

Enthalpies of Formation of Squaric Acid and the Corresponding Diethyl Ether

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Enthalpies of combustion have been measured for squaric acid (dihydroxycyclobutenedione) and diethoxycyclobutenedione. The following enthalpies of formation were derived:

	$\Delta H_f^\circ/\text{kJ mol}^{-1}$
Squaric acid (c)	-598.2 ± 0.4
Diethoxycyclobutenedione (l)	-552.1 ± 1.4

Using estimated values of enthalpies of sublimation and vaporization, the values are discussed in terms of strain energies and delocalization energies. The strain energy in a four-membered ring with four sp^2 -hybridized carbon atoms is discussed.

Diketocyclobutenediol (3,4-dihydroxy-cyclobut-3-ene-1,2-dione) was first synthesized in 1959,¹ and was later given the trivial name squaric acid.² The compound was found to be a strong acid, and the dianion was later shown to be a member of a new class of aromatic compounds, $C_nO_n^{2-}$, symmetrical resonance stabilized anions.³ The name oxocarbons⁴ was suggested for this class of compounds, in which all, or nearly all, of the carbon atoms bear ketonic functions or their equivalents.

Compounds possessing the cyclobutadienoquinone structure have been the subject of many recent investigations, since they are molecules which should have the same degree of strain as cyclobutadiene, which has not yet been isolated. Thermochemical data have been determined so far for only one member of this class of compound, phenylcyclobutenedione,⁵ and the present work was carried out to provide more information on such systems. The diethyl ether derivative of squaric acid was included to avoid the hydrogen bonding effects which exist in the acid itself.

EXPERIMENTAL

Compounds. Squaric acid (Fluka) was purified following the procedure given in Ref. 2, the recrystallization process being repeated 3 times. The compound was dried at 120°C and stored in a desiccator over P_2O_5 . The water content of the sample was determined, using a coulometric Karl Fischer method,⁶ and found to be 0.003 wt.%. The density of the sample was 2.119 g ml⁻¹ at 25°C.

1,2-Diethoxycyclobutenedione (Fluka, pract.) was purified by distillation under reduced pressure, and then dried over molecular sieves 4A. The purity of the sample was checked by GLC on a SE-30 column. No organic impurities were detected. The water content of the sample was determined on ampoules filled under vacuum, using a gas chromatographic method,⁷ and found to be 0.007 wt.%. The density of the sample was 1.1588 g ml⁻¹ at 25°C.

Combustion calorimetry – apparatus and procedure. The apparatus and calorimetric procedure were as described previously.⁸ The squaric acid sample was pressed into pellets for the combustion experiments. It was not found necessary to enclose the pellets; the substance has a very low vapour pressure at 25°C, and is not hygroscopic (no significant weight changes after 1/2 h on a microbalance).

The diethoxycyclobutenedione was filled into soda-glass ampoules under vacuum.

Enthalpies of vaporization and sublimation. No experimental values could be obtained at the present time. Instead, calculated values were derived, using a group-incremental method.

RESULTS

The results are expressed in terms of absolute joules. Symbols and calculational procedure used were as given previously.^{8,9} All weighings were reduced to mass, and the molecular weights computed from the 1969 Table of Atomic Weights.¹⁰ The values used for the specific heat capacities and $(\delta V/\delta T)_p$ for squaric acid and the diethoxy compound were 1.40 J K⁻¹g⁻¹ and 0.400 mm³ K⁻¹g⁻¹, and 1.67 J K⁻¹g⁻¹ and 0.646 mm³ K⁻¹g⁻¹, respectively.

Auxiliary data used and estimation of the final over-all precision were as previously.^{8,9} Data for a typical combustion experiment for each compound

Table 1. Summary of typical combustion experiments.

$\varepsilon^\circ(\text{calor}) = (28167.0 \pm 2.3) \text{ J K}^{-1}$		
$(\Delta U_c^\circ/M)(\text{oil}) = -(45.9459 \pm 0.0042) \text{ kJ g}^{-1}$		
$(\Delta U_c^\circ/M)(\text{fuse}) = -(16.807 \pm 0.004) \text{ kJ g}^{-1}$		
	Squaric acid	Diethoxycyclobutenedione
$m'(\text{comp.})/\text{g}$	1.846528	0.514665
$m''(\text{oil})/\text{g}$	—	0.176886
$m'''(\text{fuse})/\text{g}$	0.002120	0.001277
$m(\text{Pt})/\text{g}$	11.915	11.915
$\Delta\theta/\text{K}$	0.732197	0.724204
$m^i(\text{cont.})/\text{g}$	24.932	23.837
$e^i(\text{cont.})/\text{J K}^{-1}$	15.17	13.88
$\Delta U_{\text{dec}}^i(\text{HNO}_3)/\text{J}$	5.21	7.65
$\Delta U_\Sigma/\text{J}$	36.73	11.02
$[-\Delta U_c^\circ/M(\text{comp.})]/\text{J g}^{-1}$	11091.6	23645.0

Table 2. Results of combustion experiments at 25°C.

	$-(\Delta U_c^\circ/M)\text{kJ g}^{-1}$	$-(\Delta U_c^\circ/M)\text{kJ g}^{-1}$
	Squaric acid	Diethoxycyclobutenedione
	11.0967	23.6508
	11.0961	23.6450
	11.0921	23.6413
	11.0916	23.6507
	11.0932	23.6378
	11.0949	
Mean	11.0941	23.6451
Standard deviation	0.0009	0.0026
		$-\Delta U_c^\circ/M = 23.6468 \text{ kJ g}^{-1}$

Table 3. Results and derived quantities at 25°C.

