Thermochemical study of some cubane derivatives

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The thermochemical study of cubane-1,4-dicarboxylic acid (**1**), diethyl cubane-1,4-dicarboxylate (**2**), diisopropyl cubane-1,4-dicarboxylate (**3**), and bis(2-fluoro-2,2-dinitro)ethyl cubane-1,4-dicarboxylate (**4**) was performed. The standard enthalpies of combustion ($\Delta_c H°$) and formation ($\Delta_f H°$) of these compounds were estimated using the method of combustion in a calorimetric bomb in an oxygen atmosphere. Using the additive group method, calculated values for $\Delta_f H°$ of these substances which agreed satisfactorily with the experimental ones were obtained. The strain energies (E_s) of the cubic structure of derivatives **1—4** were calculated. It was concluded that E_s did not change on substitution of hydrogen atoms in cubane for various functional groups and was equal to E_s of the structure of cubane itself. The reliability of the single published value of $\Delta_f H°$ in the cubane crystal state, 541.8 kJ mol^{-1} (129.5 kcal mol^{-1}), was confirmed.

Key words: thermochemical study, cubane, derivatives, enthalpy of combustion, enthalpy of formation, strain energy, additive group contributions, calculation.

Few cubane (pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane) derivatives have been synthesized to date due to the considerable difficulties of synthesis both of cubane and its derivatives.

The structures in which eight carbon atoms form the cube along C—C bonds have also been studied insufficiently in the thermochemical aspect. There is only one work[1] devoted to determination of the enthalpy of formation ($\Delta_f H°$) and enthalpy of sublimation (ΔH(s)) of cubane ($\Delta_f H°$(cr) = 541.8±3.3 kJ mol^{-1}; ΔH(s) = 80.4 kJ mol^{-1}). Data from the thermochemical study[2] of dimethyl cubane-1,4-dicarboxylate (**2**) ($\Delta_f H°$(cr) **2** = −218.99±2.12 kJ mol^{-1}) were published later, and the results presented in Ref. 1 have been critically analyzed. One of the studies[3] is devoted to homocubane derivatives, whose structure differs considerably from that of cubane: one of the C—C bonds linking the vertices of the cube is cleaved by the CH_2 group introduced. In this case, homocubane derivatives can be of interest only for comparison of the changes in the thermochemical properties of the compounds on going from one structure to another.

The purpose of this work is to reveal whether the value of E_s remains constant for each of the cubane derivatives, including cubane itself, or where each compound has a characteristic value of E_s.

Experimental

Cubane-1,4-dicarboxylate **1** and its esters, dimethyl ester **2**, diisopropyl ester **3**, and bis(2-fluoro-2,2-dinitro)ethyl ester **4**, were synthesized by the procedures published previously.[4]

Some properties of the compounds studied are presented in Table 1.

The method of the calorimetric experiments, apparatus, and methods for calculation of the main and auxiliary values are similar to those used in our previous works.[5,6]

The combustion of cubane derivatives **1—4** in an oxygen atmosphere (p = 30 atm, T = 298.15 K, and V = const) is described by the equations

Table 1. Properties of cubane derivatives

Compound	Molecular weight/g	M.p./K	d_4^{20}	Purity from analyses of CO_2 (wt.%)
$C_8H_6(COOH)_2$ (**1**)	192.17	499—500	1.640	100.5
$C_8H_6(COOMe)_2$ (**2**)	220.22	436—437	1.424	99.9
$C_8H_6[COOCHMe_2]_2$ (**3**)	276.33	383—384	1.275	99.95
$C_8H_6[COOCH_2C(NO_2)_2F]_2$ (**4**)	464.25	422—423	1.665	99.8

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Table 2. Results of determination of $\Delta_f H^\circ$ of compounds **1—4** under the conditions of a calorimetric bomb

Compounds	Experiment	$-\Delta_c U^b$	$n\Delta RT + \pi$	$-\Delta_c H^\circ$	$-\Delta_f H^\circ_{exp}$	$\Delta_f H^\circ_{calc}$[7]
1	*8*	4764.6	−4.0	4760.6	318.5±12.6	312.0
2	*7*	6207.4	−1.5	6205.9	231.2±2.5	224.4
3	*7*	8770.5	3.1	8773.6	381.0±2.1	376.0
4	*5*	6573.0	−23.5	6549.5	747.8±6.3	749.9

Note. All values are presented in kJ mol^{-1}.

