THE VALUES OF Δ fHo298.15 AND So298.15 OF THE RADICALS, FORMED BY THE ABSTRACTION OF H ATOM FROM THE p-BENZYLPHENOL AND DIMETHYL PHTHALATE

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Abstract

In the present work, the standard thermochemical properties of the most thermochemically stable radicals (p-Benzylenephenol and 1-Methyl-2-methylene phthalate), formed by abstraction of the hydrogen atom from the p-Benzylphenol and Dimethyl phthalate are determined using the results of B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p) and RO/CBS-4M calculations. The consistent values of the standard enthalpies of formation of these structures are determined using the corrected thermochemistry of the homodesmotic and atomization reactions. The values of the standard entropies of these compounds and the temperature dependencies of their thermochemical properties are also calculated in the present work. It is found that the H-transfer reaction of HO2 with p-Benzylenephenol is thermochemically favorable and can lead to the chain oxidation of p-Benzylenephenol at relatively low temperatures.

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Abstract. In the present work, the standard thermochemical properties of the most thermochemically stable radicals (p-Benzylenephenol and 1-Methyl-2-methylene phthalate), formed by abstraction of the hydrogen atom from the p-Benzylphenol and Dimethyl phthalate are determined using the results of B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p) and RO/CBS-4M calculations. The consistent values of the standard enthalpies of formation of these structures are determined using the corrected thermochemistry of the homodesmotic and atomization reactions.

The values of the standard entropies of these compounds and the temperature dependencies of their thermochemical properties are also calculated in the present work.

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Keywords: p-Benzylenephenol, 1-Methyl-2-methylene phthalate, Enthalpy, Entropy

1. INTRODUCTION

The bio-oil is the intermediate product, formed during the conversion of biomass to the end products such as chemicals or fuels. Development of the technology of conversion of the bio-oil to the end products requires the definition of the target compounds as well as the optimization of conditions for their production. At the present moment, the main products of non biochemical conversion of bio-oil are the synthesis gas and diesel fuel. However, the production of other chemical compounds from such chemical rich composition is not excluded.

The computer modeling of the chemical processes using the detailed physico-chemical mechanism is one of the possible approaches for the determination of the possible products, as well as for the optimization of the conditions for the conversion of the bio-oil. This modeling cannot be done without simplification of the composition of bio-oil, contained several hundreds different chemicals [1]. The main problem for that is the deficit of the reaction kinetics and thermochemical data, related to the mechanism and the energy of decomposition and oxidation of these compounds. As a result, the simplified composition (surrogate), for which this information is seems feasible, must be used instead [2-7].

Ones of the main components of such surrogate mixture, considered previously [8-10], are the phenol and benzene derivatives (2,4-dimethylphenol (2,4-xylenol), 2-methoxy-4-methylphenol, 3-methoxy-4-formylphenol (vanillin), p-Benzylphenol, Dimethyl phthalate), produced during the fast pyrolysis of the wood based biomass [1] capable to imitate the main physico-chemical properties of the products of pyrolytic decomposition of lignin. The structure and thermochemical properties of the first three of these components, as well as of the radicals, formed by abstraction of H atom from them, are measured [11-13] and calculated using the modern quantum mechanical approaches [13–15]. Thus, the structure and thermochemical properties of the radicals formed by the abstraction of H atom from the first three compounds are studied previously [16, 17]. The thermochemical properties of last two components (p-Benzylphenol and Dimethyl phthalate) are also measured [18-20] and calculated [21]. However, the thermochemical properties of the radicals, formed by abstraction of H atom from these two components, are still unknown.

The reactions of H atom transfer from substrate to the radicals are ones of the most important processes of decomposition and oxidation of organic compounds during their combustion. In many cases, the rates of these reactions depend on their thermochemistry. Therefore, the determination of thermochemical properties of radicals is important part of development of mechanism of the combustion of substrates. Thus, the knowledge of the thermochemical properties of radicals, involved in these reactions, can be used for the estimation of effect of these reactions on the whole process, as well as for determination of the temperature effect on it.

In the current study, the structures and thermochemical properties of the radicals, formed by abstraction of H atom from these two components (Dimethyl phthalate and p-Benzylphenol) of the considered surrogate bio-oil, are optimized and calculated using the B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p)) and RO/CBS-4M quantum mechanical (QM) approaches, as well as using the methodology, proposed in [17, 21].

2. METHODS AND APPROACHES

In the present work, the geometries of the considered radicals (Y) were optimized using the DFT (B3LYP/6-311++G(d,p) [22] and M06-2X6-311++G(d,p) [23]) and composites RO/CBS-4M [24, 25] QM approaches (corresponded, in the last case, to the HF/3-21G* (3-21G(d) level of theories)), while, in the last case, the CBS-4M potential energies of these structures, as well as their values of $H^{\circ}_{298.15}$, $S^{\circ}_{298.15}$ and $G^{\circ}_{298.15}$, were determined using the Møller-Plesset (MPn) correlation energy correction [26–29] (RO/CBS-4M), as well as the CBS extrapolation [30, 31]). The methods used in the present work for the calculations of these values were the same as those used in the previous work [21] for the determination of the thermochemical properties of p-Benzylphenol and Dimethyl phthalate. The more accurate methods (such as CBS-Q, CBS-QB3, Gn, CCSD) for the calculation of $H^{\circ}_{T}(X)$ values of the considered radicals were not used, due to the limitation of the available computational facilities. The calculations were done using the Gaussian program [32]. Posted on Authorea 23 Apr 2021 — The copyright holder is the author/funder. All rights reserved. No reuse without permission. — https://doi.org/10.22541/au.161916995.54945577/v1 — This a preprint and has not been peer reviewed. Data may be prelix

The values of $\Delta_{\rm f}H^{\circ}_{298.15}$ (Y, CALC/CORR)_{atom} and $\Delta_{\rm f}H^{\circ}_{298.15}$ (Y, CALC/CORR)_{REAC} of the radicals were determined, respectively, using the thermochemistry of atomization ($\Delta_{\rm r}H^{\circ}_{298.15}$ (Y)_{atom}) and homodesmotic ($\Delta_{\rm r}H^{\circ}_{298.15}$ (Y)_{REAC}) reactions. In the first case, the values of $H^{\circ}_{298.15}$, $S^{\circ}_{298.15}$ and $G^{\circ}_{298.15}$ of C_(g), H_(g), O_(g) and Y_(g), were used for the determination of $\Delta_{\rm r}H^{\circ}_{298.15}$ (Y, CALC)_{atom}. These values of $\Delta_{\rm r}H^{\circ}_{298.15}$ (Y, CALC)_{atom} were corrected to the values of $\Delta_{\rm r}H^{\circ}_{298.15}$ (Y, CORR)_{atom} using the linear dependencies (= A + B× $\Delta_{\rm r}H^{\circ}_{298.15}$ (Y, CALC)_{atom}), determined previously [17,21], between the tabulated values of $\Delta_{\rm r}H^{\circ}_{298.15}$ (X, TAB)_{atom} (where X = C_nH_mO_p (n, m, p)) and the calculated values of $\Delta_{\rm r}H^{\circ}_{298.15}$ (X, TAB), as well as their calculated values of $H^{\circ}_{298.15}$ (X, CALC), used for the determination of these dependencies, are reported in *SI*, *Note 1* (in bold, when several values is available) and in work [21]. Both the aromatic molecules and radicals were mainly used for the determination of the mentioned correction dependencies.

The corrected values of $\Delta_{\rm r} H^{\circ}{}_{298.15}$ (Y, CORR)_{atom} and the tabulated values of $\Delta_{\rm f} H^{\circ}{}_{298.15}(^3\text{C}, \text{TAB})$, $\Delta_{\rm f} H^{\circ}{}_{298.15}(^3\text{O}, \text{TAB})$ and $\Delta_{\rm f} H^{\circ}{}_{298.15}(\text{H}, \text{TAB})$ [33] (SI, Note 1) were used for the determination of the values of $\Delta_{\rm f} H^{\circ}{}_{298.15}(\text{Y}, \text{CORR})_{\text{atom}}$. The errors introduced by the calculated values of the $H^{\circ}{}_{298.15}$ of atoms were considered insignificant [21, 34, 35]. The effects of isotopes and isomers on the thermochemical values were not considered. Thus, in the last case, the effect of the less thermochemically favorable structures on the integral values of $\Delta_{\rm f} H^{\circ}{}_{298.15}(\text{Y})$ was considered not exceeding 2-3 kJ/mol [36]. This is due to the low contribution of the value of the $T \times \Delta_{\rm r} S^{\circ}{}_{298.15}$ of their isomerization reactions to the value of the equilibrium constant at T = 298.15 K and to the exponential dependence of the value of equilibrium constant upon corresponding value of $\Delta_{\rm r} H^{\circ}{}_{298.15}$.

The alternative values of $\Delta_{\rm f} H^{\circ}_{298.15}$ (Y, CALC)_{REAC} and $\Delta_{\rm f} H^{\circ}_{298.15}$ (Y, CORR)_{REAC} of the considered compounds were calculated using the B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p) and RO/CBS-4M thermochemistry of the homodesmotic reactions ($\Delta_{\rm r} H^{\circ}_{298.15}$ (Y, CALC)_{REAC}). The tabulated values of $\Delta_{\rm f} H^{\circ}_{298.15}$ (X, TAB) [33, 37] of the components of the homodesmotic reactions, used for these calculations, were compiled in [17, 21] (*SI*, *Note 1*). The values of $\Delta_{\rm r} H^{\circ}_{298.15}$ (Y, CORR)_{REAC} were determined by conversion of the calculated values of $\Delta_{\rm r} H^{\circ}_{298.15}$ (Y, CALC)_{REAC} using the correction dependencies, reported previously for the thermochemistry of 19 homodesmotic reactions [17, 21].

The accuracies of B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p) and RO/CBS-4M approaches, used for the calculation of the values of $\Delta_{\rm r} H^{\circ}{}_{298.15}({\rm Y, CALC})_{\rm atom}$ and $\Delta_{\rm r} H^{\circ}{}_{298.15}({\rm Y, CALC})_{\rm REAC}$ of considered aromatic radicals, were determined using the root mean squared error (RMSE), calculated previously [17, 21] on the basis of the tabulated and theoretical values of $\Delta_{\rm r} H^{\circ}{}_{298.15}({\rm X})$ defined, respectively, for the atomization and homodesmotic reactions. For each used quantum mechanical approach, the uncertainties of the corrected values of $\Delta_{\rm r} H^{\circ}{}_{298.15}({\rm Y, CORR})_{\rm atom}$ and $\Delta_{\rm f} H^{\circ}{}_{298.15}({\rm Y, CORR})_{\rm atom}$, as well as of $\Delta_{\rm r} H^{\circ}{}_{298.15}({\rm Y, CORR})_{\rm REAC}$ and $\Delta_{\rm f} H^{\circ}{}_{298.15}({\rm Y, CORR})_{\rm REAC}$, were accepted equal to three values of standard error (SE), reported for the correction dependencies of X.

The most consistent and accurate values of $\Delta_{\rm f}H^{\circ}{}_{298,15}(Y, \text{CORR})_{\text{atom}}$ and $\Delta_{\rm f}H^{\circ}{}_{298,15}(Y, \text{CORR})_{\text{REAC}}(Y, \text{CORR})_{\text{REAC}}(Y, \text{CORR})_{\text{REAC}}(Y, \text{CORR})_{\text{REAC}}(Y, \text{CORR})_{\text{REAC}}(Y, \text{CORR})_{\text{REAC}})$ were determined using the 99.7% confidence intervals of these values, calculated using the different QM approaches. In this case, the values of 3SE, corresponded to 99.7% confidence interval of considered correction dependencies, were used as the uncertainty for the corrected values of $\Delta_{\rm f}H^{\circ}{}_{298.15}(Y, \text{CORR})_{\text{atom}}$ or $\Delta_{\rm f}H^{\circ}{}_{298.15}(Y, \text{CORR})_{\text{REAC}}$. These uncertainties, calculated using the different QM approaches, were united for each Y. For this, the crossing area, which was common for the considered 99.7% confidence intervals of the values of $\Delta_{\rm f}H^{\circ}{}_{298.15}(Y, \text{CORR})_{\text{REAC}}$ (±3SE), calculated using all quantum mechanical approaches, was determined. The size of this area was considered as the 99.4-99.7% confidence interval (6SE) [21] for the values of $\Delta_{\rm f}H^{\circ}{}_{298.15}(Y, \text{CORR})_{\text{MEAN}}$ or $\Delta_{\rm f$

Since, the upper and the lower limits of this crossing area were defined only by the uncertainty ranges of one or two of all those values of $\Delta_{\rm f} H^{~o}_{298.15}({\rm Y, CORR})_{\rm atom}$ or $\Delta_{\rm f} H^{~o}_{298.15}({\rm Y, CORR})_{\rm REAC}$, calculated using the considered QM approaches for each Y, then the values of their uncertainties were corresponded to 99.4-99.7%

confidential interval and were similar or close to the value of 3SE.

The values of uncertainties of $\Delta_{\rm f} H \,^{\rm o}_{298.15}$ (Y, CORR)_{MEAN} and $\Delta_{\rm f} H \,^{\rm o}_{298.15}$ (Y, CORR)_{REACMEAN} were compared, and their most accurate values were recommended as the most reliable and were used in the present work for the determination of the temperature dependencies of $\Delta_{\rm f} H \,^{\rm o}_{\rm T}$ (Y, CORR).

Multireferences calculations, successfully applied for the determination of the bonds dissociation energies of the several components of bio-oil/diesel previously [38 - 40], were not considered in the present work. It was assumed that the underestimation of the contribution of static (electronic) correlation introduces the systematic error to the thermochemistry of the atomization and homodesmotic reactions. As a result, the contribution of the static correlation effect to uncertainty was minimized due to the considered correction dependencies.