	$\Delta U_c^\circ/\text{kJ mol}^{-1}$	$\Delta H_c^\circ/\text{kJ mol}^{-1}$	$\Delta H_f^\circ(\text{c or l})/\text{kJ mol}^{-1}$	$\Delta H(\text{sub or v})/\text{kJ mol}^{-1}$	$\Delta H_f^\circ(\text{g})/\text{kJ mol}^{-1}$
Squaric acid	-1265.37 ± 0.33	-1261.67 ± 0.33	-598.20 ± 0.38	83.7 ± 16.7	-514.5 ± 16.7
Diethoxycyclo- butenedione	-4023.88 ± 1.37	-4025.11 ± 1.37	-552.11 ± 1.43	73.6 ± 3.8	-478.5 ± 4.1

Table 4. Observed and calculated enthalpies of formation.

	$\Delta H_f^\circ(\text{g})(\text{obs.})/\text{kJ mol}^{-1}$	$\Delta H_f^\circ(\text{g})(\text{calc.})/\text{kJ mol}^{-1}$	$\Delta(\text{obs.} - \text{calc.})/\text{kJ mol}^{-1}$
Squaric acid	-515	-545	+30
Diethoxycyclobutenedione	-478	-535	+57
Phenylcyclobutenedione	-30	-89	+59

are given in Table 1. The results from the different series of measurements are summarized in Table 2, where the given uncertainties are the standard deviations of the means. The $\Delta U_c^\circ/M$ mean value for diethoxycyclobutenedione given in Table 2 refers to the pure sample after correction for the water content.

Table 3 gives the standard energies, ΔU_c° , and enthalpies, ΔH_c° , of combustion, together with the estimated enthalpies of vaporization and sublimation, ΔH_v and ΔH_{sub} , and derived enthalpies of formation, ΔH_f° , for the liquid or solid and gaseous states. The errors given are twice the final over-all standard deviation of the mean, except for ΔH_v , ΔH_{sub} and $\Delta H_f^\circ(g)$, where estimated uncertainties in the calculated values are included.

DISCUSSION

The enthalpies of vaporization and sublimation calculated for the compounds are associated with fairly large errors, especially in the case of squaric acid, where hydrogen bonding in the crystal¹¹ makes the estimation particularly difficult. These errors, however, will not be as serious as would normally be the case, since, as will be seen below, uncertainties associated with the reference systems are also high, and only a qualitative picture of the effects under investigation can be obtained.

In order to derive information regarding strain and delocalization energies in the molecules, it is necessary to calculate values for a reference system. No data are available for suitable reference compounds, and the bond energy schemes usually most satisfactory for the calculation of reference data¹² are not applicable in the present case; parameters for some of the bonds and interactions are not known. It has therefore been necessary to resort to a simpler scheme, namely that of Klages,¹³ which enables the calculation of the enthalpy of combustion, and thus enthalpy of formation, in the vapour state of the strain-free and non-resonating molecules. This method was also used by Roberts and co-workers⁵ in the case of phenylcyclobutenedione, so that some uniformity in the method of approach will be maintained.

Table 4 shows the experimental and calculated enthalpies of formation for the compounds concerned, with the data for the above-mentioned phenyl compound included for comparison. The last column gives the difference between the observed and calculated values, where a correction has been made in the case of the phenyl compound for the delocalization energy of the phenyl group, 151 kJ mol⁻¹. The results indicate that for all three compounds, the strain energy of the four-membered ring exceeds the delocalization energy of the ring, and, considering the uncertainties in the corrections to the vapour state and calculations on reference systems, the results are in good agreement.

In the paper where the results for the phenyl compound were originally presented,⁵ Roberts deduced that the delocalization energy in the four-membered ring would be between about 130 and 250 kJ mol⁻¹. This was based on theoretical calculations of the strain energy in cyclobutadiene,^{14,15} which gave the strain energy as being between 190 and 310 kJ mol⁻¹, and assuming the ring strain in the dione to be the same. Further support for a high value of the strain energy in a four-membered ring with four trigonal carbon atoms is provided by the work of Bedford *et al.*,¹⁶ who deduced a strain

energy of the four-membered ring of biphenylene of between 270 and 315 kJ mol⁻¹, using a comparison with biphenyl.¹⁷ In a footnote in Ref. 5, Roberts implied that perhaps the relevant strain energy should be much lower, and in other publications^{18,19} he has suggested a value of between 75 and 126 kJ mol⁻¹, that is, of about the same order as that in a "normal" four-membered ring. If this is the case, then the delocalization energy of the systems given in Table 4 would be of the order of 40 kJ mol⁻¹. There have been some theoretical calculations of the delocalization energies in such systems, using a simple LCAO approach.^{5,20} These calculations indicate a delocalization energy in the parent cyclobutadienoquinone of about 90 kJ mol⁻¹, and in the phenyl compound of about 125 kJ mol⁻¹. These values, combined with the data of Table 4, support the high figure for the strain energy in the rings under study, but too much weight should not be put on them, since they are crude approximations.

The situation is thus rather confused, and no definite conclusions can be drawn. The present author is inclined to the view that the strain energy in question should be considerably higher than that in cyclobutane, but not as high as that quoted for the ring in biphenylene. A more definite answer to the problem can be obtained only when theoretical calculations can be refined and data obtained for molecules studied, which are uncompromised by effects other than strain.

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