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Heats of Combustion and Formation of 4-Methylthiazole and 4-Cyanothiazole

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The heats of combustion of 4-methylthiazole and 4-cyanothiazole have been determined and used to obtain values of the standard enthalpies of formation, $\Delta Hf°$(liq) and $\Delta Hf°$(c), respectively, at 25.0°C. Enthalpies of vaporization and sublimation (respectively) have been measured and these data were used to calculate standard enthalpies of formation for the gaseous compounds, $\Delta Hf°$(g). The obtained data are

4-methylthiazole: + 16.32(liq) and + 26.80(g);
4-cyanothiazole: + 52.64(c) and + 70.31(g) kcal.mole^{-1}.

EXPERIMENTAL

Compounds. Samples of 4-methylthiazole and 4-cyanothiazole were supplied by Merck Sharp & Dohme (Division of Merck & Co., Inc.) through the courtesy of Dr. Thomas J. Webb.

4-Methylthiazole: The substance had been purified by fractional distillation and a check on the purity by means of precise gas chromatography had shown no detectable impurities. Density: $d_4^{25} = 1.1101_4$ g ml^{-1}. The substance was treated with calcium hydride under vacuum for about 30 h and then transferred into a receiver containing the evacuated glass ampoules that were to be used in the combustion experiments. The ampoules were filled completely and sealed immediately after being removed from the vacuum line.[1] Six combustion experiments were carried out, one of which was unsuccessful due to incomplete combustion.

4-Cyanothiazole: Purification of the substance had been achieved by repeated re-sublimation and precise gas chromatography showed no detectable impurities. Density: $d_4^{25} = 1.46_9$ g ml^{-1}. The substance was treated several times in a closed system with Linde's molecular sieves 5A to remove any trace of water, filtered through a built-in fritted glass filter and sublimed in high vacuum into an attached tube, which could be disconnected and opened in a dry box. The sample was melted and transferred into semispherical glass bulbs to be used in the combustion experiments. Six combustions were performed.

Combustion calorimetry; apparatus and procedure. The calorimetric system used was that described by Bjellerup.[2] The benzoic acid used in calibration experiments was National Bureau of Standards standard sample 39h. The paraffin oil used as auxiliary

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material was designated USBM-P3a (*cf.* Ref. 3). Calibration experiments were performed according to standard procedure, whereas in combustion experiments with the sulphur-containing substances the bomb was charged with 10 ml of water. All weighings have been reduced to mass and the molecular weights have been computed from the 1961 table of atomic weights.[4] For further details see Ref. 1.

Vaporization calorimetry. Enthalpies of vaporization and sublimation at 25.0°C have been measured in this laboratory using two different methods, one applicable in the vapour pressure range 100—1 mm Hg,[5] the second in the range $1-10^{-3}$ mm Hg.[6] The results have been included in Table 2.

RESULTS

The results are expressed in terms of the defined thermochemical calorie equal to 4.1840 abs.joules. All symbols used are those introduced by Hubbard, Scott and Waddington.[7] Auxiliary thermochemical data have been taken from Ref. 8.

Table 1. Heat of combustion experiments.

$-\Delta E_c^\circ/M(\text{Oil}) = 10984.7 \pm 1.1$ cal.g^{-1}
$-\Delta E_c^\circ/M$ (Fuse) $= 3971 \pm 4$ cal.g^{-1}
ε°(Calor) $= 5733.17 \pm 0.25$ cal.deg^{-1}
P^i(gas) = 30.0 atm. $t_h = 25.00$°C

