

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 Roth³ who found $\Delta H = -222.5 \pm 0.7$ kcal./mole. Previous work by Ditte⁴ as corrected by Becker and Roth³ 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 $10,095.2 \pm 4.2$ 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 $4,016.1 \pm 7.5$ 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 $\Delta E_{24.6}^\circ = -921.8 \pm 1.6$ 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's⁶ value of $(\Delta E/\Delta P)_{298.15^\circ\text{K.}} = -6.51$ joules/atm./mole for oxygen and taking $\Delta H = \Delta E + \Delta(PV)$ we have for the heat of formation of In_2O_3 , $\Delta H_{25}^\circ = -925.8 \pm 1.6$ absolute kilojoules/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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- (1) This work was done under the auspices of the A.E.C.
- (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.
- (3) G. Becker and W. A. Roth, *Z. physik. Chem.*, **A161**, 69 (1932).
- (4) A. Ditte, *Compt. rend.*, **72**, 858 (1871).
- (5) C. E. Holley, Jr., and E. J. Huber, Jr., *THIS JOURNAL*, **73**, 5577 (1951).
- (6) F. D. Rossini and M. Frandsen, *J. Research Natl. Bur. Standards*, **9**, 733 (1932).

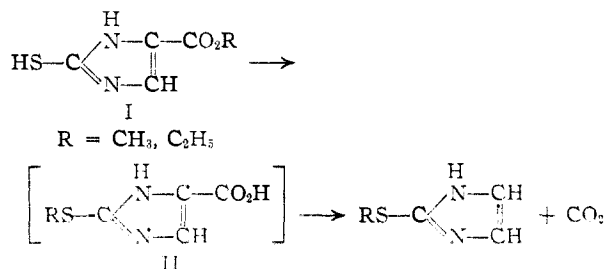
Juanita Pena and Oliver Simi in the spectroscopic analysis of the indium metal.

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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)-imidazolecarboxylate¹ 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)-imidazolecarboxylate¹ 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-methylmercaptoimidazole³ 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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- (2) R. G. Jones, E. C. Kornfeld, K. C. McLaughlin and R. C. Anderson, *ibid.*, **71**, 4000 (1949).
- (3) W. Markwald, *Ber.*, **25**, 2360 (1892).

m.p. was 103–104° and was not depressed when mixed with an authentic sample.⁴

*Anal.*⁵ Calcd. for C₈H₈N₂S: C, 46.83; H, 6.29; N, 21.83; S, 25.05. Found: C, 47.27; H, 6.36; N, 21.61; S, 24.54.

2-Mercaptoimidazole and Ethyl Benzoate.—A suspension of 8 g. of 2-mercaptoimidazole in 20 g. of ethyl benzoate was heated up to the boiling point (215°) and held at reflux for ten minutes. The cooled mixture was extracted with 50 ml. of 2 N hydrochloric acid. After separation and washing with ether the aqueous extract was made basic with sodium carbonate and a crystalline precipitate of 2-ethylmercaptoimidazole separated. The product was recrystallized from ether–petroleum ether. It melted at 103–104° and the m.p. was not depressed when mixed with authentic 2-ethylmercaptoimidazole.⁴ The yield was 4 g. (39%).

From the ethyl benzoate solution was isolated benzoic acid by extraction with sodium bicarbonate solution and acidification of the aqueous extract.

(4) Prepared from 2-mercaptoimidazole and ethyl iodide by the procedure of ref. 3; m.p. 103.5–104.5°.

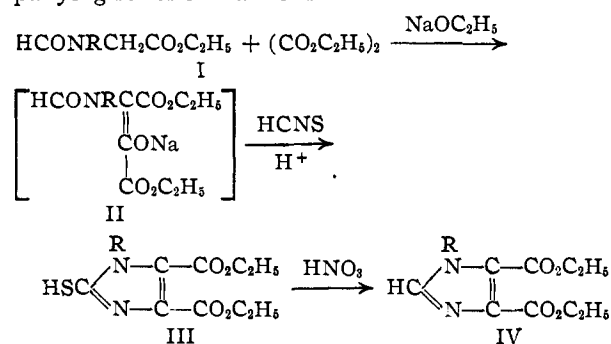
(5) The author is indebted to W. L. Brown, H. L. Hunter and W. J. Schenck for the analysis.

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Studies on Imidazoles. VI. Synthesis of 4,5-Imidazoledicarboxylates

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Imidazoledicarboxylic acids and their derivatives with substituents in the 1-position (III and IV) are of interest for the preparation of purines¹ and related compounds. A general method for the synthesis of such 1-substituted-4,5-imidazoledicarboxylic acid derivatives is reported here. This is an extension of an earlier method for the synthesis of 1-substituted-4(or 5)-imidazolecarboxylates.² The steps involved are indicated by the accompanying series of reactions.



