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Thermochemistry of Organic and Organohalogen Compounds†

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The advances in the thermochemistry of organic compounds, mainly cyclic and organohalogen derivatives, are examined. Studies on the thermodynamics of the polymerisation reactions of cyclic compounds, the determination of the standard enthalpies of formation of cyclic and organohalogen compounds, and the determination of relations between the standard enthalpies of formation and the strain energies of molecules, on the one hand, and their structure, on the other are analysed in detail.
The bibliography includes 213 references.

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I. INTRODUCTION

Fundamental research into the thermochemical properties of organic compounds is traditional in Russian thermochemistry. The determination of the heats of combustion of organic compounds in a bomb calorimeter was the fundamental experimental method at the Laboratory of Thermochemistry founded at Moscow State University (1891) by V.F.Luginin.[1,2]

After Luginin, his student and collaborator P.V.Zubov continued the research into the thermochemistry of organic compounds.[3-7] M.M.Popov made a major contribution to the development of the methods for the determination of heats of combustion. Together with W.Świetosławski, he proposed in 1914 that a single primary standard, benzoic acid, be used for the calibration of calorimeters.[8] In 1934 Popov and Shirokikh[9] constructed the first calorimeter with a moving bomb and thereby introduced into calorimetric practice a new method, which proved to be exceptionally useful for the investigation of organohalogen, organosulphur, organosilicon, and organometallic compounds as well as many other substances with a relatively complex composition.

The studies of S.M.Skuratov and his co-workers, in the course of which a self-sealing bomb calorimeter was constructed and a new model of a highly sensitive mercury thermometer was used, led to the creation of precision calorimetric apparatus which differed little from modern apparatus.[10,11] The sharp increase in the accuracy of the determination of the heats of combustion made it possible to observe extremely fine energetic effects (the mutual influence of atoms and groups, the differences between the properties of isomers, etc.). Further improvement of the apparatus and methods for stationary bomb calorimeters involved the improvement of the means for the measurement of temperature, the technique of the calorimetric experiment, and the analytical part of the thermochemical experiment.[12-14]

†In 1984, 150 years elapsed since the date of the birth of the famous Russian chemist, V.F.Luginin, who was a student of M.Berthelot and professor of Moscow University. The review has been written to commemorate this jubilee.

The standard enthalpies of formation of gaseous lower fluoro- and chlorofluorohydrocarbons have been determined mainly by two methods: by measuring the enthalpy of reaction with alkali metals (ΔH) [15,16] and by measuring the standard enthalpy of combustion in oxygen (ΔH_c°).[17,18]

Table 1. The specific combustion energies of standard substances at 298 K.

Substance*	$-\Delta U_c^0/M$, J g^{-1}			
	data from Laboratory of Thermochemistry at Moscow State University	refs.	data of other workers	refs.
Succinic acid (s)	12638.3±3.4	[10]	12638.5±1.5**	[28]
p-Chlorobenzoic acid (s)	19569.4±3.8	[19]	19566.6±1.9**	[28]
α-D-Glucose (s)	15559.7±3.0	[26]	15557.9±1.6	[29]
ααα-Trifluorotoluene (l)	23058.6±2.9	[27]	23064±14	[30]
			23051.2±2.8	[31]

*Here and henceforth the state of the substance is indicated in brackets: (l) = liquid, (s) = solid, and (g) = gaseous.
**Values recommended by the Mendeleev All-Union Institute of Metrology.

As the range of substances investigated was extended and the experimental technique improved, the importance of the method of combustion in oxygen increased continuously in view of its universality. The improvement of the method of determining the energies of combustion in rotating bomb calorimeters made it possible to apply it in the study of a whole series of new groups of organohalogen compounds: for substances containing different groups of halogens (for example, $CF_3CHClBr$ and $CF_2BrCHFCl$), for gaseous and volatile Freons (for example, $CF_2ClCFCl_2$, CF_2ClCCl_3, and CF_2ClCF_2Cl), for perfluoro-compounds, etc.[19-21] The development of methods for the combustion of gaseous substances in the liquefied state in a bomb calorimeter, first used in experiments designed to determine the combustion energy of chlorotrifluoroethylene,[22] occupies a special place.

The validity of the results obtained has been confirmed by the analysis of the literature data.[20,23-25] The method for the determination of the enthalpies of combustion of liquefied gases has led to extensive possibilities for the investigation of the thermochemical properties of substances which are not fully combusted in the gaseous state in the bomb.

The reliability of the methods for the determination of the energies of combustion of organic and organohalogen substances in stationary and rotating bomb calorimeters has been demonstrated by measuring the energies of combustion of secondary standards and highly pure specimens of thoroughly investigated substances (Table 1).

In the present review we were naturally unable to analyse all the available experimental data on the thermochemistry of organic and organohalogen compounds and we were obliged to confine ourselves to the aspects of the field which have been developed at the Laboratory of Thermochemistry at Moscow State University with inclusion of literature data for related thermochemical fields. Almost the entire data in the review can be arranged in terms of three principal branches of thermochemistry: the thermochemistry of the polymerisation reactions of heterocyclic compounds, the thermochemistry of cyclic hydrocarbons and their derivatives, and the thermochemistry of organohalogen compounds. The development of each has been stimulated by the urgent requirements of industry.

II. UNITS OF MEASUREMENT, AUXILIARY QUANTITIES, AND CALCULATION OF THE STRAIN ENERGY

The enthalpies of formation of organic and organohalogen compounds (ΔH_f°) quoted in this review constitute a system of mutually consistent quantities. In order to ensure this, all the enthalpies of formation have been recalculated on the basis of key quantities selected by the International Commission from the most reliable studies carried out in recent years and recommended by CODATA.[32] Since the values recommended by CODATA for certain key quantities (for example the ΔH_f° for HF solutions) differ significantly from those adopted earlier,[33,34] the values of ΔH_f° for organofluorine compounds presented in this review also frequently differ from those published in experimental or review communications.

All the thermochemical quantities in the present review are expressed in Joules in conformity with the international SI system of units. The data quoted in the original communications in calories have been recalculated on the basis of the relation 1 cal = 4.184 J.[35] The atomic weights have been adopted on the basis of IUPAC tables.[36] The enthalpies of dilution of HF and HCl solutions have been taken from Johnson et al.[37] and Cox et al.[38] respectively. The heat capacities of the individual substances have been taken from a handbook[33] and the heat capacities of solutions from Parker.[39]

The strain energies E_S of cyclic compounds, considered in this review, were obtained as differences between the experimental ΔH_f° and quantities calculated assuming additivity for unstrained acyclic molecules with the same number and character of bonds:

$$E_s = \Delta H^\circ_{f,(g),e} - \Delta H^\circ_{f,(g),c},$$

where ΔH_f°, (g), e is the experimental standard enthalpy of formation of the gaseous compound and ΔH_f°, (g), c the calculated value equal to the sum of the corresponding group contributions taken from Benson et al.[40] For certain groups of compounds, the E_S were calculated analogously as the differences between the experimental and calculated enthalpies of combustion. The contribution of the $-CH_2-$ groups to $\Delta H^\circ_{c(g)}$ in these calculations was assumed to be -658.63 kJ mol^{-1};[40] the contributions due to other groups are listed in the corresponding Tables in this review. In certain specially stipulated cases it proved possible to calculate the E_S only for the liquid state; in this case the contributions of the $-CH_2-$ group were taken from Prosen and Rossini[41] and Skuratov.[42]

Such calculation yields conventional values of E_S, because the result depends on the choice of the additive scheme for the calculation of the ΔH_f° for the unstrained analogue and in addition the calculation does not take into account the difference between the thermal and zero-point energies and also the difference between the internal energies and the enthalpies for the real cyclic molecule and the hypothetical molecule adopted as the unstrained species. The influence of these energy differences, which have not been allowed for, on E_S has been examined;[43] it is relatively small and is approximately constant in each series of cyclic compounds, so that, when the values of E_S are compared for compounds of a single series, the error arising due to the failure to take them into account is insignificant.

Questions associated with the nature of the strain and the complications arising in the quantitative analysis of the E_S have also been examined in a number of studies.[44-46]. The conventional nature of the E_S does not preclude the comparison and discussion of the reactivities of compounds of a single series[47] and of the dependence of the ΔH_f° on their structure.[43,48]

The values of ΔH_c°, ΔH_f°, and E_S presented below refer to 298.15 K (except for specified cases). The errors in the thermochemical quantities are expressed in terms of a 95% confidence interval.

III. THERMOCHEMISTRY OF THE POLYMERISATION REACTIONS OF HETEROCYCLIC COMPOUNDS

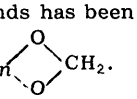
The study of the thermodynamic properties of lactams and their *N*-methyl-substituted derivatives is of great interest from the standpoint of the investigation of the capacity of these compounds for polymerisation. The reactivity of heterocyclic compounds is known to depend greatly on the number of members in the ring. This has also been observed for a series of lactams whose capacity for polymerisation diminishes consistently on passing from an eight-membered ring (ζ-enantholactam) to a five-membered ring (α-pyrrolidinone).[49] The ability of lactams to polymerise can be rigorously characterised by the Gibbs free energy of polymerisation at the corresponding temperature. In order to determine this quantity, direct measurement of the enthalpy of polymerisation and the measurement of the absolute entropies of the monomers and polymers are normally required; both sets of measurements are extremely laborious and are not always possible.

However, it is possible to make a significant approach to the solution of this problem by employing the enthalpies of combustion of the monomers. Thus it has been shown[49] that one of the factors determining the different capacities of lactams for polymerisation is the ring strain energy E_S. The values of E_S calculated[49] from the experimental enthalpies of combustion of lactams using data[50] for ζ-enantholactam, ε-caprolactam, α-piperidinone, and α-pyrrolidinone at 75 °C are 22.2, 15.9, 9.2, and 4.6 kJ mol^{-1} respectively. The decrease of E_S with decrease in the number of members in the ring ($8 > 7 > 6 > 5$) varies in parallel with the capacity of lactams for polymerisation.

Direct measurement of the enthalpies of polymerisation of caprolactam and enantholactam[42,51] and also the calculation of the enthalpies of polymerisation of these substances from the experimental ΔH_c° of the polymer and monomer[52] led to values which agreed, within the limits of error, with the E_S taken from Strepikheev et al.[49]. Strepikheev et al.[49] also demonstrated, in relation to 5- and 7-methylcaprolactams, that the substitution of a hydrogen atom in the methylene group by the methyl group does not affect significantly the ring strain.

Substitution at the N atom reduces the capacity of lactams for polymerisation to a greater extent than substitution at a C atom.[53] It has been suggested that N-substituted lactams are in general unable to polymerise, but it was later established that *N*-methylenantholactam nevertheless undergoes the polymerisation reaction.[54] The strain energies of *N*-methyl-lactams have been calculated[55] from the experimental enthalpies of combustion ΔH_c°(liq.); at 298 K they are 16.1, 9.2, −2.6, and −2.7 kJ mol^{-1} for compounds containing between 8 and 5 members in the ring respectively. These data show that *N*-methyl lactams have significantly lower E_S than their unsubstituted analogues. The highest E_S has been observed for *N*-methylenantholactam; it is approximately equal to E_S for the unsubstituted ε-caprolactam. In both series of compounds, at temperatures in the range 200–250 °C and a pressure of 100 kPa, the substances do not polymerise in the presence of activators if E_S < 12 kJ mol^{-1}.[55]

For a more accurate description of the ability of substances to polymerise, it is necessary to take into account the entropy of this reaction. Since the entropies for unsubstituted lactams and certain polymers have been measured experimentally,[52] there is a possibility of testing and revising earlier conclusions. Comparison of the thermodynamic functions calculated[52] for the polymerisation reactions of four lactams shows that there is no significant difference between the ΔH and ΔG for the polymerisation of caprolactam and enantholactam and that in these cases allowance for the entropy term does not influence the conclusions reached above on the basis of the analysis of the E_S alone. For the polymerisation reactions of α-pyrrolidinone and α-piperidinone, the difference between the enthalpies and Gibbs free energies is appreciably greater, because in this case the entropy of reaction ΔS is large. However, here too the qualitative conclusions reached from the analysis of the E_S remain in force. Furthermore, since the entropies of α-pyrrolidinone and α-piperidinone are greater than the entropies of the corresponding linear polymers, allowance for the entropy term for the polymerisation reactions of these substances makes the Gibbs free energies of both reactions positive.