The results of QM calculations were also used for the determination of the values of $S_{298.15}(Y, CALC) = (H_{298.15}(Y)-G_{298.15}(Y))/298.15$. The values $S_{298.15}(Y, CALC)$, calculated using the B3LYP and CBS-4M QM approaches, were corrected using the correction dependencies, reported in [17]. The correction dependence for the M062X/6-311++G(d,p) approach was determined in the present work for the list of compounds similar those, used previously for results of B3LYP and CBS-4M calculations. The using of the correction dependencies, in this case, was need for taking into account the contribution of the internal rotation part of entropy [36], not calculated in the present study, as well as to the determination the uncertainty of these calculations. The corrected values of $S_{298.15}(Y, CORR)$ were used as their recommended values. The values of 2SE, determined using the correction dependencies, were considered as the uncertainties for the values of $S_{298.15}(Y, CORR)$.

The accuracy of calculations of vibration frequencies for each of QM approaches was determined from the comparison of the measured [33] and calculated IR spectra, with and without scaling factors. The QM approach, predicted the most accurate values of vibration frequencies of these compounds, was used for determination of the values of $S^{\circ}_{298.15}$ (Y, CALC) and temperature dependencies of their thermochemical properties, using the ChemRate program [41]. In this case, the scaling factor, recommended by the NIST computational chemistry comparison and benchmark database [42], was used for the correction of the calculated vibration frequencies.

3. RESULTS AND DISCUSSION

3.1. Structures of Y radicals.

In the present work, the structures of radicals, formed by the abstraction of H atom from the Dimethyl phthalate (1C-12C) and p-Benzylphenol (1D-21D), are optimized using the RO/CBS-4M (at HF/3-21G* level of theory), M06-2X/6-311++G(d,p) and B3LYP/6-311++G(d,p) approaches. Their optimized structures and the main geometry parameters, determined using the CBS-4M calculations, are reported in Table 1. The most thermochemically favorable structures, optimized using the B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p) and ROCBS-4M approaches, are presented, respectively, in SI, Notes 2 (Table A and B) and \mathcal{G} .

Table 1. The structures (bond length (bl) in nm.) and values of $H^{\circ}_{0,H} \circ_{298.15}^{\circ}$ and $G^{\circ}_{298.15}$ (in Hartree) of CH₃OC(O)C₆H₄(O)COCH₂(1C-13C) and C₆H₅CHC₆H₄OH (1D-9D), optimized and determined using the CBS-4M approach.

| $1C H^{\circ}_{0}(1C) = -686.374556 H^{\circ}_{298.15}(1C) = -686.359911 G^{\circ}_{298.15}(1C) = -686.416399$ | $2C H^{o}_{0}(2C) = -686.374329 H^{o}_{0}(2C)$ |
|--------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------|
| $4C H^{\circ}_{0}(4C) = -686.372791 H^{\circ}_{298.15}(4C) = -686.358159 G^{\circ}_{298.15}(4C) = -686.414614$ | 5C $H^{\circ}_{0}(5C) = -686.352124 H^{\circ}_{0}(5C)$ |
| 7C $H^{\circ}_{0}(7C) = -686.351228 H^{\circ}_{298.15}(7C) = -686.336482 G^{\circ}_{298.15}(7C) = -686.393725$ | $8C H^{o}_{0}(8C) = -686.351394 H^{o}_{0}(8C)$ |
| $10C H^{\circ}_{0}(10C) = -686.350641 H^{\circ}_{298.15}(10C) = -686.335886 G^{\circ}_{298.15}(10C) = -686.393155$ | $11C H^{\circ}_{0}(11C) = -686.349287$ |
| 1D $H^{\circ}_{0}(1D) = -576.275792 H^{\circ}_{298.15}(1D) = -576.263125 G^{\circ}_{298.15}(1D) = -576.314688$ | $2D H^{o}_{0}(2D) = -576.275511 H^{o}_{10}(2D)$ |
| 4D $H^{\circ}_{0}(4D) = -576.224107 H^{\circ}_{298.15}(4D) = -576.211552 G^{\circ}_{298.15}(4D) = -576.264506$ | $5D H_0^0(5D) = -576.222070 H^0$ |
| 7D $H^{\circ}_{0}(7D) = -576.220702 \ H^{\circ}_{298.15}(7D) = -576.207909 \ G^{\circ}_{298.15}(7D) = -576.261547$ | $8D H^{o}_{0}(8D) = -576.219901 H^{o}_{1}$ |

| $1C H^{o}_{0}(1C) = -686.374556 H^{o}_{298.15}(1C) = -686.359911 G^{o}_{298.15}(1C) = -686.416399$ | $2C H^{o}_{0}(2C) = -686.374329 H^{o}_{2}$ |
|--------------------------------------------------------------------------------------------------------------------|--------------------------------------------|
| $10D H^{\circ}_{0}(10D) = -576.219762 H^{\circ}_{298.15}(10D) = -576.207000 G^{\circ}_{298.15}(10D) = -576.260425$ | 11D $H^{\circ}_{0}(11D) = -576.219758 H$ |
| 13D $H^{\circ}_{0}(13D) = -576.219436 H^{\circ}_{298.15}(13D) = -576.206645 G^{\circ}_{298.15}(13D) = -576.260350$ | 14D $H^{\circ}_{0}(14D) = -576.219423 H$ |
| 16D $H^{\circ}_{0}(16D) = -576.218815 H^{\circ}_{298.15}(16D) = -576.205991 G^{\circ}_{298.15}(16D) = -576.259871$ | $17D H^{\circ}_{0}(17D) = -576.218743 H$ |
| 19D $H^{\circ}_{0}(19D) = -576.217549 H^{\circ}_{298.15}(19D) = -576.204725 G^{\circ}_{298.15}(19D) = -576.258328$ | $20D H^{o}_{0}(20D) = -576.216116 H$ |
| 1K $H^{\circ}_{0}(1K) = -686.384766 \ H^{\circ}_{298.15}(1K) = -686.370480 \ G^{\circ}_{298.15}(1K) = -686.426044$ | $2K H^{o}_{0}(2K) = -686.384698 H^{o}$ |
| 2L $H^{\circ}_{0}(2L) = -576.275867 H^{\circ}_{298.15}(2L) = -576.263210 G^{\circ}_{298.15}(2L) = -576.314715$ | $3L H^{o}_{0}(3L) = -576.275711 H^{o}_{2}$ |

As can be seen, the significant difference between the geometries of the considered radicals, optimized using the restricted and unrestricted open shell wavefunctions, is not observed for the products of H atom abstraction from both the Dimethyl phthalate and p-Benzylenephenol. Thus, the integral differences between the bond lengths (*bl*) of structures, optimized using the CBS-4M and ROCBS-4M, vary from zero (for the structure 2C, 1D, 2D and 3D) to 0.1 (for the structure 4C) Å. At the same time, the discrepancy between the values of $H^{\circ}_{298.15}$, determined using these two approaches for the most thermochemically favorable structures (1C-4C, 1D-3D), is not observed only in the case of the structures 2C, 1D-3D. In all other cases, the values of $H^{\circ}_{298.15}$, calculated using the open shell configuration, are nearly 0.004 Hartree ([?] 10 kJ/mol) lower those, determined using the ROCBS-4M approach (*SI*, *Note 3*).

This discrepancy could be attributed to the small difference between the optimized geometries of these structures, which could be attributed to the spin contamination of wavefunctions [43], observed in the case of the CBS-4M calculations of the structures 1C, 3C, 4C. From this point of view, the ROCBS-4M structures 1C, 3C, 4C could be considered as the most reliable, while, the structure 2C as the less important or thermochemically unstable, compared to its conformers. The last statement partially agree with the results of B3LYP/6-311++G(d,p) calculations, for which the spin contamination of wavefunctions is not observed. Thus, the formation of the structure 2C, similar those determined using the CBS-4M approach (Table 1 and *SI*, *Note* 3), is not predicted by the B3LYP/6-311++G(d,p) (*SI*, *Note* 2, Table A), as well as by the UHF/6-311++G(d,p) (*SI*, *Note* 4) and B3LYP/aug-cc-pVDT (not presented) calculations.

However, the optimization of this structure using the same functional and basis sets (B3LYP/CBSB7 (*SI*, *Note 5*), B3LYP/6-31G(d,p), B3LYP/6-311G(d,p) and B3LYP/cc-pVDT), but excluding diffuse function, on the contrary, predicts the formation of structure 2C similar those, reported in Table 1 and *SI*, *Note 3*. Since, the resulting wavefunctions, determined in these calculations, are not spin contaminated, then the mentioned discrepancy between the existence of 2C structure, predicted using the B3LYP and UHF approaches, is rather must be attributed to the using of the diffuse functions, and not to the spin contamination, as it is assumed initially. As a result, it can be concluded, that the difference between the results of CBS-4M and ROCBS-4M approaches, in context of the structure 2C, is not related to the diffuse functions. Moreover, the values of RMSE, determined for the X compounds using the CBS-4M (RMSE = 31.4 kJ/mol [21]) and ROCBS-4M (RMSE = 47.1 kJ/mol [21]) approaches demonstrate that the accuracy of determination of $\Delta_r H^{\circ}_{298.15}(X)$ is higher in the first case, despite of the spin contamination of wavefunctions.

The mentioned effect of diffuse function on the optimized geometry of studied radical is also depending on the used QM approach. Thus, the formation of structure 2C, similar those reported in Table 1 and SI, Note 3, is supported by the results of M06-2X/6-311++G(d,p) (SI, Note 2, Table B), M06-2X/6-31G(d,p) and B3LYP/6-31G(d,p) calculations, which, are more accurate (their values of RMSE_{atomi} are, respectively, 48 [21], 25.7 and 19.5 kJ/mol [44]) than those (= 90 kJ/mol [21]), determined using the B3LYP/6-311++G(d,p) approach, as well as by the results of MP2(full)/6-311++G(d,p) and B3LYP-GD3/6-311++G(d,p) calculations, included, in the last case, the empirical D3 version of Grimme's dispersion. As a result, the observed discrepancy, most probably, must be attributed to the accuracy of the used QM approaches, particularly, for the calculations of the long distance interactions between the atoms. From this point of view, the structures 2C, optimized using the M06-2X/6-311++G(d,p), MP2/6-311++G(d,p) and B3LYP-GD3/6-311++G(d,p) approaches, are look like more reliable, than those, determined by the B3LYP/6-311++G(d,p) calculations.

The concluded higher accuracy of M06-2X/6-311++G(d,p) for the geometry optimization of considered radicals, is also indicating that the CBS-4M geometry of structures 1C, 3C and 4C must be slightly more reliable in comparison with the results of ROCBS-4M calculations. Thus, the geometries of the radicals, optimized using the M06-2X/6-311++G(d,p) approach, are slightly closer those, determined using the CBS-4M calculations, than using the ROCBS-4M. This is also in agreement with the values of RMSE, reported previously for the CBS-4M and ROCBS-4M approaches [21]. The last observation is indicating that the negative effect of spin contamination of wavefunction on the accuracy of calculation of potential energy and determination of geometry of the considered radicals is less significant than the effect on them of the restrictions, used in the ROSBS-4M approach.

On the contrast to the radicals formed from Dimethyl phthalate, the optimized structures of the radicals formed by the abstraction of H atom from p-Benzylphenol are consistent for all considered QM approaches. Thus, the integral difference between the values of bl of these structures, optimized using the considered QM approaches, is below 0.13 Å and is mainly due to the length of C-H bonds. Moreover, this difference can even be 2-3 times smaller, because the used values of the bond lengths are rounded with the accuracy of 0.01 Å.

As can be seen, in the case of Dimethyl phthalate, the most thermochemically favorable pathway of H atom abstraction is due to the dissociation of C-H bond of the ending methyl groups (structures 1C, 3C and 4C). This conclusion is correct for the results, determined using all the considered QM approaches. The same conclusions are also applicable for the radicals formed by the abstraction of H atom from the p-Benzylenephenol. Thus, the dissociation of C-H bond of the methylene group (structures 1D, 2D) is also the most thermochemically favorable pathway for the considered reactions. This route of H atom abstraction is even more thermochemically favorable than the formation of phenoxy radical (structure 3D), concluded previously as the best for the products of H atom abstraction from the different substituted phenols [17] with the single aromatic ring. The difference between the results of this and previous work is due to the conjugation of the unpaired electron, localized at CH group, with π electrons of two aromatic rings of the p-Benzylenephenol, instead of the single ring of the substituted phenols, considered in [17].

This explanation is supported by the almost planar structures of these radicals (1D, 2D), in contrast with the nearly orthogonal position of aromatic rings in the structure 3D (Table 1). The detailed description of these structures is presented in SI, Note 6.

The thermochemical properties of radicals, produced by abstraction of H atom from meta and para isomers of Dimethyl phthalate, as well as from ortho and meta isomers of p-Benzylphenol, are out of scope of this work. However, the values of $H^{\circ}_{298.15}$ for the several structures, expected to be the most thermochemically favorable (due to the higher thermochemical stability of these isomers [21]), are also determined. In this case, the structures of the possible conformers of the considered radicals and their values of potential energy are determined using the CBS-4M calculations. The structures of the most thermochemically stable of these conformers (1K, 2K, 1L – 4L) are presented in Table 1. The values of $\Delta_{\rm f} H^{\circ}_{298.15}(Y)_{\rm atom}$ of these radicals are also calculated in the present work using the thermochemistry of atomization reactions.

3.2. Thermochemical properties of the radicals

3.2.1. Standard entralmies of formation of the radicals $(\Delta_{\varphi}H^{o}_{298.15}(\Psi))_{atom}$

The values of $H^{\circ}_{298.15}(Y)$ of the structures of radicals, considered in the present work (Table 1), as well as their calculated values of the standard enthalpies of atomization ($\Delta_r H^{\circ}_{298.15}(Y, CALC)_{atom}$), have used for the determination of $\Delta_f H^{\circ}_{298.15}(Y, CALC)_{atom}$. The value of $\Delta_r H^{\circ}_{298.15}(Y, CALC)_{atom}$, calculated using the different QM approaches, are presented in Table 2.

