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ENERGETICS OF INTER- AND INTRAMOLECULAR BONDS IN ALKANEDIOLS. IV. THE THERMOCHEMICAL STUDY OF 1,2-ALKANEDIOLS AT 298.15 K

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ABSTRACT

The 1,2-alkanediols, $HO-CH_2-CHOH-(CH_2)_n-H$ ($1 \leqslant n \leqslant 4$) have been investigated by combustion and vaporisation calorimetry. The standard molar enthalpies of vaporisation, of combustion and of formation in the liquid state at 298.15 K, as well as the standard molar enthalpies of formation in the gas phase and of atomisation at 298.15 K, were determined. The enthalpies of an intermolecular hydrogen bond (about 22.5 kJ mol^{-1}) and of intramolecular C–C (346.7 kJ mol^{-1}) and C–OH (827.0 kJ mol^{-1}) bonds were derived and discussed in comparison with the ω-isomers. The stabilisation of the 1,2-alkanediols in comparison with the ω-isomers is probably due to the interaction between adjacent hydroxyl groups.

INTRODUCTION

In previous papers [1–5], we have reported the thermochemical properties of the ω-alkanediols, $HO-(CH_2)_n-OH$ ($2 \leqslant n \leqslant 10$), and the derived enthalpies of inter- and intramolecular bonds in these compounds. In ω-alkanediols, with long carbon chains, the two hydroxyl groups are separated by a number of methylene groups and can be supposed to have no interaction, except in the case of 1,2-ethanediol and probably 1,3-propanediol. In 1,2-alkanediols, $HO-CH_2-CHOH-(CH_2)_n-H$, on the contrary, the two hydroxyl groups are situated in adjacent positions; there is certainly an interaction between them.

Thermochemical investigations on 1,2-alkanediols are practically absent from the literature: in 1937, Moureu and Dodé [6] investigated enthalpies of combustion of 1,2-propanediol and 1,2-butanediol; and Gardner and Hussain [7] reported enthalpies of combustion and vaporisation of 1,2-propane-

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diol in 1972. In order to verify the influence of the relative positions of the hydroxyl groups on the thermochemical properties, we have investigated the 1,2-isomers ($1 \leqslant n \leqslant 4$) by combustion and vaporisation calorimetry of small amounts of the substances. The energetics of the inter- and intramolecular bonds in α-alkanediols are reported below and are compared with the corresponding ω-isomers.

EXPERIMENTAL

Materials

Commercial 1,2-propanediol (99 + %, Gold Label, Aldrich), 1,2-pentanediol (95%, Aldrich) and DL-1,2-hexanediol (98 + %, Aldrich) were used. 1,2-Pentanediol and DL-1,2-hexanediol were further purified by fractional distillation over a rotating-band column with 30 theoretical plates (Büchi, Dr Abegg-type).

Combustion calorimetry

The enthalpies of combustion were measured with a CRMT calorimeter equipped with a microbomb. The microbomb was filled with pure oxygen (mole fraction purity 0.99995, N_2 content $< 10^{-5}$, L'air liquide N45) under a pressure of 3.04 MPa. The apparatus and the method of operation have been previously described [4]. The specific energy of combustion of cotton thread was taken as $-(16\,399 \pm 23)$ J g^{-1} [8], and that of the polyethene tube as $-(46\,369 \pm 8)$ J g^{-1} [4]. The calorimeter was calibrated with benzoic acid standard sample 39i of the National Bureau of Standards ($\Delta_c u^{\ominus}$(s,298.15 K) $= -(26\,414 \pm 3)$ J g^{-1}). The energy equivalent of the calorimeter U_{calor} (298.15 K) $=$ (15.992 ± 0.004) J V^{-1} s^{-1} [4]. The buoyancy and Washburn corrections were performed by computer programs. The relevant physical properties of the investigated substances are summarised in Table 1. The results are based on the 1987 atomic masses [9].