$C_{10}H_8O_4(cr) + 10\ O_2(g) = 10\ CO_2(g) + 4\ H_2O(l)$

$C_{12}H_{12}O_4(cr) + 13\ O_2(g) = 12\ CO_2(g) + 6\ H_2O(l)$

$C_{16}H_{20}O_4(cr) + 19\ O_2(g) = 16\ CO_2(g) + 10\ H_2O(l)$

$C_{14}H_{10}O_{12}N_4F_2(cr) + 10\ O_2(g) = 14\ CO_2(g) +$

$+ 4\ H_2O(l) + 4\ N_2(g) + 2\ HF(s).$

The samples studied were burned without auxiliary combustible materials, using samples weighing 0.15—0.22 g, which were weighed on an electronic balance with an accuracy of up to 10^{-5} g. After the experiment, CO and CO_2 were analyzed in the gas phase. CO was not found in all of the experiments, combustion was complete, as a rule, in all experiments, and carbon black traces were observed in two experiments on combustion of compound **4**. The corresponding corrections (~2.8—3.0 J) were made in the results obtained and were included in the general data set.

The values of heats of combustion of compounds **1—4** obtained experimentally under conditions of the calorimetric bomb ($-\Delta_c U^b$), the values of heats of combustion corrected with the Washborn corrections (π) and ΔnRT ($\Delta_c H^\circ$), the values of $\Delta_f H^\circ_{exp}$ calculated on the basis of them, and $\Delta_f H^\circ_{calc}$ calculated by the Kizin—Dvorkin method of the additive group contribution for organic substances in the liquid state[7] are presented in Table 2. The data necessary for calculation of $\Delta_f H^\circ_{exp}$ were taken from a handbook,[8] and $\Delta_f H^\circ$ of HF(s) of the required concentration was taken from a well-known source.[9]

Results and Discussion

Cubane with a cubic structure has a high degree of strain, indicated by the high positive value of $\Delta_f H^\circ$.[1] We attempted to estimate this value by a calculation method used in thermochemistry for various classes of organic compounds. For these purposes, we chose the Tatevskii method[10] for cyclic hydrocarbons in the gaseous state and the Kizin—Dvorkin scheme[7] for organic compounds in the molten (liquid) state. $\Delta_f H^\circ(g)$ (C_8H_8) = 619.2 kJ mol^{-1} was obtained with the first method, and $\Delta_f H^\circ(l)$ (C_8H_8) = 530.8 kJ mol^{-1} was obtained with the second method (for the molten state). The calculated and experimental values[1] of $\Delta_f H^\circ$ of cubane agree satisfactorily.

In studying the thermochemical properties of cubane derivatives **1**—**4**, it was of interest to find the effect of the functional fragments introduced on the value of the contribution of the cubic C_8H_{8-n} fragment itself (n is the number of functional fragments). The factor used to find this effect can be E_s, calculated as the difference between $\Delta_f H^\circ_{exp}$ and the sum of the contributions of the groups of which the compound under consideration can be constructed. Using the necessary additive group contributions (see Ref. 7) and that of the $C(NO_2)_2F$ fragment (see Ref. 6), the following values of E_s/kJ mol^{-1} were determined for compounds **1**—**4**: **1** = 568.1; **2** = 567.8; **3** = 570.0; and **4** = 576.8. The value of E_s of cubane calculated by the same method is equal to 574.6 kJ mol^{-1}. The results show that the cubic fragment in these compounds is stable and does not undergo any energy changes compared to cubane within the calculation error.

