

Heats of Combustion

2,4,6-Trimethyl-3,5-dioxaheptane and
6-Ethyl-5,7-dioxaundecaneKALEVI PIHLAJA and TAUNO
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The heats of combustion of several cyclic and acyclic acetals were recently determined in our laboratory.¹⁻⁶ In order to calculate the heats of formation of alcohols and ethers a bond-bond interaction scheme based on experimental data of several authors has been derived.^{7a} However, to extend this scheme to acetals,^{7b} for which the preliminary results were promising,^{7a} more experimental data were needed. This paper reports the heats of formation of 2,4,6-trimethyl-3,5-dioxaheptane, $\text{CH}_3\text{CH}(\text{OCH}(\text{CH}_3)_2)_2$, and 6-ethyl-5,7-dioxaundecane, $\text{CH}_3\text{CH}_2\text{CH}(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2$, determined by combustion calorimetry.

2,4,6-Trimethyl-3,5-dioxaheptane (I) and 6-ethyl-5,7-dioxaundecane (II) were kindly donated by Dr. Ilmari Jansson. They were further purified by careful distillation from calcium hydride and then several times from sodium. The purities were checked on a Shandon Universal gas chromatograph fitted with a 6-foot-long copper tube containing Carbowax 1500 on Chromosorb W. As no impurities were observed, the sensitivity of the apparatus was gradually increased and the purification was continued until no impurities were found at a hundredfold sensitivity when using the same sample volume. I boiled at 128.0°C and had a n_D^{20} of 1.3898 and a d_4^{20} of 0.8123. II boiled at 204°C and had a n_D^{20} of 1.4118 and a d_4^{20} of 0.8347.

The samples were sealed in thin gelatin capsules and burned in oxygen in an adiabatic bomb calorimeter No. 1221 manufactured by Parr Instruments Co., Illinois, U.S.A., as described earlier.^{3,5} The energy equivalent of the standard calorimeter system, $e^o(\text{calor})$, was determined by burning Parr standard benzoic acid.³

The average energy of combustion of the gelatin capsules was determined by measuring the heats of combustion of six random samples (5 capsules per sample) chosen from a lot of 100 capsules ($-\Delta E_c^o/M = 4586.66 \text{ cal/g}$). The other corrections are stated in Ref. 3.

Heats of combustion, $-\Delta H_c^o(l)$, were calculated on an IBM 1130 computer at the Computer Center, University of Turku, Turku.⁵ The heats of vaporization were calculated using the equation proposed by Klages⁸ as improved by Wadsö.⁹ It is worth mentioning that this equation does not yield very satisfactory values for the heats of vaporization of compounds boiling above 170°C.⁹ Hence the value derived for the heat of vaporization of II is somewhat tentative. The results of the combustion experiments are shown in Tables 1 and 2.

In order to test the results the heats of formation of I and II were calculated by using the group increments reported by Kankare and one of us (KP).⁷ The values, -125.81 and $-133.74 \text{ kcal/mole}$, were derived for the heats of formation of I and II, respectively, taking into account the minimum number of different interactions.^{7,10} Experimentally, the values -125.70 and $-132.10 \text{ kcal/mole}$ were obtained. In the case of 2,4,6-trimethyl-3,5-dioxaheptane (I), both values are in fairly good agreement, but in the case of 6-ethyl-5,7-dioxaundecane (II), the difference is about 1.6 kcal/mole.

Skuratov *et al.*¹¹ have reported the value, $-1412.4 \text{ kcal/mole}$, for the heat of combustion of gaseous 5,7-dioxaundecane, $\text{CH}_2(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_3)_2$, (III) at 20°C, which gives the value, -117.5 kcal/mole , for the heat of formation when corrected to 25°C. The calculated value^{7,10} for this compound is -119.2 kcal/mole , which again differs about 1.7 kcal/mole from the experimental value.

The similar differences between the observed and calculated values of II and III may be due either to experimental error or to additional increments in acetals having long alkoxy chains. More work is needed to decide between these possibilities.^{7b}

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- Pihlaja, K. and Heikkilä, J. *Acta Chem. Scand.* **21** (1967) 2390.
- Pihlaja, K. and Heikkilä, J. *Acta Chem. Scand.* **21** (1965) 2430.
- Pihlaja, K. and Luoma, S. *Acta Chem. Scand.* **22** (1968) 2401.
- Pihlaja, K. and Heikkilä, J. *Acta Chem. Scand.* **22** (1968) 2731.
- Pihlaja, K. and Heikkilä, J. *Acta Chem. Scand.* **23** (1969) 1053.

Table 1. Combustion data for 2,4,6-trimethyl-3,5-dioxaheptane (I).