Table 2. The values of $-\Delta_r H^{o}_{298.15}(Y, CALC)_{atom}$ and $-\Delta_r H^{o}_{298.15}(Y, CORR)_{atom}$ of atomization reactions, determined using the different QM approaches and corresponded them correction dependencies.

$$\frac{Y}{B3LYP} = \frac{-\Delta_{r}H^{o}_{298.15}(Y, CALC)_{atom}, kJ/mol}{M06-2X} = \frac{-\Delta_{r}H^{o}_{298.15}(Y, CALC)_{atom}, kJ/mol}{CBS-4M}$$

F

| Y | $-\Delta_{\rm r} H^{\rm o}_{298.15}({\rm Y,\ CALC})_{\rm atom},{\rm kJ/mol}$ | $-\Delta_{\rm r} H^{\rm o}_{298.15}({\rm Y, \ CALC})_{\rm atom}, {\rm kJ/mol}$ | $-\Delta_{\rm r} H^{\rm o}{}_{298.15} ({\rm Y, \ CALC})_{\rm atom}, \rm kJ/mol$ | |
|---------------|------------------------------------------------------------------------------|---------------------------------------------------------------------------------|----------------------------------------------------------------------------------|---|
| 1C | -10350.2 | -10461.5 | -10566.6 | - |
| 2C | -10350.1 | -10453.4 | -10566.6 | - |
| 3C | -10350.1 | -10458.6 | -10562.8 | - |
| $4\mathrm{C}$ | -10348.7 | -10457.1 | -10562 | - |
| $5\mathrm{C}$ | -10286.8 | -10405.0 | -10507.6 | - |
| 6C | -10287.1 | -10401.7 | -10505.9 | - |
| 7C | -10283.2 | -10399.4 | -10505.1 | - |
| 8C | -10287.6 | -10404.1 | -10505.6 | - |
| 9C | -10287.4 | -10403.9 | -10505.1 | |
| 10C | -10284.4 | -10398.9 | -10503.6 | - |
| 11C | -10284.4 | -10396.5 | -10500.2 | - |
| 12C | -10287.6 | -10399.4 | -10499.9 | - |
| 1D | -11658.7 | -11756.0 | -11922.4 | - |
| 2D | -11658.7 | -11755.8 | -11921.6 | - |
| 3D | -11646.3 | -11740.7 | -11902.6 | - |
| 4D | -11525.2 | -11639.9 | -11787 | - |
| 5D | -11522.8 | -11637.9 | -11781.6 | - |
| 6D | -11525.4 | -11639.1 | -11777.7 | - |
| 7D | -11525.7 | -11639.4 | -11777.4 | - |
| 8D | -11523.3 | -11636.5 | -11775.3 | - |
| 9D | -11522.7 | -11635.9 | -11775.1 | - |
| 10D | -11525.0 | -11639.6 | -11775 | - |
| 11D | -11524.9 | -11639.5 | -11775 | - |
| 12D | -11525.2 | -11639.8 | -11774.5 | - |
| 13D | -11525.7 | -11639.3 | -11774.1 | - |
| 14D | -11525.4 | -11639.5 | -11774 | - |
| 15D | -11525.7 | -11638.0 | -11772.8 | - |
| 16D | -11524.5 | -11637.8 | -11772.4 | - |
| 17D | -11525.4 | -11638.1 | -11772.3 | - |
| 18D | -11522.8 | -11637.9 | -11769.7 | - |
| 19D | -11515.7 | -11629.4 | -11769 | - |
| 20D | -11515.4 | -11629.2 | -11765.3 | - |
| 21D | -11524.5 | -11638.0 | -11741.9 | - |
| 1K | -10380.5 | -10484.2 | -10594.4 | - |
| 2K | -10379.3 | -10485.4 | -10592.2 | - |
| 1L | -11658.3 | -11755.9 | -11922.6 | - |
| 2L | -11657.7 | -11755.1 | -11922.6 | - |
| 3L | -11657.6 | -11757.5 | -11922.4 | - |
| 4L | -11654.3 | -11758.5 | -11919.8 | - |
| | | | | |

The values of $\Delta_r H^{\circ}_{298.15}(Y)$, CALC)_{atom}, presented in Table 2, are determined using the values of $H^{\circ}_{298.15}(Y)$, $H^{\circ}_{298.15}(C)$, $H^{\circ}_{298.15}(O)$ and $H^{\circ}_{298.15}(H)$, calculated in this and in the previous works [17, 21]. Their CBS-4M values of $H^{\circ}_{298.15}(Y)$ are reported in Table 1. The M06-2X and B3LYP values of $H^{\circ}_{298.15}(Y)$ for the most thermochemically stable structures are presented, respectively, in *SI*, *Note* 2 and 3. The M06-2X and B3LYP values of $H^{\circ}_{298.15}(C)$, $H^{\circ}_{298.15}(O)$ and $H^{\circ}_{298.15}(H)$ are demonstrated in *SI*, *Note* 1. Their RO/CBS-4M values can be found in [17].

As can be seen, the values of $\Delta_{\rm r} H^{\rm o}_{298.15}$ (Y, CALC)_{atom}, calculated in the present work using the different QM approaches, are not consistent. Thus, for the most thermochemically stable radicals (structures 1C,

3C, 4C, 1D-3D), the highest differences between their values of $\Delta_r H^{o}_{298.15}$ (Y, CALC)_{atom}, observed in the cases of using the CBS-4M and B3LYP/6-311++G(d,p) approaches, reaches 200 kJ/mol.

Such high differences are mainly due to the values of $\Delta_{\rm r} H^{\circ}_{298.15}$ (X, CALC)_{atom}, calculated using the QM approaches at the low level of theory, assuming the high contribution of the systematic errors to the results of calculations [45-48]. Thus, the more accurate CBS-4M, ROCBS-4M and M06-2X approaches lead, respectively, to the significantly smaller values of RMSE_{atomi} = 31.3, 47.0 and 47.8 kJ/mol [17, 21].

The correction of these values of $\Delta_r H^{\circ}_{298.15}$ (Y, CALC)_{atom} according to the dependencies (*SI*, *Note* 7), reported previously [17, 21], decreases significantly the mentioned differences between the values of $\Delta_r H^{\circ}_{298.15}$ (Y, CORR)_{atom} (Table 2), determined using the different QM approaches. Thus, the differences between the corrected CBS-4M and ROCBS-4M or M06-2X values of $\Delta_r H^{\circ}_{298.15}$ (Y, CORR)_{atom} do not exceed, respectively, 25 and 32 kJ/mol. The even smaller difference, below 16 kJ/mol, is observed between those values, calculated using the CBS-4M and B3LYP/6-311++G(d,p) approaches. These values of differences are consistent with the values of SE_{atomi} = 8.4 (CBS-4M), 9.4 (ROCBS-4M), 11.8 (B3LYP) and 3.8 (M06-2X) kJ/mol, determined using their correction dependencies previously (*SI*, *Note* 7) [17, 21].

Table 3. The values of $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y, CORR})_{\rm atom}$, determined using the different QM approaches, as well as their mean values of $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y, CORR})_{\rm MEAN}$, determined using the upper and lower limits of the common area of the uncertainty ranges of the values of $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y, CORR})_{\rm MEAN}$. (The errors correspond to the values of 3SE, determined for the correction dependencies [17, 21] (SI, Note 7)).

| Y | $\begin{array}{c} \Delta_{\rm f} H^{\rm o}{}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm atom},\\ {\rm kJ/mol} \end{array}$ | $\begin{array}{c} \Delta_{\rm f} {H^{\rm o}}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm atom},\\ {\rm kJ/mol} \end{array}$ | $\begin{array}{c} \Delta_{\rm f} H^{\rm o}{}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm atom},\\ {\rm kJ/mol} \end{array}$ | $\begin{array}{c} \Delta_{\rm f} {H^{\rm o}}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm atom},\\ {\rm kJ/mol} \end{array}$ | $\begin{array}{c} \Delta_{\rm f} {H^{\rm o}}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm atom},\\ {\rm kJ/mol} \end{array}$ | $\begin{array}{c} \Delta_{\rm f} {H^{\rm o}}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm atom},\\ {\rm kJ/mol} \end{array}$ | $\frac{\Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y}}{\rm CORR})_{\rm MEAN}}{\rm kJ/mol}$ |
|---------------|----------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| | B3LYP | M06-2X | CBS-4M | ROCBS-4M | Lower | Upper | |
| | (± 33.6) | (± 11.4) | (± 25.2) | (± 27.6) | | | |
| 1C | -395.3 | -414.2 | -384.1 | -400.6 | -409.3 | -402.8 | -406.1 ± 3 |
| $2\mathrm{C}$ | -395.2 | -406.1 | -384.1 | -388.7 | -409.3 | -394.7 | -402 ± 7 |
| $3\mathrm{C}$ | -395.2 | -411.3 | -380.2 | -397.0 | -405.4 | -399.9 | -402.6 ± 3 |
| $4\mathrm{C}$ | -393.8 | -409.8 | -379.6 | -395.8 | -404.8 | -398.4 | -401.6 ± 3 |
| $5\mathrm{C}$ | -330.7 | -357.4 | -325.5 | -351.2 | -350.7 | -346.0 | -348.4 ± 3 |
| $6\mathrm{C}$ | -331.0 | -354.1 | -323.8 | -345.1 | -349.0 | -342.7 | $\textbf{-345.9}{\pm3}$ |
| $7\mathrm{C}$ | -327.0 | -351.7 | -323.0 | -345.1 | -348.2 | -340.3 | -344.2 ± 4 |
| $8\mathrm{C}$ | -331.5 | -356.4 | -323.5 | -348.2 | -348.7 | -345.2 | -346.9 ± 2 |
| $9\mathrm{C}$ | -331.3 | -356.3 | -322.9 | -347.6 | -348.1 | -344.9 | -346.5 ± 2 |
| 10C | -328.3 | -351.2 | -321.5 | -342.8 | -346.7 | -339.8 | -343.2 ± 3 |
| 11C | -328.3 | -348.9 | -318.1 | -338.3 | -343.3 | -337.5 | -340.4 ± 3 |
| 12C | -331.5 | -351.8 | -317.8 | -341.6 | -343.0 | -340.4 | -341.7 ± 1 |
| 1D | 110.6 | 121.0 | 107.1 | 91.1 | 109.6 | 118.7 | 114.2 ± 5 |
| 2D | 110.7 | 121.3 | 107.8 | 91.2 | 109.9 | 118.8 | 114.4 ± 4 |
| 3D | 123.3 | 136.5 | 126.8 | 142.4 | 125.1 | 149.9 | $136.5 {\pm} 11$ |
| 4D | 246.6 | 237.9 | 241.7 | 223.1 | 226.5 | 249.3 | $237.9{\pm}11$ |
| $5\mathrm{D}$ | 249.1 | 239.9 | 247.0 | 225.5 | 228.5 | 251.3 | $239.9{\pm}11$ |
| 6D | 246.4 | 238.7 | 250.9 | 225.0 | 227.3 | 250.1 | 238.7 ± 11 |
| $7\mathrm{D}$ | 246.2 | 238.4 | 251.2 | 219.4 | 227.0 | 247.0 | $237.0{\pm}10$ |
| 8D | 248.6 | 241.3 | 253.2 | 224.9 | 229.9 | 252.5 | $241.3{\pm}11$ |
| 9D | 249.1 | 241.9 | 253.5 | 226.1 | 230.5 | 252.7 | $241.6{\pm}11$ |
| 10D | 246.8 | 238.2 | 253.5 | 222.9 | 226.8 | 249.6 | $238.2{\pm}11$ |
| 11D | 246.9 | 238.3 | 253.5 | 218.6 | 226.9 | 246.2 | $236.7 {\pm} 10$ |
| 12D | 246.6 | 238.0 | 254.0 | 222.6 | 226.6 | 249.4 | $238.0{\pm}11$ |
| 13D | 246.1 | 238.5 | 254.5 | 223.7 | 227.1 | 249.9 | $238.5{\pm}11$ |
| 14D | 246.4 | 238.3 | 254.6 | 224.7 | 226.9 | 249.7 | $238.3{\pm}11$ |

| Y | $\Delta_{\rm f} H^{\rm o}{}_{298.15}({\rm Y}, {\rm CORR})_{\rm atom}, {\rm kJ/mol}$ | $\begin{array}{l} \Delta_{\rm f} H^{\rm o}{}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm atom},\\ \rm kJ/mol \end{array}$ | $\begin{array}{l} \Delta_{\rm f} H^{\rm o}{}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm atom},\\ \rm kJ/mol \end{array}$ | $\begin{array}{l} \Delta_{\rm f} H^{\rm o}{}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm atom},\\ \rm kJ/mol \end{array}$ | $\begin{array}{l} \Delta_{\rm f} H^{\rm o}{}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm atom},\\ \rm kJ/mol \end{array}$ | $\begin{array}{l} \Delta_{\rm f} H^{\rm o}{}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm atom},\\ \rm kJ/mol \end{array}$ | $\begin{array}{l} \Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y}\\ {\rm CORR})_{\rm MEAN}\\ \rm kJ/mol \end{array}$ |
|-----|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|
| 15D | 246.1 | 239.8 | 255.7 | 225.7 | 228.4 | 252.2 | 239.8 ± 11 |
| 16D | 247.3 | 240.0 | 256.2 | 226.4 | 228.6 | 251.4 | $240.0{\pm}11$ |
| 17D | 246.4 | 239.7 | 256.3 | 220.9 | 228.3 | 248.5 | $238.4{\pm}10$ |
| 18D | 249.0 | 239.9 | 258.8 | 225.1 | 228.5 | 251.3 | $239.9{\pm}11$ |
| 19D | 256.3 | 248.4 | 259.5 | 232.8 | 237.0 | 259.8 | $248.4{\pm}11$ |
| 20D | 256.6 | 248.7 | 263.2 | 232.2 | 238 | 259.8 | $248.9 {\pm} 11$ |
| 21D | 247.4 | 239.8 | 286.4 | 226.2 | 228.4 | 251.2 | $239.8{\pm}11$ |
| 1K | -426.5 | -437.4 | -412.3 | -416.9 | -437.5 | -426.0 | -433.8 ± 6 |
| 2K | -425.2 | -438.6 | -412.1 | -416.9 | -437.3 | -427.2 | -433.3 ± 5 |
| 1L | 110.7 | 120.8 | 106.2 | 89.2 | 109.4 | 116.8 | 113.1 ± 4 |
| 2L | 111.3 | 121.6 | 106.2 | 90.1 | 110.2 | 117.7 | 113.9 ± 4 |
| 3L | 111.4 | 119.2 | 106.4 | 91.4 | 107.8 | 119.0 | 113.4 ± 6 |
| 4L | 114.8 | 118.2 | 109.0 | 93.6 | 106.8 | 121.2 | 114.0±7 |

The corrected values of $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y, CORR})_{\rm atom}$, determined using the values of $\Delta_{\rm r} H^{\rm o}_{298.15}({\rm Y, CORR})_{\rm atom}$, calculated in the present work, and the tabulated values of $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm C, TAB})$, $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm O, TAB})$ and $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm H, TAB})$ (SI, Note 1 [33]), are presented in Table 3. The reported uncertainties correspond to the values of 3SE_{atomi} (99.7% confidence interval).