The thermochemistry of the polymerisation reactions of oxygen-containing compounds has been studied in relation to the cyclic formals . The enthalpies of combustion and the strain energies for these substances are presented in Table 2. In the calculation of E_S, the contribution of the -O–CH_2–O- group to the standard enthalpy of combustion in the gaseous state ΔH_c°(gas) = −395.1 kJ mol^{-1} was calculated as the difference between the values of ΔH_c°(gas) for di-n-butyl formal (Table 2) and n-octane (−5512.05 ± 2.9 kJ mol^{-1} [50]). The enthalpies of evaporation required for the calculation of ΔH_c°(gas) have been calculated[57] from the semiempirical formulae quoted by Heukelom.[60] The standard enthalpies of evaporation ΔH_v were adjusted to 298 K on the basis of Watson's formula.[61] For comparison, the E_S for cyclanes are also quoted in Table 2; the similarity of the dependences of E_S on *n* for these two series is evident.

It follows from Table 2 that the strain energies of the formals investigated depend greatly on the number of members in the ring and decrease in the sequence 8 > 5 > 7 > 6. The equilibrium polymerisation of cyclic formals at 100–150 °C has been investigated[62] and it follows from the results that the capacity of cyclic formals for polymerisation decreases in the sequence 8 > 7 > 5 > 6 as a function of the number of members in the ring, i.e., as in the case of lactams, is largely determined by the strain energy.

Table 2. The enthalpies of combustion and evaporation and the strain energies of cyclic formals at 298 K (in kJ mol^{-1})**.

Substance	*n* *	$-\Delta H_c^0$(l)	$\Delta H_v^?$	$-\Delta H_c^0$(g)	E_S	
					formals	cyclanes
Ethylene formal (l)	5	1700.4±4.2 [56]	35.6±0.4 [56]	—	—	—
	5	1704.8±0.5 [57]	33.5 [57]	1738.3	25.7	26.4
Trimethylene formal (l)	6	2322.1±5.8 [56]	35.6±0.8 [56]	—	—	—
	6	2340.8±0.6 [58]	—	—	—	—
	6	2331.9±0.8 [59]	—	—	—	—
	6	2331.4±0.8 [57]	38.5 [57]	2369.9	−1.1	0
Tetramethylene formal (l)	7	3008.8±0.9 [57]	40.2 [57]	3049.0	19.4	26.8
Pentamethylene formal (l)	8	3697.7±1.1 [57]	43.9 [57]	3741.6	53.3	41.4
Di-n-butyl formal (l)	—	5850.2±1.8 [57]	56.9 [57]	5907.1	—	—

Note. In this and subsequent tables the references are given to the original studies in which the experimental ΔH_c° or ΔH_v° were obtained. The values calculated by the authors of the present review from the tabulated data are quoted without references. When several experimental studies have been made, the E_S were evaluated from the most reliable data and are given in the corresponding row.

The error of the initial experimental quantities is quoted after the original communications. The error of the calculated quantities is given in those cases where they have been obtained from reliable experimental data accompanied by the authors' estimate of the error.

If the experimental data referred to a temperature other than 298 K, we recalculated them for the standard temperature.

*The number of members in the ring.

**Here and henceforth the numerals in square brackets denote references (Ed.of Translation).

Indeed, the E_S for five- and seven-membered rings are similar and the equilibrium yields of polymers also do not differ very greatly. On the other hand, the transposition of the formals with five and seven members in the ring can probably be accounted for by the effect of the entropy of polymerisation. It follows from general considerations that, with decrease of the number of members in the ring, the difference between the entropies of the linear polymer (calculated for the corresponding unit) and the monomer should diminish. The experimental entropies of polymerisation of lactams confirmed this. It has been shown that,[52] with decrease of the number of members in the ring from 8 to 5, ΔS gradually diminishes, changing sign at the same time. Whereas the entropy change is favourable for the polymerisation process in the case of eight- and seven-membered rings, in the case of five- and six-membered rings, it becomes unfavourable and the polymerisation reaction takes place by virtue of the enthalpy change or, in other words, the strain energy E_S. One can assume with

complete justification that the dependence of ΔS for polymerisation on n has the character as for cyclic formals.

We may note that, although the thermochemistry of heterocyclic compounds has been investigated in order to elucidate and refine our knowledge about their capacity for polymerisation, the measurement of strain energies is of wider importance. It is to be expected that, for comparatively high values of E_S, other reactions involving the opening of the ring and the formation of straight-chain products will also take place more readily. Many instances of different reactivities of substances as a function of ring size are known for heterocyclic compounds. Thus tetrahydrofuran is more reactive than tetrahydropyran; five-membered glucosides are more reactive than six-membered glucosides and five-membered γ-monosaccharides are so unstable, in contrast to the six-membered compounds, that they have not even been isolated in a free state.[26]

The enthalpies of combustion of several monosaccharides as well as certain other oxygen-containing cyclic compounds are listed in Table 3. The contribution to the ΔH_C° by the -O- group, found as the difference between ΔH_C° for di-*n*-butyl ether (Table 3) and *n*-octane [50] and amounting to 125.0 kJ mol^{-1} in the gaseous state, was used to calculate the E_S for cyclic oxygen-containing compounds. Comparison of data obtained for the simplest oxygen-containing heterocycles (tetrahydrofuran and tetrahydropyran) shows that the strain energy of the six-membered ring is close to zero, while the strain energy of the five-membered ring is ~24 kJ mol^{-1}. Similar results are quoted above for cyclic formals and lactams.

Table 3. The enthalpies of combustion and evaporation and the strain energies of certain oxygen-containing cyclic compounds at 298 K (in kJ mol^{-1}).

Substance	n	$-\Delta H_C^0$	ΔH_V°	$-\Delta H_C^\circ$ (gas)	E_S
Tetrahydrofuran (l)	5	2501.2±0.4 [26]	32.5±0.2 [63]	2533.7±0.5	24.2
	5	—	—	2533.2±0.7 [64]	—
Tetrahydropyran (l)	6	3137.6±0.8 [26]	34.9±0.8 [65]	3172.5±1.1	4.3
	6	—	—	3173.3±1.0 [64]	—
2-Methoxytetrahydropyran (l)	6	3633.8±1.2 [26]	—	—	—
α-D-Xylose (s)	6	2338.9±0.8 [26]	—	—	—
α-D-Glucose (s)	6	2803.2±0.6 [26]	—	—	—
	6	2802.7±0.6 [50]	—	—	—
Methyl β-D-glucofuranoside (l)	5	3552.6±0.8 [26]	—	—	(22.0)*
Methyl β-D-glucopyranoside (s)	6	3517.9±0.4 [26]	—	—	—
Methyl α-D-glucopyranoside (s)	6	3522.1±0.8 [26]	—	—	—
Di-n-butyl ether (l)	—	5343.4±3.3 [26]	44.4 [66]	5387.8	—
	—	5342.6±0.9 [67]	44.4 [66]	5387.0	—

*Here and in the subsequent Tables the quantities calculated from insufficiently reliable data or calculated using approximate methods are enclosed in round brackets.

Analysis of the ΔH_C° for carbohydrates and other oxygen-containing cyclic compounds led to the conclusion[26,68] that the relations characteristic of compounds of other classes are typical also for them. Thus the simplest additive calculation of thermodynamic quantities is entirely feasible for carbohydrates whose molecules contain a large number of polar functional groups. On this basis, the authors[26,68] estimated the E_S for the five-membered methyl β-D-glucofuranoside by comparing its enthalpy of combustion with the ΔH_C° for the six-membered methyl β-D-glucopyranoside assuming that $E_S \approx 0$ for the latter, by analogy with other six-membered rings. Since the ΔH_V° for these substances are unknown, the estimate could be carried out only for the liquid state. Table 3 shows that the ΔH_C° for these two glucosides differ by ~30 kJ mol^{-1} despite their overall formulae being identical. Having taken into account the enthalpy of fusion of methyl α-D-glucopyranoside, the authors[26,68] obtained the strain energy of methyl β-D-glucofuranoside, amounting to ~22 kJ mol^{-1}, which is very close to E_S for tetrahydrofuran and other five-membered rings. The higher reactivity of five-membered rings can apparently be also explained by the appreciable strain energy. The polymerisation of γ-monosaccharides as well as other low-molecular-weight cyclic compounds, which is possible by virtue of the high E_S, probably plays an appreciable role in the biosynthesis of higher carbohydrates in nature.

The study of the mutual influence of the amino-groups and oxygen-containing groups is closely related to the investigation of cyclic lactams. Measurements have been made[69] of the ΔH_C° for aliphatic aminoacids and the interaction energies of the amino- and carboxy-groups, amounting to ~13 kJ mol^{-1}, have been estimated. The similarity of the ΔH_C° for different aminocaproic acids with different positions of the amino-group is evidence of the approximate constancy of the energy of this interaction.

IV. ENTHALPIES OF COMBUSTION OF BRANCHED ALKANES

The measurement of the enthalpies of combustion and formation of branched alkanes made it possible to estimate the contribution of the interaction of hydrogen atoms in close proximity, for example in the methyl groups at quaternary carbon atoms separated by one methylene group. This interaction was not taken into account by the constants of the additive scheme proposed for the calculation of the enthalpies of formation of hydrocarbons.[70] On the other hand, the average difference between the experimental and calculated[70] ΔH_C° amounted to ±2 kJ mol^{-1}; in three cases, namely for 2,2,4-trimethylpentane, 2,2,3,4-tetramethylpentane, and 2,2,4,4-tetramethylpentane, discrepancies between the calculated and experimental values exceeding the experimental error were noted. A prediction has been made[70,71] that the interaction of the methyl groups in such substances may be significant. It has been noted[72] that the distance between the closest hydrogen atoms of the CH_3 groups in the 2- and 4-positions in 2,2,4,4-tetramethylpentane, calculated on the assumption of a "staggered" configuration, is 0.0729 nm, whereas, for example, in the methyl group it is 0.1786 nm. Such an anomalous approach of the hydrogen atoms should alter the internal energy, by an amount which remains considerable even if one takes into account the fact that it is reduced somewhat owing to the rotation of methyl groups, which distort the valence angles.

The energy of interaction has been determined quantitatively[73] by measuring the enthalpies of combustion of several branched alkanes. The validity of the determination of the ΔH_C° for 2,2,4,4-tetramethylpentane [73] has been confirmed by the satisfactory agreement of this value with the results of Johnson et al.[74]. The data obtained were used to calculate the correction which must be taken included in the calculation, by an additive scheme taking into account the first interaction sphere,[70] of the ΔH_C° for all alkanes containing hydrogen atoms in close proximity, i.e. the C(3)–C–C(4) or C(4)–C–C(4) fragments. Taking into account this correction, the enthalpies of combustion of branched alkanes at 298 K can be calculated from the formula[72]

$$\Delta H_c^0 \text{ (kJ mol}^{-1}) = \sum_{i=1}^{4}\sum_{j=i}^{4} n_{ij} H_{ij(c)} - 10.13k$$

where $k = 1$ for each C(3)–C–C(4) fragment and $k = 2$ for each C(4)–C–C(4) fragment; $j \neq 1$.

V. THERMOCHEMISTRY OF CYCLIC HYDROCARBONS AND THEIR DERIVATIVES

In recent years much attention has been devoted in the thermochemistry of organic compounds to the study of cyclic hydrocarbons and their simplest derivatives. The special interest in the thermochemistry of cyclic compounds is determined mainly by two causes: (1) the high specific combustion energy of a number of substances belonging to this class; (2) the specific thermochemical relations which are characteristic of cyclic compounds but have so far been little investigated.

