Acta Chemica Scandinavica B 28 (1974) 905—908

Non-bonded Oxygen—Oxygen Interaction in Ethoxymethyl Propionate

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The energy of combustion and enthalpy of vaporization at 298.15 K have been measured for ethoxymethyl propionate. Standard enthalpies of formation at 298.15 K have been derived for the compound in the liquid and gaseous states. The results are:

$\Delta H_f°(l) = -(667.2 \pm 1.1)$ kJ mol^{-1}
$\Delta H_f°(g) = -(617.4 \pm 1.1)$ kJ mol^{-1}

Ethoxymethyl propionate is shown to have an additional stabilization energy of 8 kJ mol^{-1} relative to the stabilization energy in ethyl propionate.

Next-nearest-neighbour oxygen atoms in an aliphatic straight-chain compound, $-O-CH_2-O-$, give rise to a stabilization energy of 17.$_6$ kJ mol^{-1}* relative to aliphatic monoethers,[1,3] whereas the next-next-nearest-neighbour arrangement brings about a 10 kJ mol^{-1} destabilization.[1] With three oxygens in "1,3,5"-positions, $-O-CH_2-O-CH_2-O-$, the total stabilization due to non-bonded oxygen-oxygen interaction, within experimental uncertainty, is twice that in the "1,3"-dioxa compound.[1] The stabilizing effect of an $-O-CH_2-O-$ arrangement can be rationalized in terms of electrostatic interactions.[4] The calculational model used so far correctly reproduces the additivity found for consecutive pairs of next-nearest-neighbour oxygens, but does not satisfactorily account for the large destabilizing oxygen-oxygen interaction in 3,6-dioxaoctane.

Gaseous enthalpies of formation for diethyl carbonate and ethyl propionate were used to estimate the stabilization ("resonance") energy of an alkyl carbonate relative to that of an alkyl ester.[5] The calculated stabilization energies were 129 and 80 kJ mol^{-1}, respectively. The possibility of a contribution to the calculated stabilization energy in diethyl carbonate due to oxygen-oxygen interaction of the same nature as that found in "1,3"-diethers is an interesting question which cannot be answered at the present time. However, a knowledge of the $-O-CH_2-O-$ interaction energy, if any, in an alkoxymethyl ester, $-O-CH_2-O-CO-$, might help in attempts to explain the nature and origin of the above mentioned non-bonded oxygen-oxygen interactions. In this paper energy of combustion and enthalpy of vaporization measurements on ethoxymethyl propionate are reported.

EXPERIMENTAL

Compounds. Ethoxymethyl propionate was synthesized essentially as described in Ref. 6. The chloromethyl ethyl ether was prepared from ethanol, s-trioxane and dry HCl, and after removal of water and excess HCl the crude ether product was reacted with (fused) sodium propionate under as moisture-free conditions as possible. The reacted material was distilled twice at reduced pressure through an all-glass column filled with helices, the main fractions of the second distillation boiling at ~339 K/40 Torr.* GLC analysis on this material showed the presence of three impurities, two of which were identified as ethanol and propionic acid, respectively. All of the observed impurities

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

* Torr = (101.325/760) kPa.

were removed by preparative GLC (Carbowax; 343 K). The identity of the purified compound was confirmed by the NMR and mass spectra. No additional impurities were found when the purified material was tested by GLC on polyethylene glycol (PEG 20M) and diethylene glycol succinate polyester columns. However, GLC analysis on an SE-30 silicone column indicated that about 0.5 % of yet another impurity was present. Unfortunately this particular type of column caused decomposition of the compound when the column and/or injector temperature was increased above ~340 K. Tests on a different silicone (OV-17) column showed no such decomposition, but again the impurity could not be separated from the main component at any of the conditions tried. In an attempt to remove this additional impurity the material was run through the preparative gas chromatograph on an SE-30 column with injector and column temperatures at 333 K. The amount of impurity could, however, only be reduced by about 50 % in this way and therefore its nature and concentration had to be established reasonably well to allow the appropriate correction to be applied to the measured energy of combustion. Mass spectrometric analysis, coupled with GLC, indicated a molecular weight of the impurity of 116. The fragmentation pattern gave several indications of the presence of an ethoxy group as well as strong support for two oxygens in the molecule.[7] The composition $C_6H_{12}O_3$ and the structure of ethoxymethyl ethyl ketone were in accord with the obtained mass spectrum, whereas for instance a structure such as that of ethyl butyrate could be ruled out.[8]

The response of the flame ionization detector, used in the GLC analysis, to 1 mol of impurity was estimated to be very nearly the same as that per mol of ethoxymethyl propionate.[9] From the measured areas under the GLC peaks the amount of impurity was calculated as 0.25 mass per cent with an assigned uncertainty of ±0.03 mass per cent.