These uncertainties intervals of the values of $\Delta_{\rm f} H \,^{\circ}_{298.15}(Y, \text{CORR})_{\text{atom}}$ are used for the determination of the values of $\Delta_{\rm f} H \,^{\circ}_{298.15}(Y, \text{CORR})_{\text{MEAN}}$, according to the procedure, described in [17, 21]. Thus, the uncertainty ranges of the values of $\Delta_{\rm f} H \,^{\circ}_{298.15}(Y, \text{CORR})_{\text{atom}}$, determined using the different QM approaches for the same structures (Y), are compared one with other. As a result, the lower and upper limit of the values of $\Delta_{\rm f} H \,^{\circ}_{298.15}(Y, \text{CORR})_{\text{atom}}$ for the particular structure are determined as the limits of the crossing area (Table 3) of all 99.7% confidence intervals. By other word, it is assumed that the target value belong simultaneously to 3SE intervals of all values, determined using the considered QM approaches. This procedure is applied for the each of the considered radicals (Y). The mean values ($\Delta_{\rm f} H \,^{\circ}_{298.15}(Y,$ CORR)_{MEAN}) of these limits are considered as the most accurate estimate of that values (Table 3), while, the half of the corresponding range as their uncertainty.

Since, the upper and lower limits of the crossing area for each considered structure Y is defined by the intervals of only one or two of the corrected values of $\Delta_{\rm f}H^{~0}_{298.15}(Y, {\rm CORR})_{\rm atom}$ then the probability of these events, corresponded to the result of the multiplications of the individual probabilities (0.997, 3SE), is equal to 99.7 % (= 100%*0.997¹) or 99.4 % (= 100%*0.997²), i.e. [?] 3SE. In this context, the M06-2X approach must be considered as the most accurate among those considered in the present study. Thus, all intervals for the values of $\Delta_{\rm f}H^{~0}_{298.15}(Y, {\rm CORR})_{\rm MEAN}$, reported in Table 3, correspond to one or both values of limits (upper and/or lower), determined for the M06-2X values of $\Delta_{\rm f}H^{~0}_{298.15}(Y, {\rm CORR})$.

This conclusion agrees with dependencies (Figures 1 and 2), observed between the values of $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y}, {\rm CORR})_{\rm MEAN}$ and corresponded them values of $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y}, {\rm CORR})_{\rm atom}$, determined using the different QM approaches for the products of H atom abstraction, respectively, from Dimethyl phthalate and p-Benzylphenol.

Figure 1. The dependencies between the values of $\Delta_{\rm f}H^{\circ}_{298.15}(Y, {\rm CORR})_{\rm MEAN}$ and corresponding them values of $\Delta_{\rm f}H^{\circ}_{298.15}(Y, {\rm CORR})_{\rm atom}$, determined using the B3LYP (closed squares, solid line, = 49+1.1× $\Delta_{\rm f}H^{\circ}_{298.15}(Y, {\rm CORR})_{\rm MEAN}$), M06-2X (open squares, dot-dashed line, = -19+0.972× $\Delta_{\rm f}H^{\circ}_{298.15}(Y, {\rm CORR})_{\rm MEAN}$), CBS-4M (open circles, dashed line, = $30.1+1.02\times\Delta_{\rm f}H^{\circ}_{298.15}(Y, {\rm CORR})_{\rm MEAN}$) and ROCBS-4M (closed circles, dotted line, = $-46.5+0.867\times\Delta_{\rm f}H^{\circ}_{298.15}(Y, {\rm CORR})_{\rm MEAN}$) approaches for the products of abstraction of H atom from Dimethyl phthalate. Figure 2. The dependencies between the values of $\Delta_{\rm f}H^{\circ}_{298.15}(Y, \text{CORR})_{\rm MEAN}$ and corresponding them values of $\Delta_{\rm f}H^{\circ}_{298.15}(Y, \text{CORR})_{\rm atom}$, determined using the B3LYP (closed squares, solid line, = -19.5+1.11× $\Delta_{\rm f}H^{\circ}_{298.15}(Y, \text{CORR})_{\rm MEAN}$), M06-2X (open squares, dot-dashed line, = -10.8+0.953× $\Delta_{\rm f}H^{\circ}_{298.15}(Y, \text{CORR})_{\rm MEAN}$), CBS-4M (open circles, dashed line, = -29.7+1.18× $\Delta_{\rm f}H^{\circ}_{298.15}(Y, \text{CORR})_{\rm MEAN}$) and ROCBS-4M (closed circles, dotted line, = -14.1+0.997× $\Delta_{\rm f}H^{\circ}_{298.15}(Y, \text{CORR})_{\rm MEAN}$) approaches for the products of abstraction of H atom from p-Benzylphenol.

As can be seen the most consistent dependencies are also observed in the case of using the M06-2X approach. Thus, both dependencies, determined using this approach, have the closest values of intercepts and slopes. Moreover, their absolute values of intercepts are closest to zero.

At the same time, in the case of Dimethyl phthalate, the value of slope, closest to the unity, is observed for the CBS-4M dependence, while, in the case of p-Benzylphenol, for the ROCBS-4M dependence. However, the differences between those values and the values, determined using the M06-2X approach, are insignificant, compared to consistency between the dependencies, determined in the last case for Dimethyl phthalate and p-Benzylphenol.

3.2.2. The homodesplotic reactions and the adves of $\Delta_{\varphi}H^{\circ}_{298.15}(\Psi)_{PEA^{\circ}}$.

Alternatively, the same compounds (SI, Note 1) are used for the determination of the correction dependencies [17, 21] and for the calculation of the values of $\Delta_r H \,^{o}_{298.15}$ (Y, CALC)_{REAC} of homodesmotic reactions (Table 4).

The homodesmotic reactions, used for the determination of their tabulated values of $\Delta_r H$ °_{298.15}(R_i,TAB)_{REAC}, as well as their values of $\Delta_r H$ °_{298.15}(R_i,CALC)_{REAC}, calculated using different QM approaches, are reported in [17, 21]. The accuracy of these calculations, corresponded to RMSE_{REAC}, is determined previously [17, 21], using the homodesmotic reactions, for which, the thermochemical properties of all components are known (*SI*, *Note* 7, *Table B*).

The same reactions have also used in [17, 21] for the determination of their correction dependencies (*SI*, *Note* 7, *Table B*). The values of $\Delta_{\rm r} H^{\rm o}_{298.15}$ (Y, CORR)_{REAC}, determined using these correction dependencies, are also presented in Table 4.

Table 4. The homodesmotic reactions and their values of $\Delta_{\rm r} H^{\rm o}_{298.15}$ (Y, CALC)_{REAC}/ $\Delta_{\rm r} H^{\rm o}_{298.15}$ (Y, CORR)_{REAC}, determined for the most thermochemically favorable isomers of Y (= 1C (*i* = 1, 2), 1D (*i* = 3-5), 3D (*i* = 6, 7), 4D (*i* = 8) and 6C (*i* = 9)) using the different QM approaches.

| i | Reaction, $(\mathbf{R}_{\mathbf{x}})_i$ | $\Delta_{\rm r} H^{\rm o}_{298.15}({\rm Y, CALC})_{\rm REA}$ |
|---|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|
| | | B3LYP |
| 1 | $C_6H_4(C(O)OCH_3)_2 + HC(O)OCH_2 = C_6H_4(C(O)OCH_3)C(O)OCH_2 + HC(O)OCH_3$ | -3.2/-5.4 |
| 2 | $C_6H_4(C(O)OCH_3)_2 + CH_3C(O)OCH_2 = C_6H_4(C(O)OCH_3)C(O)OCH_2 + CH_3C(O)OCH_3$ | -1.5/-3.9 |
| 3 | $CH_2(C_6H_5)_2 + C_6H_5OH + C_6H_5CH_2 = C_6H_5CHC_6H_4OH + C_6H_6 + C_6H_5CH_3$ | -33.6/-32.3 |
| 4 | $CH_2(C_6H_5)_2 + C_6H_5OH + CH_2CCH = C_6H_5CHC_6H_4OH + C_6H_6 + CH_3CCH$ | -35.9/-34.3 |
| 5 | $CH_2(C_6H_5)_2 + C_6H_5OH + CH_2CHCH_2 = C_6H_5CHC_6H_4OH + C_6H_6 + CH_3CHCH_2$ | -22.6/-17.5 |
| 6 | $CH_2(C_6H_5)_2 + C_6H_5O = C_6H_5CH_2C_6H_4O + C_6H_6$ | -5.8/-7.7 |
| 7 | $\mathrm{CH}_2(\mathrm{C}_6\mathrm{H}_5)_2 + \mathrm{CH}_3\mathrm{O} = \mathrm{C}_6\mathrm{H}_5\mathrm{CH}_2\mathrm{C}_6\mathrm{H}_4\mathrm{O} + \mathrm{CH}_4$ | -120.7/-109.2 |
| 8 | $CH_2(C_6H_5)_2 + C_6H_5OH + C_6H_5 = C_6H_5CH_2C_6H_3OH (4Dn) + 2C_6H_6$ | 0.4/-2.2 |
| 9 | $C_6H_4(C(O)OCH_3)_2 + C_6H_5 = C_6H_3(C(O)OCH_3)_2(6C) + C_6H_6$ | 2.7/-0.2 |

The values of $\Delta_{\rm f}H^{\circ}_{298.15}({\rm Y, CORR})_{\rm REAC}$ of these structures, determined using the theoretical values of $\Delta_{\rm r}H^{\circ}_{298.15}((R_x)_{\rm i}, {\rm CORR})_{\rm REAC}$ and tabulated values of $\Delta_{\rm f}H^{\circ}_{298.15}({\rm X} = {\rm H, C}$ and O, TAB), are compiled in Table 5. Their lower and upper limits are determined according to the procedure, described in [17, 21], and by the analogy with those, used above for the determination of the values of $\Delta_{\rm f}H^{\circ}_{298.15}({\rm Y, CORR})_{\rm MEAN}$ (Table 3). The uncertainty ranges for the values of $\Delta_{\rm f}H^{\circ}_{298.15}({\rm Y, CORR})_{\rm REAC}$, reported in Table 5,

correspond to the values of $3SE_{REACi}$, where the values of SE_{REACi} have determined using the reported correction dependencies [17, 21] (*SI*, Note 7, Table B). As it is mentioned above, the crossing area of these 99.7% confidential intervals, defined for each of the considered QM approaches, has used for the determination of the lowest and upper limits of the target values. In this case, the differences between the lower and upper limits of crossing area of these confidential intervals also correspond to 6SE. The averaging of the limits of those crossing areas has used for the determination of the values of $\Delta_{\rm f} H^{\rm o}_{298.15}$ (Y, CORR)_{REACMEAN}, also reposrted in Table 5.

Table 5. The values of $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y, CORR})_{\rm REAC}$ (±3SE), determined for the most thermochemically stable radicals using the B3LYP, M06-2X and RO/CBS-4M thermochemistry of the homodesmotic reactions, as well as the values of $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y, CORR})_{\rm REACMEAN}$ (±3SE), corresponded to the mean of their crossing area.

| i | $\begin{array}{c} \Delta_{\rm f} H^{\rm o}{}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm REAC},\\ {\rm kJ/mol} \end{array}$ | $\begin{array}{c} \Delta_{\rm f} H^{\rm o}{}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm REAC},\\ {\rm kJ/mol} \end{array}$ | $\begin{array}{c} \Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm REAC},\\ {\rm kJ/mol} \end{array}$ | $\begin{array}{c} \Delta_{\rm f} H^{\rm o}{}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm REAC},\\ {\rm kJ/mol} \end{array}$ | $\begin{array}{c} \Delta_{\rm f} H^{\rm o}{}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm REAC},\\ {\rm kJ/mol} \end{array}$ | $\begin{array}{c} \Delta_{\rm f} H^{\rm o}{}_{298.15}({\rm Y},\\ {\rm CORR})_{\rm REAC},\\ {\rm kJ/mol} \end{array}$ | $\frac{\Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y} {\rm CORR})_{\rm REACN}}{\rm kJ/mol}$ |
|----|----------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|
| | B3LYP | M06-2X | CBS-4M | ROCBS-4M | Lower | Upper | |
| | (± 19) | (± 10.2) | (± 16.5) | (± 15.6) | | | |
| 1C | 1C | 1C | 1C | 1C | 1C | 1C | 1C |
| 1 | -410 | -410.7 | -394.4 | -408.6 | -400.5 | -410.9 | -405.7 ± 5 |
| 2 | -421.6 | -421.9 | -405.4 | -419.2 | -411.7 | -421.9 | -416.9 ± 5 |
| 1D | 1D | 1D | 1D | 1D | 1D | 1D | 1D |
| 3 | 114.5 | 116.9 | 121.0 | 99.5 | 106.7 | 115.1 | $116.4{\pm}10$ |
| 4 | 117.2 | 116.4 | 130.8 | 99.6 | 114.3 | 115.2 | 120.5 ± 6 |
| 5 | 115.4 | 115.4 | 124.1 | 106.0 | 107.6 | 122.5 | $115.4{\pm}10$ |
| | | | | | 114.3 | 115.1 | $114.7{\pm}0.4$ |
| 3D | 3D | 3D | 3D | 3D | 3D | 3D | 3D |
| 6 | 130.3 | 130.8 | 134.7 | 130.9 | 120.6 | 141.0 | $130.8 {\pm} 10$ |
| 7 | 152.1 | 140.7 | 136.0 | 135.0 | 130.5 | 150.9 | 140.7 ± 10 |
| | | | | | 130.5 | 141.0 | $135.8{\pm}5$ |
| 4D | 4D | 4D | 4D | 4D | 4D | 4D | 4D |
| 8 | 237.2 | 241.4 | 236.6 | 239.7 | 231.2 | 241.6 | $241.4{\pm}10$ |
| 5C | $5\mathrm{C}$ | $5\mathrm{C}$ | $5\mathrm{C}$ | $5\mathrm{C}$ | $5\mathrm{C}$ | $5\mathrm{C}$ | $5\mathrm{C}$ |
| 9 | -352.4 | -352.0 | -349.6 | -351.8 | -341.8 | -362.2 | $-352.0{\pm}10$ |

As can be seen from Table 5, the value of $\Delta_{\rm f} H^{\circ}_{298.15}$ (Y, CORR)_{REACMEAN}, calculated using the thermochemistry of reaction 2, is significantly lower (outside of the 3SE uncertainties ranges), than those values, determined using the thermochemistry of atomization reactions (Table 3) and homodesmotic reaction 1 (Table 5). This discrepancy can be attributed to the uncertainty, reported for the value of $\Delta_{\rm f} H^{\circ}_{298.15}$ (CH₂OC(O)CH₃) (= -221.6±8 kJ/mol) in [37]. Thus, the values of $\Delta_{\rm f} H^{\circ}_{298.15}$ (CH₂OC(O)CH₃)_{atom}, calculated in the present work using the different QM approaches (Table 6, 1F), are consistent one with others as well as are systematically (6-23 kJ/mol) higher than its tabulated value. However, both the tabulated ($\Delta_{\rm f} H^{\circ}_{298.15}$ (CH₂OC(O)CH₃)) and the calculated ($\Delta_{\rm f} H^{\circ}_{298.15}$ (CH₂OC(O)CH₃)_{MEAN}) values are lying within their uncertainties ranges.