m' g	m'' g	Δt deg	$\Delta E^f_{dec.}(HNO_3 + HNO_2)$ cal.	ΔE_Σ cal.	$-\Delta E_c^\circ/M$ cal.g^{-1}
4-Methylthiazole					
M = 99.155					
0.528883	0.096171	0.85007	9.08	3.15	7118.35
0.540176	0.099551	0.87085	10.06	3.18	7117.21
0.476979	0.145804	0.88054	12.98	3.52	7119.29
0.483741	0.140395	0.87939	10.25	3.50	7119.28
0.543817	0.101191	0.87863	8.75	3.22	7118.93
			$-\Delta E_c^\circ/M = 7118.61 \pm 0.39$ * cal.g^{-1}		
4-Cyanothiazole					
M = 110.138					
0.473213	0.201950	0.87643	14.69	4.47	5813.39
0.500255	0.188183	0.87750	14.39	4.40	5815.41
0.497608	0.189453	0.87726	15.39	4.39	5815.69
0.500135	0.187758	0.87679	15.21	4.39	5815.59
0.432466	0.224535	0.87801	13.80	4.60	5815.93
0.442072	0.219320	0.87775	13.77	4.58	5813.40
			$-\Delta E_c^\circ/M = 5814.90 \pm 0.48$ * cal.g^{-1}		

* The given uncertainties are the standard deviations of the means.

The results of the combustion experiments are summarized in Table 1. The ΔE_c° values refer to reactions in which all reactants and products are in their thermodynamic standard states at 25.0°C. (Sulphur as $H_2SO_4 \cdot 115\ H_2O$.) The final over-all precision of the ΔE_c° mean values was estimated by the method of Bjellerup;[9] (also see Ref. 1, p. 1868).

Table 2. Results and derived data at 25.0°C. In kcal.mole^{-1}.

4-Methylthiazole	$\Delta E_c°$(liq)	$= -705.85 \pm 0.14$ **
	$\Delta H_c°$(liq)	$= -707.18 \pm 0.14$ **
	$\Delta Hf°$(liq)	$= +16.32 \pm 0.14$ **
	ΔH_v	$= +10.48 \pm 0.05$ *
	$\Delta Hf°$(g)	$= +26.80 \pm 0.17$ **
4-Cyanothiazole	$\Delta E_c°$(c)	$= -640.44 \pm 0.19$ **
	$\Delta H_c°$(c)	$= -641.03 \pm 0.19$ **
	$\Delta Hf°$(c)	$= +52.64 \pm 0.19$ **
	$\Delta H_{subl.}$	$= +17.67 \pm 0.10$ *
	$\Delta Hf°$(g)	$= +70.31 \pm 0.28$ **

* The given uncertainties are the final over-all standard deviations.
** The given uncertainties are equal to twice the final over-all standard deviation.

Table 2 gives the standard energies, $\Delta E_c°$, and enthalpies, $\Delta H_c°$, of combustion together with enthalpies of vaporization, ΔH_v, and sublimation, ΔH_{subl}, and derived standard enthalpies of formation, $\Delta Hf°$, at 25.0°C.

THE RESONANCE ENERGY OF THE THIAZOLE RING

From the obtained result for methylthiazole and Cottrell's bond energy terms [10] the resonance energy of this compound is calculated to be 15 kcal.mole^{-1}. A methyl substitution leads to an apparent *** increase in resonance energy: toluene has 44 kcal. compared to 41 for benzene; 2-picoline 29 compared to 24 for pyridine, and 3-methylthiophene 25 whereas thiophene has 22 kcal.mole^{-1}. It seems therefore reasonable to conclude that the unsubstituted thiazole should have a resonance energy of approximately 10—12 kcal.mole^{-1}.

For 4-cyanothiazole the resonance energy becomes 10 kcal. if Cottrell's values are used with one exception: E(C≡N) is calculated from Evans and Skinner's [11] data on butyronitrile to be 215.1 kcal. instead of 212.6 as given by Cottrell. It is of interest to note that the resonance energy of benzonitrile [11] is calculated to be 41 kcal. or the same value as is obtained for benzene.

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*** In a simple bond energy scheme like Cottrell's the effect of a branched carbon chain is not accounted for. A structural similarity approach should give a different result: a comparison between the pairs cyclohexane-methylcyclohexane and benzene-toluene indicates no change in resonance energy within the limits of error.

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