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Non-bonded Oxygen—Oxygen Interactions in 2,4,10-Trioxaadamantane and 1,3,5,7,9-Pentoxecane

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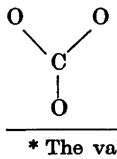
Enthalpies of combustion, utilizing a micro combustion calorimetric technique, and enthalpies of sublimation have been determined for 2,4,10-trioxaadamantane and 1,3,5,7,9-pentoxecane (pentoxane). Standard enthalpies of formation for the compounds in the gaseous state, ΔH_f°(g), have been derived and are $-(499.2 \pm 2.2)$ and $-(779.8 \pm 1.3)$ kJ mol^{-1}, respectively. The calculated stabilization energy due to next-nearest-neighbour oxygen-oxygen interaction in trioxaadamantane, relative to adamantane and aliphatic monoethers, is 53 kJ mol^{-1}. The gaseous enthalpy of formation per $-CH_2O-$ unit in pentoxane is very nearly the same as that in trioxane and tetroxane.

One pair of next-nearest-neighbour oxygen atoms in an aliphatic straight-chain compound gives rise to a stabilization energy as large as 17.$_6$ kJ mol^{-1} relative to monoethers,* whereas the stabilization in an $-O-CH_2-O-CH_2-O-$ arrangement, within experimental uncertainties, is twice that of one pair.[1] Addition of another $-CH_2-O-$ group likewise increases the total stabilization energy to three times that for a single pair.[1] This means that consecutive pairs of next-nearest-neighbour oxygens in straight-chain compounds give rise to the same stabilization energy per pair even though some of the oxygens are simultaneously engaged in two interactions. The orthoester arrangement



in 2,4,10-trioxaadamantane can similarly be looked upon as a three pair oxygen-oxygen next-nearest-neighbour interaction system. Does the fact that the interacting oxygens are all attached to the same carbon atom, and moreover rather rigidly locked into fixed positions, have a marked influence on the resulting stabilization energy in this tricyclic ortho ester?

In s-trioxane (1,3,5-trioxacyclohexane) the stabilization from the three pairs of oxygen atoms appears to be only 28 kJ mol^{-1}, when the aliphatic ether increment is used in the calculations.[1,3] However, if the ether increment is instead evaluated from the enthalpies of formation for gaseous cyclohexane and tetrahydropyran, the calculated stabilization energy in trioxane due to the oxygen-oxygen interactions becomes 42 kJ mol^{-1}. This is a good illustration of the importance of clearly defining the reference system in calculations and discussions of thermochemical stabilization or destabilization (strain) energies. In the study of trioxane and the formaldehyde tetramer tetroxane it was found that the gaseous enthalpies of formation per $-CH_2O-$ unit in the two compounds were not significantly different.[3]

In this paper energy of combustion and enthalpy of sublimation measurements are reported for 2,4,10-trioxaadamantane (2,4,10-trioxatricyclo[3.3.1.1^{3,7}]decane) and pentoxane (1,3,5,7,9-pentoxecane). A recently developed micro-bomb (4.5 cm^3) combustion calorimeter together with an ampoule technique for milligram quantities of material has been used in the combustion studies.[4]

* The value given in Ref. 1 is 16.9 kJ mol^{-1}. A recalculation with parameters for the ether increment taken from Ref. 2 yields 17.6 kJ mol^{-1}.

EXPERIMENTAL

Compounds. 2,4,10-Trioxaadamantane, a gift from Dr. Kjell Olsson, The Royal Agricultural College, Uppsala, Sweden, was synthesized from *cis,cis*-cyclohexane-1,3,5-triol and excess triethylformate in methanolic HCl.[5] The crude product was recrystallized from petroleum ether and the obtained crystals then sublimed at approximately 10 Torr * and 323 K to remove traces of solvent. A concentrated ether solution of purified material was analyzed by GLC on Apiezon, silicone (SE-30), and Carbowax columns. No trace of any impurity could be found. The above described material was used in series A. However, water analysis by a coulometric method[6] indicated 0.07_3 mass per cent of water. A second preparation of trioxaadamantane was therefore sublimed through activated molecular sieves. The dried material was handled in a small plastic glove bag, which had been flushed several times with dry nitrogen and which also housed a large dish with freshly activated molecular sieves. Pellets for the combustion experiments of series B were made inside the glove bag whereas when pellets for series A were prepared no real precautions to avoid moisture had been taken (relative humidity 25 – 30 %). However, the water content of the second preparation was determined to be 0.06_9 mass per cent. Evidently "dry conditions" have to be maintained much more rigorously when one wants to prevent contamination by water while working with milligram quantities of "slightly hygroscopic"[5] materials. A correction for $0.07_0 \pm 0.00_5$ mass per cent of water has been applied to the measured energy of combustion of trioxaadamantane.