N-Formylglycine esters (I) are readily obtained by methods previously outlined.² The esters such as I have been found to undergo the Claisen condensation with oxalic acid esters to give the intermediates, II. As in the related reactions described previously,² it is possible to use N-acetylglycine esters in place of the N-formyl esters (I). Compounds II have not been isolated but have been allowed to react with thiocyanic acid in aqueous solution, and 1-substituted-2-mercapto-4,5-imidazoledicarboxylates, III, have been obtained in good yields. Oxidation of compounds III with

nitric acid² led to the 1-substituted-4,5-imidazoledicarboxylates, IV.

Several of the compounds had unexpected solubility properties. Whereas 1-methyl-4,5-imidazoledicarboxylic acid, like 4,5-imidazoledicarboxylic acid³ itself, was rather sparingly soluble in water; 2-mercapto-4,5-imidazoledicarboxylic acid and 1-phenyl-2-mercapto-4,5-imidazoledicarboxylic acid were soluble in water. They were precipitated when the solution was made strongly acidic with hydrochloric acid. Dimethyl 1-methyl-4,5-imidazoledicarboxylate was soluble in water, but dimethyl 1-phenyl-4,5-imidazoledicarboxylate and diethyl 4,5-imidazoledicarboxylate were water insoluble.

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Experimental

Diethyl 2-Mercapto-4,5-imidazoledicarboxylate.—In a dry, three-liter, three-necked flask provided with a stirrer, dropping funnel and reflux condenser were placed 700 ml. of anhydrous ether and 29 g. (1.25 g. atom) of clean sodium cut in small pieces. Absolute ethanol, 58 g. (1.25 moles), was added followed by 182 g. (1.25 moles) of ethyl oxalate added slowly so that the reaction did not become too vigorous. To the resulting solution was added from the dropping funnel with stirring 131 g. (1.0 mole) of N-formylglycine ethyl ester.³ A precipitate formed which turned to a dark red-brown gummy mass after standing. After the mixture had stood overnight 1 liter of ice water was added, and the mixture was agitated until the solid dissolved. The aqueous layer was separated, and to it was added 170 g. (1.75 moles) of potassium thiocyanate followed by 240 ml. (3.0 moles) of 12 N hydrochloric acid.

The resulting solution was warmed on the steam-bath under reduced pressure for a few minutes to remove dissolved ether, and then it was kept at about 40–60° for five or six hours during which time a heavy yellow crystalline precipitate separated. The mixture was cooled, and the product was collected on a filter and washed with a little ice-water. By evaporating the filtrate under reduced pressure to a volume of about 700 ml. an additional quantity of the product was obtained. The total yield of crude product was 165 g. (68%), and the yield from a similar experiment in which N-acetylglycine ethyl ester was used in place of N-formylglycine ethyl ester was 54%.

The diethyl 2-mercapto-4,5-imidazoledicarboxylate was appreciably soluble in water or alcohol, and recrystallization from either of these solvents resulted in large losses of material. A sample for analysis was recrystallized from water m.p. 204–205° dec. (uncor.).

Anal. Calcd. for C₉H₁₂N₂O₄S: C, 44.25; H, 4.95; N, 11.47. Found: C, 44.50; H, 4.93; N, 11.62.

2-Mercapto-4,5-imidazoledicarboxylic Acid.—A solution of 9 g. of crude diethyl 2-mercapto-4,5-imidazoledicarboxylate in 30 ml. of 6 N sodium hydroxide was heated on the steam-bath for one hour. The solution was clarified with carbon, filtered and the carbon washed with 20 ml. of water. The combined filtrate and washing was acidified with 17 ml. of 12 N hydrochloric acid. A canary-yellow, crystalline precipitate separated. The product was recrystallized by dissolving in 125 ml. of cold water and adding 100 ml. of 12 N hydrochloric acid. After standing, 5 g. (71% yield) of yellow crystalline powder separated; m.p. 251–252° dec. (uncor.).

Anal. Calcd. for C₈H₈N₂O₄S: N, 14.90. Found: N, 15.02.

Diethyl 4,5-Imidazoledicarboxylate.—Diethyl 2-mercapto-4,5-imidazoledicarboxylate was oxidized with dilute nitric acid in a manner previously described for the oxidation of similar 2-mercaptoimidazoles.² When the reaction was complete the solution was treated with excess sodium carbonate. An oil separated which quickly crystallized.

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