Among these substances, compounds with small rings (three- and four-membered) are especially interesting because of their unusual structural and chemical features. For this reason special attention has been devoted to them in this review. We shall not dwell on the analysis of the thermochemical data for other monocyclanes and their derivatives, since they are few in number and in addition are well known.[50,75]

Table 4. The enthalpies of combustion, formation, and evaporation (sublimation) and strain energies of cyclopropane, cyclopropene, and their substituted derivatives at 298 K (in kJ mol^{-1}).

Substance	$-\Delta H_c^0$	ΔH_f^0 (l or s)	ΔH_v^0 or ΔH_s^0	ΔH_f^0 (g)	E_s
Cyclopropane (g)	2091.3±0.5 [80]	—	—	53.3±0.5	115.4
Methylcyclopropane (l)	2719.1±0.6 [81]	1.7±0.6	22.6*	24.3	115.8
cis-1,2-Dimethylcyclopropane (l)	3370.4±0.6 [81]	−26.3±0.6	28.0*	1.7	122.7
trans-1,2-Dimethylcyclopropane (l)	3366.0±0.8 [81]	−30.7±0.8	26.9*	−3.8	117.2
1,1-Dimethylcyclopropane (l)	3363.4±0.7 [82]	−33.3±0.7	25.1±0.8 [83]	−8.2±1.2	115.5
1,1,2-Trimethylcyclopropane (l)	3979.9±0.8 [81]	−96.2±0.8	30.5*	−65.7	87.4
1,1,2,2-Tetramethylcyclopropane (l)	4635.6±0.8 [81]	−119.8±0.8	33.6*	−86.2	99.0
Ethylcyclopropane (l)	3371.9±0.8 [81]	−24.8±0.8	28.2*	3.4	115.7
	3384.0 [84]	—	—	—	—
1-Ethyl-2,2-Dimethylcyclopropane (l)	4665.2±0.8 [85]	−90.2±0.8	33.5*	−56.7	117.1
2,2-Dimethyl-1-propylcyclopropane (l)	5318.7±1.7 [85]	−116.0±1.7	38.9*	−77.1	117.4
Hexylcyclopropane (l)	5513.7** [84]	−314.5	—	—	—
1-Hexyl-2,2-dimethylcyclopropane (l)	7279.0±1.7 [85]	−193.0±1.7	51.6*	−141.4	115.2
cis-1,2-Diethylcyclopropane (l)	4675.5±1.3 [86]	−79.9±1.3	35.4±0.8 [86]	−44.5±1.5	117.9
trans-1,2-Diethylcyclopropane (l)	4672.1±2.1 [86]	−83.3±1.2	34.3±0.8 [86]	−49.0±2.3	113.4
cis-1,2-Dimethyl-3,3-dichlorocyclopropane (l)	3071.3±0.9 [87]	−86.9±0.9	(39.5)***	−47.4	(134.4)
trans-1,2-Dimethyl-3,3-dichlorocyclopropane (l)	3067.9±1.1 [87]	−90.2±1.1	(39.5)***	−50.7	(131.1)
Bicyclopropyl (l)	3886.0±3.0 [88]	95.9±3.0	33.5±1.2 [88]	129.4±3.2	228.1
Vinylcyclopropane (l)	3213.3±0.8 [89]	102.5±0.8	28.7±1.3 [89]	131.2±1.5	116.7
	3233.4 [84]	122.6	—	—	—
	—	98.7 [90]	—	—	—
Isopropenylcyclopropane (l)	3851.4±1.3 [91]	61.2±1.3	28.4±0.2 [91]	89.6±1.3	109.9
3-Cyclopropylbuta-1,2-diene (l)	4379.5±1.7 [91]	195.8±1.7	37.7*	233.5	110.7
Ethynylcyclopropane (l)	3086.1±0.8 [89]	261.1±0.8	30.9±1.5 [89]	292.0±1.7	112.7
Methylenecyclopropane (g)	2632.1±1.8 [92]	—	—	200.5±1.8	170.9
Trimethylenecyclopropane (g)	—	—	—	395.8 [93]	(205.4)
1,1-Diethynylcyclopropane (l)	4113.0±0.8 [91]	500.9±0.8	37.6*	538.5	113.5
Dicyclopropyldiacetylene (l)	5869.5±1.7****	505.2±1.7	58.2±1.0****	563.4±2.0	183.0
Phenylcyclopropane (l)	5071.0±0.9 [94]	100.3±0.9	50.22±0.10 [95]	150.5±0.9	103.9
	5076.4 [84]	105.7	—	—	—
1,1-Diphenylcyclopropane (l)	8088.9±3.3 [94]	185.4±3.3	65.5*	250.9	—
cis-1,2-Diphenylcyclopropane (l)	8082.2±0.8 [94]	178.7±2.1	—	—	—
trans-1,2-Diphenylcyclopropane (l)	8059.7±2.5 [94]	166.2±3.2	66.6*	232.8	77.4
1-Cyclopropyl-2-methylbenzene (l)	5725.4±0.8 [96]	75.4±1.2	52.0*	127.4	113.8
1-Cyclopropyl-2,4-dimethylbenzene (l)	6366.0±1.3 [96]	36.4±1.3	55.0*	91.4	110.7
1-Cyclopropyl-2,4,6-trimethylbenzene (l)	7014.1±2.1 [96]	5.4±2.1	58.3*	63.7	115.9
1-Cyclopropyl-4-isopropylbenzene (l)	7022.8±1.7 [96]	14.2±1.7	—	—	—
Cyclopropyl methyl ketone (l)	2956.2±1.0 [97]	154.7±1.0	39.41±0.09 [98]	−115.3±1.0	106.3
cis-2-Carboxy-1-phenylcyclopropane (s)	5043.4±2.1 [99]	−320.9±2.1	103.3±0.6 [91]	−217.6±2.2	115.1
trans-2-Carboxy-1-phenylcyclopropane (s)	5032.1±2.1 [99]	−332.1±2.1	104.8±0.2 [91]	−227.4±2.1	101.2
cis-2-Ethoxycarbonyl-1-phenylcyclopropane (l)	6423.1±1.2 [91]	−299.9±1.2	70.7±0.6 [91]	−229.2±1.3	101.7
trans-2-Ethoxycarbonyl-1-phenylcyclopropane (s)	6385.8±1.2 [91]	−337.2±1.2	96.9±0.4 [91]	−240.3±1.3	90.6
Cyclopropene (g)	2029.2±2.5 [50]	—	—	277.1±2.5	225.2
Methylcyclopropene (g)	2675.1±1.1 [92]	—	—	243.6±1.1	224.5
1,3,3-Trimethylcyclopropene (l)	3927.9±0.8 [91]	137.7±0.8	26.8±1.7 [91]	164.5±1.9	199.8
Spiropentane (l)	3296.0±0.7 [100]	—	—	185.1±0.7	265.8
	3258.4±1.3 [101]	147.5±1.3	27.53±0.04 [102]	175.0±1.3	--

*The enthalpy of evaporation was calculated from the Klages formula.[103]

**The value of ΔH_C° for hexylcyclopropane, given by Fierens and Nasielski[84] and also quoted by Pedley and Rylance,[50] deviates sharply from the series of ΔH_C° for other substituted cyclopropanes.

***The ΔH_V° were estimated from the group contributions quoted by Lebedev and Miroshnichenko.[83] The contribution of the three-membered ring to ΔH_V°, amounting to 3.3 kJ mol^{-1}, was obtained from a comparison of the experimental and calculated ΔH_V° for cyclopropane and 1,1-dimethylcyclopropane.

****Determined by S.M.Pimenova in the Laboratory of Thermochemistry at Moscow State University.

1. Three- and Four-Membered Rings

The variation of the strain energy of the three-membered ring in substituted cyclopropanes and cyclopropenes is illustrated in Table 4. The nature of the bonds in cyclopropane and the interaction of the ring with substituents have been the subject of numerous theoretical studies.[76-79] For example, the interaction of the three-membered ring with various substituents, in the first place π-donors and π-acceptors, has been examined[79] within the framework of perturbation methods using molecular orbitals. The effect of the interaction was estimated[79] mainly from the change in the geometry of the ring. However, as can be seen from the same investigation, this criterion is by no means always sufficiently sensitive.

Thermochemical data for cyclopropane derivatives are fairly numerous and are of undoubted interest. The results of the measurements of the ΔH_c° and E_S for substituted cyclopropanes, presented in Table 4, show that the interaction of the substituent with the three-membered ring is complex and that the effect of the stabilisation (or destabilisation) of the ring does not always agree with the postulated effect. The substitution of hydrogen by one or two methyl groups gives rise to a relatively small effect. An appreciable decrease of E_S has been observed for 1,1,2-trimethylcyclopropane and 1,1,2,2-tetramethylcyclopropane, going far beyond the limits of experimental error. However, this effect has not been noted for 2-n-alkyl-1,1-dimethylcyclopropanes. It has been shown[85] that the presence of the strained three-membered ring in the molecules of compounds of this series does not affect the bond energies in the side chain; this enabled the authors[85] to put forward a formula for the calculation of the ΔH_c° for liquid 1-n-alkyl-2,2-dimethylcyclopropanes, starting with 1-ethyl-2,2-dimethylcyclopropane:

$$-\Delta H_c^0 \text{ (liq.) (kJ mol}^{-1}) = 4665.2 + (n-7)\,653.7,$$

where $n \geq 7$ is the number of carbon atoms in the molecule.

The strain energies of the *cis*- and *trans*-isomers of 3,3-dichloro-1,2-dimethylcyclopropane proved to be much greater than the E_S for their hydrocarbon analogues. This conclusion must be regarded as preliminary, since the ΔH_v° for these compounds are approximate estimates and the energy contribution of the $C-(Cl)_2(C)_2$ group (taken from Benson et al.[40]) used in the calculation of ΔH_f°(gas) for the hypothetical unstrained compound is not entirely reliable.

The introduction of an exocyclic double bond appreciably increases the strain energy of the ring, which can be seen in relation to methylenecyclopropane. In the calculation of E_S for trimethylenecyclopropane it was assumed that the contribution of the $C_d-(C_d)_2$ group to ΔH_f° is equal to the contribution of the $C_d-(C_d)(C)$ group; furthermore, the accuracy of the measurement of ΔH_f°(gas) is low. This makes it necessary to regard the result of the calculation of E_S as approximate. However, the appreciable increase of E_S in this case too can be hardly open to doubt (see Table 4). On the other hand, the strain energies of alkenyl- and alkynyl-cyclopropanes, in which the double (or triple) bond is separated from the ring by a single bond, are close to the E_S for cyclopropane; for the majority of compounds, the difference is within the limits of the experimental error. This indicates the absence in most cases of an appreciable effect of the conjugation of the cyclopropane ring. However, there are also exceptions: the decrease of E_S in cyclopropyl methyl ketone greatly exceeds the experimental error, while the strain energy of dicyclopropyldiacetylene calculated for a single ring is only 91.5 kJ mol^{-1}. The conjugation of the triple bonds probably plays a major role in the latter case.

When an endocyclic double bond is introduced, the strain energy of the three-membered ring increases even more than that after the introduction of the exocyclic bond. The same behaviour has been observed for methylcyclopropenes as for methylcyclopropanes: the E_S for methylcyclopropene hardly differs from that for cyclopropene itself and the E_S for 1,3,3-trimethylcyclopropene is significantly lower.

Phenylcyclopropanes have an even lower strain energy compared with the unsubstituted cyclopropane. For phenylcyclopropanes and 1,1-diphenylcyclopropanes, this decrease is approximately the same. The effect of the interaction of the phenyl group with the three-membered ring in 1,2-diphenylcyclopropanes depends on their relative positions: for the *trans*-isomer, E_S is appreciably lower than for the *cis*-isomer. It is of interest that this feature is retained also in oxygen-containing phenyl-substituted derivatives: in phenylcyclopropanoic acids and their ethyl esters.

