

The Enthalpies of Combustion and Formation of Some 3,3-Disubstituted Oxetanes

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Enthalpies of combustion and vaporization at 25.0°C have been measured for some 3,3-disubstituted oxetanes. Enthalpies of formation at 25.0°C have been derived for the compounds in the liquid and gaseous states. The results are:

	$\Delta H_f^\circ(l)/\text{kJ mol}^{-1}$	$\Delta H_f^\circ(g)/\text{kJ mol}^{-1}$
3,3-Dimethyloxetane	-182.2 ± 1.6	-148.2 ± 1.7
3-Ethyl-3-chloromethyloxetane	-243.0 ± 1.6	-193.3 ± 1.6
3,3-Bis-chloromethyloxetane	-260.0 ± 1.8	-204.0 ± 1.9

The strain energies in these compounds have been compared with that in the parent oxetane.

The present work is a continuation of a study on strain in small ring compounds of theoretical as well as practical interest.^{1,2} The possible use of oxetane and 3,3-disubstituted oxetanes as monomers in polymerization processes³⁻⁶ makes these compounds an attractive choice for an investigation of the influence of substitution on thermochemical strain energy in a four-membered ring system.

EXPERIMENTAL

Compounds. 3,3-Dimethyloxetane⁷ (I) and 3-ethyl-3-chloromethyloxetane⁸ (II) were synthesized at this laboratory. 3,3-Bis-chloromethyloxetane (III) was a commercial sample (Toyobo Co. Ltd., Japan).

The compounds were purified by fractional distillation followed by preparative gas chromatography (Autoprep A-700, 20' × 3/8", 25 % Carbowax 20M on Chromosorb W). No impurities could be detected by analytical GLC in any of the samples used. All samples were carefully dried over Type 4A Molecular Sieves. (Calcium hydride caused decomposition.) In no case was decomposition due to this treatment observed (GLC). The water content of the different compounds was determined by GLC⁹ on samples sealed into ampoules filled at the same time as ampoules used in combustion measurements.

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The accuracy of the water determinations is equal to or better than 0.002 mass per cent. No correction was applied if the analysis indicated less than 0.005 mass per cent H₂O. Densities of the pure materials are given in Table 1.

Table 1. Densities.

Compound	$\rho/\text{g cm}^{-3}$	
	20°C	25°C
3,3-Dimethyloxetane	0.83101	0.82620
3-Ethyl-3-chloromethyloxetane	1.08889	1.08408
3,3-Bis-chloromethyloxetane	1.29796	1.29276

Combustion calorimetry – apparatus and procedure. A rotating-bomb calorimeter TKL-2¹⁰ was used with two different platinum-lined bombs, 2A and 2B, both with an internal volume of 0.2622 dm³. Details of the calorimetric procedure have been given previously.¹¹ Calibration experiments were performed according to the standard procedure using the National Bureau of Standards sample 39i of benzoic acid.

After drying, the different substances were transferred in vacuum from Molecular Sieves to a receiver containing the ampoules to be filled for the combustion experiments.¹² Soft-glass ampoules were used in all experiments and the mass of the ampoules varied between 45 and 95 mg.

The combustions of 3,3-dimethyloxetane were carried out under standard conditions with 0.79 cm³ of water in the bomb. The chlorine-containing samples were burned with 10.02 cm³ of a 0.0656 M * arsenious oxide solution in the initial state.¹³ The amount of chlorine in all experiments did not exceed 6×10^{-3} g atoms. The paraffin oil used as auxiliary material was designated USBM-P3a.¹⁴

The chlorinated compounds tended to deposit soot. Experiments in which the substance did not burn completely were rejected.

All weighings were reduced to mass and the molecular weights computed from the 1961 table of atomic weights.¹⁵ The corrected temperature rise, $\Delta\theta$, and the energy equivalent of the calorimetric system were calculated as described by Bjellerup.¹⁶

Details of the different analyses of the final bomb solutions have been described recently.¹⁷

Vaporization calorimetry. The enthalpies of vaporization at 25.0°C for the compounds studied here were measured using the Wadsö calorimeter.¹⁸

RESULTS

All symbols used are those introduced by Hubbard, Scott and Waddington¹³ except that internal energy is now represented by U and temperature by θ . For 3,3-dimethyloxetane the Washburn corrections, ΔU_{Σ} were calculated using a computer program based on a slightly modified version of the calculational procedure given by Hubbard *et al.*¹³ For the chlorinated compounds a program for halogen compounds was used.¹⁷ The solubilities of oxygen in the initial and final bomb solutions and of carbon dioxide in the final bomb solution were estimated as given in Ref. 17. The enthalpies of solution of oxygen and carbon dioxide in pure water were taken from Ref. 19 with 1 cal = 4.184 J.** The value used for the energy of decomposition of arsenic

* M = mol dm⁻³.