Table 6. The values of $\Delta_{\rm f} H^{\circ}{}_{298.15}({\rm CH}_2{\rm OC}({\rm O}){\rm CH}_3, {\rm CORR})_{\rm atom}$ (±3SE), determined using the different QM approaches, as well as their mean values of $\Delta_{\rm f} H^{\circ}{}_{298.15}({\rm CH}_2{\rm OC}({\rm O}){\rm CH}_3, {\rm CORR})_{\rm MEAN}$ (±3SE), determined using the upper and lower limits (6SE) of the common area of the uncertainty ranges of the values of $\Delta_{\rm f} H^{\circ}{}_{298.15}({\rm CH}_2{\rm OC}({\rm O}){\rm CH}_3, {\rm CORR})_{\rm MEAN}$ (±3SE), determined using the upper and lower limits (6SE) of the common area of the uncertainty ranges of the values of $\Delta_{\rm f} H^{\circ}{}_{298.15}({\rm CH}_2{\rm OC}({\rm O}){\rm CH}_3, {\rm CORR})_{\rm atom}$. (The values of errors correspond to 3SE, determined for the correction dependencies reported in [21] (SI, Note 7)).

| | $\begin{array}{l} \Delta_{\rm f} {H^{\rm o}}_{298.15}({\rm Y}' \\ {\rm CORR})_{\rm atom}, \\ {\rm kJ/mol} \end{array}$ | , $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y'},$ CORR) _{atom} , kJ/mol | , $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y'})$ CORR) _{atom} , kJ/mol | , $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y'},$ CORR) _{atom} , kJ/mol | , $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y'},$ CORR) _{atom} , kJ/mol | $\Delta_{\rm f} H^{\rm o}{}_{298.15}({\rm Y'}, {\rm CORR})_{\rm atom}, kJ/{\rm mol}$ | , $\Delta_{\rm f} H^{\rm o}_{298.15} ({\rm Y} {\rm CORR})_{\rm MEAN}$ kJ/mol |
|----------|------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| | B3LYP (±33.6) | M06-2X (± 11.4) | $\begin{array}{c} \text{CBS-4M} \\ (\pm 25.2) \end{array}$ | ROCBS- 4M (±27.6) | Lower | Upper | |
| 1F 2F | -215.2 -157.1 | -215.2 -161.8 | -198.6 -146.3 | -200.5 -149.0 | -223.8 -171.5 | -203.8 -150.4 | -213±10 -161±11 |

On the contrary, the values of $\Delta_{\rm f} H^{\rm o}_{298.15}$ (CH₂OC(O)CH, CORR)_{atom}, calculated using the same QM approaches (Table 6, 2F), are not systematically lower or higher its tabulated value (= -156.9±1.7 kJ/mol, *SI*, *Note 1*) and are rather demonstrating their dispersion around it. As a result, the value of $\Delta_{\rm f} H^{\rm o}_{298.15}$ (Y, CORR)_{REACMEAN}, determined using the thermochemistry of the homodesmotic reaction i = 1 (Table 5), is considered as the more reliable than hose value, derived on the basis of reaction i = 2 (Table 5). This conclusion agrees with the value of $\Delta_{\rm f} H^{\rm o}_{298.15}$ (Y, CORR)_{MEAN}, determined using the corrected thermochemistry of atomization reactions.

The most accurate and consistent values of $\Delta_{\rm f} H^{\rm o}_{298.15}$ (Y, CORR)_{REACMEAN} (marked bold in Tables 3 and 5) that agree with the other theoretical values, determined in the present study, are considered as the most reliable. Most of these values are determined using thermochemistry homodesmotic reactions ($\Delta_{\rm f} H^{\rm o}_{298.15}$ (Y, CORR)_{REACMEAN}), Table 5). However, in the case of structures 1C and 5C, the uncertainties ranges for their values of $\Delta_{\rm f} H^{\rm o}_{298.15}$ (Y, CORR)_{REACMEAN}), Table 5). However, in the case of structures 1C and 5C, the uncertainties ranges for their values of $\Delta_{\rm f} H^{\rm o}_{298.15}$ (Y, CORR)_{MEAN}, calculated using the thermochemistry of atomization reactions, are recommended due to their smaller 99.7% confidence intervals than those, determined using the thermochemistry of homodesmotic reactions (Table 5, i = 1,9).

The values of $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y,\ CORR})_{\rm REACMEAN}$ of others isomers, can also be determined using the thermochemistry of their homodesmotic tautomerization reactions and the values of $\Delta_{\rm f} H^{\rm o}_{298.15}({\rm Y,\ CORR})_{\rm REACMEAN}$, reported in the present work for the structures 1C, 5C, 1D, 3D and 4D.

Noticeably, in the case of structures 8D and 9D, the rotation of OH group leads to formation of the 6-10 kJ/mol less thermochemically stable conformers (respectively, 19D and 20D). This result is probably due to the interaction of unpaired electron with H atom of hydroxyl group. As a result, the lower values of entropy of the structures 8D and 9D, compared those for the structures 19D and 20D, are expected.

3.2.3. Determination of the values of $S^{o}_{298.15}(Y)$

The values of $S^{\circ}_{298.15}(Y, \text{CALC})$, determined in the present study using the values of $H^{\circ}_{298.15}(Y, \text{CALC})$ and $G^{\circ}_{298.15}(Y, \text{CALC})$, are presented in Table 7. As can be seen, these values are mainly consistent and do not depend upon used QM approach. The effect of the restricted open shell wavefunction is not observed and is not expected [17, 21]. Therefore, the only results of B3LYP, M06-2X and CBS-4M calculations of $S^{\circ}_{298.15}(Y, \text{CALC})$ are reported.

As can be seen the highest difference between the values of $S^{\circ}_{298,15}(Y, \text{CALC})$ of conformers and tautomers, determined within the same QM approach, is too small for affecting the qualitative distribution between the considered isomers of radicals, formed by abstraction of H atom from $1,2-C_6H_4(\text{CO}_2\text{CH}_3)_2(<15 \text{ J/(mol K)})$ and $p-C_6H_5\text{CH}_2C_6H_4\text{OH}(<30 \text{ J/(mol K)})$ at room or elevated temperatures. Thus, the B3LYP values of $\Delta_r S \circ_{298,15}(1\text{C}-11\text{C}) \times T = 31.2 \text{ kJ/mol and } \Delta_r S \circ_{298,15}(1\text{D}-13\text{D}) \times T = 59.4 \text{ kJ/mol at } T = 2000 \text{ K}$ are significantly smaller than the standard enthalpies of these reaction, which correspond, respectively, to 60-70 and 140 kJ/mol (Table 3). The even smaller values of $\Delta_r S \circ_{298,15}(1\text{C}-11\text{C}) \times T = 7.4 \text{ J/(mol K)}$ and $\Delta_r S \circ_{298,15}(1\text{D}-13\text{D}) \times T = 37.6 \text{ J/(mol K)}$ for these reactions (T = 2000 K) are predicted by the CBS-4M calculations. The observed differences between the values of $\Delta_r S \circ_{298,15}(1\text{C}-11\text{C})$ or $\Delta_r S \circ_{298,15}(1\text{D}-13\text{D})$, determined in the present work using the different QM approaches, is most probably due to the accuracy of calculations of the vibration frequencies. As a result, the different QM approaches predict the highest

values of $\Delta_{\rm r}S^{~o}_{298.15}$ of isomerization of the 1C and 1D for the different structures. Thus, the B3LYP and M06-2X approaches suggests its highest values for the reaction (1C-11C), while, the CBS-4M calculation for the reaction (1C-6C) ($\Delta_{\rm r}S^{~o}_{298.15}(1C-6C) \times T = 23.4 \text{ kJ/mol}$). The same discrepancy, but for all three considered QM approaches, is observed for the reaction of tautomerization of 1D. Thus, the highest values of $\Delta_{\rm r}S^{~o}_{298.15}(1D-4D) \times T = 60.6 \text{ kJ/mol}$ and $\Delta_{\rm r}S^{~o}_{298.15}(1D-17D) \times T = 47.2 \text{ kJ/mol}$ (at T = 2000 K) are determined, respectively, using the M06-2X and CBS-4M approaches. However, these observations don't affecting the qualitative distribution between the main tautomers of these radicals.

The corrections of these values of $S^{\circ}_{298.15}(Y, CALC)$ using the reported dependencies [17, 21] don't affecting significantly these differences as well. The corrected values of $S^{\circ}_{298.15}(Y, CORR)$ are presented in Table 7. The uncertainties, reported for these values in Table 7 (in parentheses), correspond to the values of 2SE, determined previously for the B3LYP (-4.47+1.015× $S^{\circ}_{298.15}(X, B3LYP)$, [21]), CBS-4M (-10.35+1.037× $S^{\circ}_{298.15}(X, RO/CBS-4M)$ [17]) and M06-2X (-21.13+1.0587× $S^{\circ}_{298.15}(X, M06-2X)$ [21]) correction dependencies.

| Table 7. The values of | ${ m of}S~{ m o}_{298.15}({ m Y},{ m G})$ | CALC) of con | sidered radical | s (1C-12C, | 1D-21D), as | well as thei | r corrected |
|----------------------------------------|-------------------------------------------|----------------|-----------------|------------|--------------------|--------------|-------------|
| values of $S^{o}_{298,15}(\mathbf{Y},$ | CORR), calcu | ulated using t | the different Q | M approach | nes ($\pm 2SE$). | | |

| | $S^{o}_{298.15}(Y, CALC)$ | $S^{o}_{298.15}(Y, CALC)$ | $S^{o}_{298.15}(Y, CALC)$ | $S^{o}_{298.15}(Y, COBB)$ | $S^{o}_{298.15}(Y, COPP)$ | $S^{o}_{298.15}(Y, COPP)$ |
|---------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| V | (ALC), | (ALC), | (ALC), | U(nn), | U(1 X) | U(1X) |
| Y | J/(mol K) |
| | B3LYP | M06-2X | CBS-4M | B3LYP | M06-2X (± 20) | CBS-4M |
| | | | | (± 17.6) | · · · · | (± 15.6) |
| 1C | 493.1 | 484.9 | 497.4 | 496.0 | 492.2 | 505.5 |
| 2C | N/A | 490.1 | 493.7 | N/A | 497.7 | 501.6 |
| 3C | 499.0 | 489.1 | 502.4 | 502.0 | 496.7 | 510.6 |
| $4\mathrm{C}$ | 496.2 | 487.6 | 497.1 | 499.2 | 495.1 | 505.2 |
| $5\mathrm{C}$ | 496.3 | 489.2 | 501.5 | 499.3 | 496.8 | 509.7 |
| $6\mathrm{C}$ | 500.1 | 491.5 | 509.1 | 503.1 | 499.2 | 517.6 |
| 7C | 501.7 | 492.9 | 504.1 | 504.8 | 500.7 | 512.4 |
| $8\mathrm{C}$ | 497.5 | 488.2 | 503.9 | 500.5 | 495.7 | 512.2 |
| 9C | 497.2 | 488.1 | 504.7 | 500.2 | 495.6 | 513.0 |
| 10C | 508.3 | 489.1 | 504.3 | 511.5 | 496.7 | 512.6 |
| 11C | 508.7 | 495.0 | 501.1 | 511.9 | 502.9 | 509.3 |
| 12C | 497.5 | 492.7 | 498.5 | 500.5 | 500.5 | 506.6 |
| 1D | 448.0 | 447.2 | 454.1 | 450.3 | 452.3 | 460.6 |
| 2D | 448.7 | 447.1 | 454.1 | 451.0 | 452.2 | 460.6 |
| 3D | 466.0 | 466.0 | 461.2 | 468.5 | 472.2 | 467.9 |
| 4D | 470.3 | 477.5 | 466.3 | 472.9 | 484.4 | 473.2 |
| 5D | 470.1 | 466.7 | 465.5 | 472.7 | 473.0 | 472.4 |
| 6D | 474.2 | 468.7 | 473.1 | 476.8 | 475.1 | 480.3 |
| 7D | 474.9 | 469.8 | 472.3 | 477.6 | 476.2 | 479.4 |
| 8D | 470.6 | 471.5 | 471.4 | 473.2 | 478.0 | 478.5 |
| 9D | 471.1 | 467.4 | 470.9 | 473.7 | 473.7 | 478.0 |
| 10D | 470.5 | 469.0 | 470.5 | 473.1 | 475.4 | 477.6 |
| 11D | 471.0 | 468.4 | 469.1 | 473.6 | 474.8 | 476.1 |
| 12D | 470.7 | 467.2 | 470.4 | 473.3 | 473.5 | 477.5 |
| 13D | 477.7 | 467.8 | 472.9 | 480.4 | 474.1 | 480.1 |
| 14D | 474.1 | 467.4 | 473.4 | 476.7 | 473.7 | 480.6 |
| 15D | 471.0 | 474.0 | 473.3 | 473.6 | 480.7 | 480.5 |
| 16D | 476.6 | 474.3 | 474.5 | 479.3 | 481.0 | 481.7 |
| 17D | 474.1 | 473.1 | 477.7 | 476.7 | 479.7 | 485.0 |
| | | | | | | |

| Y | $S^{o}_{298.15}(Y, CALC), J/(mol K)$ | $S^{o}_{298.15}(Y, CALC), J/(mol K)$ | $S^{o}_{298.15}(Y, CALC), J/(mol K)$ | $S^{o}_{298.15}(Y, CORR), J/(mol K)$ | $S^{o}_{298.15}(Y, CORR), J/(mol K)$ | $S^{o}_{298.15}(Y, CORR), J/(mol K)$ |
|-----|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| 18D | 470.0 | 469.2 | 470.2 | 472.6 | 475.6 | 477.3 |
| 19D | 469.5 | 469.2 | 472.0 | 472.1 | 475.6 | 479.1 |
| 20D | 467.9 | 469.6 | 472.2 | 470.5 | 476.0 | 479.3 |
| 21D | 477.2 | 469.5 | 473.3 | 479.9 | 475.9 | 480.5 |