The 1,3,5,7,9-pentoxecane (pentoxane) sample was a gift from Dr. Yasuhiko Miyake, Mitsui-Toatsu Chemicals, Inc., Japan. The melting point of the sample, determined on a Perkin-Elmer DSC-1B differential scanning calorimeter, was $335._3$ K; literature value 334 ± 1 K.[7] No impurities were found when a concentrated ether solution of pentoxane was carefully analyzed by GLC on silicone (SE-30) and Carbowax columns. The NMR and mass spectra were in good agreement with those reported in the literature.[8,9] Water analysis,[6] performed on a small sample that had been well exposed to laboratory air, indicated ≤ 0.01 mass per cent of water. No correction for water in pentoxane has been applied.

The Delrin ** (polyoxymethylene) ampoules used in this investigation were not manufactured from the same rod as those referred to in Ref. 4. A redetermination of the energy of combustion of this particular polyoxymethylene material was therefore required. The ampoules were cleaned and conditioned as described earlier.[4]

The benzoic acid used in calibration experiments was National Bureau of Standards SRM 39i.

Combustion calorimetry. The micro combustion calorimeter, the calorimetric and calculational procedures, and the ampoule technique have been described previously.[4] The amount of water initially in the bomb (internal bomb volume 4.50 cm^3) was 20 mm^3. The initial pressure of oxygen, $p^i(O_2)$, varied between 34.6 and 37.1 atm * in the trioxaadamantane experiments; for the pentoxane runs it varied from 35.9 to 37.5 atm. The oxygen was 99.995 % pure and in combination with an efficient flushing procedure, this resulted in negligible corrections for the formation of HNO_3 during combustions.[4] Electrical calibrations were performed after each combustion experiment.

In both series of measurements on trioxaadamantane ($p_{25} \sim 3 \times 10^{-2}$ Torr **) the compound was enclosed in thin-walled polyoxymethylene ampoules.[4] An unusually large number of failures was encountered in the combustions on trioxaadamantane, possibly due to air being trapped in the pellets. Four out of twelve runs were rejected because some trace of soot on the bomb wall indicated incomplete combustion. Five successful runs were performed in series A and three in series B.

Five combustions were performed with pentoxane ($p_{25} \sim 2 \times 10^{-2}$ Torr **) enclosed in ampoules; one was rejected. Four experiments were carried out where somewhat larger pellets of pentoxane were burned without protection. The mass loss of these pellets was determined as a function of time to allow an appropriate correction to be applied for material evaporated during assembly and closing of the bomb. 6 ± 1 μg evaporated in 10 min, while the time for mounting the crucible and closing the bomb was less than four min. In the pentoxane as well as in the trioxaadamantane series all the included successful runs were without any trace of soot.

The Delrin ampoules were weighed on a Sartorius type 4125 electronic micro balance, the linearity of which has been verified. The sensitivity was checked several times during a series of weighings. A Mettler M5 micro balance, carefully calibrated against standard weights,[4] was used when the pelleted samples were weighed either into closed ampoules or in the open crucible. The sensitivity of the Mettler balance was checked before and after each series of weighings.

All weighings have been reduced to masses and molar masses computed from the 1969 table of atomic weights.[10] The energy equiva-

* Torr = (101.325/760) kPa

** "DELRIN acetal resin"; reg. trade name. E. I. du Pont de Nemours & Co. (Inc.), U.S.A.

* atm = 101.325 kPa. ** Estimated from enthalpy of sublimation measurements.

Table 1. Auxiliary quantities used in the calculations.

Compound	ϱ/g cm^{-3}	$(\partial v/\partial T)_p$/mm^3 K^{-1} g^{-1}	c_p/J K^{-1} g^{-1}
2,4,10-Trioxaadamantane	1.1	0.39	1.3
1,3,5,7,9-Pentoxecane	1.48[a]	1.7	1.14[b]
Delrin	1.43	1.0	1.3

[a] Ref. 9. [b] Ref. 7.