** It seems probable that the value for carbon dioxide, $\Delta U_{\text{soln}}(\text{CO}_2) = -17.824$ kJ mol⁻¹ may be changed in the near future. When available, an average correction may be applied: for (II) and (III), add to the given value of $\Delta H_c^\circ/M [(a/-17.824) - 1] \times 37$ J g⁻¹, where a is the revised $\Delta U_{\text{soln}}(\text{CO}_2)$ -value. For (I) the correction is not significant (*ca.* 0.2 J g⁻¹).

oxide was that given by Bjellerup *et al.*²⁰ Corrections have been applied for the ionization of arsenic acid.²¹ Enthalpy of decomposition of H_2PtCl_6 was taken from Ref. 22. For the specific heat capacity of the compounds a common value of $1.88 \text{ J K}^{-1}\text{g}^{-1}$ was chosen. For paraffin oil and benzoic acid the values used were 2.22 and $1.20 \text{ J K}^{-1}\text{g}^{-1}$, respectively. $(\partial V/\partial T)_p$ -Values were calculated from the density measurements at 20 and 25°C . For paraffin oil $0.850 \text{ mm}^3 \text{ K}^{-1}\text{g}^{-1}$ was used. The final over-all precision of the ΔU_c° mean values was estimated as given in Ref. 17. Enthalpies of formation at 25.0°C for gaseous carbon dioxide and liquid water have been taken from Ref. 19.

Table 2. Summary of typical combustion experiments.

$$(\Delta U_c^\circ/M)(\text{oil}) = -(45.9587 \pm 0.0038) \text{ kJ g}^{-1}$$

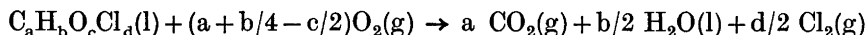
$$(\Delta U_c^\circ/M)(\text{fuse}) = -(16.807 \pm 0.004) \text{ kJ g}^{-1}$$

	3,3-Dimethyloxetane	3-Ethyl-3-chloro- methyloxetane	3,3-Bis-chloro- methyloxetane
Bomb	2A	2B	2B
$m'(\text{comp.})/\text{g}$	0.310320	0.476427	0.498756
$m''(\text{oil})/\text{g}$	0.203449	0.249931	0.249837
$m'''(\text{fuse})/\text{g}$	0.001521	0.001180	0.001198
$m(\text{Pt})/\text{g}$	11.009	11.920	9.183
$\Delta\theta/\text{K}$	0.744725	0.877809	0.744495
$\varepsilon^\circ(\text{calor})/\text{J K}^{-1}$	28215.8 ^a	28203.0 ^b	28201.3 ^b
$m^1(\text{cont.})/\text{g}$	22.754	32.816	30.177
$\varepsilon^1(\text{cont.})/\text{J K}^{-1}$	13.54	52.24	51.972
$\Delta U_{\text{soln}}^f(\text{CO}_2)/\text{J}$	2.17	19.97	17.05
$\Delta U_{\text{oxid}}^f(\text{HX})/\text{J}$	0	80.32	143.75
$\Delta U_{\text{dec}}^f(\text{As}_2\text{O}_5)/\text{J}$	0	23.39	104.06
$\Delta U_{\text{dec}}^f(\text{HNO}_3)/\text{J}$	4.00	3.44	2.13
$\Delta U_{\text{dec}}^f(\text{H}_2\text{PtCl}_6)/\text{J}$	0	0.02	0.71
$\Delta U_{\Sigma}^f/\text{J}$	6.83	24.70	21.62
$[-\Delta U_c^\circ/M(\text{comp.})]/\text{J g}^{-1}$	37270.4	27379.0	18377.6

^a The standard deviation of the mean for the calibration series was 2.4 J K^{-1} .

^b The standard deviation of the mean for the calibration series was 3.2 J K^{-1} .

Data for a typical combustion experiment for each compound are given in Table 2. Small differences in the $\varepsilon^\circ(\text{calor})$ -values for the same calorimeter system are due to minor changes in the calorimeter. The results of the different series of measurements are summarized in Table 3. The ΔU_c° -values refer to the idealized combustion reaction



in which all reactants and products are in their thermodynamic standard states at 25°C .

Table 4 gives the standard energies, ΔU_c° , and enthalpies, ΔH_c° , of combustion for the compounds in the liquid state together with the enthalpies of formation, ΔH_f° , for the liquid and gaseous states at 25.0°C .