$t_h = t_i = 25.00^\circ\text{C}$
 $e^\circ(\text{calor}) = 1360.08 \pm 0.19 \text{ cal/}^\circ\text{F}$
 $M = 146.232$

m g	m'_{gel} g	Δt °F	ΔE_{ign} cal	ΔE_{dec}^f (HNO ₃) cal	ΔE_{dec}^f (H ₂ SO ₄) cal	ΔE_{gel} cal	$\Delta E\Sigma$ cal	$e^f(\text{cont})$ cal/°F	$-\Delta U_c^\circ/M$ cal/g
0.630013	0.121845	4.319	17.00	12.35	0.96	558.86	2.05	2.39	8401.90
0.628676	0.127395	4.327	12.74	12.37	1.00	584.32	2.06	2.39	8403.20
0.653640	0.119245	4.457	16.85	12.56	1.94	546.94	2.12	2.40	8403.99
0.618763	0.126905	4.269	18.56	12.68	1.00	582.07	2.02	2.38	8403.91
0.624706	0.126705	4.309	20.36	10.84	1.00	581.15	2.07	2.39	8412.72
0.608054	0.124235	4.183	8.40	11.81	0.98	569.82	1.99	2.38	8397.52
0.624090	0.131925	4.315	7.99	12.51	1.04	605.10	2.06	2.39	8412.86
0.629277	0.120485	4.314	13.43	12.36	0.95	552.62	2.04	2.39	8416.50
0.602046	0.122015	4.143	15.39	12.17	0.96	559.64	1.95	2.37	8395.53

^a Standard deviation of the mean.

^b Over-all standard deviation.³

^c Twice the over-all standard deviation.³

$-\Delta U_c^\circ/M = 8405.34 \pm 2.40^a \text{ cal/g}$

$-\Delta U_c^\circ(l) = 1229.13 \pm 0.42^b \text{ kcal/mole}$

$-\Delta H_c^\circ(l) = 1231.20 \pm 0.84^c \text{ kcal/mole}$

$-\Delta H_f^\circ(l) = 136.05 \pm 0.84^c \text{ kcal/mole}$

$-\Delta H_f^\circ(g) = 125.70 \pm 1.14 \text{ kcal/mole}$

Table 2. Combustion data for 6-ethyl-5,7-dioxaundecane (II).

$t_h = t_i = 25.00^\circ\text{C}$
 $e^\circ(\text{calor}) = 1360.08 \pm 0.19 \text{ cal/}^\circ\text{F}$
 $M = 188.313$

m g	m'_{gel} g	Δt °F	ΔE_{ign} cal	ΔE_{dec}^f (HNO ₃) cal	ΔE_{dec}^f (H ₂ SO ₄) cal	ΔE_{gel} cal	$\Delta E\Sigma$ cal	$e^f(\text{cont})$ cal/°F	$-\Delta U_c^\circ/M$ cal/g
0.631675	0.123480	4.639	15.74	11.82	0.97	566.36	2.16	2.41	9060.90
0.631510	0.121400	4.622	3.00	13.16	0.95	556.82	2.13	2.40	9059.75
0.649563	0.125270	4.762	17.40	13.25	0.98	574.57	2.20	2.42	9051.97
0.654269	0.124225	4.795	17.09	13.56	0.98	569.78	2.22	2.42	9062.87
0.642234	0.128290	4.731	21.96	13.73	1.01	588.42	2.19	2.41	9059.98
0.632847	0.118240	4.626	12.86	13.00	0.93	542.33	2.12	2.40	9056.84
0.637748	0.124670	4.687	19.62	12.97	0.98	571.82	2.16	2.41	9060.70

^a Standard deviation of the mean.

^b Over-all standard deviation.³

^c Twice the over-all standard deviation.³

$-\Delta U_c^\circ/M = 9059.00 \pm 1.35^a \text{ cal/g}$

$-\Delta U_c^\circ(l) = 1705.93 \pm 0.40^b \text{ kcal/mole}$

$-\Delta H_c^\circ(l) = 1708.89 \pm 0.79^c \text{ kcal/mole}$

$-\Delta H_f^\circ(l) = 145.46 \pm 0.79^c \text{ kcal/mole}$

$-\Delta H_f^\circ(g) = 132.10 \pm 1.60 \text{ kcal/mole}$

- Pihlaja, K. and Heikkilä, J. *Suomen Kemistilehti* **B 42** (1969) 338.
- (a) Pihlaja, K. and Kankare, J. *Acta Chem. Scand.* **23** (1969) 1745; (b) Pihlaja, K. *Unpublished data.*
- Klages, P. *Chem. Ber.* **82** (1949) 358.
- Wadsö, I. *Acta Chem. Scand.* **20** (1966) 544.

- Eliel, E. L. *Svensk Kem. Tidsskr.* **89** (1969) 22. *Personal communication.*
- Skuratov, S., Strepikheev, A., Shtekher, S. and Volokhina, A. *Dokl. Akad. Nauk. SSSR* **117** (1957) 263.

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