Vaporisation calorimetry

The enthalpies of vaporisation of the substances were determined at 298.15 K with a Tian–Calvet calorimeter equipped with a Knudsen effusion cell. The apparatus and the method of operation have been previously reported [12]; the calorimeter is electrically calibrated. 1,2-Propanediol was investigated with an effusion orifice diameter of 0.2 mm, 1,2-pentanediol and DL-1,2-hexanediol with an effusion orifice diameter of 0.5 mm.

The saturated vapour pressures of the 1,2-alkanediols can be calculated using relation (1), provided Knudsen effusion conditions are fulfilled during

TABLE 1

Molar masses M and densities ρ

Substance	Formula	M (g mol^{-1})	ρ (g cm^{-3})
1,2-Propanediol	$HOCH_2CHOHCH_3$	76.0953	1.036 [a]
1,2-Pentanediol	$HOCH_2CHOH(CH_2)_3H$	104.1491	0.971 [a]
DL-1,2-Hexanediol	$HOCH_2CHOH(CH_2)_4H$	118.1760	0.951 [a]
Polyethene	$(CH_2)_n$	14.0269	0.92 [b]
Cotton	$CH_{1.833}O_{0.828}$	27.1061	1.5 [c]

[a] Indicated by Aldrich.
[b] Ref. 10.
[c] Ref. 11.

the experiments

$$P \approx \Delta P = dm/dt(1/aF)(2\pi RT/M)^{1/2} \tag{1}$$

where ΔP is the pressure difference between the inside and outside of the effusion cell, nearly equal to the saturated vapour pressure P of the substance if P is not too small, dm/dt is the effusion rate, a is the effusion orifice area, F is the Clausing factor, R is the ideal gas constant, T is the absolute temperature and M is the molar mass of the substance.

RESULTS

The molar enthalpies of vaporisation and the saturated vapour pressures at 298.15K of the investigated 1,2-alkanediols are summarised in Table 2. The $\Delta_{vap}H_m$ (298.15 K) is assumed to be identical with $_{vap}H_m^\ominus$ (298.15 K) because of the relatively low vapour pressures of the 1,2-alkanediols. The results of the combustion experiments at 298.15 K which correspond to the general reaction

$$\begin{aligned}&HO{-}CH_2{-}CHOH{-}(CH_2)_n{-}H(l) + 1/2(3n+5)O_2(g)\\&\quad = (n+2)CO_2(g) + (n+3)H_2O(l)\end{aligned} \tag{2}$$

are given in Table 3. The standard molar enthalpies of formation in the condensed phase were calculated using $\Delta_f H_m^\ominus$ (l, 298.15 K) = $-(285.830 \pm 0.042)$ kJ mol^{-1} for H_2O (l) and $\Delta_f H_m^\ominus$ (g, 298,15 K) = $-(393.51 \pm 0.13)$ kJ mol^{-1} for CO_2 (g) [13]. In all cases the experimental uncertainties represent standard deviations of the mean.

The standard molar enthalpies of formation in the gas phase at 298.15 K were calculated with the standard molar enthalpies of vaporisation. The standard molar enthalpies of atomisation, which are the enthalpies of the dissociation reaction in the ideal gas state of a molecule into atoms, at

TABLE 2

Molar enthalpies of vaporisation of the 1,2-alkanediols at 298.15 K

Substance	$m \times 10^6$ (kg)	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}^{\ominus}$ (298.15 K) (kJ mol^{-1})	ΔP (298.15 K) (Torr)
1,2-Propanediol	21.0045	70.80	0.8×10^{-1}
	22.2072	71.31	2.1×10^{-1}
	20.8405	71.14	1.4×10^{-1}
	17.4748	71.34	0.7×10^{-1}
	27.7718	71.28	1.1×10^{-1}
	29.6142	71.46	1.2×10^{-1}
		71.2 ± 0.1	1.5×10^{-1}
1,2-Pentanediol	13.5670	81.99	0.21×10^{-1}
	23.4906	81.97	0.18×10^{-1}
	15.1680	81.33	0.34×10^{-1}
	20.7606	81.34	0.33×10^{-1}
	28.7003	81.69	0.33×10^{-1}
	26.6916	81.42	0.29×10^{-1}
		81.6 ± 0.2	0.3×10^{-1}
DL-1,2-Hexanediol	11.6316	85.93	–
	19.7577	86.99	11.0×10^{-3}
	20.5964	87.09	9.6×10^{-3}
	19.5828	86.87	7.8×10^{-3}
	21.9128	86.83	–
	19.1126	88.12	9.7×10^{-3}
	16.9547	87.68	11.0×10^{-3}
	21.0086	86.40	9.9×10^{-3}
		87.0 ± 0.3	10×10^{-3}

298.15 K were calculated using the standard molar enthalpies of formation of gaseous carbon, hydrogen and oxygen [13] (Table 4).