Table 3. Results of combustion experiments at 25.0°C.
 $-(\Delta U_c^\circ/M)/\text{kJ g}^{-1}$

	3,3-Dimethyloxetane	3-Ethyl-3-chloro- methyloxetane	3,3-Bis-chloro- methyloxetane
	37.2392	27.3940	18.3827
	37.2754	27.3891	18.3776
	37.2944	27.3870	18.3824
	37.2643	27.3812	18.4031
	37.2704	27.3808	18.3890
	37.2569	27.3688	18.3723
	37.2355		18.3668
Mean	37.2623	27.3818	18.3820
Standard deviation	0.0078	0.0034	0.0045

Table 4. Results and derived quantities at 25.0°C.

	$\Delta U_c^\circ/\text{kJ mol}^{-1}$	$\Delta H_c^\circ/\text{kJ mol}^{-1}$	$\Delta H_f^\circ(\text{l})/\text{kJ mol}^{-1}$	$\Delta H_v/\text{kJ mol}^{-1}$	$\Delta H_f^\circ(\text{g})/\text{kJ mol}^{-1}$
3,3-Di- methyloxetane	-3209.59 ± 1.60	-3214.54 ± 1.60	-182.16 ± 1.63	33.94 ± 0.29	-148.22 ± 1.66
3-Ethyl-3-chloro- methyloxetane	-3685.78 ± 1.58	-3690.11 ± 1.58^a	-243.01 ± 1.62	49.71 ± 0.15	-193.30 ± 1.63
3,3-Bis-chloro- methyloxetane	-2849.67 ± 1.80	-2850.91 ± 1.80^b	-259.96 ± 1.84	55.98 ± 0.38	-203.98 ± 1.88

The uncertainties given are twice the final over-all standard deviation of the mean. The ΔH_c° values corresponding to a final state with the chlorine in the form of $\text{HCl}(600 \text{ H}_2\text{O})(\text{l})$ are ^a -3713.81 and ^b -2898.31 kJ mol^{-1} , respectively.

THE RING STRAIN IN THE SUBSTITUTED OXETANES

Pilcher determined the enthalpy of formation of the parent oxetane, using a flame calorimeter²³ and calculated a conventional ring-strain energy (C.R.S.E.) * in the four-membered ring of $106.3 \text{ kJ mol}^{-1}$. The question arises as to how the C.R.S.E. changes with the introduction of the different substituents in the ring. Both kinetic and thermochemical evidence support the generally accepted idea that alkyl substituents stabilize small ring structures.

From thermochemical studies on thiacyclopropanes,^{24,25} the C.R.S.E. in thiacyclopropane itself is calculated to 82.8 kJ mol^{-1} . Substitution with one methyl group decreases the C.R.S.E. with *ca.* 16 kJ mol^{-1} . The introduction of a second methyl group on the same carbon atom leads to a further decrease of $2-3 \text{ kJ mol}^{-1}$.

* Defined as $[\Delta H_a(\text{estimated}) - \Delta H_a(\text{observed})]$ at 298.15 K. This convention has been adopted here.

The C.R.S.E. in (I) relative to that in the parent oxetane may be derived by using the method of structural similarity. The difference in enthalpy of formation between (I) and oxetane is $-(67.7 \pm 1.8)$ kJ mol⁻¹. If this value is compared with the difference in enthalpy of formation between 3,3-dimethylpentane and pentane, $-(54.4 \pm 1.4)$ kJ mol⁻¹,²⁶ then the C.R.S.E. in (I) is found to be 13.3 kJ mol⁻¹ lower than that in oxetane.

A similar approach may be used to estimate C.R.S.E. in the two halogen substituted oxetanes. The difference in enthalpy of formation between (II) and (I) is $-(45.1 \pm 2.3)$ kJ mol⁻¹. For the reference substances chosen, 1-chlorobutane and propane, the corresponding difference is $-(43.1 \pm 4.0)$ kJ mol⁻¹.²⁶ Thus, within the limits of error of the data the C.R.S.E. in (II) is the same as in (I).

The difference in enthalpy of formation between (III) and (I) is $-(55.8 \pm 2.5)$ kJ mol⁻¹. For the reference compounds, 1,3-dichloropropane and propane, the corresponding difference is $-(56.1 \pm 4.0)$ kJ mol⁻¹.²⁶ The C.R.S.E. in (III) is, again, the same as it is in (I).

Thus, it has been found that the C.R.S.E. in the investigated 3,3-disubstituted oxetanes is approximately the same and *ca.* 14 kJ mol⁻¹ less than in the parent oxetane.

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