Enthalpy of Formation of Tetramethyl-1,3-cyclobutane-dione

PETER SELLERS

Thermochemistry Laboratory, Chemical Center, University of Lund, S-220 07 Lund 7, Sweden

The enthalpies of combustion and sublimation have been determined for tetramethyl-1,3-cyclobutanedione. The following enthalpies of formation at 25°C were derived:

$\Delta H_f^\circ(c) = -379.9 \pm 1.5$ kJ mol^{-1}
$\Delta H_f^\circ(g) = -307.7 \pm 1.6$ kJ mol^{-1}

The results have been used in a discussion of the strain energy in the molecule, and compared with other four-membered ring compounds.

In previous papers from this Laboratory, results have been presented for enthalpies of formation of four-membered ring compounds with different degrees of sp^2-hybridization, and strain energies have been calculated. Thus, Börjesson *et al.*[1] found the strain energy in β-propiolactone to be 94 kJ mol^{-1}, similar to that in cyclobutane, 111 kJ mol^{-1}.[2] The strain energy in diketene,[3] a four-membered ring with 2 sp^2-hybridized carbon atoms, was found to be essentially the same as that in β-propiolactone, with only 1 sp^2-hybridized carbon atom. These results were somewhat surprising, and it was decided that data for other compounds with sp^2-hybridized ring carbon atoms would be of value in a consideration of the strain energies of such compounds. Tetramethyl-1,3-cyclobutanedione (I) was chosen as a suitable compound, since it was easily available and there would be no problems caused by keto-enol tautomerisation.

EXPERIMENTAL

Compounds. Tetramethyl-1,3-cyclobutanedione (Fluka, practical grade) was purified by fractional crystallization from absolute ethanol (repeated 3 times), followed by drying at 60°C overnight. The sample was then sublimed twice under vacuum and stored in a desiccator over P_2O_5.

The water content of the sample was determined, using a microcoulometric Karl Fischer technique, and found to be 0.021 wt.%.

Solutions of the substance in absolute ethanol were analyzed by gas chromatography on a Carbowax 20M column at 100°, and no organic impurities were detected.

The purity of the sample was further checked by analysis of the melting peaks obtained by differential scanning calorimetry (Perkin-Elmer DSC-1B). The melting point derived from the DSC curve was 115.3°C, and the purity was found to be 99.9 ± 0.1 mol %,[4] in reasonable agreement with the results from the GLC and water content measurements described above.

Table 1. Results of the combustion experiments.

$\varepsilon°(calor) = 28167.0 \pm 2.3$ J deg^{-1};
$m(Pt) = 11.915$ g;
$(\Delta U_c°/M)(mylar) = -[(22.8969 - 0.0011 \times RH) \pm 0.0033]$ kJ g^{-1};
$(\Delta U_c°/M)(fuse) = -(16.807 \pm 0.004)$ kJ g^{-1}.

$m'(comp.)/g$	$m''(mylar)/g$ RH=40%	$m'''(fuse)/g$	$\Delta\theta/K$	$m_i(cont.)/g$	$\varepsilon^i(cont.)/J\ K^{-1}$	$\Delta U_{dec}^f(HNO_3)/J$	$\Delta U\Sigma/J$	$[-\Delta U_c'°/M(comp.)]/J\ g^{-1}$
0.620127	0.048158	0.001593	0.745987	23.764	13.52	7.69	11.13	31932.3
0.619790	0.049121	0.001480	0.746668	23.764	13.52	5.52	11.18	31951.5
0.619813	0.047259	0.001690	0.744999	23.763	13.52	7.58	11.11	31934.4
0.619440	0.047250	0.001598	0.744520	23.762	13.52	3.34	11.16	31941.5
0.615443	0.051304	0.001612	0.743311	23.762	13.52	8.31	11.10	31934.9

Mean $-\Delta U_c'°/M(comp.)$
$= 31938.9 \pm 3.5$ J g^{-1}

$-\Delta U_c°/M(comp.)$
$= 31945.6 \pm 3.8$ J g^{-1}

The density of the pure compound was 1.108 g ml^{-1} at 25°C.

Combustion calorimetry — apparatus and procedure. The apparatus and calorimetric procedure were as described previously, using a Hewlett Packard Quartz Thermometer for temperature measurement.[5]

The sample was pressed into pellets and sealed into polyester bags made from Du Pont's 100 gauge Mylar Type A, using the technique described in Ref. 6. The bags were weighed before filling at a known relative humidity. The substance was not particularly hygroscopic, and the use of a dry-box was not considered necessary.

