

Low Temperature Oxidation of Cyclohexane: Uncertainty of Important Thermo-Chemical Properties

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Abstract

The study of the standard formation enthalpy, entropy, and heat capacity for key species relevant to the low-temperature combustion of cyclohexane has been performed by applying the group additivity method of Benson. The properties of 18 Benson groups (8 of them for the first time), and 10 ring correction factors for cyclic species were estimated through different empirical and semi-empirical methods. The method validation proceeded through comparison of predicted values for certain number of newly estimated groups and available literature data derived from quantum chemistry estimations. Further validations of the estimated properties of groups have been provided by comparing estimated properties of test species with data in literature and kinetic databases. Also the standard deviation between prediction and reported values has been evaluated for each validation case. A similar approach has been applied for validation of the estimated ring correction groups. For selected well-studied cyclic molecules the predicted values and the literature data have been compared with each other, and the standard deviations have been also reported. The evaluated properties of the cyclohexane relevant species were also compared with similar ones available in other kinetic models and in databases. At the end the estimated properties have been presented in a tabulated form of NASA polynomial coefficients with extrapolation up to 3500 K.

1. Introduction

Performance and emissions of any combustion devices are strongly dependent on the fuel and the underlying chemistry. Practical fuels such as kerosene are a complex mixture of several hundred individual species, which can be divided into four hydrocarbon families (n-/i-paraffins, naphthenes (cyclo-paraffins) and aromatics). The focus of this work is an evaluation of the thermodynamic data for species occurring in the reaction model of cyclohexane (cyC₆H₁₂) oxidation. The chemistry of cyC₆H₁₂ oxidation is the basis for the reaction mechanisms of combustion of different naphthenes, including substituted cyclo-molecules. The present study revises the thermodynamic data for the molecules and radicals involved in the low-temperature chemical kinetics of cyC₆H₁₂ [1] and estimates thermodynamic properties for molecules adopted in the model during modifications and extensions.

Figure 1 depicts the main reaction paths and species of the low-temperature sub-mechanism of the DLR cyclohexane combustion model [1]:

- 1) Addition reaction with O₂
- 2) Isomerization of cyclic peroxy to hydroperoxy radical
- 3) Decomposition cyC₆H₁₀OOH· radicals to cyclohexene and HO₂
- 4) Decomposition of cyC₆H₁₀OOH· and formation of cyclohexanone and bicyclic ethers
- 5) O₂ addition to cyC₆H₁₀OOH· with formation of O₂QOOH· type radicals
- 6) Decomposition of O₂QOOH· to cyclic ketohydroperoxides
- 7) Isomerization of cyOOC₆H₁₀OOH to cyC₆H₉(OOH)₂
- 8) Isomerization of cyOOC₆H₁₀OOH and formation of cyclic carbonyl hydroperoxide
- 9) Decomposition of cyC₆H₉O
- 10) Decomposition of OcyC₆H₉OOH

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11) Formation of $\text{cyC}_6\text{H}_{11}\text{O}\cdot$ from $\text{cyC}_6\text{H}_{11}\text{OO}\cdot$ and $\text{cyC}_6\text{H}_{11}$

12) Decomposition of $\text{cyC}_6\text{H}_{11}\text{O}\cdot$

13) Oxidation of cyclic olefin $\text{cyC}_6\text{H}_{10}$.

The current reaction mechanism [1] has been extended for the cyclohexene low-temperature schemes (step 13), for cyclohexenyl peroxy formation and isomerization of hydroperoxy peroxy radical, through the internal hydrogen transfer yielding more stable $\text{cyC}_6\text{H}_9(\text{OOH})_2$ (step 7).

The reaction paths of low-temperature cyclohexane oxidation have been investigated in other works [2–4]. Silke et al. [2] used the thermodynamic properties calculated with the THERM program of Ritter and Bozzelli [5], which implements the group-additivity method of Benson [6]. Buda et al. [3] presented a kinetic model with thermochemical data calculated using the software THERGAS [7], also based on the group-additivity method [6]. An update of this model was performed by Serinyel et al. [4], which used thermodynamic properties calculated with CBS-QB3 by Sirjean et al. [8, 9]. Sirjean et al. [8] studied the gas-phase reactions of cyclopentylperoxy and cyclohexylperoxy radicals and determined the required thermodynamic properties (14 species, see Table 1 of [8]) by means of quantum chemistry at the CBS-QB3 level and based on the isodesmic reactions.

Table 1 integrates the information about the standard formation enthalpies and entropies of species involved in the low-temperature chemistry of our model, and also reported in other kinetic studies of cyclohexane [2–4, 8, 9], in the databases of the National Institute of Standards and

Technology (NIST) [10] and in Burcat et al. [11]. The scatter in the literature data has also been evaluated and included in Table 1 (2 last columns). As shown, none of the sources reports data for all required species and the uncertainty of the data is remarkably high.

This fostered our interest to revise, re-estimate and evaluate thermodynamic properties with an in-house developed numerical tool to (a) complete the dataset for all species needed in the kinetic scheme and (b) to assess the uncertainty of the values obtained. There are several methods available to calculate thermodynamic properties: experimental determinations and extrapolations, quantum chemistry approaches, and empirical and semi-empirical methods. The latter are favoured over quantum chemistry methods in terms of computational costs. They are extensive, fast and compatible with a range of computational resources, but due to the dependency on experimental data, unlike the quantum chemistry approaches, their application is often limited. A combination of experimental measurements with their extrapolations was applied by Rossini et al. [12] and Wilhoit et al. [13] to estimate enthalpies and heat capacities for 38 different species. Goldsmith et al. [14] used the quantum chemistry RQCISD (T)/cc-PV ∞ QZ//B3LYP/6-311++G (d,p) method for 219 small molecules, including radicals, bi-radicals, and triplet species. The group additivities, which is based on molecular mechanics, was later developed by Benson et al. [6, 15, 16, 17] and extensively extended by other [18–24] investigators. However, there are several groups in hydrocarbon molecules, i.e. radicals of oxygenated compounds and radicals of multiple bound structures, remained unknown.

