The Heat of Combustion of Indium[1,2]

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Introduction.—The heat of formation of In_2O_3 as determined from its heat of combustion in oxygen has been measured by Becker and Roth[3] who found $\Delta H = -222.5 \pm 0.7$ kcal./mole. Previous work by Ditte[4] as corrected by Becker and Roth[3] gave $\Delta H = -220$ kcal./mole. The purpose of this note is to report on some recent work which essentially confirms the results of Becker and Roth and which is of somewhat greater precision.

Method.—The method involved the determination of the heat evolved from the burning of a weighed sample of the metal in an oxygen bomb calorimeter at 25 atmospheres pressure. The energy equivalent of the calorimeter was determined from the heat of combustion of standard benzoic acid and also electrically. The completeness of combustion was determined by treating the combustion products with 6 *N* hydrochloric acid and measuring the amount of hydrogen evolved from any unburned metal present. The uncertainties are given as twice the standard deviation.

Apparatus.—The details of the construction and calibration of the calorimeter have been described.[5] The energy equivalent of the calorimeter was 10,095.2 ± 4.2 absolute joules/°C.

Combustion of Indium.—The indium used was in the form of very high purity sheets. A spectroscopic analysis showed the presence of traces (< 0.01%) of Mg and Fe. Other metals were absent.

The combustion took place on discs of sintered In_2O_3 of high purity. In the first five runs indium fuse wire was used. However, the percentage of misfires was so great with indium fuse wire that for the subsequent runs magnesium fuse wire was used. No significant difference in the results was noticed when magnesium wire was used instead of indium wire. The initial temperature was 24.6° and the average final temperature was 25.8°. The results may be summarized as follows: number of runs, 14; mass of indium, 2.59 to 3.20 g.; % burned, 97.60 to 98.59; temperature rise, 1.0093 to 1.2528°; energy from indium, 3,989.8 to 4,033.3 joules/g.; average = 4,016.1 joules/g.; average deviation from the mean, 10.7 joules/g.; standard deviation of the mean, 3.6 joules/g. The final average value for the heat of combustion of indium, taking into account the uncertainty in the energy equivalent of the calorimeter, is 4,016.1 ± 7.5 absolute joules/g. In calories this is 959.8 ± 1.8 calories/g.

Heat of Formation of In_2O_3.—The heat of combustion reported above gives a value of $\Delta E_{24.6}° = -921.8 \pm 1.6$ absolute kilojoules/mole. The correction of this value to 25° is less than the uncertainty in the result. To obtain the heat of formation it is necessary to correct for the deviation of oxygen from the perfect gas law and to convert from ΔE to ΔH. Using Rossini and Frandsen's[6] value of $(\partial\Delta E/\Delta P)_{301°K.} = -6.51$ joules/atm./mole for oxygen and taking $\Delta H = \Delta E + \Delta(PV)$ we have for the heat of formation of In_2O_3, $\Delta H_{25}° = -925.8 \pm 1.6$ absolute kjoules/mole where the uncertainty given includes the uncertainty in the energy equivalent. In defined calories this is -221.27 ± 0.40 kcal./mole.

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(2) For detailed data order Document 3413 from American Documentation Institute, 1719 N Street, N.W., Washington, 6 D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

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Studies on Imidazoles. V. The S-Alkylation of 2-Mercaptoimidazoles with Esters

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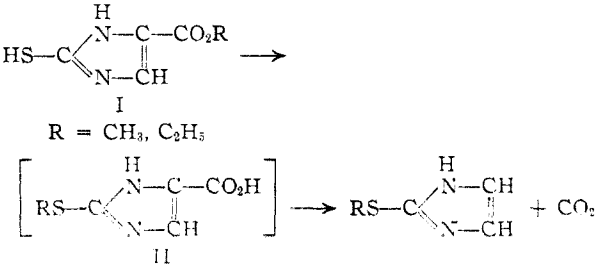
It was observed that in melting point capillaries the esters (I) of 2-mercapto-4(or 5)-imidazolecarboxylic acid decomposed and evolved gas at the melting points (185–190°).[1] This behavior was difficult to explain, since 2-mercaptoimidazole itself was shown to be entirely stable at temperatures up to 250°.[2] In order to investigate the products of decomposition, a larger quantity of methyl 2-mercapto-4(or 5)-imidazolecarboxylate[1] was heated to about 200° for a few minutes. The evolved gas was collected and found to be carbon dioxide. From the residue in the flask the only product isolated was 2-methylmercaptoimidazole. Ethyl 2-mercapto-4 (or 5)-imidazolecarboxylate[1] behaved in the same way when it was decomposed by heating to 200°. The products were carbon dioxide and 2-ethylmercaptoimidazole. Most probably the sulfur atom at position 2 was alkylated by the ester groups followed by loss of carbon dioxide from the resulting acid, II. Such acids are known to undergo decarboxylation readily.[2]



One additional experiment was carried out in which 2-mercaptoimidazole was heated with ethyl benzoate. The products from this reaction were 2-ethylmercaptoimidazole and benzoic acid.

Experimental

Pyrolysis of 2-Mercapto-4(or 5)-imidazolecarboxylic Esters.—In a small round-bottom flask was placed 10 g. of methyl 2-mercapto-4(or 5)-imidazolecarboxylate.[1] The flask was carefully heated with a small flame until the contents melted. Gas was evolved, and the mixture darkened. Heating was continued until foaming had largely stopped. The evolved gas was collected and shown by the usual methods to be carbon dioxide. The mixture was cooled, and the partially crystalline residue was taken up in 50 ml. of warm acetone. After the acetone solution had been clarified with carbon and filtered it was evaporated to dryness. The residue was treated with 20 ml. of water, and the crystalline solid was collected and air dried. A sample was recrystallized from water; m.p. 134–135°. A mixture with an authentic sample of 2-methylmercaptoimidazole[3] melted at 135–135.5°. The yield was 4.0 g. (55%).

The experiment was repeated using ethyl 2-mercapto-4 (or 5)-imidazolecarboxylate in place of the methyl ester. 2-Ethylmercaptoimidazole was isolated in 28% yield. The

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