Short Communications

Non-bonded Oxygen—Oxygen Interactions. 3,7-Dioxanonane

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A straight chain diether with the two oxygen atoms separated by just one methylene group is stabilized by 17 kJ mol^{-1} as compared to aliphatic monoethers.[1] When a second carbon atom is "added" between the two ether oxygens the 17 kJ mol^{-1} stabilization turns into a destabilization (apparent strain) as large as 11 kJ mol^{-1}; again aliphatic monoethers constitute the reference system. Thus there seems to be a change of 28 kJ mol^{-1} in the non-bonded oxygen — oxygen interaction when going from a $-O-CH_2-O-$ to a $-O-CH_2-CH_2-O-$ arrangement. This rather puzzling result is supported by the enthalpy of isomerization for 1,3-dioxane (g) and 1,4-dioxane (g), which amounts to 25.9 ± 1.5 kJ mol^{-1} (*cf.* Ref. 1). Will there still be a noticeable non-bonded interaction between the ether oxygens when a third carbon atom is introduced between them? If so, what "sign" does it have? These questions prompted a determination of the enthalpy of formation of 3,7-dioxanonane (1,3-diethoxypropane) *via* enthalpy of combustion measurements.

Compound. 3,7-Dioxanonane was synthesized by Dr. Klas Nyberg (Department of Organic Chemistry, Chemical Center, Lund) from trimethylene glycol *via* its disodium salt, which was converted with ethyl iodide to the diether. The two major impurities remaining after the first distillation, tetrahydrofuran (solvent) and trimethylene glycol monoether, were removed completely by distillation at reduced pressure, 70 mmHg, in an annular Teflon spinning band

column followed by preparative gas chromatography. The purity was checked by GLC on Carbowax, Apiezon and silicone (SE—30) columns, respectively. No trace of any organic impurities was found in the purified material. The identity of the compound was ascertained by NMR. Amplification of the NMR spectrum revealed no signs of impurities.[1] Before the ampoule filling procedure the sample was dried for about 5 min with activated molecular sieves. No change in purity was observed due to this treatment. The water content, as determined by a GLC method[2] on the contents of two combustion ampoules, was 0.007 mass per cent in either case. $d_4^{20} = 0.83576$, $d_4^{25} = 0.83093$.

Combustion calorimetry. The rotating-bomb calorimeter TKL-2 with platinum-lined bomb 2B, internal bomb volume 0.2622 dm^3, was used with 0.79 cm^3 of water initially in the bomb and P^i(gas) = 30.0 atm at 25°C. The calorimetric procedures followed those already described[1] with one major difference. Temperatures were measured using a Hewlett Packard HP—M40—2801A Quartz Thermometer with a 2850D probe. The thermometer was used in the 100 sec range (resolution 10^{-5} K) with minimum time between readings. Fore-, main-, and after-periods were all of 20 min duration. Paraffin oil, designation USBM-P3a, was used as auxiliary material. Calibration experiments were performed with benzoic acid, National Bureau of Standards SRM 39i, under certificate conditions.

The dried sample of 3,7-dioxanonane was transferred in vacuum to a receiver containing the Pyrex glass ampoules for the combustion experiments.[3] The ampoule mass varied between 50 and 68 mg. Ten combustion experiments were carried out with the diether, two of which were rejected because of soot being trapped in the glass. The nitric acid content in the final bomb solutions was determined by titration with carbonate-free sodium hydroxide solution.

Molecular weights were computed from the 1961 table of atomic weights. All weighings were reduced to mass and the calculations carried out as described in Ref. 1.

Vaporization calorimetry. The enthalpies of vaporization at 25°C were measured using the Wadsö calorimeter.[4]

Results and discussion. All symbols used are those of Hubbard, Scott and Waddington.[5] The corrections to standard states, ΔU_{Σ}, (Washburn corrections) were calculated using a computer program based on the procedure by Hubbard *et al.*[5] with $\Delta U_{dec}(HNO_3) = 58.89$ kJ mol^{-1}, $\Delta U_{soln}(CO_2) = -17.09$ kJ mol^{-1},[6] and $K(CO_2) = 0.03440$ mol dm^{-3} atm^{-1}.[6] The values used for c_p and $(\partial v/\partial T)_p$ for 3,7-dioxanonane were 1.88 J K^{-1} g^{-1} and 1.374 mm^3 K^{-1} g^{-1}, respectively. A summary of a typical combustion experiment is given in Table 1. The results of the individual com-

Table 1. Summary of a typical combustion experiment.

$\varepsilon°(calor) = (28170.5 \pm 1.3^a)$ J K^{-1}
$\Delta u_c°(oil) = -(45942.3 \pm 3.0^a)$ J g^{-1}
$\Delta u_c°(fuse) = -(16807 \pm 4^a)$ J g^{-1}

$m'(comp)/g$	0.425090
$m''(oil)/g$	0.135964
$m'''(fuse)/g$	0.001194
$m(Pt)/g$	10.359
$\Delta\theta/K$	0.744734
$m^i(cont)/g$	22.164
$\varepsilon^i(cont)/J$ K^{-1}	13.52
$\Delta U_{dec}^f(HNO_3)/J$	8.70
$\Delta U_{\Sigma}/J$	6.42
$-\Delta u_c°(comp)/J$ g^{-1}	34436.5

[a] Uncertainties are standard deviations of the mean.

bustion experiments in terms of $-\Delta u_c°/kJ$ g^{-1} at 25.0°C were: 34.4365, 34.4398, 34.4092, 34.4344, 34.4375, 34.4157, 34.4101, 34.4322, with the mean value and standard deviation of the mean equal to 34.4269 ± 0.0046 kJ g^{-1}. The standard molar energy, $\Delta U_c°$, and enthalpy, $\Delta H_c°$, of combustion, referring to the idealized reaction in which all reactants and products are in their thermodynamic standard states at 25.0°C, are given in Table 2 together with the molar enthalpy of vaporization, ΔH_v, and derived molar enthalpies of formation, $\Delta H_f°$, for the compound in the liquid and gaseous states at 25.0°C. The final overall precision of the results was estimated as recommended by Rossini, *cf.* Ref. 1.

Table 2. Results and derived quantities at 25.0°C. The uncertainties given are twice the final overall standard deviation of the mean.

$\Delta U_c°/kJ$ mol^{-1}	-4551.7 ± 1.4^a
$\Delta H_c°/kJ$ mol^{-1}	-4559.1 ± 1.4
$\Delta H_f°(l)/kJ$ mol^{-1}	-482.1 ± 1.5
$\Delta H_v/kJ$ mol^{-1}	45.9 ± 0.2
$\Delta H_f°(g)/kJ$ mol^{-1}	-436.2 ± 1.5

[a] Corrected for 0.007 mass per cent water.

Enthalpies of formation at 25°C for gaseous carbon dioxide and liquid water were taken from Ref. 7 with 1 cal = 4.1840 J.

The average enthalpy of formation change, $\Delta(\Delta H_f°(g))$, when a methylene group in an alkane is replaced by an ether oxygen is -104.8 kJ mol^{-1}. With ether oxygens replacing the two $-CH_2-$ groups in the 3 and 7 positions in nonane the calculated enthalpy of formation becomes -438.3 kJ mol^{-1}, while $\Delta H_f°(g)$ as determined in this work is -436.2 ± 1.5 kJ mol^{-1}. This implies a destabilization of 2 kJ mol^{-1} in 3,7-dioxanonane, which is, however, hardly a significant amount when the uncertainties of the reference data as well as that of the measured value are taken into account.

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