In this work, based on the group additivity method of Benson et al. [6], the standard heat of formation ΔH_f^0 , standard entropy S^0 , and the heat capacity C_p have been evaluated for oxygenated cyclohexane species and for certain Benson additivity groups found in the structure of studied molecules and transient complexes. The properties for certain number of these groups and species, were not found in our comprehensive literature review [6, 15–24] and are only available in the quantum chemistry calculations of [20–22].

The paper is organized as follows: The first part describes the utilized approaches for estimation of the properties of new Benson groups. The second part highlights the estimation of ring correction groups. In the next section, comparisons of new estimated properties of ten Benson groups with

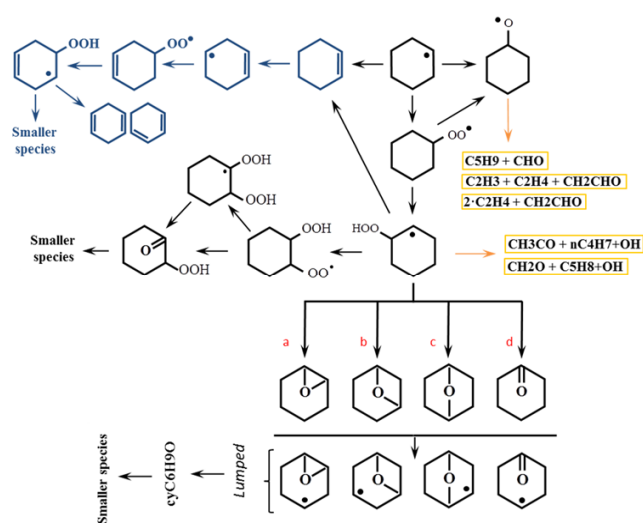


Fig. 1. Principal scheme of the low temperature $\text{cyC}_6\text{H}_{12}$ oxidation.

Table 1
Comparison between predicted values and existing properties in other cyclohexane models, NIST [10] and Burcat [11] databases, for certain low temperature intermediates

Species	Silke et al. [2]		Buda et al. [3]		Serinyel et al. [4]		Sirjean et al. [8], [9]		NIST [10], Burcat [11]		Uncertainty%	
	ΔH_f^0 *	S^0 *	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0
cyC ₆ H ₁₁	70.35	326.81	74.70	317.93	71.22	318.95	71.48	325.2	75.82 ^b	317.75 ^b	3.3	1.4
cyC ₆ H ₁₀	-4.62	316.23	-	-	-5.73	310.68	-0.41	304.3	-4.32 ^a	310.45 ^a	61.6	1.6
cyC ₆ H ₁₁ O	-	-	71.48	314.46	-71.56	314.74	-	-	-	-	0.1	0.1
cyC ₆ H ₁₁ O	-87.18	378.94	-81.26	370.89	-84.21	371.25	-93.21	366.59	-	-	5.9	1.4
cyC ₆ H ₁₀ OOH (1)	-31.99	402.33	-29.84	400.53	-36.22	401.92	-18.39	380.80	-	-	26.2	2.6
cyOOC ₆ H ₁₀ OOH	-190.32	449.34	-183.08	453.03	-185.08	453.48	-	-	-	-	2.0	0.5
cyOC ₆ H ₉ OOH	-339.65	409.62	-	-	-353.12	377.49	-	-	-	-	2.8	5.8
a-cyC ₆ H ₁₀ O	-30.52	272.51	-118.09	312.7	-126.80	322.97	-126.65	322.70	125.52 ^a	-	39.9	7.8
b-cyC ₆ H ₁₀ O	-37.80	261.93	-	-	-	-	-107.00	316.43	-	-	67.6	13.3
c-cyC ₆ H ₁₀ O	-121.6	253.44	-177.44	312.71	-183.28	313.34	-183.08	313.08	-	-	18.0	10.0
d-cyC ₆ H ₁₀ O	-236.80	338.24	-	-	-230.52	322.10	-232.83	334.82	-231.10 ^a	335.53 ^a	1.2	2.2
cyC ₆ H ₉ -1,3	106.50	309.67	-	-	126.92	321.35	-	-	131.45 ^b	313.65 ^b	10.9	1.9
cyC ₆ H ₉ -1,4	109.18	291.06	-	-	192.81	322.32	-	-	-	-	39.2	7.2

*: ΔH_f^0 , S^0 are in kJ·mol⁻¹ and J·mol⁻¹·K⁻¹, respectively. a: NIST [10] b: Burcat [11]

quantum chemistry calculations reported by Khan et al. [22] are provided. The following section presents results of comparisons of the predicted thermochemistry (p.w.) and previously published literature values for a select list of species. The next section describes the final step of the applied methodology validation.

2. Computational methods for calculation of new Benson groups and correction groups

2.1. Determination of properties of the new groups G1-G17

To evaluate values of the enthalpy ΔH_f^0 , entropy ΔS^0 , and heat capacity C_p terms for new Benson groups (G1-G17) in Table 2 and the [C-(C_d)(CO)(H)₂] group, an empirical combinative approach was used, which is based on the Benson contribution rules [25]. To highlight this approach, the estimation of properties of the new unknown group [C·-(O)(H)₂] will be described in detail. This is a radical-centered group, representing a radical of carbon, bonded with oxygen and 2 other hydrogen atoms. Firstly, the appropriate “parent” (or reference) molecule is to be found. In this case, it would be the CH₂COCH₃ molecule, which consists of this unknown group, and two other known Benson

groups: [O-(C)(C·)] and [C-(O)(H)₃]. Based on the additivity rules, ΔH_f^0 of the unknown group can be estimated:

$$\Delta H_f^0[\text{C} \cdot -(\text{O})(\text{H})_2] = \Delta H_f^0[\text{CH}_3\text{OCH}_2] - \Delta H_f^0[\text{O} - (\text{C})(\text{C} \cdot) - \Delta H_f^0[\text{C} - (\text{O})(\text{H})_3] \quad (1)$$

The S^0 and C_p values are estimated in a similar way. Table 2 provides a list of 17 newly introduced groups and their thermodynamic properties within the range 300–1500 K, along with their parent compounds. The reference molecules have been selected to be the simplest available one and not larger than C₅, with the aim to reduce the uncertainty of calculations.