As can be seen, the CBS-4M values of $S_{298.15}(1C, CORR)$ and $S_{298.15}(1D, CORR)$, determined in the present study, are 5-6 kJ/mol higher and lower those values estimated, respectively, for Dimethyl phthalate $(500.9\pm15.6~(\pm 2SE)~J/(mol~K~)~[21])$ and p-Benzylphenol ($465.0\pm15.6~(\pm 2SE)~J/(mol~K)~[21]$). At the same time, the difference between their B3LYP values is close to 1 J/(mol K~) in the case of Dimethyl phthalate ($494.6\pm17.6~(\pm 2SE)~J/(mol~K~)~[21]$), and is near 12 J/(molK~)~ for the p-Benzylphenol ($462.6\pm17.6~J/(mol~K~)~[21]$). In the case of M06-2X calculations, the difference near 1 kJ/mol, similar those determined using the B3LYP approach, is only observed for the Dimethyl phthalate (491.3~J/(mol~K~)~[21]), while, for the p-Benzylphenol, the difference (=19 kJ/mol) between the value of $S_{298.15}(1B, CORR)$ [21] and the value of $S_{298.15}(1D, CORR)$, determined in the present work, is higher those derived from CBS-4M and B3LYP calculations.

At the same time, the consistent differences between the values of $S^{\circ}_{298.15}$ (p-Benzylphenol) [21] and $S^{\circ}_{298.15}$ (3D, CORR) are calculated using all considered approaches. Thus, the CBS-4M value of this difference (2.9 J/(mol K)) is slightly higher and lower, respectively, those values, determined using the M06-2X (0.8 J/(mol K)) and B3LYP (4.9 J/(mol K)) approaches. These values are not far away from the difference of -3 J/(mol K), determined using the tabulated values of phenol and phenoxy radical ($S^{\circ}_{298.15}$ (C₆H₅OH, TAB) (= 315 J/(mol K)) and $S^{\circ}_{298.15}$ (C₆H₅O, TAB) (= 312 J/(mol K)) [37]). The same result is also observed for the tabulated values of $S^{\circ}_{298.15}$ (C₆H₅CH₃, TAB) (= 320 J/(mol K)) and $S^{\circ}_{298.15}$ (C₆H₅CH₂, TAB) (= 318 J/(mol K), or $S^{\circ}_{298.15}$ (CH₃OH, TAB) (= 239 J/(mol K)) and $S^{\circ}_{298.15}$ (C₆H₅CH₂, TAB) (= 318 J/(mol K), or $S^{\circ}_{298.15}$ (CH₃OH, TAB) (= 239 J/(mol K)) and $S^{\circ}_{298.15}$ (CH₃O, TAB) (= 234 J/(mol K)) [37]. The observed slight discrepancy between these and calculated values can be explained by the uncertainties of calculations. From this point of view, the CBS-4M values of $S^{\circ}_{298.15}$ (p-Benzylphenol) [21] and $S^{\circ}_{298.15}$ (1D, CORR) have the smallest uncertainty range and are considered as the most reliable. Thus, generally speaking, the removing of one atom from compound should decrease the entropy, due to the lost of mass, lost of one (or more) vibration component, as well as due to the slightly smaller size of radical. However, in some cases, such logical line does not work and some correction of these values can also be expected.

For example, the removing of H atom from Benzaldehyde (336 J/(mol K)) leads to the formation of $C_{6}H_{5}CO$, for which the tabulated value of $S^{\circ}_{298,15}(C_{6}H_{5}CO, TAB) = 342 J/(mol K)$ [37] is 6 J/(mol K) higher. The same effect can also be demonstrated for the pairs of $CH_{3}(S^{\circ}_{298,15}(CH_{3}, TAB) = 194 J/(mol K))$ and $CH_{4}(S^{\circ}_{298,15}(CH_{4}, TAB) = 186 J/(mol K))$, or $CH_{2}OH$ ($S^{\circ}_{298,15}(CH_{2}OH, TAB) = 244 J/(mol K)$) and $CH_{3}OH$ ($S^{\circ}_{298,15}(CH_{3}OH, TAB) = 239 J/(mol K)$) [37]. These observations are, most probably, due to the effect of H atom abstraction on the symmetry and the vibration frequencies of atoms in the formed radicals, and cannot be attributed to the internal rotations, which are not considered in this study for the entropies calculations [36], but corrected using the correction dependencies. Thus, the $C_{6}H_{5}$ and $C_{6}H_{6}$ do not have the internal rotations, but the value of $S^{\circ}_{298,15}(C_{6}H_{5}, TAB)$ (= 286.1 J/(mol K)) is 17 J/(mol K) higher than the value of $S^{\circ}_{298,15}(C_{6}H_{6}, TAB)$ (= 269.2 J/(mol K)) [37].

The last pair of values is slightly better consistent with the results of B3LYP and M06-2X calculations than with results, determined using the CBS-4M approach. Thus, the differences between the values of $S^{\circ}_{298.15}$ (p-Benzylphenol)_{CBS-4M} (= 465.0±15.6 J/(mol K)) and $S^{\circ}_{298.15}$ (4D, CORR)_{CBS-4M} corresponds to 8.2 J/(mol K), while, the differences between those values, determined using the B3LYP and M06-2X approaches, are, respectively, 10.3 and 13 J/(mol K). However, all these values are lying within reported uncertainties and cannot be used as the argument for preference of one of the determined values.

The same conclusion can be made for the values of $S^{\circ}_{298.15}$, calculated using the CBS-4M approach for the radicals, formed by the abstraction of H atom from Dimethyl phthalate. Thus, the difference of 5-6 J/(mol K) between the values of $S^{\circ}_{298.15}$ (Dimethyl phthalate)_{CBS-4M} and $S^{\circ}_{298.15}$ (1C, CORR)_{CBS-4M} is closer those values, determined for pairs CH₄/CH₃ or CH₃OH/CH₂OH, than that value determined using the B3LYP approach. However, the difference of 16-18 J/(mol K) between the values of $S^{\circ}_{298.15}$ (Dimethyl phthalate) [21] and $S^{\circ}_{298.15}$ (Y, CORR), calculated using the CBS-4M (Y = 6C), as well as the B3LYP (Y = 11C) approaches, are both consistent with the tabulated values of $S^{\circ}_{298.15}$ (C₆H₅, TAB) and $S^{\circ}_{298.15}$ (C₆H₆, TAB).

As a result, it can be concluded, that all values of entropy of considered radicals can be used within recommended uncertainties. However, CBS-4M values, as well as the corrected (using considered correction dependencies) B3LYP and M06-2X values, cannot be used for the determination of the vibration frequencies of compounds, their temperature dependencies and IR spectra. Therefore, the not corrected results of B3LYP calculations are used for these purposes instead.

3.2.4. IR spectra of the most thermochemically stable radicals.

The IR spectra of the most thermochemically favorable isomers of these radicals, determined using B3LYP/6-311++G(d,p), are presented in Figures 3a and 3b, respectively, for the structures 1C and 1D/3D. The values of wavenumber, used for these spectra, correspond to their original vibration frequencies, not corrected using the recommended scaling factor. Unfortunately, the spectra of these radicals are not measured or not reported in the literature. Therefore, the spectra of Dimethyl phthalate and p-Benzylphenol are used for the comparison with the calculated IR spectra of most thermochemically stable radicals instead.

Figure 3. The IR spectra of $C_6H_4(CO_2CH_2)CO_2CH_3(1C, black, a)$, $C_6H_5CHC_6H_4OH$ (1D, black, b) and $C_6H_5CH_2C_6H_4O$ (3D, dark red, b), calculated using the B3LYP/6-311++G(d,p) approach.

As it is expected, the spectra, presented in Figures 3a and 3b, are very close those reported for the Dimethyl phthalate and p-Benzylphenol. In the case of Dimethyl phthalate, the difference between its measured spectrum [33] and the spectrum, calculated for the structure 1C, is mainly observed at 300 and 1020 cm⁻¹. This difference corresponds, respectively, to the frequencies of the angular vibration of [?]HCH group and to the vibration of RC-OCH₂ bonds.

In the case of p-Benzylphenol, the main difference between its measured spectrum [33] and the spectra, calculated for the most thermochemically favorable structures 1D/3D, is due to the vibration of C-H bonds of methylene group (~3020 and ~3050 cm⁻¹), not presented in these radicals. In addition, the calculated spectrum of C₆H₅CH₂C₆H₄O (structure 3D), also presented on Figure 3b, does not have absorption at ~3840 cm⁻¹, corresponded to the vibration of O-H bond, but demonstrates the vibration of CH₂ group at ~3020 and ~3050 cm⁻¹.

As a result, it can be concluded, that the calculated vibration frequencies must not introduce significant error to the values of entropies, presented above (Table 7). This conclusion is due to the consistency between the calculated IR spectra of radicals and the spectra, reported for the Dimethyl phthalate and p-Benzylphenol.

3.2.5. Temperature dependencies

Temperature dependencies of the main thermochemical properties of the most stable radicals (1C, 1D and 3D), considered in the present work, are determined using their values of $\Delta_{\rm f}H$ °_{298.15}, determined above, as well as the B3LYP/6-311++G(d,p) geometry and vibration frequencies, scaled according to NIST recommendations [42]. In addition, the temperature dependencies for their isomers with the lowest values of $\Delta_{\rm f}H$ °_{298.15} (structures 5C and 4D) or the highest corrected CBS-4M values of S °_{298.15} (6C and 17D) are also determined. The results of these calculations are presented in Tables 8 and 9.

Table 8. Temperature dependencies of the thermochemical properties ((C_p)_T (J/(mol K), S^o_T (J/(mol K), $\Delta_{\rm f} H^{\rm o}_{\rm T}$ (kJ/mol), $\Delta_{\rm f} G^{\rm o}_{\rm T}$ (kJ/mol)) of structures (1C) and (1D), determined using the B3LYP/6-311++G(d,p) geometries and scaled (0.996) frequencies.

| T, K | (1C) | (1C) | (1C) | (1C) | (1D) | (1D) | (1D) | (1D) |
|--------|-----------------------|---------------|--------------------------------------|--------------------------------------|-----------------------|---------------|--------------------------------------|--------------------------------------|
| | $(C_{\rm p})_{\rm T}$ | $S^{o}{}_{T}$ | $\Delta_{\rm f} H^{\rm o}{}_{\rm T}$ | $\Delta_{\rm f} G^{\rm o}{}_{\rm T}$ | $(C_{\rm p})_{\rm T}$ | $S^{o}{}_{T}$ | $\Delta_{\rm f} H^{\rm o}{}_{\rm T}$ | $\Delta_{\rm f} G^{\rm o}{}_{\rm T}$ |
| 0 | 0.000 | 0.000 | -378.286 | -378.286 | 0 | 0 | 146.867 | 146.867 |
| 100 | 101.900 | 324.844 | -391.628 | -343.167 | 77.241 | 306.332 | 133.549 | 168.225 |
| 200 | 160.492 | 414.129 | -399.617 | -291.413 | 135.274 | 376.865 | 123.545 | 206.889 |
| 298.15 | 214.072 | 488.215 | -406.1 | -236.754 | 201.207 | 443.074 | 114.700 | 249.858 |
| 300 | 215.070 | 489.542 | -406.21 | -235.836 | 202.453 | 444.322 | 114.547 | 250.561 |
| 400 | 266.428 | 558.591 | -411.333 | -178.229 | 265.995 | 511.476 | 107.275 | 297.046 |
| 500 | 310.251 | 622.906 | -414.961 | -119.504 | 318.946 | 576.732 | 101.773 | 345.160 |
| 600 | 345.955 | 682.743 | -417.368 | -60.169 | 361.175 | 638.763 | 97.657 | 394.243 |
| 700 | 374.897 | 738.322 | -418.737 | -0.51 | 394.893 | 697.065 | 94.686 | 443.929 |
| 800 | 398.617 | 789.981 | -419.194 | 59.269 | 422.279 | 751.644 | 92.707 | 493.956 |
| 900 | 418.321 | 838.104 | -418.862 | 119.071 | 444.93 | 802.729 | 91.587 | 544.196 |
| 1000 | 434.872 | 883.060 | -417.851 | 178.787 | 463.938 | 850.619 | 91.205 | 594.504 |
| 1100 | 448.894 | 925.183 | -416.278 | 238.384 | 480.058 | 895.614 | 91.436 | 644.834 |
| 1200 | 460.851 | 964.768 | -414.234 | 297.809 | 493.833 | 937.99 | 92.181 | 695.111 |
| 1300 | 471.102 | 1002.071 | -411.824 | 357.046 | 505.674 | 977.997 | 93.327 | 745.304 |
| 1400 | 479.931 | 1037.315 | -409.125 | 416.106 | 515.903 | 1015.855 | 94.790 | 795.423 |
| 1500 | 487.571 | 1070.693 | -406.201 | 474.939 | 524.779 | 1051.758 | 96.507 | 845.396 |
| 1600 | 494.210 | 1102.377 | -403.118 | 533.59 | 532.513 | 1085.879 | 98.402 | 895.272 |
| 1700 | 500.002 | 1132.516 | -399.928 | 592.03 | 539.278 | 1118.37 | 100.420 | 945.005 |
| 1800 | 505.077 | 1161.242 | -396.671 | 650.289 | 545.219 | 1149.366 | 102.515 | 994.628 |
| 1900 | 509.540 | 1188.673 | -393.38 | 708.364 | 550.455 | 1178.988 | 104.662 | 1044.135 |
| 2000 | 513.481 | 1214.911 | -390.084 | 766.261 | 555.089 | 1207.343 | 106.820 | 1093.518 |
| 2100 | 516.975 | 1240.050 | -386.826 | 823.991 | 559.202 | 1234.527 | 108.946 | 1142.792 |
| 2200 | 520.082 | 1264.173 | -383.612 | 881.581 | 562.868 | 1260.628 | 111.033 | 1191.981 |
| 2300 | 522.856 | 1287.354 | -380.454 | 939.029 | 566.144 | 1285.722 | 113.072 | 1241.082 |
| 2400 | 525.341 | 1309.660 | -377.382 | 996.323 | 569.083 | 1309.88 | 115.024 | 1290.074 |
| 2500 | 527.573 | 1331.151 | -374.4 | 1053.499 | 571.727 | 1333.165 | 116.889 | 1338.999 |
| 2600 | 529.585 | 1351.883 | -371.523 | 1110.56 | 574.113 | 1355.636 | 118.646 | 1387.850 |
| 2700 | 531.405 | 1371.904 | -368.754 | 1167.504 | 576.272 | 1377.345 | 120.295 | 1436.624 |
| 2800 | 533.054 | 1391.261 | -366.106 | 1224.358 | 578.231 | 1398.338 | 121.819 | 1485.356 |
| 2900 | 534.554 | 1409.993 | -363.592 | 1281.111 | 580.013 | 1418.661 | 123.201 | 1534.025 |
| 3000 | 535.920 | 1428.138 | -361.198 | 1337.792 | 581.639 | 1438.352 | 124.461 | 1582.660 |