Drying the material with molecular sieves before it was transferred to the vacuum line for the ampoule filling procedure caused no detectable change in the purity. The water content, determined by GLC[10] on the sample in one of the combustion ampoules, was 0.002_5 mass per cent. No correction for water has been applied. Densities at 293.15 and 298.15 K were 0.9642_7 and 0.9593_0 g cm^{-3}, respectively. $n_D^{25} = 1.3961$.

The paraffin oil, laboratory designation TKL-66, used as auxiliary material in the combustions, has been described.[11] The benzoic acid, used in the calibration experiments, was National Bureau of Standards SRM 39i.

Combustion calorimetry – apparatus and procedure. The rotating-bomb calorimeter TKL-3 was used with the platinum-lined bomb 3B;[12] internal bomb volume 0.2609 dm^3. All combustions were carried out with 0.79 cm^3 of water initially in the bomb that was flushed with oxygen (99.995 % pure; less than 10 ppm. of nitrogen) for three min before charging to the initial pressure of oxygen $p^i(\text{gas}) = 30.0$ atm* at 298.2 K. Calibrations were carried out under certificate conditions and the other experiments designed to give close to the same temperature rise. Further details of the calorimetric procedure have been given previously.[1] A Hewlett Packard HP-M40-2801A Quartz Thermometer with 2850D probes was used for the temperature measurements. It was used in the 100 s mode (resolution 10^{-5} K) with minimum time between readings. Fore-, main-, and after-periods were all of 20 min duration.

The dried sample was transferred in vacuum to the receiver containing the Pyrex glass ampoules to be filled for the combustion experiments.[13] The ampoule mass varied between 26 and 44 mg. Five combustions were carried out on ethoxymethyl propionate. In all experiments tests were made for carbon monoxide in the final bomb gases. The detection limit of the test is well below 1 ppm of CO in the bomb gas [14] corresponding to a correction of about 4 ppm of the total heat evolved in a combustion. No evidence of CO was found in any of the experiments. The almost negligible amount of nitric acid in the final bomb solution was determined spectrophotometrically [15] at wavelength $\lambda = 202$ nm.

All weighings were reduced to masses and molar masses computed from the 1969 table of atomic weights.[16] The corrected temperature rise, $\Delta\theta$, and the energy equivalent of the standard calorimetric system, ε°(calor), were calculated as outlined by Bjellerup.[17] ε°(calor) was recalculated to air density 1.2 g dm^{-3}, since variations in air density affect the amount of water in the calorimeter.

Vaporization calorimetry. The enthalpy of vaporization at 298.15 K of ethoxymethyl propionate was measured using the Wadsö calorimeter.[18] Five experiments were performed.

RESULTS AND DISCUSSION

All symbols used are those of Hubbard, Scott and Waddington.[19] The Washburn corrections, ΔU_Σ, were calculated using a computer program based on the procedure in Ref. 19. The energy of solution of carbon dioxide in water, $\Delta U_{\text{soln}}(CO_2)$, and the solubility constant, $K(CO_2)$, were taken as −17.09 kJ mol^{-1} and 0.03440 mol dm^{-3} atm^{-1}, respectively, at 298.15 K.[20] The $(\partial v/\partial T)_p$ value for ethoxymethyl propionate was calculated from measured densities, whereas the value used for the

* atm = 101.325 kPa.

specific heat capacity, $c_p = 1.8$ J K^{-1} g^{-1}, is an estimate. The final overall precision of the ΔU_c° mean value was estimated as recommended by Rossini.[21] The enthalpies of formation at 298.15 K for gaseous carbon dioxide and liquid water, used in the calculation of the enthalpy of formation, are from Ref. 22.