However, the mentioned method is not appropriate for the [C-(C_d)(CO)(H)₂] group, which is one of the constructive groups of the transient complexes cyC₆H₈O with one conjugated carbon bond and a carbonyl group. No “parent” molecules with completely “known” properties was found in this case. The best matching case for a reference molecule could be 3-butenal. Its properties are partially known and have the potential to be completed and improved using different strategies, which are described in the following section.

Table 2
New determined groups via combination method

No.	Group	$\Delta H_f^0 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$S^0 / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$C_p(T) / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$						Reference Species	Structure	Ref.
				300	400	500	600	800	1000			
G1	C-(C)(C)(O)(H)	-10.77	-49.75	24.63	30.87	35.06	38.28	41.67	42.00	47.20		[26]
G2	C-(C_d)(C)(O)(H)	-43.42	-55.59	16.35	26.37	34.24	40.10	45.71	44.82	47.26		[26]
G3	C-(C_d)(C)(O)(H)	-12.40	-43.94	14.01	23.14	30.79	36.87	43.14	43.14	46.48		[26]
G4	C-(O)(H)_2	147.50	127.10	26.19	29.00	32.90	36.16	39.90	44.04	50.15		[11]
G5	O-(C)(H)	-148.06	126.00	22.28	25.00	26.23	27.57	31.39	33.35	37.30		[11]
G6	C-(C)(O)(H)	134.68	41.09	15.76	19.00	23.41	27.09	30.58	32.07	34.66		[26]
G7	CO-(C_d)(C)	-146.52	52.20	24.72	29.61	34.06	37.86	41.10	42.36	45.75		[26]
G8	C-(CO)(H)_2	140.44	126.21	23.82	28.54	32.59	36.08	40.40	44.06	49.00		[11]
G9	C-(C)(C_d)(H)_2	-25.19	37.95	21.18	26.64	32.71	38.19	45.61	51.44	59.95		[11]
G10	C-(C_d)_2(H)	81.19	25.46	16.60	24.20	30.87	35.66	40.85	45.86	50.07		[11]
G11	C-(C)(O)(H)_2	-32.41	42.88	18.29	25.82	31.50	36.42	44.20	52.29	61.38		[11]
G12	C-(C)(C_d)(O)	84.01	-59.86	11.28	15.31	19.96	23.24	24.86	25.52	27.17		[26]
G13	CO=C	-84.75	126.70	30.39	32.81	34.38	35.28	36.73	37.71	39.06		[11]
G14	CO-(C)(H)	-123.81	137.04	29.60	33.23	37.20	41.00	46.63	50.80	56.00		[11]
G15	CO-(C)(H)	-115.24	141.92	31.31	34.83	38.37	41.72	48.73	53.61	62.35		[26]
G16	O-(C)(O)	-11.51	32.92	15.40	19.63	22.25	24.71	29.69	30.80	34.62		[26]
G17	C-(CO)(C)(H)_2	-7.43	51.38	23.17	28.71	33.11	37.05	44.06	50.21	56.62		[26]

*Deviations for ΔH_f^0 are assumed to be $\pm 5.00 \text{ kJ} \cdot \text{mol}^{-1}$, whereas uncertainties for S^0 and $C_p(T)$ are assigned to be about $\pm 10.00 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, due to implemented combinative approach and the recommendation of Benson [6] for additivity method, and considering 10% of uncertainty for parents molecule from literature.

2.2. Estimation of properties of [C-(C_d)(CO)(H)₂] Benson group

Three different methods are considered to derive ΔH_f^0 , S^0 and C_p for [C-(C_d)(CO)(H)₂] from the properties of the “parent” molecule: i) Additivity of Bond Properties, ii) Statistical Mechanical Estimation and iii) Group Contribution Method. None of these methods can provide a full set of thermodynamic requirements. Only using those in combination does the different contributions to the studied properties. The results, obtained with methods i)-iii), have been compared with each other and with the average values. The predicted uncertainties have been assigned to each new group, see Table 4.

2.2.1. Additivity of Bond Properties

Based on this method, developed by S.W. Benson 1976 [6], properties of gas phase species at the standard condition ($p = 1$ atm, $T = 300$ K) can be estimated from their bond contribution properties. This method is applicable to approximate ΔH_f^0 with an accuracy of 10 kJ·mol⁻¹, and for S^0 and C_p^0 with accuracy of 5.00 J·mol⁻¹. A larger error in the case of heavy branched structures is expected. Moreover, bond additivity is not able to distinguish the property differences between isomers. With this method, ΔH_f^0 , S^0 and C_p^0 of 3-butenal have been calculated only at the standard condition (*Supplement 1, Sheet 1 i*).