Table 9. Temperature dependencies of the thermochemical properties ((C_p)_T (J/(mol K), S^o_T (J/(mol K), $\Delta_{\rm f}H$ o_T (kJ/mol), $\Delta_{\rm f}G$ o_T (kJ/mol)) of structures (3D), determined using the B3LYP/6-311++G(d,p) geometries and scaled (0.996) frequencies.

| T, K | (3D) | (3D) | (3D) | (3D) |
|--------|-----------------------|---------------|--------------------------------------|--------------------------------------|
| | $(C_{\rm p})_{\rm T}$ | $S^{o}{}_{T}$ | $\Delta_{\rm f} H^{\rm o}{}_{\rm T}$ | $\Delta_{\rm f} G^{\rm o}{}_{\rm T}$ |
| 0 | 0 | 0 | 167.966 | 167.966 |
| 100 | 79.134 | 326.578 | 155.201 | 187.852 |
| 200 | 131.937 | 396.629 | 145.097 | 224.488 |
| 298.15 | 195.791 | 461.027 | 135.800 | 265.605 |
| 300 | 197.021 | 462.242 | 135.637 | 266.275 |
| 400 | 260.53 | 527.797 | 127.809 | 311.052 |
| 500 | 314.251 | 591.909 | 121.796 | 357.595 |
| 600 | 357.456 | 653.17 | 117.259 | 405.201 |
| 700 | 392.128 | 710.97 | 113.964 | 453.473 |

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| T, K | (3D) | (3D) | (3D) | (3D) |
|------|---------|----------|---------|----------|
| 800 | 420.355 | 765.236 | 111.752 | 502.127 |
| 900 | 443.706 | 816.137 | 110.476 | 551.017 |
| 1000 | 463.271 | 863.928 | 110.001 | 599.990 |
| 1100 | 479.819 | 908.88 | 110.187 | 648.992 |
| 1200 | 493.914 | 951.25 | 110.925 | 697.942 |
| 1300 | 505.988 | 991.274 | 112.092 | 746.808 |
| 1400 | 516.382 | 1029.161 | 113.594 | 795.598 |
| 1500 | 525.371 | 1065.102 | 115.366 | 844.239 |
| 1600 | 533.179 | 1099.264 | 117.323 | 892.779 |
| 1700 | 539.989 | 1131.796 | 119.410 | 941.172 |
| 1800 | 545.953 | 1162.834 | 121.578 | 989.450 |
| 1900 | 551.198 | 1192.495 | 123.798 | 1037.608 |
| 2000 | 555.828 | 1220.888 | 126.031 | 1085.639 |
| 2100 | 559.93 | 1248.108 | 128.230 | 1133.557 |
| 2200 | 563.579 | 1274.242 | 130.390 | 1181.386 |
| 2300 | 566.836 | 1299.368 | 132.499 | 1229.123 |
| 2400 | 569.752 | 1323.555 | 134.519 | 1276.749 |
| 2500 | 572.373 | 1346.867 | 136.450 | 1324.306 |
| 2600 | 574.734 | 1369.363 | 138.270 | 1371.785 |
| 2700 | 576.869 | 1391.094 | 139.980 | 1419.186 |
| 2800 | 578.804 | 1412.109 | 141.562 | 1466.541 |
| 2900 | 580.563 | 1432.451 | 143.001 | 1513.832 |
| 3000 | 582.166 | 1452.161 | 144.314 | 1561.087 |

The slight differences, observed between the values of $S^{\circ}_{298.15}$ (Y, CALC)_{B3LYP} (Table 7) and the values of S°_{T} (at T = 298.15 K, Tables 8, 9 and *SI*, *Note 8* (Tables A and B)), are due to the using, in the last case, of the scaling factor, recommended by NIST database [41], for the correction of vibration frequencies.

As can be seen, in most of the cases, the increase of temperature does not qualitatively affecting the equilibrium distribution between the radicals. Thus, the same structures of these radicals (1C, 1D-3D) are the most thermochemically favorable at temperatures 298.15 and 3000K. The significant difference is only observed between the structures 1D and 3D. In this case, the most thermochemically stable structure, predicted for the temperatures above 2000 K, is 3D, but is not the structures 1D and 2D.

The small inconsistency between the values of $S^{\circ}_{298.15}$, recommended in the present work (Table 7, in bold), and their, not corrected, B3LYP values, used for the reported temperature dependencies, is insignificant and can be adjusted by addition of the values of $S^{\circ}_{298.15}$ (Y, CORR)_{CBS-4M} - $S^{\circ}_{298.15}$ (Y, CALC)_{B3LYP} to the scaled values of S°_{T} (Y, CALC)_{B3LYP}. Thus, the significant differences between the values of S°_{3000} (Y, CALC) - $S^{\circ}_{298.15}$ (Y, CALC), determined using the different QM approaches, are not observed (Table 10).

Table 10. Temperature effect on the values of S $^{\rm o}{}_{\rm T}$ of the most thermochemically stable structures 1C, 1D and 3D.

| QM | $S^{o}_{3000}(Y, CALC) - S^{o}_{298.15}(Y, CALC), J/(mol K)$ | $S^{o}_{3000}(Y, CALC) - S^{o}_{298.15}(Y, CALC), J/(mol K)$ | $S^{o}{}_{30}$ |
|--------|--------------------------------------------------------------|--------------------------------------------------------------|----------------|
| | 1C | 1D | 3D |
| B3LYP | 939.9 | 995.3 | 991.1 |
| CBS-4M | 935.2 | 1000.4 | 992.2 |
| M06-2X | 932.6 | 989.9 | 986.0 |

The NASA polynomial form for the most thermochemically favorable structures are reported below.

| C6H4(CO2CH2) | H 9C 10O 4 0g 300.00 5000.00 1000.00 | |
|--------------|--------------------------------------|--|
| | | |

| $2.61925331E + 01 \ 3.90153651E - 02 - 1.53874921E - 05 \ 2.77271165E - 09 - 1.87516226E - 13$ | 2 |
|------------------------------------------------------------------------------------------------|---|
| $-6.06140178E + 04 - 1.06885434E + 02\ 7.34068835E - 01\ 1.00177216E - 01 - 5.44073621E - 05$ | 3 |
| $4.70975205E-09 \ 1.05223290E-11-5.30311753E+04 \ 2.71041634E+01$ | 4 |

1

1

C6H5CHC6H4OH_1D H 11C 13O 1 0g 300.00 5000.00 1000.00

| $2.58261199 \pm +01\ 4.46658587 \pm -02-1.75098213 \pm -05\ 3.14286073 \pm -09-2.11992719 \pm -13$ | 2 |
|----------------------------------------------------------------------------------------------------|---|
| $1.42429281E + 03 - 1.12958631E + 02 - 8.73432400E + 00\ 1.38156180E - 01 - 1.00164238E - 04$ | 3 |
| $2.18497804E-08\ 4.70746911E-12\ 1.10969737E+04\ 6.61076246E+01$ | 4 |

| C6H5CH2C6H4O_3D H 11C 13O 1 0g 300.00 5000.00 1000.00 | 1 |
|------------------------------------------------------------------------------------------------|---|
| 2.49221685E+01 4.60393038E-02-1.81770211E-05 3.27776273E-09-2.21787754E-13 | 2 |
| $4.09498659E + 03 - 1.06193269E + 02 - 8.15775498E + 00 \ 1.29079520E - 01 - 7.81334086E - 05$ | 3 |
| $1.63173469E-09 \ 1.13165088E-11 \ 1.37083149E+04 \ 6.68738078E+01$ | 4 |

3.3. Potentially important reactions of the formation of Y radicals.

As it is shown above, the abstraction of H atom from the CH_n group of the considered compounds (Dimethyl phthalate and p-Benzylphenol) is the most thermochemically favorable pathway. In the case of Dimethyl phthalate this conclusion agrees with the results of work [16,17], which demonstrate that the value of BDE of C_6H_5R -H increase according to the following order BDE(R = O) < BDE($R = CH_2$) < BDE($R = OCH_2$) < BDE(C_6H_5 -H, no R). However, in the present work, some contradiction with this order is observed for p-Benzylphenol. Thus, the value of BDE($R = C_6H_5CH$) is not higher, but is lower than the value of BDE(R = O). The noted discrepancy has explained above and is due to the conjugation of the electron of CH group with π -electrons of two aromatic rings.

As a result of the low value of BDE(R = C₆H₅CH), the reactions of H atom abstraction (transfer) from CH₂ group of p-Benzylphenol can be very important for the pyrolysis, combustion and ignition processes. The values of $\Delta_r H^{\circ}_{298,15}((R_H)_i)$, $\Delta_r S^{\circ}_{298,15}((R_H)_i)$ and $\Delta_r G^{\circ}_{298,15}((R_H)_i)$ of the reactions of these components of the surrogate bio-oils, potentially important for the combustion chemistry, are presented in Table 11 (j = 1-18).

The measured value of $\Delta_{\rm f} H^{\rm o}_{298.15}$ (Dimethyl phthalate, TAB) = -606.1 [18] and the estimated value of $\Delta_{\rm f} H^{\rm o}_{298.15}$ (p-Benzylphenol)_{REACMEAN}(= -11.9±10 kJ/mol) are used for the determination of the values of $\Delta_{\rm r} H^{\rm o}_{298.15}$ ((R_H)_i), $\Delta_{\rm r} S^{\rm o}_{298.15}$ ((R_H)_i) and $\Delta_{\rm r} G^{\rm o}_{298.15}$ ((R_H)_i) of their reactions. The values of $\Delta_{\rm f} H^{\rm o}_{298.15}$ and $S^{\rm o}_{298.15}$ of radicals (NO, NO₂, HNO, HNO₂, NH₂, NH₃, NO₃, HNO₃, HO₂, H₂O₂, CH₃O₂ and CH₃O₂H), used for the calculations of the $\Delta_{\rm r} H^{\rm o}_{298.15}$ ((R_H)_j), $\Delta_{\rm r} S^{\rm o}_{298.15}$ ((R_H)_j) and $\Delta_{\rm r} G^{\rm o}_{298.15}$ ((R_H)_j), are taken from JANAF-NIST [48] and Burcat [37] databases.