Comparatively few experimental enthalpies of combustion and strain energies are available for cyclobutane and cyclobutene derivatives (Table 5). So far as can be judged from the few reliable data, features similar to those noted above for cyclopropane and cyclopropene derivatives are characteristic of these compounds. Thus the strain energies of the alkyl-substituted derivatives differ little from the E_S for cyclobutane. When a double bond is introduced, E_S increases but the change in the E_S for the four-membered ring is much smaller than for the three-membered ring.

Table 5. The enthalpies of combustion, formation, and evaporation and the strain energies of cyclobutane, cyclobutene, and their substituted derivatives at 298 K (in kJ mol^{-1}).

Substance	$-\Delta H_c^0$ (l)	ΔH_f^0 (l)	ΔH_v^0	ΔH_f^0(g)	E_S
Cyclobutane (l)	2721.1±0.5 [104, 105]	3.7±0.5	24.64±0.04 [106]	28.4±0.5	111.2
Methylcyclobutane (l)	3352.2±1.3* [101]	−44.5±1.3	—	—	—
Ethylcyclobutane (l)	4017.1±0.7 [82]	−58.9±0.7	32.6±0.8 [82]	−26.3±1.1	106.7
	—	—	31.24±0.03 [98]	—	—
Bicyclo[1.1.0]-butane (g)	2648.7±0.8 [92]	—	—	217.2±0.8	274.5
Isopropenylcyclobutane (l)	4489.4±2.1**	19.9±2.1	—	—	—
trans-1,2-Divinylcyclo-butane (l)	4990.8±1.6 [91]	127.7±1.9	38 7±0.6 [91]	166.4±2.0	95.9
	4964.3±3.3 [107]	101.2±3.5	—	—	—
1-Vinylbicyclo-[1.1.0] butane (l)	3725.8±5.4**	221.3±5.4	—	—	—
Isobutylcyclobutane (l)	5317.4±1.7**	−117.3±1.7	41 1***	−76.2	106.9
Cyclobutene (g)	2588.2±1.5 [92]	—	—	156.7±1.5	124.7
Methylenecyclobutane (l)	3204.7±0.5 [82]	93.9±0.5	27.7±0.4 [82]	121.6±0.7	—
	3206.0±0.6 [109]	95.1±0.6	23.9 [109]	124.4±0.8	115.5

*The value of ΔH_c° for methylcyclobutane appears to be doubtful.

**Determined by L.P.Timofeeva and L.V.Kulakova in the Laboratory of Thermochemistry at Moscow State University.

***Calculated from the Klages formula.[103]

2. Bicyclic Hydrocarbons with Separated Rings and Spirans

Table 6 presents the enthalpies of combustion and formation and the strain energies for bicyclic hydrocarbons in which two rings are separated by one or two σ-bonds and also for spirans. As was to be expected, the E_S for the

individual rings in bicyclanes without a common carbon atom hardly differ from the E_S for the corresponding monocyclanes. Thus the strain energy of one three-membered ring in bicyclopropyl is equal to the E_S for cyclopropane within the limits of experimental error. The same feature has been observed also for other bicyclanes with analogous structures. It has been shown[11] that the difference between the enthalpies of combustion of a bicyclane and the corresponding monocyclanes in the liquid state is constant in all the known instances and amounts to 251.5 ± 1.6 kJ mol^{-1}. Thus the enthalpies of combustion of liquid bicyclanes in the molecules of which the rings are separated by one σ-bond can be calculated from the formula

$$\Delta H_c^0(\text{liq.})\ (\text{kJ mol}^{-1}) = [\Delta H_c^0(\text{liq.})]' + [\Delta H_c^0(\text{liq.})]'' + 251.5,$$

where $[\Delta H_C^\circ(\text{liq.})]'$ and $[\Delta H_C^\circ(\text{liq.})]''$ are the enthalpies of combustion of the corresponding monocyclanes.[11]

The difference between the enthalpies of combustion of dicyclopentylmethane and bicyclopentyl is −649.8 kJ mol^{-1} according to Kozina et al.[11] Using this value and the data quoted above, it is possible to calculate approximately the ΔH_C° for bicyclanes, in the molecules of which the rings are separated by the $-CH_2-$ group, from the formula

$$\Delta H_c^0(\text{liq.})\ (\text{kJ mol}^{-1}) = [\Delta H_c^0(\text{liq.})]' + [\Delta H_c^0(\text{liq.})]'' - 398.3,$$

where, as in the previous formula, $[\Delta H_C^\circ(\text{liq.})]'$ and $[\Delta H_C^\circ(\text{liq.})]''$ are the enthalpies of combustion of the corresponding monocyclanes. Presumably the interaction between the rings does not affect the thermodynamic quantities also in those cases where the number of rings separated by σ-bonds is greater than two.

Table 6. The enthalpies of combustion, formation, and evaporation and the strain energies of spiro-hydrocarbons and certain bicyclic hydrocarbons at 298 K (in kJ mol^{-1}).

Substance	$-\Delta H_c^0$	ΔH_f^0 (l)	ΔH_v^0	ΔH_f^0 (g)	E_S
Bicyclopropyl (l)	3886.0±3.3 [88]	95.8±3.3	33.5±1.3 [88]	129.3±3.6	228.0
Bicyclopentyl (l)	6332.5±2.9 [111]	−175.1±3.2	51.0*	−124.1	—
	6328.3±0.8 [110]	−179.3±0.8	—	−128.3	53.3
Dicyclopentylmethane (l)	6981.8±2.1 [11]	−205.1±2.1	52.7*	−152.4	49.9
Cyclopentylcyclohexane (l)	6956.7 [11]	−230.2	55.2*	−175.0	27.3
Bicyclohexyl (l)	7593.0±0.8 [110]	−273.3±0.8	—	—	—
Cyclopentylcycloheptane (l)	7640.0±3.8 [11]	−226.3±3.8	58.6*	−167.7	55.3
Bicycloheptyl (l)	8940.0±2.5 [11]	−285.0±2.5	63.3*	−221.7	42.7
Spiropentane (g)	3296.0±0.7 [100]	—	—	185.1±0.7	265.8
Spiropentane (l)	3258.4±1.3 [101]	147.5±1.3	27.53±0.04 [102]	175.0±1.3	—
Spiro[4,4]nonane (l)	5684.4±1.3 [111]	−143.8±1.3	46.2*	−97.6	67.0
Spiro[4,5]decane (l)	6307.4±1.3 [111]	−200.2±1.3	54.9±0.1 [113]	−145.3±1.3	39.0
	6307.5±2.0 [112]	−200.0±2.1	54.9±0.1 [113]	−145.1±2.1	—
Spiro[5,5]undecane (l)	6938.7±2.1 [111]	−248.2±2.1	56.1±0.1 [113]	−192.1±2.1	12.9
	6942.4±2.8 [112]	−244.5±3.0	56.1±0.1 [113]	−188.4±3.0	—
Spiro[5,6]dodecane (l)	7613.2±0.8 [111]	−253.0±0.8	57.3*	−195.7	30.0
	7613.8±2.3 [112]	−252.4±2.5	57.3*	−195.1	—

*Calculated from the Klages formula.[103]

On the other hand, the strain energies of spiro-hydrocarbons are greater than some of the E_S for the individual rings. For example, the strain energy of one three-membered ring in spiropentane is 132.8 kJ mol^{-1}, which exceeds by ~17 kJ mol^{-1} the strain energy of cyclopropane. The increase of E_S relative to the additive value has been observed also for other spiro-hydrocarbons, although the effect for these substances is smaller than for spiropentane (Table 6).

It has been shown[111] that, when the strain energies of individual rings in spiro-hydrocarbons are assumed to be equal to the values of E_S for the corresponding monocyclanes, then the contribution introduced by the quaternary carbon atom to ΔH_C° and ΔH_f° is found to be constant for all four spirans investigated by Kozina et al.[111] This contribution naturally differs from that adopted by Benson et al.[40] since account was taken of the thermochemical characteristics of spirans in its calculation. By taking into account the data of Subach and Zvolinski,[112] the following formulae have been obtained for the approximate calculation of ΔH_C° and ΔH_f° for spirans (apart from those containing three- and four-membered rings):

$$-\Delta H_c^0(\text{gas})\ (\text{kJ mol}^{-1}) = 406.2 + 658.63n + \Sigma E_s,$$
$$\Delta H_f^0(\text{gas})\ (\text{kJ mol}^{-1}) = 12.8 - 20.71n + \Sigma E_s,$$

where n is the number of $-CH_2-$ groups and E_S the strain energies of the constituent rings of the given molecule according to Benson et al.[40]

3. Bridged and Condensed Bicyclic Hydrocarbons

The study of bicyclic hydrocarbons and their simplest derivatives has aroused much interest in recent years. The experimental measurement of the standard enthalpies of formation and of the strain energies calculated from them occupies an important place in such research. The special interest in the strain energies of these compounds is determined, in particular, by the fact that an increase in the rigidity of the molecular skeleton on passing from monocyclic to bicyclic and polycyclic compounds entails a change in the geometry of the individual rings, which greatly affects E_S. Thus, measurement of E_S in combination with conformational analysis and electron diffraction and spectroscopic studies makes it possible to investigate the nature of the strain.[114–117] On the other hand, there remains the problem of the empirical study of ΔH_f° and E_S in order to investigate the influence of substituents, the introduction of a double bond, etc. on the latter with the aim of establishing the thermochemical relations for predicting the thermodynamic properties of compounds which have not been investigated. This Section deals with the results of thermochemical studies on compounds of two classes: bridged bicyclic hydrocarbons and their derivatives, i.e. [*n.m.k*]bicyclic compounds, and condensed bicyclic compounds, i.e. [*n.m.*0]-bicyclic compounds.

The thermochemical data for bridged bicyclic hydrocarbons and their simplest derivatives are presented in Table 7. The greatest number of experimental data are available for derivatives of bicyclo[2.2.1]heptane (norbornane). Table 7 shows that the strain energies of norbornane derivatives depend greatly not only on the number but also on the positions of the substituents. Even when hydrogen atoms are replaced by one or two methyl groups, E_S varies from ~55 to ~80 kJ mol^{-1}. The introduction of the CH_3 group in the 2-position or even two CH_3 groups in the 2- and 3-positions, which are most remote from the "bridge" has comparatively little effect on the strain energy. On the other hand, E_S for 1-methylnorbornane is lower by almost 10 kJ mol^{-1} than for the unsubstituted norbornane. The introduction of two methyl groups at tertiary carbon atoms, i.e. in the 1- and 4-positions stabilises the molecule to an even greater extent. On the other hand, E_S for 7,7-dimethylnorbornane is ~10 kJ mol^{-1} higher than for norbornane.

Table 7. The enthalpies of combustion, formation, and evaporation (sublimation) and the strain energies of bridged bicyclic hydrocarbons and their derivatives at 298 K (in kJ mol^{-1}).