2.2.2. Statistical Mechanics Estimation

With this method S^0 and C_p^0 can be estimated with reliable uncertainties [6], but it is not able to approximate the standard heat of formation directly. From statistical mechanics, thermodynamics of compounds can be described by partition functions, obtained from contributions of four degrees of freedom: translational, rotational, vibrational and electronic contributions [6]. With certain assumptions, (an ideal gas, non-linearity of the molecule) the heat capacity would be mainly described by its vibrational contribution [6]:

$$C_p \cong 4R + C_{p,vib}, \quad C_{p,vib} = R \cdot x^2 e^x / (e^x - 1)^2 \quad (2)$$

where $x = hcv/kT$ is a dimensionless scalar, representing vibrational frequencies, h is Planck's constant, c is the speed of light and k is the Boltzmann constant. The values for x at different temperatures were tabulated and are available in Benson, 1976 [6]. Similarly the standard entropy can

be determined with its translational, rotational and vibrational contributions. For simplification of estimations, the calculation of properties of the target molecule ϕ_{target} can be provided for two terms: properties of the model (or reference) molecule ϕ_{model} , with an analogous structure and known properties, and a correction $\Delta\phi$, calculated as the partition functions for differences in translational, rotational and vibrational contributions:

$$\phi_{target} = \phi_{model} + \Delta\phi \quad (3)$$

In case of 3-butenal, 1,4-pentadiene (1,4-C₅H₈) would be the closest molecule to the parent (Fig. 2). Therefore, for each entropy contribution, and for heat capacity vibrational contribution ($\Delta C_{p,vib}$) the correction terms are calculated. The total correction of standard entropy will be the summation of the corrections for each translational (ΔS_{tran}^0), rotational (ΔS_{rot}^0) and vibrational (ΔS_{vib}^0) contribution. Since the translational contribution varies as $\frac{3}{2} R \ln M$ here M (g·mol⁻¹) is the molecular weight, ΔS_{tran}^0 can be estimated as follows [6]:

$$\Delta S_{tran}^0 = \frac{3}{2} R \ln \left(\frac{M_{target}}{M_{model}} \right) \quad (4)$$

The rotational contribution, ΔS_{rot}^0 , would be negligible in this case [6]. The vibrational contribution of entropy and heat capacity are highly dependent on stretching and bending frequencies. Therefore both terms of ΔS_{vib}^0 and $\Delta C_{p,vib}$ follow the differences in vibrational frequencies of the model and target molecules, i.e. 1,4-C₅H₈ and 3-C₄H₆O, respectively. The model molecule (1,4-C₅H₈) has additional 6 stretching and deformation frequencies compared to 3-butenal. Therefore ΔS_{vib}^0 is seen as the largest contribution, forming the total ΔS^0 between target and model molecule. Also the symmetry difference between 1,4-C₅H₈ and 3-C₄H₆O and its influence on entropy should be taken into account. The correction due to this feature, known as symmetry correction is obtained by subtracting $R \ln \sigma$ where σ is the symmetry number [6]. Thus the symmetry difference between the model and target molecule is evaluated as follows:

$$\Delta S_{sym} = R \ln \frac{\sigma_{model}}{\sigma_{target}} \quad (5)$$

Details of the calculations are provided in the supplemental information (*Supplement 1, Sheet 3 ii*); the final results of statistical mechanics estimations for 3-C₄H₆O are summarized in Table 3 in standard units.

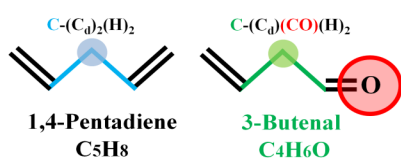


Fig. 2. Comparison between structures of the unknown group C-(C_d)(CO)(H)₂ (green) and C-(C_d)₂(H)₂ (blue).

2.2.3. Group Contribution Method

This method was developed by Joback et al. [27] and can estimate eleven physical properties, including standard entropy of formation and heat capacities over temperature ranges. 3-C₄H₆O contains the following groups: (=CH₂), (=CH-), (-CH₂-), (O=CH-). The values for ΔH_f^0 and C_p are estimated with the method and equations described in [27], in units kJ·mol⁻¹ and J·mol⁻¹·K⁻¹, respectively. Details of calculations with the mentioned methods are provided in supplemental information (see Supplement 1, Sheet 3 iii).

The final results of the Group Contribution Method application to 3-C₄H₆O are summarized in Table 3. After estimations of the properties of the parent molecule 1,4-C₅H₈, the properties of the target group [C-(C_d)(CO)(H)₂] are extracted through application of the combination rule (section 2.1). In Table 4 the group values obtained using all three described above methods are presented. The mean value of these 3 methods are set as the final re-

ported ones (marked with bold numbers), and the standard deviations are considered as uncertainty of calculation (written in *italic*). Details of approximations are included in the supplemental information, Supplement 1, Sheet 4 and Sheet 5. Since most of the studied intermediates related to the low- and high-temperature oxidation sub-mechanism of cyclohexane species are cyclic, the 18 newly determined groups are insufficient to estimate their properties, and the influence of a ring structure on the thermodynamic properties has to be estimated.

2.3. Ring strain correction groups

A strain energy term is often used in the case of highly branched or cyclic molecules [6]. Most of the ring structures require unique strain corrections which cannot be derived from groups themselves [21]. However, this term can be considered as an additive value to the strain energy of non-branched hydrocarbons, defined as “unstrained”, but assigned to be zero [6]. On these grounds, the difference between the observed ΔH_f^0 and the formation enthalpy estimated from the unstrained standard group additivity is assigned as the strain energy [6], F_n . Cohen et al. [28] applied the same approach:

$$\Delta H_f^0(C_n H_{2n}) = n[\Delta H_{f,s}^0] + F_n \quad (6)$$

Table 3

Thermodynamic properties of 3-C₄H₆O calculated with three semi-empirical methods, introduced in section 2.2.