The corresponding calculation has shown the virtual coincidence of the C—C bond energies for cubane and ethylene (301.2 kJ per arbitrary bond in cubane and 303.7 kJ in ethylene). This fact also attests to the sufficient stability of the cubic structure and to the possibility of synthesizing other stable cubane derivatives. The necessary data on the C—C and C—H bond energies were taken from works published previously.[11—12]

The authors of the work[2] devoted to the thermochemistry of compound **2** obtained the value of $\Delta_f H^\circ$, which is 12 kJ more positive than that determined by us. The purity of their sample was 99.7±0.1 mol.%, m.p. was 437.6—438.6 K, d = 1.36 g cm^{-3}, ΔH_m = 41±3 kJ mol^{-1}, and the d value of the sample was obtained from measurements of the size of the molded brick. In our work, the density was determined by two methods: calculation based on X-ray diffraction data (D_x) and pycnometrically, d_4^{20} g cm^{-3} (see Table 1). The coincidence of the values was 0.001 g cm^{-3}. It is noteworthy that the value of ΔH_m of the sample is sufficiently high, which is rare for organic compounds.

In this case, the calculation by the Kizin—Dvorkin scheme,[7] which works satisfactorily for the estimation of $\Delta_f H^\circ$ of molten compounds of various classes, gives a difference of ~46 kJ mol for the liquid state, which makes repeated determination of $\Delta_f H^\circ$ and ΔH_m of compound **2** necessary.

A conclusion was made[2] concerning the change in E_s of the cubic structure of cubane on going to its derivatives (E_s of cubane is equal to 632.8, E_s of **2** is equal to 590.7 kJ mol^{-1}), and the reliability of the value of $\Delta_f H^\circ$ of cubane obtained by Kybett[1] was in doubt.

We believe that this conclusion was based on incorrect methods of the analysis performed previously.[2] The calculated increment in $\Delta_f H^\circ$ of methyl ester of cyclobutanecarboxylic acid and cyclobutane, of methyl ester of bicyclobutanecarboxylic acid and bicyclobutane was used, and this increment was transferred to the **2**—cubane pair. The "corrected" values of $\Delta_f H^\circ$ of cubane in the crystalline state were obtained by the reverse calculation. Therefore, in this transfer, all changes in $\Delta_f H^\circ$ and E_s of cyclic planar structures turned out to be transferred to $\Delta_f H^\circ$ of the steric structure of cubane. A simple calculation which takes into account the changes in the bond structure on going from $C-(C)_2(H)_2$ and $C-(C)_2(CO)(H)$ bonds to $C-(C)_3(H)$ and $C-(C)_3(CO)$ bonds, and the change in the E_s values of cyclo- and bicyclobutane determined experimentally for these compounds relative to their methyl esters result in a total error of 44.04 kJ. Introduction of the correction to this value of the calculation of $\Delta_f H^\circ$(cr) of cubane (see Ref. 2) results in 542±4.5 kJ mol^{-1} (541.8±3.3).[1] We performed this calculation using only the data obtained previously.[2]

Thus, the insertion of substituents into the exo-position instead of a hydrogen atom does not change the E_s value of the cubic structure. This conclusion can be illustrated using additive group contributions (see Ref. 2), which were used by the authors in their calculations, and the experimental value of $\Delta_f H^\circ$ of compound **2**. Omitting the arithmetic transformations, we obtain E_s **2** (cr) = 590.76 kJ mol^{-1}, and for cubane according to Kybett,[1] E_s(cubane)(cr) = 589.6 kJ mol^{-1}. The coincidence of the values of E_s to 1 kJ mol^{-1} confirms our conclusion and refutes the previous statement.[2] In our opinion, the work by Kybett[1] was performed at a rather low level from the viewpoint of thermochemical requirements, and the values should be determined repeatedly. However, we cannot rigorously reject the results obtained in this work.

The calculation[7] of homocubane derivatives ($\Delta_f H^\circ$ was determined previously[3]) was also performed for 4-carbomethoxyhomocubane and homocubane-4-carboxylic acid and produced satisfactory results, when the replacement of two four-membered rings in the cubane structure for two five-membered rings when insertion of a CH_2 group between adjacent atoms $C(C)_3$ was taken into account. This decreases E_s of the final structure by 155 kJ mol^{-1}.

Unfortunately, the number of cubane and homocubane derivatives studied is not large and, therefore, a more correct consideration of the regularities of the change in their thermochemical properties is presently difficult.

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