No.	Substance	$-\Delta H_c^0$	ΔH_f^0 (l or s)	ΔH_v^0 or ΔH_s^0	ΔH_f^0 (g)	E_s
1	Bicyclo[2.2.1]heptane (norbornane) (s)	4377.5±2.2 [118]	−92.1±2.2	40.1±0.8 [119]	−52.0±2.3	67.4
		4367.5±3.3 [120]	−102.0±3.3	40.4±0.8 [120]	−61.6±3.4	—
2	*exo*-2-Methylnorbornane (l)	5026.4±1.1 [121]	−122.5±1.1	41.8*	−80.7	68.2
3	*endo*-2-Methylnorbornane (l)	5026.8±1.2 [121]	−122.1±1.2	41.0*	−81.1	67.8
4	1-Methylnorbornane (l)	5018.0±1.0 [121]	−131.0±1.0	38.1±0.2 [122]	−92.8±1.0	58.8
5	1,4-Dimethylnorbornane (l)	5660.8±1.3 [123]	−167.5±1.3	38.9±0.4 [124]	−128.6±1.4	55.1
6	*trans*-2,3-Dimethylnorbornane (l)	5678.0±1.9 [123]	−150.3±1.9	42.3±0.5 [124]	−108.0±2.0	70.3
7	7,7-Dimethylnorbornane (s)	5680.0±1.5 [125]	−148.2±1.5	47.0±1.0 [125]	−101.2±1.8	79.8
8	2-Ethylnorbornane (l) (mixture of isomers: 36% *exo*-, 64% *endo*-)	5688.0±1.8 [125]	−140.3±1.8	—	—	—
9	Bicyclo[2.2.1]hept-2-ene (norbornene) (s)	4213.5±1.7 [126]	29.7±1.7	33.6±0.1 [126]	63.3±1.7	—
		4225.1±1.3 [127]	41.4±1.3	38.7±0.4 [127]	80.1±1.4	82.7
		4237.2±3.2 [120]	53.5±3.2	37.7±0.8 [120]	91.2±3.3	—
		—	—	—	89.5±2.6 [128]	—
		—	—	—	86.6** [130]	—
10	2-Methylenenorbornane (l)	4859.0±1.7 [46]	−4.1±1.7	39.4±0.1 [122]	35.3±1.7	63.8
11	7-Methylenenorbornane (l)	4882.7±2.1 [129]	19.7±2.1	40.7*	60.4	86.2
12	2-Methylnorbornene (l)	4867.5±1.7 [123]	4.4±1.7	39.4±0.2 [122]	43.8±1.7	82.3
13	6-Methylnorbornene (l) (mixture of isomers: 44% *exo*-, 56% *endo*-)	4878.9±1.2 [46]	15.8±1.2	—	—	—
14	Bicyclo[2.2.1]hepta-2,5-diene (s)	4076.7±1.0 [126]	178.7±1.0	32.9±0.1 [126]	211.7±1.0	—
		—	—	—	233.0 [130]**	—
		4111.7±3.0 [120]	213.8±3.0	33.8±0.8 [120]	247.6±3.2	—
		—	—	—	240.2±2.8 [128]	129.5
15	*trens*-5-Ethylidenebicyclo[2.2.1]hept-2-ene (l)	5358.5±1.5 [46]	101.9±1.5	44.6±1.1 [124]	146.5±1.9	90.6
16	*cis*-5-Ethylidenebicyclo[2.2.1]hept-2-ene (l)	5363.2±1.7 [46]	106.6±1.7	44.5±0.5 [124]	151.1±1.8	95.2
17	5-Vinylbicyclo[2.2.1]hept-2-ene (l) (mixture of isomers: 35% *exo*-, 65% *endo*-)	5371.7±1.4 [46]	115.1±1.4	—	—	—
18	2,2-Dimethyl-3-methylenenorbornane (s)	6146.4±2.1 [129]	−75.3±2.1	46.9±0.5 [129]	−28.4±2.2	55.7
19	Bicyclo[3.3.1]nonane (s)	5650.1±0.8 [108]	−178.1±0.8	50.6±2.1 [108]	−127.5±2.3	33.4
20	Bicyclo[3.3.1]non-2-ene (s)	5445.1±1.3 [131]	−97.3±1.3	48.2±0.4 [132]	−49.1±1.4	−4.1
21	Bicyclo[4.2.1]non-3-ene (s)	5496.3±0.9 [131]	−46.1±0.9	49.7±0.8 [132]	3.6±1.2	54.2
22	Bicyclo[2.2.1]heptan-7-one (s)	4002.4±2.3 [133]	−181.3±2.3	47.3±2.1 [133]	−134.0±3.1	94.1
23	Bicyclo[2.2.1]heptan-2-one (s)	3967.1±2.7 [133]	−216.6±2.7	48.9±1.7 [133]	−167.7±3.2	60.2
24	1-Methylbicyclo[2.2.1]heptan-2-one (l)	4611.1±2.5 [97]	−252.0±2.5	47.6±0.2 [122]	−204.4±2.5	52.5
25	1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one (s)	5902.5±2.5 [134]	−319.2±2.5	51.9±1.3 [134]	−267.3±2.9	64.4
26	7-Oxabicyclo[2.2.1]heptane (l)	3566.3±1.5 [118]	−223.9±1.5	40.0*	−183.3	54.3
27	*exo*-2-Methyl-7-oxabicyclo[2.2.1]heptane (l)	4215.7±1.7 [118]	−253.8±1.7	42.7*	−211.1	56.0
28	*endo*-2-Methyl-7-oxabicyclo[2.2.1]heptane (l)	4219.3±1.6 [118]	−250.3±1.6	43.5*	−206.8	60.3
29	*exo*-2-Cyanobicyclo[2.2.1]heptane (l)	4739.8±1.3*** [135]	19.7±1.3	—	—	—
30	*endo*-2-Cyanobicyclo[2.2.1]heptane (s)	4740.4±1.5 [135]	20.3±1.5	—	—	—
31	2,3-Diazabicyclo[2.2.1]hept-2-ene (s)	3262.9±2.6 [140]	152.1±2.6	55.3±0.6 [140]	207.4±2.7	64.4
32	Bicyclo[2.2.2]octane (s)	5001.9±0.8 [136]	−147.0±0.8	48.0±0.4 [137]	−99.0±1.0	41.2
33	Bicyclo[2.2.2]oct-2-ene (s)	4839.7±0.7 [136]	−23.4±0.7	43.8±0.4 [137]	20.4±0.8	43.7
		—	—	—	19.4 [130]**	—
34	2-Methylenebicyclo[2.2.2]octane (l)	5488.0±2.4 [138]	−54.4±2.4	45.2*	−9.2	38.2
35	2-Methylbicyclo[2.2.2]oct-2-ene (l)	5480.4±2.1 [138]	−62.0±2.1	43.3±0.7 [139]	−18.7±2.2	39.5
36	Bicyclo[3.2.2]non-6-ene (s)	5490.9±2.1 [131]	−51.5±2.1	48.0±1.6 [132]	−3.5±2.3	41.5
37	1-Azabicyclo[2.2.2]octane (s)	4557.4±1.2 [136]	−55.1±1.2	50.8±0.5 [137]	−4.3±1.3	46.5
38	1,4-Dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene (s)	4883.5±4.4 [140]	20.4±4.4	72.0±0.5 [140]	92.4±4.4	42.3
39	3-Oxabicyclo[3.2.2]nonane (s)	4873.3±0.8 [136]	−275.6±0.8	53.1±0.6 [137]	−222.5±1.0	43.6
40	3-Azabicyclo[3.2.2]nonane (s)	5191.2±0.7*** [136]	−100.6±0.7	57.9±0.4 [137]	−42.7±0.8	46.8
41	Bicyclo[3.3.2]decane (s)	6343.4±7.1 [108]	−164.2±7.1	58.2±2.1 [108]	−106.0±7.4	75.6
42	Bicyclo[3.3.3]undecane (s)	7034.3±1.7 [141]	−152.6±1.7	63.6±0.8 [141]	−89.0±1.9	113.3

*Calculated from the Klages formula.[103]

**In the calculation of ΔH_f° from the enthalpy of hydrogenation, the values of ΔH_f° for the corresponding saturated compounds, taken from Pedley and Rylance,[50] were used here and henceforth.

***Recalculated by ourselves for 298 K.

The introduction of an endocyclic double bond appreciably increases E_S but not to the extent observed for the three-membered ring. The influence of an exocyclic double bond depends on the position of the methylene group: the strain energy of 2-methylenenorbornane is a little lower and that of 7-methylenenorbornane is significantly higher than the E_S for the initial molecule. E_S is even greater for *cis*- and *trans*-ethylidenenorbornanes. The influence of the substitution of a hydrogen atom by the oxo-group is similar to the influence of the $=CH_2$ group: the oxo-group in the 7-position significantly increases while in the 2-position it slightly diminishes the strain energy. The introduction of the methyl group in the 1-position in the molecule of bicyclo[2.2.1]heptan-2-one, reduces E_S still further, analogously to such substitution in norbornane. The replacement of the $-CH_2-$ group in the bridge by an ether oxygen atom entails some decrease of the E_S for the 7-oxabicyclo[2.2.1]heptane molecule, in contrast to the three-membered ring, whose strain energy E_S remains almost unaltered following such substitution.[40]

Bicyclo[2.2.2]octane is an interesting compound for the investigation of the nature of strain. Its molecule can be imagined as being made up of, as it were, two six-membered rings, but its strain energy proved to be unexpectedly extremely high, amounting to ~40 kJ mol^{-1}. It has been suggested[136] that this strain is mainly determined by the presence of three pairs of hydrogen atoms in the "eclipsed" conformation. The influence of the methyl substitution and also of exocyclic and endocyclic double bonds on the E_S for bicyclo[2.2.2]octane is qualitatively similar to that noted above for norbornane derivatives, but is much weaker.

The marked dependence of E_S on the structure of the molecule and on the position of the double bond is evident from the example of certain saturated hydrocarbons (Nos.1, 19, 41, and 42) and three bicyclononene isomers (Nos.20, 21, and 36, Table 7).

Table 8. The enthalpies of combustion, formation, and evaporation (sublimation) and the strain energies of condensed bicyclic hydrocarbons and their derivatives at 298 K (in kJ mol^{-1}).