DISCUSSION

Enthalpies of vaporisation

The molar enthalpies of vaporisation may be expressed by a linear relation of n

$$\Delta_{\mathrm{vap}}H_{\mathrm{m}}^{\ominus}(298.15\ \mathrm{K})/(\mathrm{kJ\ mol^{-1}}) = 65.9 + 5.26n \qquad (3)$$

The methylene group increment is lower here than in the ω-isomers (7.0 kJ mol^{-1} [1]). In accordance with identical previous observations [14], this may be due to the fact that in the ω-isomers the electron-attracting hydroxyl groups are situated at both ends of the carbon chain. The extrapolated value

TABLE 3

Combustion experiments for 1,2-alkanediols at 298.15 K

m (sample) (mg)	m (polyethene) (mg)	m (cotton) (mg)	$-\Delta U$ [a] (J)	$-W_1$ [b] (J)	W_2 [c] (J)	$-\Delta_c U_m^\ominus$ (l, 298.15 K) (kJ mol^{-1})
1,2-Propanediol						
7.0193	10.2712	1.964	648.860	479.487	0.404	1831.78
6.0149	10.4914	1.858	633.570	489.523	0.393	1817.38
6.7148	10.5975	1.184	652.938	493.338	0.407	1804.07
7.0922	10.7468	1.652	670.647	501.028	0.418	1815.42
6.9042	10.9947	1.048	678.448	511.532	0.421	1835.04
7.1572	11.1581	1.751	693.114	520.262	0.431	1833.17
5.9218	10.7948	1.780	646.278	503.464	0.399	1830.04
6.4483	10.3777	1.158	637.133	483.103	0.396	1813.02
6.5111	9.9465	1.845	618.981	464.236	0.386	1804.01
$\Delta_c U_m^\ominus$ (l, 298.15 K) $= -(1820.4 \pm 4.1)$ kJ mol^{-1} $\Delta_c H_m^\ominus$ (l, 298.15 K) $= -(1822.9 \pm 4.1)$ kJ mol^{-1} $\Delta_f H_m^\ominus$ (l, 298.15 K) $= -(501.0 \pm 4.1)$ kJ mol^{-1}						
1,2-Pentanediol						
5.8940	9.6975	1.319	630.199	451.827	0.383	3145.14
6.1782	9.6616	1.315	637.597	450.156	0.387	3153.26
6.9138	11.4660	1.153	740.931	533.558	0.453	3117.03
6.4601	11.0134	1.413	706.478	512.998	0.431	3112.31
6.8711	11.3446	1.871	738.291	529.107	0.450	3163.90
6.7884	11.2543	1.742	727.647	524.708	0.446	3106.70
6.3904	10.2166	1.548	669.363	476.256	0.408	3140.56
6.8497	11.1028	2.216	725.371	518.461	0.443	3139.32
6.7330	10.9126	2.268	710.550	509.726	0.436	3099.69
$\Delta_c U_m^\ominus$ (l, 298.15 K) $= -(3130.9 \pm 7.5)$ kJ mol^{-1} $\Delta_c H_m^\ominus$ (l, 298.15 K) $= -(3135.8 \pm 7.5)$ kJ mol^{-1} $\Delta_f H_m^\ominus$ (l, 298.15 K) $= -(546.7 \pm 7.5)$ kJ mol^{-1}						
DL-1,2-Hexanediol						
6.4296	11.2931	1.462	730.621	526.048	0.444	3751.88
6.3620	10.4359	2.066	691.360	487.291	0.420	3782.85
6.0884	9.8872	1.551	657.162	461.004	0.398	3799.73
5.4620	10.1963	1.434	651.748	475.144	0.393	3812.51
7.1943	11.3634	1.029	758.985	528.597	0.462	3776.85
6.8398	11.5760	1.426	738.156	519.706	0.449	3766.57
6.1383	10.7630	1.654	698.725	501.783	0.424	3783.43
6.1416	10.7228	1.743	697.312	500.065	0.423	3787.29
6.4576	10.0733	2.011	675.490	470.387	0.412	3745.91
$\Delta_c U_m^\ominus$ (l, 298.15 K) $= -(3778.6 \pm 7.1)$ kJ mol^{-1} $\Delta_c H_m^\ominus$ (l, 298.15 K) $= -(3784.8 \pm 7.1)$ kJ mol^{-1} $\Delta_f H_m^\ominus$ (l, 298.15 K) $= -(577.1 \pm 7.1)$ kJ mol^{-1}						

