are necessary before a definite proposal can be made for the use of thianthrene as a standard substance.

The heat of combustion of thianthrene to carbon dioxide and a diluted sulfuric acid ($H_2SO_4$, 115 $H_2O$) was determined to be $-\Delta Ec$ ($p = 1$; 293.16) = $1\ 729.3_0 \pm 0.32$ * kcal per mole.

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\* Twice the "overall" standard deviation [13].