No.	Substance	$-\Delta H_c^0$	ΔH_f^0 (l or s)	ΔH_v^0 or ΔH_s^0	ΔH_f^0 (g)	E_s
1	Bicyclo[1.1.0]butane (g)	2648.7±0.8 [92]	—	—	217.2±0.8	274.5
2	Bicyclo[2.1.0]pentane (l)	3241.6±1.3 [91]	130.7±1.3	28.0±0.3 [124]	158.7±1.3	236.7
		—	—	—	152.3±1.7 [142]	—
3	Bicyclo[3.1.0]hexane (l)	3795.3±2.1 [143]	5.1±2.1	33.5±0.4 [143]	38.6±2.1	137.3
4	1-Methylbicyclo[3.1.0]hexane (l)	4436.4±1.2 [123]	−33.1±1.2	34.6±0.4 [124]	1.5±1.3	132.4
5	1,3,5-Trimethylbicyclo[3.1.0]hexane (l)	5726.2±2.1*	−102.0±2.1	41.5**	−60.5	131.9
6	5-Ethyl-1-methylbicyclo[3.1.0]hexane (l)	5730.0±2.1*	−98.2±2.1	42.8**	−55.4	128.3
7	Bicyclo[3.1.0]hex-3-ene (l)	3625.0±2.9 [46]	120.6±2.9	—	—	—
8	Bicyclo[4.1.0]heptane (norcarane) (l)	4442.3±1.2 [46]	−27.2±1.2	38.8±0.6 [124]	11.6±1.3	131.0
		4432.7±2.6 [143]	−36.8±2.6	38.1±0.8 [143]	1.3±2.7	—
9	1-Methylnorcarane (l)	5089.0±1.4 [123]	−59.9±1.4	39.5±0.6 [124]	−20.4±1.5	131.2
10a	*cis*-3,7,7-Trimethylnorcarane (carane) (l)	6391.6±2.6 [144]	−116.0±2.6	47.1±1.2 [124]	−68.9±2.9	141.5
10b	*trans*-Carane (l)	6389.1±2.5 [144]	−118.5±2.5	48.1±1.1 [124]	−70.4±2.7	140.0
11	Bicyclo[4.1.0]hept-2-ene (l)	4258.4±2.8*	74.7±2.8	41.5±0.6 [124]***	116.2±3.0	119.8
12	3,7,7-Trimethylbicyclo[4.1.0]hept-2-ene (2-carene) (l)	6199.1±2.3 [145]	−22.6±2.3	47.8 [146]	25.2	125.2
13	3,7,7-Trimethylbicyclo[4.1.0]hept-3-ene (3-carene) (l)	6192.1±1.8 [145]	−29.6±1.8	48.3±3.1 [146]	18.7±3.6	119.7
14	*cis*-7-Methylenebicyclo[4.1.0]hept-2-ene (l)	4786.0±1.1 [91]	208.8±1.0	43.2**	252.0	121.2
15	*cis*-7-Oxabicyclo[4.1.0]heptane (l)	3624.2±1.1 [149]	−166.8±1.1	40.5±0.2 [149]	−126.3±1.1	111.3
16	*cis*-Caran-3-ol (s)	6178.4±3.0 [147]	−329.2±3.0	79.5±1.3 [83]	−249.7±3.3	138.9
17	*trans*-Caran-3-ol (s)	6164.1±2.4 [147]	−343.5±2.4	84.3±0.4 [83]	−259.2±2.5	129.4
18	*cis*-Caran-2-ol (l)	6200.1±1.8 [148]	−307.5±2.3	77.2****	−230.3	147.2
19	*cis*-Caran-4-ol (l)	6195.5±1.2 [148]	−312.1±1.8	78.0±3.9 [148]	−234.1±4.3	143.4
20	*cis*-Bicyclo[5.1.0]octane (l)	5088.6±1.3 [143]	−60.3±1.3	43.5±0.8 [143]	−16.8±1.5	123.4
21a	*cis*-Bicyclo[6.1.0]nonane (l)	5747.1±2.5 [143]	−81.1±2.5	49.4±0.8 [143]	−31.7±2.6	—
		5748.4±3.7 [150]	−79.8±3.7	49.8±0.8 [150]	−30.0±3.8	—
		5758.2±1.5 [86]	−70.0±1.5	49.4±0.8 [86]	−20.6±1.7	140.3
21b	*trans*-Bicyclo[6.1.0]nonane (l)	5745.9±3.2 [150]	−82.3±3.2	42.7±0.6 [150]	−39.6±3.3	—
		5760.3±1.5 [86]	−67.9±1.5	49.4±0.8 [86]	−18.5±1.7	142.4
22	*cis*-9-Oxabicyclo[6.1.0]nonane (s)	4936.4±2.2 [149]	−212.6±2.2	47.4±1.0 [149]	−165.1±2.4	113.8
23	*cis*-Bicyclo[4.2.0]octane (l)	5080.6±2.5 [143]	−68.3±2.5	42.7±1.2 [143]	−25.6±2.8	114.7
24a	*cis*-Bicyclo[3.3.0]octane (l)	5016.0±2.8 [151]	—	—	—	—
		5012.8±1.3 [143]	−135.5±1.2	43.1±0.8 [143]	−92.4±1.5	47.8
24b	*trans*-Bicyclo[3.3.0]octane (l)	5041.7±5.0 [151]	—	—	—	—
		5039.6±1.7 [143]	−109.0±1.6	42.7±0.8 [143]	−66.4±1.8	73.8
25a	*cis*-Bicyclo[4.3.0]nonane (l)	5655.1±1.5 [152]	−173.1±1.5	46.0±1.3 [152]	−127.1±2.0	33.8
25b	*trans*-Bicyclo[4.3.0]nonane (l)	5652.0±1.7 [152]	−176.2±1.7	44.8±1.3 [152]	−131.4±2.1	29.5
26	*cis*-Bicyclo[4.3.0]nona-3,7-diene (l)	5320.9±1.0 [153]	64.3±1.0	45.0±0.9 [124]	109.3±1.4	39.4
27	*cis*-Bicyclo[5.3.0]decane (l)	6323.7±3.3 [143]	−183.9±3.8	53.6±1.2 [143]	−130.3±5.0	51.3
28a	*cis*-Bicyclo[4.4.0]decane (l)	6288.2±0.9 [154]	−219.4±1.1	50.2±2.1 [155]	−169.2±2.3	12.4
28b	*trans*-Bicyclo[4.4.0]decane (l)	6277.0±0.9 [154]	−230.6±1.1	48.5±2.1 [155]	−182.1±2.3	−0.5
29	*trans*-3-Methylbicyclo[4.4.0]decane (l)	6922.0±2.1 [11]	−264.9±2.1	53.5**	−211.4	−0.4
30a	*cis*-2-Methylbicyclo[4.4.0]decane (l)	6943.1±1.9 [156]	−243.8±2.0	—	—	—
30b	*trans*-2-Methylbicyclo[4.4.0]decane (l)	6937.2±1.7 [156]	−249.7±1.8	—	—	—
31	Pyrrolizidine (l)	4564.2±3.0 [157]	−48.3±3.0	44.4**	−3.9	53.8
32	3,5-Dimethylpyrrolizidine (l)	5856.8±2.0 [157]	−114.4±2.0	47.7±1.7 [157]	−66.7±2.5	63.7

*Obtained by L.P.Timofeeva in the Laboratory of Thermochemistry at Moscow State University.
**Calculated from the Klages formula.[103]
***The value of ΔH_v° measured for bicyclo[4.1.0]hept-3-ene is quoted.
****Estimated group contributions taken from Lebedev and Miroshnichenko.[83]

The results of the measurement of the enthalpies of combustion and strain energies of condensed bicyclic hydrocarbons and their derivatives are presented in Table 8. Unsubstituted bicyclo[*n.m.*0]alkanes are also extremely interesting objects for the study of strain in cyclic compounds. The strain energies of condensed rings do not in general consist of the sum of the contributions of the constituent monocyclic moieties of the molecule, but are fairly close to this value. Two factors affecting the strain energy on formation of a bicyclic compound have been noted:[143] the change in the conformation of the rings leading to an increase of E_S and the disappearance of torsional interactions causing a decrease of E_S. The effects of these factors approximately cancel out for many real molecules. A more rigorous approach makes it necessary to reconcile data on the enthalpies of formation, molecular geometries, and vibrational frequencies. In many cases it has been possible to calculate fairly accurately the enthalpies of formation of cyclic hydrocarbons,[114–117] but this requires a knowledge of numerous accurately measured parameters, which are in practice not always known.

In relation to unsubstituted cyclic hydrocarbons of different classes, the dependence of the strain energy on the geometrical structure of the molecules has been analysed and correlation equations have been derived.[43] It has been found that the E_S in the given series of compounds is determined mainly by the change of some one structural parameter. For example, in bridged bicyclic compounds E_S is determined by the change of the dihedral angle, while in condensed bicyclic compounds it is determined by the deformation of the angles at the tertiary carbon atom. This may account for the characteristic variation of E_S in each series of cyclic compounds after the introduction of the same substituents.

The empirical dependence of the enthalpies of formation of bicyclo[*n*.1.0]alkanes on their structure has been examined.[46]

The influence of substitution on the strain energy of bicyclo[*n.m.*0]alkanes can be traced in relation to bicyclo-[4.1.0]heptane (norcarane), for the derivatives of which numerous experimental data have been obtained (Table 8). The substitution of a hydrogen atom at the tertiary carbon atom of the methyl group does not affect the E_S, in contrast

to norbornane. The introduction of an endocyclic double bond entails an appreciable decrease of E_S, i.e. it exerts the opposite effect compared with norbornane and cyclopropane. On the other hand, the effect of an exocyclic double bond is small.

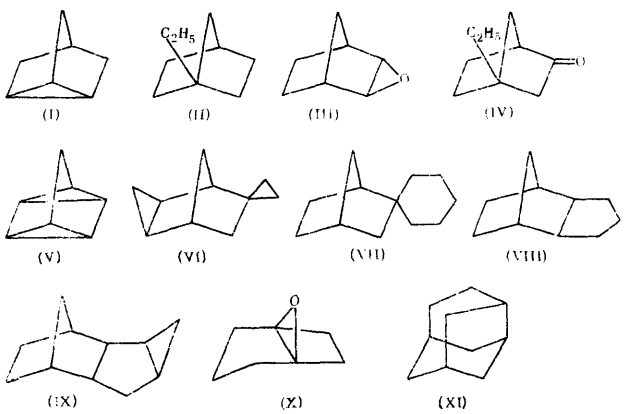
Table 8 shows that the strain energies of carane and carene (trimethyl-substituted derivatives of norcarane and norcarene) are somewhat greater than those of the initial compounds. It is of interest to note that the E_S for 2-carene, whose double bond is conjugated with the three-membered ring, is greater than for 3-carene.

Many of the bicyclic compounds investigated are known only in the *cis*-form. However, in many cases ΔH_f° and E_S have been determined for the *cis*- and *trans*-isomers. The difference between these quantities for certain bicyclic hydrocarbons proved to be very considerable, amounting to ~10–20 kJ mol^{-1} (Table 8)—see, for example, the strain energies of the *cis*- and *trans*-isomers of bicyclo[3.3.0]-octane, bicyclo[4.4.0]decane, etc.

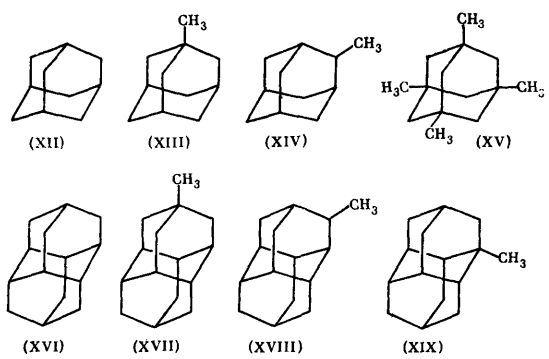
The introduction of oxygen into the three-membered ring of condensed bicyclic hydrocarbons leads to some increase in E_S, as in bridged bicyclic compounds. On the other hand, the presence of the OH group in the *cis*-carane structure entails an appreciable change in the strain energy regardless of its position and orientation.

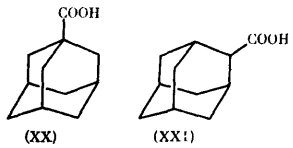
4. Polycyclic Hydrocarbons and Their Derivatives

Until recently, the thermochemical properties of polycyclic compounds were little investigated. However, in the last decade a number of studies, mainly of bridged polycyclic compounds (I)–(XI) containing small rings with less than six atoms in the ring have been published.

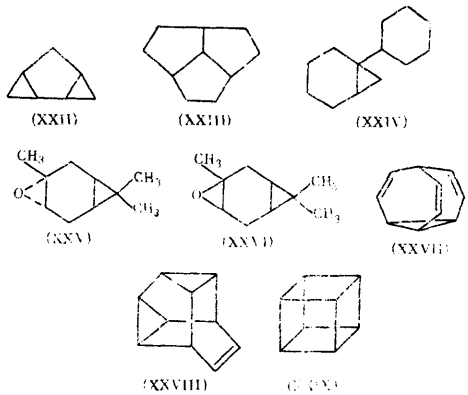


The bridged polycyclic compounds (XII)–(XXI) containing only six-membered rings (adamantane, diadamantane, and their derivatives) constitute a separate group.





A few data are available for the condensed polycyclic compounds (XXII)–(XXIX) containing different rings, including seven-membered rings.



The study of polycyclic compounds has been partly induced by practical needs, because many of them enter into the composition of petroleum and their physicochemical properties are close to those of components of lubricating oils.[165] These compounds are of even greater interest for the investigation of the influence of the structural features of molecules on the energy properties of the given substance.

Thermochemical data for polycyclic hydrocarbons and their derivatives are presented in Table 9. It has been observed for the compounds investigated that the strain energies of the majority of these molecules are smaller than the sums of the contributions of the strain energies of the individual rings constituting the molecule. In some cases the strain energy may be much higher, for example, in cubane (XXIX) and spiro{tricyclo[3.2.1.0^{2,4}]octane-6,1′-cyclopropane} (VI) (Table 9).

It was initially assumed that the adamantane (XII) and diadamantane (XVI) molecules are unstrained, but the experimental determination of ΔH_c° showed that their strain energies are appreciable (~20–40 kJ mol^{-1}). This finding has been explained[115,170] by the presence of angular strain and by the interaction of non-bonded carbon atoms.

It is noteworthy that the substitution of a hydrogen atom at a tertiary carbon atom by an alkyl group in nortricyclene (VII), adamantane, and diadamantane leads to an appreciable decrease in E_S. The introduction of the methyl group in the 2-position, causes, on the other hand, an increase in E_S. These effects are similar to that of alkyl substitution on the E_S for norbornane (Table 7) and can apparently be accounted for by the same causes.

VI. THERMOCHEMISTRY OF ORGANOHALOGEN COMPOUNDS

The organohalogen compounds investigated belong to different classes. A considerable proportion of them consist of fluoro-substituted lower hydrocarbons (methane, ethylene, ethane, and propane). The ΔH_c° and ΔH_f° have also been determined for many chlorofluoro-derivatives as well as bromine-containing compounds.