Method	$\Delta H_f^0/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$S^0/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$C_p(T)/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$						
			300	400	500	600	800	1000	1500
i) Benson Bond energy	-83.64	330.95	91.13	-	-	-	-	-	-
ii) Statistical Mechanics	-	341.32	94.22	116.6	134.6	149.4	172.1	188.8	213.6
iii) Joback & Reid	86.00	-	91.63	112.7	130.8	146.2	170.5	187.9	217.6

Table 4

Properties for [C-(C_d)(CO)(H)₂] by different methods

Method used for properties of parent molecule 3-C ₄ H ₆ O	$\Delta H_f^0/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$S^0/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$C_p(T)/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$						
			300	400	500	600	800	1000	1500
i) Benson Bond energy	-24.02	36.07	23.10	-	-	-	-	-	-
ii) Statistical Mechanics	-	46.43	26.20	36.26	42.11	46.04	51.09	55.25	62.04
iii) Joback & Reid	-26.38	-	23.60	32.39	38.24	42.90	49.48	54.32	66.17
Final values*	-25.20 <i>±1.20</i>	41.25 <i>±7.3</i>	24.30 <i>±1.4</i>	34.33 <i>±1.9</i>	40.17 <i>±1.9</i>	44.47 <i>±1.6</i>	50.28 <i>±0.8</i>	54.78 <i>±0.5</i>	64.10 <i>±2.1</i>

* Uncertainty values are assigned as standard deviation of all methods (see supporting information, Sheet 5 Summary)

where $\Delta H_{f,s}^0$ represents the enthalpy of formation and n is the number of the $[\text{C}-(\text{C})_2(\text{H})_2]$ group and F_n is equal to strain energy value. For the species with different groups in rings, the strain energy can also be defined as the difference between the standard formation enthalpy following from measurements or literature data and that from summation of the constructing groups. A similar approach can also be applied for S^0 and C_p to evaluate correction groups. Therefore, with the properties of the known species, reported in the literature, the correction factor can be calculated. Sabbe et al. [20] evaluated ring strain corrections for 18 species differing from each other by size of the rings, the number and locations of the endocyclic double bonds. A study by Lay et al. [29] estimated thermodynamic properties for 34 oxygenated hydrocarbons, using PM3 calculations, and extracted the ring correction groups with the aid of additivity groups. However, most of these estimations are only available for the ring strain energy (ΔH_f^0 correction), or for cyclic oxygenated compounds, such as oxirane or hydroxyran. Therefore, the required correction groups have been estimated or re-estimated based on recent available sources and correction factors F_n have been calculated Table 5. Corrections for the cyclohexene ring (RC9) have been taken to equal the values reported by Benson et al. [15]. The group RC10 presents the ring correction for each member sitting in the ring. This correction is used to

estimate the properties of multi-cyclic molecules. For example, the bicyclic a-cyC₆H₁₀O molecule is in fact a cyclic ether with three members, forming an external hydrocarbon ring with 4 other carbons. For this structure, the correction factor is considered to be an oxirane correction (RC1), added with 4 cyclohexane corrections RC10 (for each carbon atom).

3. Results and discussion

3.1. Validation and results

For ten newly estimated groups (see Table 2), namely: G1, G4, G6, G7, G8, G10, G12, G15, G14 and G16, literature data is available: Sabbe et al. [20, 21] estimated the group properties using ab-initio quantum chemistry methods; the data of Khan et al. [22] has been evaluated based on the estimated properties of the reference species, using Gaussian-3 theory with B3LYP geometries; Da Silva and Bozzelli [32] have also determined certain group additivity values for the carbon-oxygen-hydrogen groups important to aldehydes, using quantum chemistry. Table 6 provides a comparison of the calculated values in present work (p.w.) with those estimated in [20–22, 31].

The differences between predicted values and those reported in literature are on average 6.2 kJ·mol⁻¹ for ΔH_f^0 , 8.5 J·mol⁻¹·K⁻¹ for S^0 , and

Table 5
Estimated ring correction groups*

No.	Species	Ref.	Structure	$\Delta H_f^0 /$ J·mol ⁻¹ ·K ⁻¹	$S^0 /$ J·mol ⁻¹ ·K ⁻¹	$C_p(T) / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$						
						300	400	500	600	800	1000	1500
RC1	Oxirane	[30]		114.27	135.8	-8.66	-11.0	-10.0	-8.66	-8.45	-7.28	3.47
RC2	Oxetane	[11]		106.0	123.1	-16.8	-19.3	-16.6	-13.0	-11.1	-8.33	4.73
RC3	Hydro furan (iv)	[11]		23.05	111.1	-25.3	-25.6	-20.9	-15.8	-11.9	-7.91	6.11
RC4	Hydro Pyran (iv)	[11]		3.10	70.96	-28.0	-28.3	-23.4	-17.8	-12.4	-7.28	7.70
RC5	Oxepane	[31]		27.11	77.36	-25.6	-22.4	-16.0	-10.6	-3.9	1.13	18.20
RC6	Cyclohexane	[10]		-3.86	75.71	-31.94	-25.91	-18.27	-11.47	-0.83	4.60	9.45
RC7	Cyclohexene	[10]		3.73	87.87	-21.51	-18.01	-13.89	-10.72	-5.86	-3.13	2.11
RC8	1,3-cyC ₆ H ₈	[11]		17.70	107.0	-20.2	-20.5	-17.1	-13.1	-8.95	-5.56	-2.47
RC9	1,4-cyC ₆ H ₈	[11]		1.54	29.1	-14.32	-14.28	-11.08	-7.66	-4.86	-2.81	0.59
RC10	CHX/6**	[10]		-0.64	12.62	-5.32	-4.32	-3.05	-1.91	0.14	0.77	1.58

*Deviations for ΔH_f^0 are ± 13.0 kJ·mol⁻¹ and uncertainties for S^0 , C_p are assigned to be about ± 7.0 J·mol⁻¹·K⁻¹, for heavy substituted species, due to [6]. **Correction factor for each C atom, in cyC₆H₁₂ ring, based on the reported values from [17].

6.75 J·mol⁻¹·K⁻¹ for C_p over T = 300–1500 K. The maximum deviation is seen in the case of G1, where the deviations in ΔH_f^0 , S^0 and C_p (300 K) are 19.28 kJ·mol⁻¹, 15.40 J·mol⁻¹·K⁻¹ and 16.22 J·mol⁻¹·K⁻¹, respectively. Also data for the G12 and G16, despite of their good agreement with Khan et al. [22] in ΔH_f^0 values, deviate significantly in C_p . The main reasons for these deviations could be due to the existing uncertainty in the thermochemistry of the reference species, i.e. from where the group properties were extracted.