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[a] ΔU is the energy variation of the bomb and its contents.

[b] W_1 is the energy of combustion of cotton thread + polyethene.

[c] W_2 are corrections to standard state.

TABLE 4

Thermodynamic properties in kJ mol^{-1} of 1,2-alkanediols ($1 \leqslant n \leqslant 4$) at 298.15 K

	1,2-Propanediol	1,2-Pentanediol	DL-1,2-Hexanediol
$-\Delta_c H_m^\ominus$ (l, 298.15 K)	1822.9 ± 4.1	3135.8 ± 7.5	3784.8 ± 7.1
$-\Delta_f H_m^\ominus$ (l, 298.15 K)	501.0 ± 4.1	546.7 ± 7.5	577.1 ± 7.1
$\Delta_{vap} H_m^\ominus$ (298.15 K)	71.2 ± 0.1	81.6 ± 0.2	87.0 ± 0.3
$-\Delta_f H_m^\ominus$ (g, 298.15 K)	429.8 ± 4.1	465.1 ± 7.5	490.1 ± 7.1
$\Delta_{a,exp} H_m^\ominus$ (298.15 K)	4822.1 ± 4.2	7162.8 ± 7.6	8340.4 ± 7.2

for $n = 0$, which corresponds to the enthalpy of vaporisation of 1,2-ethanediol, is in good agreement with the experimental value (65.6 ± 0.3 kJ mol^{-1}) previously found [1]. The saturated vapor pressures of the 1,2-alkanediols are generally higher and their enthalpies of vaporisation are always slightly lower than those of the corresponding ω-isomers. This is probably related to the existence of an intramolecular hydrogen bond in the 1,2-isomers, weakening the intermolecular cohesion. The difference seems to increase with increasing number of methylene groups. As mentioned in the introduction, an intramolecular interaction between the hydroxyl groups probably exists in 1,3-propanediol, the difference between 1,2- and ω-isomers is thus rather small (about 1 kJ mol^{-1}). On the contrary, the intramolecular interaction should be absent in 1,5-pentanediol, the difference with the intramolecularly hydrogen-bonded 1,2-pentanediol clearly being higher (about 5 kJ mol^{-1}).

As previously shown [1], we may calculate the energy contribution of the intermolecular hydrogen bonds (Table 5) by comparison of the enthalpies of vaporisation of the 1,2-alkanediols with those of isoelectronic n-alkanes [15] (representing the energetical contribution of London-type interactions). We see that the mean difference amounts to about 46 kJ mol^{-1}. This difference includes the energetical contribution of dipole–dipole interactions (Keesom), dipole-induced dipole interactions (Debye) and intermolecular hydrogen bonds between the 1,2-alkanediols molecules. When we assume, as in the

TABLE 5

Comparison of the molar enthalpies of vaporisation of 1,2-alkanediols with those of isoelectronic n-alkanes

Substance	$\Delta_{vap} H_m^\ominus$ (298.15 K) [a] (kJ mol^{-1})					
$n =$	0	1	2	3	4	
$HO\text{-}CH_2\text{-}CH(OH)\text{-}(CH_2)_n\text{-}H$	65.6	71.2	(76.4)	81.6	87.0	
$H_3C\text{-}CH_2\text{-}CH(CH_3)\text{-}(CH_2)_n\text{-}H$	21.0	25.2	30.5	35.2	39.9	
Difference	44.6	46.0	45.9	46.4	47.1	mean value: 46

[a] The value in parentheses is calculated from eqn. (3).