It is noteworthy that there are still many obscure problems and even contradictions in the thermochemistry of organohalogen compounds. This can be explained mainly by the methodological difficulties noted above. In recent years determinations of ΔH_c° and ΔH_f° for organohalogen compounds have been made in order to establish the thermochemical properties of the compounds of greatest importance for technology, to elucidate and resolve the contradictions in the available data, and also to investigate new promising classes of organohalogen compounds (tertiary perfluoroamines, fluoro- and chlorofluoro-ethers, fluorinated diketones, etc.). For example, the measurement of the ΔH_c° and ΔH_f° for 1,2,2-trichloro-1,1,2-trifluoroethane, 1-bromo-2-chloro-1,1,2-trifluoroethane, and chlorotrifluoroethylene made it possible to correct (by 40–50 kJ mol^{-1}) the incorrect values present in the literature and to solve one of the most complex problems of the thermochemistry of organohalogen compounds.[22]

Table 9. The enthalpies of combustion, formation, and evaporation (sublimation) and the strain energies of polycyclic compounds at 298 K (in kJ mol^{-1}).

Substance	$-\Delta H_c^0$	ΔH_f^0 (l or s)	ΔH_v^0 or ΔH_s^0	ΔH_f^0 (g)	E_s
(I) (s)	4207.8±2.1 [126]	24.1±2.1	38.0±0.1 [126]	62.1±2.1	—
	4214.8±1.0 [127]	31.1±1.0	39.2±1.1 [127]	70.3±1.5	164.2
	4227.1±2.0 [120]	43.4±2.0	38.7±0.6 [120]	82.1±2.1	—
(I) (g)	—	—	—	84.3±3.2 [128]	—
	—	—	—	82.3 [142]	—
(II) (l)	5510.0±2.1 [162]	−32.4±2.1	42.0±0.1 [162]	9.6±2.1	156.4
(III) (s, *exo*-)	4086.9±2.6 [149]	−96.8±2.6	44.1±0.5 [149]	−52.7±2.7	180.1
(IV) (l)	5115.1±1.8 [162]	−141.5±1.8	49.8±0.8 [162]	−91.7±2.0	165.6
(V) (s)	4114.3±1.1 [126]	216.4±1.1	37.0±0.1 [126]	253.4±1.2	—
	4200.0±2.2 [120]	302.1±2.2	37.0±0.8 [120]	339.1±2.3	238.8
(V) (g)	—	—	—	332.7±2.9 [128]	—
	—	—	—	333.0 [142]	—
(VI) (l, *cis*-)	6058.5±1.6 [162]	122.6±1.6	47.8±0.1 [162]	170.4±1.6	303.7
(VII) (l)	7388.1±2.1 [46]	−192.3±2.1	57.3*	−135.0	65.2
(VIII) (l)	6108.8±2.5 [119]	−112.9±2.5	52.9±1.3 [119]	−60.0±2.8	96.1
(IX) (l, *exo*-)	6618.7±2.1**	3.4±2.1	55.2±0.5**	58.6±2.2	209.8
(X) (l)	4174.2±1.0 [163]	−9.5±1.0	36.4 [163]	26.9	281.9
(XI) (s)	6070.9±1.7 [159]	−150.8±1.7	64.8±1.8 [159]	−86.0±2.5	62.1
(XII) (s)	6024.5±0.7 [167]	−197.2±0.7	59.3±0.2 [167]	−137.9±0.7	18.2
	6033.1±2.8 [119]	−188.6±2.8	60.5±1.3 [119]	−128.1±3.1	28.0
	6033.4±3.3 [168]	−188.3±3.3	59.5±0.8 [168]	−128.8±3.4	27.3
	6029.2±0.4 [159]	−192.5±0.4	59.7±0.8 [159]	−132.8±0.9	23.3
(XIII) (s)	6663.8±1.3 [159]	−237.3±1.3	67.6±0.5 [159]	−169.7±1.4	18.5
(XIV) (s)	6684.4±1.2 [159]	−216.7±1.2	67.5±2.1 [159]	−149.2±2.4	39.0
(XV) (s)	8577.0±2.0 [159]	−362.1±2.0	81.1±0.9 [159]	−281.0±2.2	3.6
(XVI) (s)	8127.7±1.3 [159]	−239.7±1.3	95.9±0.8 [159]	−143.8±1.5	44.1
	8084.8±1.7 [169]	−282.6±1.7	87.0±1.9 [169]	−195.6±2.5	—
(XVII) (s)	8785.2±0.7 [159]	−261.5±0.7	79.4±1.2 [159]	−182.1±2.0	37.9
(XVIII) (s)	8786.4±2.0 [159]	−260.4±2.0	103.1±1.0 [159]	−157.3±2.3	60.0
(XIX) (s)	8799.4±3.3 [159]	−247.4±3.3	80.6±0.4 [159]	−166.8±3.3	53.2
(XX) (s)	5972.2±3.6 [170]	−643.1±3.6	—	—	—
(XXI) (s)	5988.1±3.8 [170]	−627.2±3.8	—	—	—
(XXII) (l, *trans*-)	4296.5±1.3 [158]	112.8±1.3	36.5±0.5 [139]	149.3±1.4	243.2
(XXIII) (s)	6662.8±3.2 [159]	−158.9±3.2	56.6±1.3 [159]	−102.3±3.6	53.8
(XXIV) (l)	8094.1±2.9 [160]	−165.7±2.9	57.2*	−108.5	112.4
(XXV) (l, α-)	6065.4±1.5 [161]	−156.3±1.5	49.4*	−106.9	228.0
(XXVI) (l, β-)	6073.7±1.6 [161]	−148.0±1.6	50.2*	−97.8	237.1
(XXVII) (s)	5626.5±3.0 [164]	262.3±3.0	71.8±0.4 [164]	334.1±3.0	146.1 [164]
(XXVIII) (s)	5610.7±2.1 [165]	246.4±2.1	—	—	—
(XXIX) (s)	4833.2±3.3 [166]	541.8±3.3	80.3±1.7	622.1±3.7	685.6

*Calculated from the Klages formula.[103]
**The measurements were carried out by L.P.Timofeeva and L.L.Pashchenko in the Laboratory of Thermochemistry at Moscow State University.

The publication of numerous new experimental data made it necessary to revise the entire set of enthalpies of formation of organohalogen compounds. This revision is particularly urgently required also because until recently there has been a considerable lack of coordination in the selection of key quantities for the calculation of ΔH_f°. This virtually precluded the analysis of the experimental data and the search for thermochemical relations on the basis of the results of different workers.

In order to represent and analyse the entire experimental thermochemical data for organohalogen compounds on a modern basis, the ΔH_f°, both those obtained in the Laboratory of Thermochemistry at Moscow State University and the available literature data, were recalculated by ourselves on the basis of a single system of key quantities developed and adopted by CODATA.[32] Analysis of the available experimental data for different groups of organohalogen compounds led Kolesov[171] to the following results. In the case of halogenomethanes, the most reliable ΔH_f° for 17 compounds were selected and on their basis the ΔH_f° for all the remaining halogenomethanes were calculated by approximate estimation methods.[171] Among the halogenoethanes, reliable ΔH_f° were selected for 37 compounds and the ΔH_f° for all the possible 210 bromochlorofluoroethanes were calculated on the basis of these reference quantities in terms of the approximation of atom–atom pair interactions.[172]

A somewhat greater number of reliable ΔH_f° values are available in the literature for the halogeno-derivatives of saturated aliphatic compounds. The enthalpies of formation of saturated fluoro- and chlorofluoro-derivatives of organic compounds ($n \geq 3$, where n is the number of carbon atoms) are presented in Table 10, which embraces all the data known at present except the ΔH_f° for methane and ethane derivatives as well as Swarts's obsolete data.[199] To facilitate the calculation of certain constants entering into computational schemes and to revise their values, Table 10 also includes two compounds without fluorine, namely propyl chloride and 1,1,1,3-tetrachloropropane. The majority of the quantities listed in Table 10 have been obtained experimentally in the Laboratory of Thermochemistry at Moscow State University. The experimental data have been analysed and the choice of the ΔH_f° for compounds Nos.1–9 and 16–19 has been justified by Kolesov.[200] The numerical differences between the ΔH_f° for the compounds in Table 10 and those quoted by Kolesov[200] can be due only to the recalculation in terms of the SI system of units and the recalculation in terms of the system of key quantities adopted by CODATA (see above). The details of the experimental determination of all the values of ΔH_f° are given in the corresponding communications quoted in Table 10. The ΔH_v° obtained from calorimetric and ebulliometric measurements were used to calculate the ΔH_f°(gas).[201–204] In those cases where the experimental data were lacking, the enthalpies of evaporation were estimated from the Klages[103] and Kistiakowsky[205] equations.

The experimental data were treated by Tatevskii's method.[70,206,207] Preliminary analysis showed[208,209] that at least a scheme taking into account the atoms in the first and second interaction spheres should be adopted as a single computational scheme which would ensure an accuracy of the calculation comparable to the experimental accuracy. However, the experimental data available at present are clearly insufficient for the calculation of all the constants involved in such a scheme. The experimental enthalpies of formation of the organofluorine compounds were therefore treated as follows.[208]

In the first place the constants necessary for the evaluation of the ΔH_f° in accordance with the scheme involving "atoms in the first interaction sphere" were calculated from the available experimental data. In setting up this computational scheme, we began with the usual classification of structural elements, i.e. we took into account the chemical nature and valence state of the given atom and also the

chemical nature and valence state of the atoms linked directly to the given atom.[72] The structural elements were designated by the system of symbols taken from Benson et al.[40], which is fully consistent with the characteristics of the structural elements in the scheme involving atoms where the first interaction sphere is taken into account. In order to limit reasonably the number of unknowns, the contributions of the structural elements not containing halogens were taken from the same investigation.[40]

The enthalpies ΔH_f° for 41 compounds (Table 10) were treated by the method of least squares. Comparison of the calculated and experimental ΔH_f° shows that the computational scheme employed is extremely approximate and that the difference between the calculated and experimental values $\Delta(\Delta H_f^\circ)$ is several times greater than the experimental error in some cases. This comparison makes it possible to discover also groups of compounds for which the deviations $\Delta(\Delta H_f^\circ)$ are a maximum. This applies in the first place to perfluoroalkanes and substances where the perfluoro-group (CF_3 or $-CF_2-$) adjoins the $-CH_2-$ group. Appreciable discrepancies have also been observed for certain ethers. For the remaining compounds, the scheme involving atoms and their first environment as a rule yields satisfactory results.

In order to reduce the most serious of the discrepancies noted above, the calculation of ΔH_f° in accordance with the "atoms in the first interaction sphere" scheme was refined by partial allowance for the second interaction sphere. Since the limited amount of experimental data precluded the complete allowance for the second interaction sphere, account was taken only of the second interaction sphere of the oxygen atom in the ethyl group and the carbon atom in the perfluoro-groups. For this purpose, the structural elements incorporating the second interaction sphere of the oxygen atom in ethers were identified, i.e. $O-(CF_2)(CF_2)$, $O-(CF_2)(CH_2)$, $O-(CF_2)(CCl_2)$, $O-(CF_2)(CCl_3)$, $O-(CF_2)(CH_3)$, and $O-(CF_2)(CF_2Cl)$. The perfluoro-groups were subdivided into two categories: the $C-(F)_3[C_F]$ and $C-(F)_2.[C_F]_2$ groups, adjoining only fluorine-containing groups even though these may not be fully fluorinated (CF_2H, CF_3, CFH, CF_2, CFCl, etc.) and the $C-(F)_3(CH_2)$ and $C-(F)_2(C).(CH_2)$ groups linked to at least one $-CH_2-$ group. Unfortunately a more detailed differentiation of the perfluoro-groups is so far impossible owing to the insufficiency of experimental data.