Further validations of the estimated properties of groups have been provided by comparison of the calculated thermochemistry of selective species with data for reference molecules used in section 2.1. Results are collected in Table S1 in the (*Supplement 2*). The selected species contain at least one of the new calculated groups of Table 2. In most cases the values estimated in this work (p.w.), and data reported from literature, mainly evaluated by quantum chemistry methods, are consistent. The mean absolute deviation (MAD) was calculated for molecules with two or more different sets of properties available in literature. If only one set of observation was available, the difference between

the estimate and observation is provided (DF). For all species, except C₃H₇O and C₄H₇O, the MAD or DF of standard heat of formation is less than 10 kJ·mol⁻¹, and for S^0 and C_p is mostly less than 5 J·mol⁻¹·K⁻¹, which are satisfactory deviations. Of note, in the case of propan-2-ol-1-yl (C₃H₇O), which contains the new estimated group G1, the properties estimation reveals a good agreement with data from Khan et al. [22], unlike the properties of G1 ([C-(C·)(C)(O)(H)]), Table 6. Excluding Holmes et al. [33], who measured ΔH_f^0 of C₃H₇O around -96.14 kJ·mol⁻¹, other observations are well aligned with the estimated properties, including S^0 and C_p values.

The C₃H₇O₂ molecule contains two new groups: G4 and G16. The estimated values for G16 disagree with the reported values from Khan et al. [22] by around 30%. Despite that, the p.w. values agree well with the mentioned reference. However, at 1500 K the heat capacity is also over-predicted by around of 11 J·mol⁻¹·K⁻¹. The discrepancy arises due to the estimation of 1-Buten-3-ol-yl (C₄H₇O radical), which contains the group G12 with the largest disagreement of the calculated properties. In this case, the standard heat of formation and

Table 6

Comparison of thermodynamic values for certain additivity groups between calculated and available literature data

No	Group	Ref.	$\Delta H_f^0 /$ J·mol ⁻¹ ·K ⁻¹	$S^0 /$ J·mol ⁻¹ ·K ⁻¹	$C_p(T) /$ J·mol ⁻¹ ·K ⁻¹						
					300	400	500	600	800	1000	1500
G1	C-(C·)(C)(O)(H)	p.w.* [22]	-10.77	-49.75	24.63	30.87	35.06	38.28	41.67	42.00	47.20
			-30.05	-59.65	32.98	39.38	42.89	45.06	47.69	49.12	51.16
G4	C·-(O)(H) ₂	p.w.* [22]	142.50	127.10	26.19	29.00	32.90	36.16	39.90	44.04	50.15
			139.78	130.17	25.37	30.68	36.16	40.38	45.06	49.20	55.89
G6	C·-(C)(O)(H)	p.w.* [22]	134.68	41.09	15.76	19.00	23.41	27.10	30.58	32.07	34.66
			140.66	46.90	20.61	25.87	30.01	33.06	36.45	38.87	42.22
G7	CO-(C _d)(C)	p.w.* [22]	-146.52	52.20	24.72	29.61	34.06	37.86	41.10	42.36	45.75
			-136.73	65.75	25.00	25.58	27.09	28.67	32.19	36.12	45.02
G8	C·-(CO)(H) ₂	p.w.* [22]	140.44	126.21	23.82	28.55	32.60	36.08	40.40	44.06	47.91
			143.67	121.30	27.96	34.40	38.83	42.18	47.19	51.41	55.68
G10	C·-(C _d) ₂ (H)	p.w.* [20], [21]	81.19	25.46	16.60	24.20	30.87	35.66	40.85	45.86	50.07
			76.57	16.48	17.36	25.77	31.59	35.48	40.29	43.35	47.66
G12	C·-(C)(C _d)(O)	p.w.* [22]	84.01	-68.99	11.28	15.32	19.97	23.24	24.86	25.52	26.06
			83.77	-53.59	27.50	33.23	35.28	35.91	35.45	34.94	35.45
G14	CO-(C)(H)	p.w.* [32]	-123.81	137.04	29.60	33.23	37.20	41.00	46.63	50.80	56.00
			-123.18	145.88	29.26	32.60	36.78	40.55	46.82	51.00	58.10
G15	CO-(C·)(H)	p.w.* [22]	-115.24	141.92	31.31	34.83	38.37	41.72	48.73	53.61	62.35
			-128.83	146.72	28.13	31.48	35.57	39.46	45.94	50.29	59.82
G16	O-(C·)(O)	p.w.* [22]	-11.51	32.92	15.40	19.63	22.25	24.71	26.69	30.80	34.62
			-13.08	42.13	24.75	24.29	22.78	21.86	22.57	22.91	23.74

* p.w.: present work.

heat capacities estimated in the current study and provided by Hansen et al. [26] are in good agreement and deviate from the prediction of [22] by $15.65 \text{ kJ}\cdot\text{mol}^{-1}$ for ΔH_f^0 and by $10 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for C_p at lower temperature.

A comparison of the predictions with the data available in literature for the selected well-studied cyclic molecules, which contain the estimated ring correction groups of Table 5 are provided in *Supplement 2* Table S2. Similar to Table S1, the MAD and DF values were calculated. It has been shown that, as species become more complex in structure, the uncertainty among literature data grows as well. For example in the case of Oxetane, 3-methylene ($\text{C}_5\text{H}_6\text{O}$), two different data sets in the RGM database [34] are available. They disagree in value for the standard heat of formation by around $20.00 \text{ kJ}\cdot\text{mol}^{-1}$, although they are well-matched in prediction of S^0 and C_p values. Also the estimations of ΔH_f^0 provided by Sabbe et al. [20] are higher than other references in most cases. Nevertheless, it can be seen from this table that, in the case of ring structured species, the provided estimations in the current study estimations lie within an acceptable margin compared to other available data and predict the thermodynamic properties of the studied ring classes with acceptable uncertainty.

