

STANDARD MOLAR ENTHALPY OF FORMATION OF $\text{CH}_3(\text{CH}_3\text{SCH}_2)\text{SO}$, METHYL METHYLTHIOMETHYL SULFOXIDE*

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The standard molar enthalpy of formation of methyl methylthiomethyl sulfoxide, $\text{CH}_3(\text{CH}_3\text{SCH}_2)\text{SO}$, at $T=298.15$ K in the liquid state was determined to be -199.4 ± 1.5 kJ mol⁻¹ by means of oxygen rotating-bomb combustion calorimetry.

Keywords: combustion calorimetry, sulfoxide, thioether

Introduction

Mixing properties of methyl methylthiomethyl sulfoxide, $\text{CH}_3(\text{CH}_3\text{SCH}_2)\text{SO}$, have been studied well [1–3], because this material is the polar amphiphilic aprotic solvent, in which many substances are solved. From thermochemical point of view, the reactivity and stability of the characteristic S–CH₂–SO structure are interesting as well [4, 5]. In the present study, the standard enthalpy of formation of $\text{CH}_3(\text{CH}_3\text{SCH}_2)\text{SO}$ in the liquid-state was determined by means of oxygen rotating-bomb combustion calorimetry.

Experimental

Purification of $\text{CH}_3(\text{CH}_3\text{SCH}_2)\text{SO}$ (Nippon Soda, Co.) was described elsewhere [1]. The water content of the sample was determined to be $4\text{--}5 \cdot 10^{-4}$ in mass fraction by Karl–Fischer titration. Therefore, the sample mass of the combustion calorimetry was corrected by multiplying the fraction, 0.9995. No signal of organic impurities was observed in ¹H N.M.R. Thianthrene (NIST, SRM 1656, Calorimetric Standard) was dried by heating under reduced pressure.

A rotating-bomb calorimeter described elsewhere was used [6, 7]. The calorimeter was calibrated by burning thermochemical standard benzoic acid (NIST, SRM 39i) in oxygen under certificated condition. The mean and standard deviation of the mean of the energy equivalent was 15360.4 ± 0.7 J K⁻¹ (six experiments). Liquid sample was filled in a polyethylene ampoule of 1 mL in volume, as similar to the previous study on dimethylsulfoxide [7]. The standard massic energy of combustion of the ampoule was de-

termined to be $-(46413.4 \pm 7.4)$ J g⁻¹ (six experiments), where the uncertainty is the standard deviation of the mean. Six combustion experiments of $\text{CH}_3(\text{CH}_3\text{SCH}_2)\text{SO}$ was carried out under the pressure of the gas mixture of oxygen (2.96 MPa) and nitrogen (0.08 MPa).

After the calorimetry, the combustion products were analyzed. The bomb gas was tested for carbon monoxide with a commercial CO detection tube (Gastec). Nitric acid in the bomb solution was determined by means of ion-chromatography [6]. Reduction to standard state at $P=0.1$ MPa was carried out following literature [8] and with the thermochemical values compiled in literature [9]. The recent values of $\Delta_{\text{decomp}}U_{\text{m}}(\text{HNO}_3)$ and $\Delta_{\text{f}}H^\circ(\text{H}_2\text{SO}_4, \text{aq})$ were used [10]. In order to confirm the whole procedure, the energy of combustion of thianthrene was determined to be $-(33464 \pm 12)$ J g⁻¹ (four experiments), where the combustion reaction was referred to $\text{C}_{12}\text{H}_8\text{S}_2(\text{cr}) + 17\text{O}_2(\text{g}) + 228\text{H}_2\text{O}(\text{l}) = 12\text{CO}_2(\text{g}) + 2\text{H}_2\text{SO}_4 \cdot 115\text{H}_2\text{O}(\text{sln})$. The value agrees well with the recommended $-(33468 \pm 4)$ J g⁻¹ [11].

Results and discussion

Auxiliary quantities in Table 1 were used for the calculation of $\Delta_{\text{c}}u^\circ$ of the materials. The results of the combustion calorimetry of $\text{CH}_3(\text{CH}_3\text{SCH}_2)\text{SO}$ are summarized in Table 2. Molar values are reported in terms of $M=124.228$ g mol⁻¹. $\Delta_{\text{c}}U_{\text{m}}^\circ(\text{C}_3\text{H}_8\text{S}_2\text{O}, \text{l})$ refers to the ideal combustion reaction: $\text{C}_3\text{H}_8\text{S}_2\text{O}(\text{l}) + 15/2\text{O}_2(\text{g}) + 228\text{H}_2\text{O}(\text{l}) = 3\text{CO}_2(\text{g}) + 2\text{H}_2\text{SO}_4 \cdot 115\text{H}_2\text{O}(\text{sln})$. The final overall uncertainty of $\Delta_{\text{c}}u^\circ(\text{C}_3\text{H}_8\text{S}_2\text{O}(\text{l}))$ was evaluated to be 12 J g⁻¹, as twice the combined standard deviation

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Table 1 Auxiliary quantities for the calculation of standard energies of combustion^a