Table 10. Comparison of the experimental and calculated $\Delta H_f^\circ(g)$ for organohalogen compounds (in kJ mol^{-1}).

No.	Substance	$-[\Delta H_f^0(g)]_{exp}$	$-[\Delta H_f^0(g)]_{c,I}$	$\Delta[\Delta H_f^0(g)]_I$	$-[\Delta H_f^0(g)]_{c,II}$	$\Delta[\Delta H_f^0(g)]_{II}$
1	$CF_3-CF_2-CF_3$	1784.7±8.8 [173]	1789.1	+4.4	1762.9	−21.8
2	$CF_3-(CF_2)_5-CF_3$	3385.4±7.1 [174]	3437.2	+51.8	3402.5	+17.1
3	$1/n[-CF_2-CF_2-]_n$	809.6 [175.176]	824.1	+14.5	819.5	+10.2
4	$CH_3-CFH-CH_3$	286.2±3.0 [177]	301.9	+15.7	286.2	0
5	$CH_3-CH_2-CH_2F$	279.1±2.6 [177]	279.1	0	279.1	0
6	$CF_3-CH_2-CF_3$	1406.1±8.1 [179]	1397.7	−8.4	1413.5	+7.2
7	$1/n[-CF_2-CH_2-]_n$	465.9 [180]	432.7	−33.2	462.8	−3.1
8	$CF_3-CH_2-CH_2Cl$	779.7±2.2 [181]	774.5	−5.2	780.6	+0.9
9	$CF_3-CH_2-CCl_3$	803.9±2.2 [181]	794.4	−9.5	799.2	−4.7
10	$CF_3-CH_2-CHCl_2$	791.3±2.7 [182]	791.3	0	791.3	0
11	$CH_3-CH_2-CH_2Cl$	132.5±1.0 [183]	128.2	−4.3	126.6	−5.9
12	$CCl_3-CH_2-CH_2Cl$	161.7±1.7 [184]	171.2	+9.5	166.3	+4.6
13	$CF_3-CFCl-CF_2Cl$	1324.7 [185.186]	1325.0	+0.3	1320.4	−4.3
14	$CF_3-CH_2-CFCl_2$	970.3 [182]	970.0	−0.3	972.9	+2.6
15	$CF_3-CH_2-CF_2Cl$	1151.5±3.6 [182]	1151.2	−0.3	1153.8	+2.3
16	$CF_3-CH_2-CH_2-OH$	921.0±2.5 [187]	903.3	−17.7	911.1	−9.9
17	$CF_2H-CF_2-CH_2-OH$	1064.8±2.7 [187]	1067.6	+2.8	1064.8	0
18	$CF_3-CF_2-CH_2-OH$	1309.1±4.3 [187]	1294.6	−14.5	1312.8	+3.7
19	$CF_3-CF_2-CF_2-CH_2-OH$	1739.7±7.9 [179.188]	1706.7	−33.0	1722.7	−17.0
20	$(CF_3-CH_2-CH_2)_2O$	1604.4±4.0 [189]	1586.1	−18.3	1601.7	−2.7
21	$(CF_3-CF_2-CF_2)_2O$	3148.2±9.5 [190]	3156.5	+8.3	3158.0	+9.8
22	$(CF_3-CF_2-CF_2-CF_2)_2O$	3979.2±12.0 [182]	3980.5	+1.3	3977.8	−1.4
23	$(CF_3-CF_2-CF_2-CF_2-CF_2)_2O$	4806.4±20.7 [191]	4804.6	−1.8	4797.6	−8.8
24	$CFCl_2-CF_2-O-CCl_3$	901.2±2.9 [192]	901.5	+0.3	898.7	−2.5
25	$CF_3-CFCl-CF_2-O-CCl_3$	1524.1±4.9 [192]	1523.8	−0.3	1526.4	+2.3
26	$CFClH-CF_2-O-CH_3$	882.3±2.1 [192]	869.4	−12.9	882.3	0
27	$CFClH-CF_2-O-CH_2-CF_2-CF_2H$	1720.7±5.0 [193]	1736.3	+15.6	1736.4	+15.7
28	$CFClH-CF_2-O-CH_2-(CF_2)_3-CF_2H$	2555.6±7.3 [193]	2560.4	+4.8	2556.2	+0.4
29	$CFClH-CF_2-O-CH_2-(CF_2)_5-CF_2H$	3391.9±11.0 [193]	3384.4	−7.5	3376.0	−15.9
30	$CF_3-CFH-CF_2-O-CH_2-CF_2-CF_2H$	2359.5±8.0 [194]	2341.1	−18.4	2351.5	−8.0
31	$CF_3-CFH-CF_2-O-CH_2-(CF_2)_3-CF_2H$	3162.4±12.4 [194]	3165.1	+2.7	3171.3	+8.9
32	$CFCl_2-CF_2-O-CF_2Cl$	1325.6±7.3 [195]	1325.6	0	1325.6	0
33	$CFCl_2-CF_2-O-CCl_2-CF_2-CF_2Cl$	1752.5±6.5 [195]	1744.5	−8.0	1746.5	−6.0
34	$CFCl_2-CF_2-O-CCl_2-(CF_2)_3-CF_2Cl$	2560.6±8.3 [195]	2568.6	+8.0	2566.3	+5.7
35	$(CF_2)_4(CH_2OH)_2$	2084.2±12.0 [196]	2036.3	−47.8	2092.4	+8.2
36	$CF_3-CF_2-COOCH_3$	1428.3±3.7 [189]	1440.4	+12.1	1433.5	+5.2
37	$CF_3-CF_2-CF_2-COOCH_3$	1843.0±7.3 [197]	1852.4	+9.4	1843.4	+0.4
38	$(CF_2)_3(COOCH_3)_2$	1926.6±5.7 [191]	1915.8	−10.8	1923.9	−2.7
39	$CF_3-N(CF_2-CF_3)_2$	2783.2±9.1 [27]	2783.2	0	2783.2	0
40	$(CF_3-CF_2)_3N$	3172.4±12.3 [198]	3172.1	−0.3	3177.2	+4.8
41	$(CF_3-CF_2-CF_2-CF_2)_3N$	5643.9±19.8 [198]	5644.3	+0.4	5636.6	−7.3

Notation. $[\Delta H_f^\circ(g)]_{exp}$ is the experimental standard enthalpy of formation of the gaseous compound, while $[\Delta H_f^\circ(g)]_{c,I}$ and $[\Delta H_f^\circ(g)]_{c,II}$ are the values calculated respectively taking into account the first environment and with partial allowance also for the second environment.

Table 11. The contribution of atoms to $\Delta H_f^\circ(g)$ taking into account their first and in some cases also the second interaction sphere (in kJ mol^{-1}).

Atoms and their environment	Contribution to $\Delta H_f^0(g)$	Atoms and their environment	Contribution to $\Delta H_f^0(g)$
$C-(F)_3[C_F]$	−676.5	$C-(Cl)(H)_2(C)$	−63.6
$C-(F)_3(CH_2)$	−696.3	$O-(CF_2)(CCl_3)$	−642.8
$C-(F)_2(Cl)(C)$	−436.8	$O-(CF_2)(CH_3)$	−619.1
$C-(F)(Cl)_2(C)$	−255.9	$O-(CF_2)(CF_2Cl)$	−1069.8
$C-(F)_2(H)(C)$	−428.2	$O-(CF_2)(CF_2)$	−985.2
$C-(F)(Cl)(H)(C)$	−263.2	$O-(CF_2)(CCl_3)$	−643.9
$C-(F)(H)_2(C)$	−216.1	$O-(CF_2)(CH_2)$	−602.8
$C-(F)_2[C_F]_2$	−409.9	$C-(H)_3(C)$	−42.2
$C-(F)_3(C)(CH_2)$	−442.2	$C-(H)_2(C)_2$	−20.7
$C-(F)(Cl)(C)_2$	−207.1	$C-(O)(C)(H)_2$	−35.6
$C-(F)(H)(C)_2$	−201.8	$O-(H)(C)$	−158.5
$C-(F)_2(CO)(C)$	−402.3	$O-(C)_2$	−96.5
$C-(F)_3(N)$	−699.1	$C-(H)_3(O)$	−42.2
$C-(F)_2(N)(C)$	−416.6	$O-(CO)(C)$	−172.8
$C-(Cl)_3(C)$	−82.1	$CO-(O)(C)$	−139.7
$C-(Cl)_2(H)(C)$	−74.3	$N-(C)_3$	+102.1

Partial allowance for the second environment led to an increase of the constants of the additive scheme from 19 to 23. They were evaluated by the method of least squares in accordance with a standard program. The constants of these, i.e. the energy contributions to the ΔH_f° from structural elements, are presented in Table 11, which includes also nine contributions taken from Benson et al.[40]. The ΔH_f° calculated from the contributions in Table 11 are given in the sixth column of Table 10. It is seen from Table 10 that the differences between the calculated and experimental ΔH_f° as a rule do not exceed the experimental error. Only for a few compounds does the discrepancy $\Delta(\Delta H_f^\circ)$ exceed 10 kJ mol^{-1}. These discrepancies can probably be accounted for by the incomplete allowance for the second environment of the atom. On the other hand, overall comparison of the experimental and calculated ΔH_f° shows that the additive computational scheme, taking into account fully the first environment and partly the second environment of the atoms, is fully applicable in the approximate calculation of the standard enthalpies of formation of fluoro- and chlorofluoro-derivatives of organic compounds.

VII. CONCLUSION

Thus it follows from the present review that the capacity of lactams, their *N*-methyl derivatives, and cyclic formals for polymerisation can be fairly fully characterised by thermodynamic functions obtained using calorimetric methods. The problem whether or not polymerisation reactions of other cyclic compounds are thermodynamically allowed still remains acute. For this reason, studies of the thermodynamics of the polymerisation reactions of cyclic compounds of different classes are being continued and will apparently continue to develop in the immediate future.[211,212] Studies carried out in recent years made it possible to generalise and refine the earlier conclusions. It has been established that the polymerisation of three-, four-, five-, seven-, eight-, and many six-membered rings of different chemical nature is thermodynamically allowed. On the other hand, the polymerisation reactions of acyclic monomers, leading to the formation of highly structured thermally stable polymers with cyclic fragments, have aroused much interest in recent years. The thermodynamics of reactions of this type, for example, the cyclotrimerisation of aryl cyanates, isocyanates, etc. has been vigorously investigated[213] and these studies will undoubtedly continue to develop.

Despite the fairly extensive experimental data, few reliably established relations are so far available in the thermochemistry of cyclic hydrocarbons and their derivatives. Some of them were noted above in the analysis of the ΔH_f° for compounds with small rings and also with rings separated by a single bond. For compounds with a more complex structure (bicyclic bridged compounds, condensed bicyclic compounds, etc.), the experimental data obtained show that, as a rule, a characteristic dependence of the ΔH_c° and E_S on the nature, positions, and numbers of substituents in the molecule has been observed for each series of compounds. Extrapolation of the relations found for any one series of cyclic compound to other groups of compounds can lead to large errors. The study of the energetic and structural characteristics of cyclic compounds is therefore inevitably associated with the need for a fairly large set of reliable experimental data, particularly for methyl- and ethyl-substituted derivatives. They should be regarded as the first series members having unusual properties, which is analogous to the consideration of methane or ethane in the series of n-alkanes.

The numerical values of the strain energy have been used in the present review mainly for the analysis of thermochemical relations for particular groups of compounds. However, they can be useful also for the parametrisation of various empirical force field methods in order to calculate the ΔH_f°(gas) for cyclic compounds.[114-117]

The set of investigations carried out in the thermochemistry of organohalogen compounds has already made it possible to set up a system of thermochemical data by means of which it is possible to calculate approximately the enthalpies of formation of numerous compounds which have not yet been investigated. The accuracy of the calculations for the fluoro- and chlorofluoro-substituted n-alkanes is comparable to the accuracy of the determination of the experimental quantities.[172,208]

The further development of the thermochemistry of organohalogen compounds will apparently be determined by the investigation of new promising classes of substances and the accumulation of reliable experimental data for "reference" compounds.

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