Figure 3 shows the heat capacities for $\text{cyC}_6\text{H}_{11}$, $\text{cyC}_6\text{H}_{10}$, $\text{cyC}_6\text{H}_{11}\text{O}$, $\text{cyC}_6\text{H}_{11}\text{OO}$, $\text{cyC}_6\text{H}_{10}\text{OOH}$, $\text{cyOOC}_6\text{H}_{10}\text{OOH}$ and $\text{a,d-cyC}_6\text{H}_{10}$ reported in other cyclohexane kinetic models, literature data, and calculated in this work with the newly estimated groups and ring correction factors. The presented species vary from each other in structure and functional groups, including linear and cyclic alkanes, radicals and oxygenated compounds. It can be seen that, there is a good consistency between literatures data and predictions. In most cases, the heat capacity values, estimated in the present work were predicted to be close to the average of the available literature data. The maximum deviation occurs for $\text{cyC}_6\text{H}_{10}\text{O}$ around $20 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, i.e. at a 5% lower value than used by Nancy's model [4] at 3500 K, see Fig. 3c. The estimated uncertainty intervals for literature data, DF and MAD, are provided in Tables 6 and 7. They are shown to be under $10.00 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for the range 300–2000 K. The uncertainty of calculations rises with increasing temperature; uncertainty intervals increase to $15 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for the range 2000–3000 K and to $20 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ above 3000 K.

Table 7 provides the results of the performed calculations of the standard heat of formation and

standard entropy for main intermediates involved in cyclohexane low temperature oxidation reaction scheme. Also, for comparison, literature data from well-established cyclohexane modelling studies, from the NIST [10], Burcat [11], and RGM database [34] have been presented in Table 7. As expected in the case of well-studied species, the method used in this work delivers good agreement with the other models. Unlike for the heat capacities (Fig. 3a-l), the deviations here increase as the intermediates become more complex in structure. For the case of bi-cyclic ethers $\text{a,b,c-cyC}_6\text{H}_{10}\text{O}$, high MAD values have been obtained for both ΔH_f^0 and S^0 .

3.2. Benson groups and NASA coefficients of low-temperature species

The “Thermo-NASA” code, written by DLR (German Aerospace Center) in Stuttgart was used to calculate thermodynamic properties, ΔH_f^0 , S^0 and $C_p(T)$, and to approximate them using the NASA polynomial coefficients. The inputs to the program are the list of Benson groups, and configuration information (linearity and symmetry). The output of the code presents estimated values for the temperature range of 300–1500 K, an extrapolation up to 3500 K and the corresponding NASA polynomial coefficients. The “Therm-NASA” code implements the FUMILI tool [35–37] for approximation and calculation of the NASA coefficients. Table A.1 in supplemental information (see *Supplement 2*) lists these values for select species important to the low temperature reaction mechanism of cyclohexane. They have been also provided in ASCII format suitable for numerical calculations, see *Supplement 3*.

4. Conclusions

The method implemented in this study to estimate the thermodynamic features of the species involved in the cyclohexane oxidation scheme at lower temperature, applies the Benson additivity rules, where the properties of a compound could be described by properties of each contributing group in the range $T = 300\text{--}3500 \text{ K}$. Since the available databases for Benson groups provided by different references do not contain all of the required groups for the aim of this work, new groups had to be determined. This was done either empirically via properties of reference species which contain these new groups, or semi-empirically if there is no