Table 2. Summary of typical combustion experiments.[a] Δu_c°(Delrin) = $-(17118._0 \pm 6._4)$ J g^{-1}.[b,c]

	2,4,10-Trioxaadamantane		1,3,5,7,9-Pentoxecane	
	Series A	Series B	In ampoules	"Pellets"
m(comp)/mg	8.526	9.078	9.437	21.492
m(Delrin)/mg	4.341	5.248	4.524	0
ε(calor,b.a.)/J K^{-1}	583.057 $\pm$ 0.093[c]	582.930[d] $\pm$ 0.076[c]	582.908 $\pm$ 0.098[c]	582.908 $\pm$ 0.098[c]
ε^i(cont)/J K^{-1}	0.295	0.288	0.295	0.284
$\Delta\theta$/K	0.49880_5	0.54958_0	0.40607_4	0.62181_3
ΔU_{ign}/J	0.212	0.202	0.189	0.206
ΔU_Σ/J	0.231	0.248	0.201	0.315
$-\Delta u_c^\circ$(comp)/J mg^{-1}	25.3609	25.3624	16.8477	16.8488

[a] For explanation of symbols *cf.* Ref. 11. [b] At 30 % relative humidity. [c] Uncertainties are standard deviations of the mean. [d] Direct calibration with benzoic acid.

Table 3. Results of combustion experiments at 298.15 K. $-\Delta u_c^\circ$/kJ g^{-1}

	2,4,10-Trioxaadamantane		1,3,5,7,9-Pentoxecane	
	Series A	Series B	In ampoules	"Pellets"
	25.3561	25.3624	16.8477	16.8416
	25.3609	25.3313	16.8587	16.8488
	25.3770	25.3481	16.8128	16.8442
	25.3825		16.8228	16.8486
Mean:	25.3691[a]	25.3473[a]	16.8355	16.8458
Standard deviation of the mean:	0.0063	0.0090	0.0107	0.0018
Final overall standard deviation of the mean:	0.0087	0.0105	0.0115	0.0035

[a] Not corrected for $0.07_0 \pm 0.00_5$ mass per cent of water.

lent, ε(calor), of the calorimetric system was calculated from the mean value of pertinent electrical calibrations, values of ε^i(cont) and the experimentally established relation between benzoic acid and electrical calibrations: ε(calor,b.a.) = ε(calor,el.) + (0.060 ± 0.070) J K^{-1}. The corrections to standard states, ΔU_Σ, were calculated using a computer program based on the procedure by Hubbard *et al.*[11] Some auxiliary quantities used in the calculations are listed in Table 1. The final overall precision of the ΔU_c° mean values was estimated as recommended by Rossini.[12] The reference temperature of the combustion experiments is 298.15 K.

Vaporization calorimetry. The enthalpies of sublimation at 298.15 K were measured using

the Morawetz calorimeter.[13] The trioxaadamantane sample was sublimed into the calorimeter. Four experiments were performed following the procedure described in Ref. 13 with around 6 mg evaporated per experiment. A molten sample of pentoxane was dropped from a heated pipette into the evaporation pan of the calorimeter. Seven experiments were performed with on the average 7 mg evaporated per experiment.

RESULTS AND DISCUSSION

In Table 2 detailed results for some typical combustion experiments are given, one from each of the four series of measurements. Values of $-\Delta u_c°$, referring to unit mass, for the individual runs are listed in Table 3. One of the trioxaadamantane values in series A has been discarded on statistical grounds. The calculated mean value for each series together with the standard deviation of the mean and the estimated final overall uncertainty are included in Table 3. No significant difference was found between the results from the two different series of measurements on each compound. Therefore the mean values were weighted proportionately to the inverse squares of their overall uncertainties. The obtained $\Delta u_c°$ values were $-(25.360_1 \pm 0.013_4)$ and $-(16.844_9 \pm 0.006_7)$ kJ g^{-1} for trioxaadamantane and pentoxane, respectively; the uncertainties are twice the final overall standard deviations of the mean. After correction for 0.07_0 mass per cent of water the trioxaadamantane value becomes -25.377_9 kJ g^{-1}. The $\Delta u_c°$ values refer to the idealized combustion reaction in which all reactants and products are in their thermodynamic standard states at 298.15 K. Table 4 gives the standard molar energies, $\Delta U_c°$, and enthalpies, $\Delta H_c°$, of combustion for the compounds in the crystalline state, together with the molar enthalpies of sublimation, ΔH_{subl}, and derived enthalpies of formation, $\Delta H_f°$, for the compounds in the crystalline and gaseous states, all at 298.15 K. The enthalpies of formation at 298.15 K for gaseous carbon dioxide and liquid water used in the calculations are from Ref. 14. No previous determinations of the enthalpies of formation of the compounds studied here have been found in the literature.