ω-isomers, that about 1 kJ mol^{-1} is due to dipolar interactions, the contribution due to hydrogen bonds amounts to about 45 kJ mol^{-1}. If it is assumed that in the case of 1,2-alkanediols, two intermolecular hydrogen bounds could be formed per molecule, we find that the enthalpy of an intermolecular hydrogen bond is slightly lower in 1,2-alkanediols (22.5 kJ mol^{-1}) than in the ω-isomers (23 kJ mol^{-1} [1]).

Enthalpies of combustion and formation

The standard molar enthalpies of combustion and of formation in the liquid phase at 298.15 K of the 1,2-alkanediols can be expressed as linear relations of n

$$\Delta_c H_m^{\ominus}(\mathrm{l}, 298.15\ \mathrm{K}) = -1169.6 - 654.3n \qquad (4)$$

$$\Delta_f H_m^{\ominus}(\mathrm{l}, 298.15\ \mathrm{K}) = -474.9 - 25.0n \qquad (5)$$

The standard molar enthalpies of formation in the gas phase at 298.15 K can also be written as a linear relation of n

$$\Delta_f H_m^{\ominus}(\mathrm{g}, 298.15\ \mathrm{K}) = -409.0 - 19.75n \qquad (6)$$

The methylene group increment in this equation is clearly higher than in the corresponding ω-isomers (16.2 kJ mol^{-1} [3]), but lower than in other aliphatic compound series (mean value, 20.75 ± 0.15 kJ mol^{-1} [16]). The difference between the enthalpies of formation in the gas phase of 1,2- and ω-alkanediols, which represents the enthalpy of isomerisation, amounts to about 25 kJ mol^{-1}.

A linear relation can also be proposed for the standard molar enthalpies of atomisation:

$$\Delta_{a,\exp} H_m^{\ominus}(298.15\ \mathrm{K}) = 3648.6 + 1172.4n \qquad (7)$$

As these enthalpies are the sum of the intramolecular bond enthalpies, we can write

$$\Delta_{a,\exp} H_m^{\ominus}(298.15\ \mathrm{K}) = 2H(\mathrm{C{-}OH}) + 4H(\mathrm{C{-}H}) + H(\mathrm{C{-}C})_{\mathrm{diol}} + n(H(\mathrm{C{-}C}) + 2H(\mathrm{C{-}H})) \qquad (8)$$

The term $H(\mathrm{C{-}C})_{\mathrm{diol}}$ indicates the enthalpy of the C–C bond situated between the two hydroxyl groups; its value should, to a first approximation, be identical to the value found in the ω-isomers (343.2 kJ mol^{-1} [3]). The enthalpy of the C–H bond is taken as 412.85 kJ mol^{-1} [2]. By solving eqns. (7) and (8), the enthalpies of the C–OH and of the C–C bonds in the carbon chain can be calculated: $H(\mathrm{C{-}C}) = 346.7$ kJ mol^{-1}; $H(\mathrm{C{-}OH}) = 827.0$ kJ mol^{-1}. Both enthalpies are thus clearly higher than in the ω-isomers. The C–C bond enthalpy is nearly the same as in n-alkanols (346.8 kJ mol^{-1} [2]), but lower than in n-alkanes (348.0 kJ mol^{-1} [2]). The destabilising effect of the hydroxyl group on the C–C bond is again shown, but the carbon chain is less disturbed when both hydroxyl groups are situated at one end of the molecule. The C–OH bond enthalpy is clearly higher than in *n*-alkanols ($814.7\ \mathrm{kJ\ mol^{-1}}$ [2]) and in ω-alkanediols ($819.5\ \mathrm{kJ\ mol^{-1}}$ [3]), reflecting the intramolecular stabilisation of the adjacent hydroxyl groups. This effect seems to stabilise the 1,2-alkanediols in comparison with their ω-isomers.

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