Using data from Ref. 2 the energy of combustion of liquid ethoxymethyl ethyl ketone, assumed to be the remaining impurity in the sample, was estimated as -3622 kJ mol^{-1}, equal to -31.18 kJ g^{-1}. An uncertainty of ± 0.5 kJ g^{-1} (58 kJ mol^{-1}) was assigned to this value to account for possible misjudgement of the identity of the impurity. Since it seems very unlikely that the impurity is an ester, the uncertainty does not fully cover the approximately 80 kJ mol^{-1} stabilization energy of an ester group.[5] The net correction to be applied to the measured Δu_c° value due to impurity is (13.5 ± 1.8) J g^{-1}, corresponding to (1.57 ± 0.21) kJ mol^{-1}, where the uncertainty also includes that assigned to the determination of the impurity concentration. This 1.8 J g^{-1} uncertainty has been taken into account in the calculation of the final overall precision of the ΔU_c° mean value.

Details of a typical combustion experiment are given in Table 1. The individual $-\Delta u_c^\circ$ values, referring to unit mass, are listed in Table 2, uncorrected for impurity. The corrected Δu_c° mean value is -25.7649 kJ g^{-1}. The ΔU_c° values refer to the idealized combustion reaction, where reactants and products are in their

Table 1. Summary of a typical combustion experiment.

ε°(calor) = (28677.3 ± 0.7) J K^{-1}[a]
Δu°_c(oil) = (−46041.7 ± 2.0) J g^{-1}[a]
Δu°_c(fuse) = (−16807 ± 4) J g^{-1}[a]

m(comp)/g	0.507371
m(oil)/g	0.166596
m(fuse)/g	0.001185
m(Pt)/g	10.298
$\Delta\theta$/K	0.726561
m^i(cont)/g	22.13
ε^i(cont)/J K^{-1}	13.64
$\Delta U^t_{dec}(HNO_3)$/J	0.17
ΔU_Σ/J	8.81
$-\Delta u_c^\circ$(comp)/kJ g^{-1}	25.7777

[a] The uncertainties are standard deviations of the mean. For explanation of symbols, *cf.* Ref. 19.

Table 2. Results of combustion experiments at 298.15 K.

	$-\Delta u_c^\circ$/kJ g^{-1}
	25.7763
	25.7808
	25.7769
	25.7777
	25.7805
Mean:	25.7784 [a]
Standard deviation of the mean:	0.0009

[a] Not corrected for impurity. See text.

Table 3. Results and derived quantities at 298.15 K. The uncertainties given are twice the final overall standard deviation of the mean.

ΔU_c°/kJ mol^{-1}	−3405.09 ± 0.70
ΔH_c°/kJ mol^{-1}	−3408.81 ± 0.70
ΔH_f°(l)/kJ mol^{-1}	−667.23 ± 1.08
ΔH_v/kJ mol^{-1}	49.88 ± 0.09
ΔH_f°(g)/kJ mol^{-1}	−617.35 ± 1.08
ΔH_f°(g)/kcal mol^{-1}	−147.55 ± 0.26

thermodynamic standard states at 298.15 K. Table 3 gives the standard energy, ΔU_c°, and enthalpy, ΔH_c°, of combustion for the compound in the liquid state, together with the enthalpy of vaporization, ΔH_v, and the derived standard enthalpies of formation, ΔH_f°, for the liquid and gaseous states at 298.15 K.

No enthalpy of formation value for ethoxymethyl propionate or any other alkoxymethyl ester was found in the literature. The calculated gaseous enthalpy of formation increment for insertion of a $-CH_2-O-$ group in an alkane is -145.9 kJ mol^{-1}.[2] From this value and the enthalpy of formation of gaseous ethyl propionate, $-(463.6 \pm 0.7)$ kJ mol^{-1},[5] a value of -609.5 kJ mol^{-1} may be "predicted" for the enthalpy of formation of ethoxymethyl propionate. This "predicted" value rests on the assumption that the total stabilization energy in ethoxymethyl propionate is the same as that in ethyl propionate.* The experimentally derived enthalpy of formation value for the

* The reference system in all the calculations referred to here consists of n-alkanes, and aliphatic monoethers and ketones.

former compound is $-(617.4 \pm 1.1)$ kJ mol^{-1}, implying that there is an extra stabilization energy in ethoxymethyl propionate of (7.9 ± 1.3) kJ mol^{-1}, relative to ethyl propionate, due to interaction between the ether type oxygen and the alkoxy oxygen in the ester group. This is only half of the stabilizing effect, 17.6 kJ mol^{-1}, found for non-bonded interaction between the two oxygens in a "1,3"-dioxa alkane.

Acknowledgements. I am very much indebted to Mr. Tore Henricsson, who synthesized the compound. The valuable assistance of Miss Monica Andersson, who did the GLC work and performed the vaporization measurements, is gratefully acknowledged.

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Received March 7, 1974.