Table 11. The values of $\Delta_{\rm r} H^{\rm o}_{298.15}(({\rm R_H})_{\rm j})$, $\Delta_{\rm r} S^{\rm o}_{298.15}(({\rm R_H})_{\rm j})$ and $\Delta_{\rm r} G^{\rm o}_{298.15}(({\rm R_H})_{\rm j})$ of reactions potentially important for the combustion chemistry and pyrolysis of the compounds of the considered surrogate bio-oil, determined using the tabulated (*SI*, *Note 1*) and calculated (Tables 5 and 7) values of $\Delta_{\rm f} H^{\rm o}_{298.15}$ and $S^{\rm o}_{298.15}$.

| j | Reactions $(R_H)_j$ | $\Delta_{\rm r} H^{\rm o}{}_{298.15}(({\rm R_H})_{\rm j}),{\rm kJ/mol}$ | $\Delta_{\rm r} S^{\rm o}{}_{298.15}($ |
|---|------------------------------------------------------------------|-------------------------------------------------------------------------|----------------------------------------|
| 1 | $CH_3 + C_6H_4((CO)OCH_3)_2 - CH_4 + CH_2O(CO)C_6H_4((CO)OCH_3)$ | -23.5 | -3.3 |

| j | Reactions $(R_H)_j$ | $\Delta_{\rm r} H^{\rm o}{}_{298.15}(({\rm R_H})_{\rm j}),{\rm kJ/mol}$ | $\Delta_{\rm r} S^{\rm o}{}_{298.15}$ |
|----|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|---------------------------------------|
| 2 | $NO_3 + C_6H_4((CO)OCH_3)_2 - HNO_3 + CH_3C_6H_3(O)CH_3$ | -8.5 | 18.4 |
| 3 | $OH + C_6H_4((CO)OCH_3)_2 - H_2O + CH_2O(CO)C_6H_4((CO)OCH_3)$ | -83.7 | 9.7 |
| 4 | $\mathrm{H} + \mathrm{C}_{6}\mathrm{H}_{4}((\mathrm{CO})\mathrm{OCH}_{3})_{2}$ - $\mathrm{H}_{2} + \mathrm{CH}_{2}\mathrm{O}(\mathrm{CO})\mathrm{C}_{6}\mathrm{H}_{4}((\mathrm{CO})\mathrm{OCH}_{3})$ | -20.9 | 20.6 |
| 5 | $NO_2 + C_6H_4((CO)OCH_3)_2 - HNO_2 + CH_2O(CO)C_6H_4((CO)OCH_3)$ | 87.7 | 14.0 |
| 6 | $\mathrm{NO} + \mathrm{C}_{6}\mathrm{H}_{4}((\mathrm{CO})\mathrm{OCH}_{3})_{2}$ - $\mathrm{HNO} + \mathrm{CH}_{2}\mathrm{O}(\mathrm{CO})\mathrm{C}_{6}\mathrm{H}_{4}((\mathrm{CO})\mathrm{OCH}_{3})$ | 206.4 | 14.0 |
| 7 | $\mathrm{NH}_2 + \mathrm{C}_6\mathrm{H}_4((\mathrm{CO})\mathrm{OCH}_3)_2$ - $\mathrm{NH}_3 + \mathrm{CH}_2\mathrm{O}(\mathrm{CO})\mathrm{C}_6\mathrm{H}_4((\mathrm{CO})\mathrm{OCH}_3)$ | -39.2 | 2.7 |
| 8 | $\mathrm{HO}_2 + \mathrm{C}_6\mathrm{H}_4((\mathrm{CO})\mathrm{OCH}_3)_2$ - $\mathrm{H}_2\mathrm{O}_2 + \mathrm{CH}_2\mathrm{O}(\mathrm{CO})\mathrm{C}_6\mathrm{H}_4((\mathrm{CO})\mathrm{OCH}_3)$ | 58.9 | 8.4 |
| 9 | $CH_3O_2 + C_6H_4((CO)OCH_3)_2 - CH_3O_2H + CH_2O(CO)C_6H_4((CO)OCH_3)$ | 58.5 | 20.9 |
| 10 | $\mathrm{CH}_3 + \mathrm{C}_6\mathrm{H}_5\mathrm{CH}_2\mathrm{C}_6\mathrm{H}_4\mathrm{OH}$ - $\mathrm{CH}_4 + \mathrm{C}_6\mathrm{H}_5\mathrm{CH}\mathrm{C}_6\mathrm{H}_4\mathrm{OH}$ | -102.9 | -12.3 |
| 11 | $\mathrm{NO}_3 + \mathrm{C}_6\mathrm{H}_5\mathrm{CH}_2\mathrm{C}_6\mathrm{H}_4\mathrm{OH}$ - $\mathrm{HNO}_3 + \mathrm{C}_6\mathrm{H}_5\mathrm{CHC}_6\mathrm{H}_4\mathrm{OH}$ | -87.9 | 9.4 |
| 12 | $OH + C_6H_5CH_2C_6H_4OH$ - $H_2O + C_6H_5CHC_6H_4OH$ | -163.1 | 0.7 |
| 13 | $\mathrm{H} + \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{C}\mathrm{H}_{2}\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{O}\mathrm{H}$ - $\mathrm{H}_{2} + \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{C}\mathrm{H}\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{O}\mathrm{H}$ | -100.3 | 11.6 |
| 14 | $NO_2 + C_6H_5CH_2C_6H_4OH$ - $HNO_2 + C_6H_5CHC_6H_4OH$ | 8.3 | 5.0 |
| 15 | $\mathrm{NO} + \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{CH}_{2}\mathrm{C}_{6}\mathrm{H}_{4}\mathrm{OH}$ - $\mathrm{HNO} + \mathrm{C}_{6}\mathrm{H}_{5}\mathrm{CHC}_{6}\mathrm{H}_{4}\mathrm{OH}$ | 127.0 | 5.6 |
| 16 | $\mathrm{NH}_2 + \mathrm{C}_6\mathrm{H}_5\mathrm{CH}_2\mathrm{C}_6\mathrm{H}_4\mathrm{OH}$ - $\mathrm{NH}_3 + \mathrm{C}_6\mathrm{H}_5\mathrm{CH}\mathrm{C}_6\mathrm{H}_4\mathrm{OH}$ | -118.6 | -6.3 |
| 17 | $\mathrm{HO}_2 + \mathrm{C}_6\mathrm{H}_5\mathrm{CH}_2\mathrm{C}_6\mathrm{H}_4\mathrm{OH}$ - $\mathrm{H}_2\mathrm{O}_2 + \mathrm{C}_6\mathrm{H}_5\mathrm{CHC}_6\mathrm{H}_4\mathrm{OH}$ | -20.5 | -0.6 |
| 18 | $\mathrm{CH}_3\mathrm{O}_2 + \mathrm{C}_6\mathrm{H}_5\mathrm{CH}_2\mathrm{C}_6\mathrm{H}_4\mathrm{OH} - \mathrm{CH}_3\mathrm{O}_2\mathrm{H} + \mathrm{C}_6\mathrm{H}_5\mathrm{CH}\mathrm{C}_6\mathrm{H}_4\mathrm{OH}$ | -20.9 | 11.9 |

As can be seen, the reactions of NO and NO₂ ((5), (6), (14) and (15)) with Dimethyl phthalate and p-Benzylphenol are not thermochemically favorable. At the same time, the reaction of NO₂ with p-Benzylphenol is only slightly endothermic, and rather should be considered as the thermoneutral. The slight exothermic effect, predicted for the reaction of NO₃ with Dimethyl phthalate (j = 2), must also be considered as an indication of thermoneutral reaction. However, the contribution of these reactions to the combustion or atmospheric chemistry must be insignificant, due to their undetectable gas phase concentration in the atmosphere and to their complete oxidation under combustion conditions at the moment of NO₂ or NO₃ formation. However, their heterogeneous reactions on the surface of atmospheric aerosols can be valuable. The last statement also corrects for the thermochemically favorable reactions (j = 1, 3, 4, 7, 10-13, 16-18), considered in the present work.

Moreover, the thermochemically favorable reactions are important for the determination of mechanisms of combustion of Dimethyl phthalate and p-Benzylphenol. Thus, the results of the present study indicate that both of these compounds can be oxidized by the H, OH, CH₃ and NH₂ radicals, formed during the ignition and combustion of fuels, contained them. The thermochemistry of these reactions is more favorable than those for the alkanes.

At the same time, the reactions with peroxy radicals (8) and (9), which are very important for the propagation of oxidation of Dimethyl phthalate, are not thermochemically favorable. However, the slightly lower values of $\Delta_r H \circ_{298.15}((R_H)_i)$ and $\Delta_r G \circ_{298.15}((R_H)_i)$ than those for the reaction of CH₃OO with CH₄, indicate that its addition to the alkane fuel must decrease the ignition delay and temperature of ignition, as well as increase the rate of combustion. The even higher effect on combustion, according to the results of the present study, is expected for the addition of p-Benzylphenol to the fuels. Thus, the reactions of HO₂ and CH₃O₂ with p-Benzylphenol are thermochemically favorable. As a results, the rate of propagation reactions must arising, as well as the temperature of ignition and ignition delay should decreasing, compared with both alkanes and Dimethyl phthalate fuels.

The reactions of $C_6H_5CHC_6H_4OH$ formation and decomposition are important not only for the combustion chemistry of fuels and for the heterogeneous processes in the atmosphere, but also for the conversion of lignine biomass to the bio-oil or others products. Thus, the p-Benzylphenol is the small piece of lignine that contains the main its functional groups. As a result, the detailed radical driven chemistry of its thermal decomposition can also be applied to the mechanism of thermal decomposition of lignines. The effect of the temperature on thermochemistry of these reactions is also estimated in the present work. However, it is found that this effect is not significant up to $T = 3000 \ K$, and qualitatively corresponds those results, demonstrated above for the standard conditions at $T = 298.15 \ K$.

4. CONCLUSIONS

In the present work, the structures of the most thermochemically stable radicals (1C, 1D and 3D), formed by the reactions of abstraction of H atom from Dimethyl phthalate and p-Benzylphenol, are determined. It is found that the most thermochemically favorable pathways for the reactions of abstraction of H atom are, respectively, formation OCH_2^* and CH^* groups.

The values of $\Delta_{\rm f} H^{\circ}_{298.15}(1{\rm C})_{\rm MEAN}$ and $\Delta_{\rm f} H^{\circ}_{298.15}(1{\rm D})_{\rm MEAN}$ of the most thermochemically stable products of H atom abstraction of Dimethyl phthalate and p-Benzylphenol, determined in the present study using the corrected thermochemistry of atomization reactions, correspond, respectively, to -406.1±3 (±3SE) and 114.1±5 (±3SE) kJ/mol. These values are consistent with those values, determined using the corrected thermochemistry of the homodesmotic reactions. Thus, nearly the same values of $\Delta_{\rm f} H^{\circ}_{298.15}(1{\rm C})_{\rm REACMEAN}$ = -405.7±5 (±3SE) kJ/mol and $\Delta_{\rm f} H^{\circ}_{298.15}(1{\rm D})_{\rm REACMEAN}$ = 114.7±0.4 (±3SE) are calculated. The values of $\Delta_{\rm f} H^{\circ}_{298.15}(1{\rm C})_{\rm MEAN}$ = -406.1±3 (±3SE) kJ/mol and $\Delta_{\rm f} H^{\circ}_{298.15}(1{\rm D})_{\rm REACMEAN}$ = 114.7±0.4 (±3SE) kJ/mol, demonstrated the lowest uncertainties ranges, are considered as the most consistent and reliable.

The contribution of other isomers to the integral values of thermochemical properties of these radicals, as well as to their IR spectra, is insignificant at room temperature. Thus, the values of $\Delta_{\rm f} H^{\circ}_{298.15}(5{\rm C})_{\rm MEAN}(=-348.4\pm3~(\pm3SE)~{\rm kJ/mol}), \Delta_{\rm f} H^{\circ}_{298.15}(3{\rm D})_{\rm MEAN}(=136.5\pm11~(\pm3SE)~{\rm kJ/mol})$ and $\Delta_{\rm f} H^{\circ}_{298.15}(4{\rm D})_{\rm MEAN}(=237.9\pm11~(\pm3SE)~{\rm kJ/mol})$, determined using the thermochemistry of atomization reactions, as well as their values of $\Delta_{\rm f} H^{\circ}_{298.15}(5{\rm C})_{\rm REACMEAN}(=-352.0\pm10~(\pm3SE)~{\rm kJ/mol}), \Delta_{\rm f} H^{\circ}_{298.15}(3{\rm D})_{\rm REACMEAN}(=135.8\pm5~(\pm3SE)~{\rm kJ/mol})$ and $\Delta_{\rm f} H^{\circ}_{298.15}(5{\rm C})_{\rm REACMEAN}(=-352.0\pm10~(\pm3SE)~{\rm kJ/mol}), \Delta_{\rm f} H^{\circ}_{298.15}(3{\rm D})_{\rm REACMEAN}(=135.8\pm5~(\pm3SE)~{\rm kJ/mol})$ and $\Delta_{\rm f} H^{\circ}_{298.15}(4{\rm D})_{\rm REACMEAN}(=241.4\pm10~(\pm3SE)~{\rm kJ/mol})$, calculated for these tautomers using the thermochemistry of homodesmotic reactions, are closest to those values of the most thermochemically stable radicals 1C and 1D, produced during the abstraction of H atom from Dimethyl phthalate and p-Benzylphenol. However, even in this case, the differences between their values of $\Delta_{\rm f} H^{\circ}_{298.15}(1{\rm C})_{\rm MEAN}$ and $\Delta_{\rm f} H^{\circ}_{298.15}(1{\rm D})_{\rm REACMEAN}$ and the corresponded them values of $\Delta_{\rm f} H^{\circ}_{298.15}(1{\rm C})_{\rm MEAN}$ and $\Delta_{\rm f} H^{\circ}_{298.15}(1{\rm D})_{\rm REACMEAN}$ and the corresponded them values of $\Delta_{\rm f} H^{\circ}_{298.15}(1{\rm C})_{\rm MEAN}$ and $\Delta_{\rm f} H^{\circ}_{298.15}(1{\rm D})_{\rm REACMEAN}$ are respectively, equal to 57.7 (54.1), 21.8 (21.1) and 123.2 (126.7)~{\rm kJ/mol}. These values are significantly larger than the difference between their values of entropies that don't exceeding 19~{\rm J/(mol~K)}~(19\times0.29815=5.7~{\rm kJ/mol}) at T=298.15~K. At the same time, the importance of contribution of 3D structure to the distribution of isomers arises with the temperature, and became significant at temperatures above 2000 K .

The significant differences between the values of $S^{\circ}_{298.15}(Y)$, calculated using the B3LYP, M06-2X and CBS-4M approaches, are not observed. Since, the contribution of the internal rotations to the values of $S^{\circ}_{298.15}$ is not calculated in the present study then the CBS-4M values of $S^{\circ}_{298.15}(1C, CORR) = 505.5\pm16$ ($\pm 2SE$) J/(mol K) and $S^{\circ}_{298.15}(1D, CORR) = 460.6\pm16$ ($\pm 2SE$) J/(mol K), determined using the correction dependencies [17], are recommended as the most accurate of calculated.

The temperature dependencies of thermochemical properties of considered compounds, calculated using the scaled B3LYP vibration frequencies, indicate that the structure 1D is the most thermochemically favorable product of H atom abstraction from p-Benzylphenol at temperatures below 2000 K, while, the 3D structure is the most thermochemically stable for the temperatures above this value.

Analysis of the thermochemistry of reactions of H atom abstraction from Dimethyl phthalate and p-Benzylphenol by the different radicals, formed during the pyrolysis of lignine, combustion of fossil fuels as well as produced in the atmosphere, indicate the high potential importance of reactions of p-Benzylphenol on the combustion and biomass pyrolysis, as well as their possible contribution to the atmospheric chemistry. In the last case, the contribution of these reactions on the heterogeneous chemistry of the atmospheric aerosols, contained lignine or its derivative, is assumed.

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