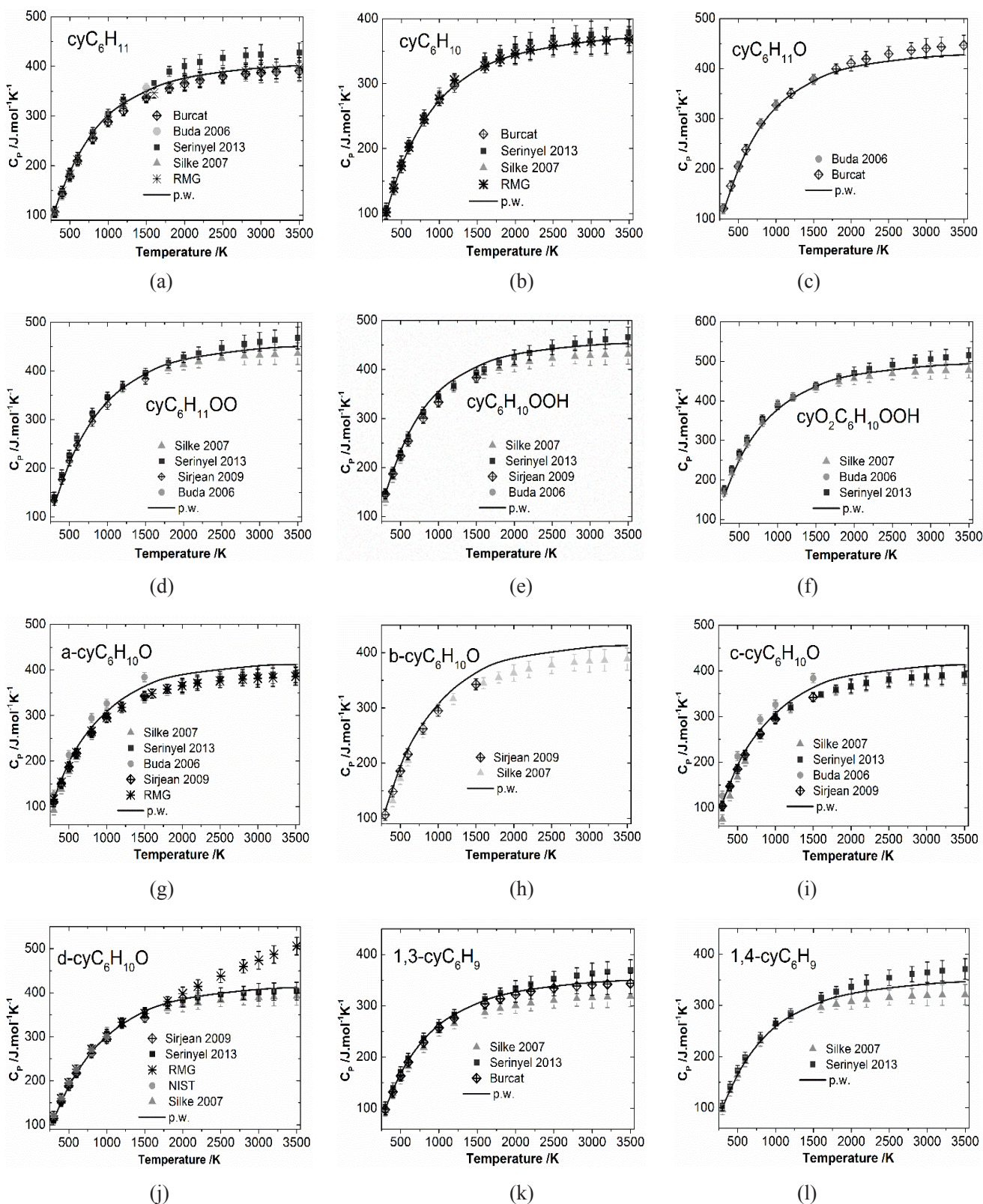


Fig. 3. Predicted values of present work (solid lines) versus data from certain kinetic models and databases [2–4], [8–11], [34] (symbols) for heat capacity values of certain important intermediates of low temperature oxidation within $T = 300\text{--}3500\text{ K}$.

known data for the model molecule with an analogous structure in the literature. In this case, calculations of bond energy and statistical mechanics analysis have been performed.

Most of the intermediates occurring in the low-temperature chemistry of cyclohexane are cyclic structured. They include oxygenated and bicyclic species as well. A precise evaluation of the

Table 7
Comparison between predicted values and existing properties in other cyclohexane models, NIST [10] and Burcat [11] databases, for certain low temperature intermediates

Species	p.w.*		Silke et al. [2]		Buda et al. [3]		Serinyel et al. [4]		Sirjean et al. [8], [9]		NIST [10], Burcat [11]		RMG [34]		MAD**	
	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0	ΔH_f^0	S^0
cyC ₆ H ₁₁	50.85	311.87	70.35	326.81	74.70	317.93	71.22	318.95	71.48	325.2	75.82 ^b	317.75 ^b	71.12	325.48	7.79	5.04
cyC ₆ H ₁₀	-4.57	309.63	-4.62	316.23	-	-	-5.73	310.68	-0.41	304.3	-4.32 ^a	310.45 ^a	-4.61	310.56	1.69	3.46
cyC ₆ H ₁₁ O	-72.09	328.48	-	-	-71.48	314.46	-71.56	314.74	-	-	-	-	-	0.27	6.54	
cyC ₆ H ₁₁ OO	-86.93	362.08	-87.18	378.94	-81.26	370.89	-84.21	371.25	-93.21	366.59	-	-	-	3.96	5.60	
cyC ₆ H ₁₀ OOH-1	-25.83	385.30	-31.99	402.33	-29.84	400.53	-36.22	401.92	-18.39	380.80	-	-	-	6.05	9.21	
cyOOC ₆ H ₁₀ OOH	-183.78	438.26	-190.32	449.34	-183.08	453.03	-185.08	453.48	-	-	-	-	-	2.84	6.14	
cyOOC ₆ H ₉ OOH	-335.83	408.48	-339.65	409.62	-	-	-353.12	377.49	-	-	-	-	-	7.42	14.88	
a-cyC ₆ H ₁₀ O	-128.14	283.15	-30.52	272.51	-118.09	312.7	-126.80	322.97	-126.65	322.70	-125.52 ^a	-	-76.36 ^c	329.73 ^c	34.72	21.57
b-cyC ₆ H ₁₀ O	-135.77	257.77	-37.80	261.93	-	-	-	-	-107.00	316.43	-	-	-	41.12	26.73	
c-cyC ₆ H ₁₀ O	-218.09	227.37	-121.6	253.44	177.44	312.71	-183.28	313.34	-183.08	313.08	-	-	-	31.09	36.53	
d-cyC ₆ H ₁₀ O	-239.27	331.32	-236.80	338.24	-	-	-230.52	322.10	-232.83	334.82	-231.10 ^a	335.53 ^a	225.68 ^d	334.52 ^d	4.41	5.18
cyC ₆ H ₉ -1,3	121.44	303.71	106.50	309.67	-	-	126.92	321.35	-	-	131.45 ^b	313.65 ^b	-	9.40	6.41	
cyC ₆ H ₉ -1,4	184.61	318.49	109.18	291.06	-	-	192.81	322.32	-	-	-	-	-	37.64	13.92	

ΔH_f^0 , S^0 are in kJ·mol⁻¹ and J·mol⁻¹·K⁻¹, respectively.

*: present work **: Mean Absolute Deviation a: NIST [10] b: Burcat [11] c: RMG, Group Additivity d: RMG, CHO

properties of these species should consider the ring strain energy for standard entropy and heat capacity values over the temperature range of $T = 300\text{--}3500$ K. Therefore, the required ring correction groups were evaluated and extended in this work. To validate the new estimation method, the predicted values for heat capacity, enthalpy of formation and entropy of selected validation species were compared with literature data. The validation species contain at least one of the newly determined Benson or ring-correction groups. The predictions were in accordance with other references, showing acceptable deviations in several thermochemical specifications. The estimation of thermodynamic properties of all main intermediates of cyclohexane low-temperature oxidation was performed applying the same algorithm for all species, with a commensurate accuracy, and using a straightforward methodology. The calculated properties have been presented in the NASA polynomial format.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in online version, at <https://doi.org/10.18321/ectj759>.

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