Materials	formula	$\rho/\text{g cm}^{-3}$	$C_p/\text{J K}^{-1} \text{g}^{-1}$	$(\partial U/\partial P)_T/\text{J g}^{-1} \text{MPa}^{-1}$
methyl sulfoxide	$\text{C}_3\text{H}_8\text{S}_2\text{O}$	1.22 ^b	1.77 ^c	(-0.25)
thianthrene	$\text{C}_{12}\text{H}_8\text{S}_2$	1.44 ^d	1.50 ^d	-0.20 ^d
benzoic acid	$\text{C}_7\text{H}_6\text{O}_2$	1.32	1.21	-0.052
polyethylene	$(\text{CH}_2)_n$	0.927 ^e	2.40 ^f	(-0.093)
cotton fuse	$\text{CH}_{1.86}\text{O}_{0.93}$	1.5	1.70	-0.29

^avalues in parentheses are estimated; ^bfrom [1]; ^cdetermined by DSC measurement; ^dfrom [12]; ^efrom [7]; ^ffrom [13]

Table 2 Summary of combustion calorimetry of methyl methylthiomethyl sulfoxide^a

$m(\text{compd})/\text{g}$	0.48625	0.44792	0.48735	0.48423	0.47204	0.49108
$m(\text{polyethylene})/\text{g}$	0.35733	0.35149	0.35770	0.35129	0.35851	0.35799
$m(\text{fuse})/\text{g}$	0.00213	0.00195	0.00218	0.00205	0.00156	0.00185
$m_c^i(\text{H}_2\text{O})/\text{g}$	9.983	9.983	9.983	9.983	9.983	9.983
$p^i(\text{gas})/\text{MPa}$	3.040	3.040	3.040	3.040	3.040	3.040
$(T_i/\text{K})-273.15$	23.1801	23.1799	23.1805	23.1808	23.1805	23.1803
$(T_f/\text{K})-273.15$	25.1254	25.0447	25.1290	25.1056	25.1054	25.1351
$\Delta T_{\text{corr}}/\text{K}$	0.02147	0.02479	0.02090	0.02239	0.02218	0.02051
$\Delta T_{\text{ad}}/\text{K}$	1.92383	1.83999	1.92758	1.90243	1.90270	1.93436
$n^f(\text{HNO}_3)/\text{mmol}$	0.7349	0.7709	0.9061	0.8087	0.8614	0.8144
$\Delta U_{\text{ign}}/\text{J}$	4.309	4.309	4.309	4.309	4.309	4.309
$\Delta U_{\Sigma}/\text{J}$	7.052	7.893	6.924	6.857	7.397	6.881
$\Delta U_{\text{decomp}}(\text{HNO}_3)/\text{J}$	43.871	46.023	54.096	48.281	51.426	48.621
$-\Delta U_{\text{dil}}(\text{H}_2\text{SO}_4)/\text{J}$	4.076	3.089	4.106	4.030	3.704	4.204
$\epsilon^i(\text{cont})/\text{J K}^{-1}$	56.585	56.506	56.588	56.567	56.562	56.595
$\epsilon^f(\text{cont})/\text{J K}^{-1}$	57.388	57.285	57.375	57.345	57.355	57.391
$-\Delta U_{\text{IBP}}/\text{J}$	29657.0	28364.2	29714.3	29327.0	29331.0	29819.3
$-\Delta_c u^\circ/\text{J g}^{-1}$	26706.3	26710.7	26706.9	26709.3	26707.1	26711.9
$-\Delta_c U^\circ/\text{kJ mol}^{-1}$	3317.67	3318.21	3317.75	3318.04	3317.77	3318.37

^aThe symbols are similar to those in [8]

of the mean, by using the equation of the error propagation [14]. $\Delta_f H_m^\circ(\text{C}_3\text{H}_8\text{S}_2\text{O}(l))$ was derived to be $-(199.4 \pm 1.5) \text{ kJ mol}^{-1}$ by using the current values of $\Delta_f H_m^\circ(\text{H}_2\text{O}, l) = -(285.830 \pm 0.042) \text{ kJ mol}^{-1}$, $\Delta_f H_m^\circ(\text{CO}_2, g) = -(393.51 \pm 0.13) \text{ kJ mol}^{-1}$, and $\Delta_f H_m^\circ(\text{H}_2\text{SO}_4 \cdot 115\text{H}_2\text{O}) = -888.146 \text{ kJ mol}^{-1}$ [9].

$\text{CH}_3(\text{CH}_3\text{SCH}_2)\text{SO}$ has been known to be a good reagent, which displaces a halogen atom with a CHO group in alkyl halides [4]. On the basis of the present result, the enthalpy changes of an ideal reaction, $\text{RI}(g) + \text{CH}_3(\text{CH}_3\text{SCH}_2)\text{SO}(l) = \text{RCHO}(l) + \text{CH}_3\text{SSCH}_3(l) + \text{HI}(g)$, were evaluated to be -43.2 , -44.5 and $-45.6 \text{ kJ mol}^{-1}$ for $R = \text{CH}_3$, $R = \text{C}_2\text{H}_5$ and $R = 1-\text{C}_3\text{H}_7$, respectively.

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