Unsubstituted adamantane forms the natural basis for a reference system in the evaluation of the non-bonded oxygen-oxygen interaction energy in trioxaadamantane. Three independent determinations of the energy of combustion of adamantane were published recently.[15–17] Two of these are in close agreement, whereas the third [15] differs by almost 9 kJ mol^{-1} from the others. The reason for this discrepancy has not yet been explained. Taking the average of the three reported determinations of the enthalpies of combustion and sublimation leads to a standard enthalpy of formation for gaseous adamantane equal to -131.6 kJ mol^{-1}. From this value and the aliphatic ether increment for the exchange of a $-CH_2-$ group by an ether oxygen $-O-$ (-104.8 kJ mol^{-1}), the predicted enthalpy of formation of gaseous 2,4,10-trioxaadamantane is -446.0 kJ mol^{-1}. The experimentally obtained value is -499.2 kJ mol^{-1} implying a stabilization energy of 53 kJ mol^{-1} in trioxaadamantane. If on the other hand the cyclohexane-tetrahydropyran based ether increment (-100.0 kJ mol^{-1}) is used, the calculated stabilization energy for the three pair oxygen-oxygen next-nearest-neighbour interaction system is 68 kJ mol^{-1} in the tricyclic ortho ester studied here.

Traditionally, adamantane was considered to be relatively free of strain, but recent calculations show that it is in fact appreciably

Table 4. Results and derived quantities at 298.15 K. The uncertainties given are twice the final overall standard deviation of the mean. cal = 4.184 J.

	2,4,10-Trioxaadamantane	1,3,5,7,9-Pentoxecane
$\Delta U_c°$/kJ mol^{-1}	-3607.60 ± 1.90	-2528.96 ± 1.01
$\Delta H_c°$/kJ mol^{-1}	-3610.08 ± 1.90	-2528.96 ± 1.01
$\Delta H_f°$(c)/kJ mol^{-1}	-573.64 ± 2.12	-867.74 ± 1.22
ΔH_{subl}/kJ mol^{-1}	74.41 ± 0.37	87.94 ± 0.53
$\Delta H_f°$(g)/kJ mol^{-1}	-499.23 ± 2.15	-779.80 ± 1.33
$\Delta H_f°$(g)/kcal mol^{-1}	-119.32 ± 0.51	-186.38 ± 0.32

strained; *cf.* for instance Refs. 18 and 19. The exact nature of the strain, however, still seems to be a matter of some controversy. Schleyer *et al.*[18] account for the strain (~ 27 kJ mol^{-1}) in terms of angle strain and C···C non-bonded repulsions, whereas Allinger *et al.*[19] state that "the strain in adamantane is largely due to an excessive number of H···H repulsions." Since only the overall effect of strain and stabilization in a compound is discernible from thermochemical measurements, a simple calculation of the oxygen-oxygen interaction energy in trioxaadamantane may well be obscured by such changes in the "strain" in adamantane that are not taken care of in the choice of ether increment.

The stabilization due to next-nearest-neighbour oxygens in straight-chain compounds can be rationalized in terms of electrostatic interactions.[20] A simple calculational model of this kind correctly reproduces the additivity found for the stabilizing effect of consecutive pairs of oxygens in $-O-CH_2-O-CH_2-O-$ chains. With parameters calibrated by the 17.$_6$ kJ mol^{-1} interaction energy for a single pair, a value of 58 kJ mol^{-1} is predicted for the stabilization energy due to non-bonded oxygen-oxygen interaction in ortho esters.

Energy of combustion measurements on trimethyl- and triethylorthoformate have been published.[21] From these, and estimates of the enthalpies of vaporization, gaseous enthalpies of formation were derived.[21] The calculated stabilization energy in these compounds is 72 * and 69 kJ mol^{-1}, respectively.**

The gaseous enthalpies of formation per $-CH_2O-$ unit in trioxane, tetroxane, and pentoxane are $-(155.3 \pm 0.2)$, $-(155.1 \pm 0.2)$ and $-(156.0 \pm 0.3)$ kJ mol^{-1}, respectively, which means that the overall stabilization per $-O-CH_2-O-$ interaction is the same in these compounds.

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* The ether increment is slightly different, -91.9 kJ mol^{-1}, when the oxygen atom is attached to a methyl group.[2] This has been taken into account in the calculations.

** The compounds were burned in gelatin capsules. No details are given about the precautions taken to prevent uptake of water when handling these extremely hygroscopic materials. Water, if not accounted for, would tend to "increase" the calculated stabilization energy.