All weighings were reduced to mass, and the molecular weights computed from the 1969 Table of Atomic Weights.[7]

Vaporization calorimetry. The enthalpy of sublimation at 25°C for the compound was measured in a modified version of the calorimeter described by Morawetz.[8]

RESULTS

The results are expressed in terms of absolute joules. Symbols and calculational procedure used were as previously described.[5],[9] The values used for the specific heat capacity, C_p, and $(\delta V/\delta T)_p$ were 1.40 J K^{-1}g^{-1} and 0.388 mm^3 K^{-1}g^{-1}, respectively.

The final overall precision of the ΔU_c° mean value was estimated as in Ref. 9. Enthalpies of formation at 25°C for gaseous CO_2 and liquid water were taken from Ref. 10. The results from the combustion experiments are shown in Table 1, where the mean $-\Delta U_c^\circ/M$ value is obtained from $-\Delta U_c'^\circ/M$ by correction for the water content of the sample. The $\Delta U_c'^\circ$ values refer to the idealized combustion reaction, in which all reactants and products are in their thermodynamic standard states at 25°C.

Table 2. Results and derived quantities at 25°C.

ΔU_c°/kJ mol^{-1}	-4478.26 ± 1.37
ΔH_c°/kJ mol^{-1}	-4483.20 ± 1.37
ΔH_f°(c)/kJ mol^{-1}	-379.86 ± 1.47
ΔH_{sub}/kJ mol^{-1}	72.2 ± 0.6
ΔH_f°(g)/kJ mol^{-1}	-307.7 ± 1.6

Table 2 gives the standard energy, ΔU_c°, and enthalpy, ΔH_c°, of combustion, together with the enthalpy of sublimation, ΔH_{sub}, and derived enthalpies of formation, ΔH_f°, for the liquid and gaseous states at 25°C. The uncertainties given are twice the final overall standard deviation of the mean.

DISCUSSION

The strain energies in four-membered ring compounds can show considerable variations due to different conformations of the ring itself and to the presence of different substituents on the ring carbon atoms.

The structure of tetramethyl-1,3-cyclobutanedione (the dimer of dimethyl ketene) has been investigated by electron diffraction[11] and X-ray crystal structure analysis.[12] These studies have shown that the molecule is essentially planar, but the possibility of considerable out-of-plane vibrations was not excluded. These results are supported by NMR studies at $-60°$ and $+40°C$ which showed no evidence of non-equivalent protons, only one sharp single peak being observed.[13] The authors of this latter paper suggested a flexible structure which oscillates through a mean plane.

Thermochemical evidence supports the idea that alkyl substituents stabilize small ring structures. This has been shown in studies on methyl substituted thiacyclopropanes [14,15] and 3,3-disubstituted oxetanes,[16] where dimethyl substitution stabilizes the rings by between 14 and 20 kJ mol^{-1}, the effect being greater for the three-membered rings. There is not such clear evidence of the effect of substitution in the case where some of the ring carbon atoms are sp^2-hybridized, but it would be expected to be similar to that in the examples mentioned above.

The strain energy in (I) may be derived by applying a bond-energy scheme calculation (here we refer to the conventional ring-strain energy, C.R.S.E., as defined in Ref. 2). Parameters for several such schemes have been given in Ref. 2, and we have used the Allen scheme with one modification. The parameter Δ_{CCC^*}, where C* is a carbonyl carbon atom, has been derived previously in a study on aliphatic branched ketones,[17] and is used in this calculation. There will be also four interactions of the type $\Delta_{CC^*C^*}$, with both the carbonyl carbons involved, but since there are no values available for this parameter it has been set equal to Δ_{CCC^*}. In this manner, the enthalpy of formation of gaseous (I) is calculated to be -403.8 kJ mol^{-1}. The C.R.S.E. in (I), the difference between the experimental and calculated enthalpies of formation, is then 96 kJ mol^{-1}, with an uncertainty of about ± 10 kJ mol^{-1}.

Despite the large uncertainties involved, it would seem reasonable to state that, assuming a degree of stabilisation in the molecule due to methyl substitution similar to the cases mentioned previously, the presence of two sp^2-hybridized carbon atoms in the ring does not significantly affect the strain energy.

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