

Structure, Intramolecular Rotation Barrier, and Thermochemical Properties of Hydroxycyclohexadienyl Radical

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Ab initio and density functional calculations are used to study the structures and thermochemical properties, $\Delta H_f^0(T)$, $S^0(T)$, and $C_p(T)$ ($100 \leq T/K \leq 5000$), of the benzene-OH adduct (hydroxycyclohexadienyl, *CHD*-OH). Molecular structures and vibrational frequencies were determined at the B3LYP/6-31G(d,p) and MP2(full)/6-31G(d) levels. Energy calculations were performed at the G3, CBS-Q, CBS-QB3, G3(MP2)//B3LYP/6-31G(d,p), CBS-Q//B3LYP/6-31G(d,p), G3(MP2)//MP2(full)/6-31G(d), and CBS-Q//MP2(full)/6-31G(d) levels. Enthalpies of formation (ΔH_{f298}^0) were determined at each calculation level using group balance isodesmic reactions. The new value of $\Delta H_{f298}^0(\text{OH}) = 8.96 \text{ kcal mol}^{-1}$ was used in this study. Standard entropy, $S^0(T)$, and heat capacity, $C_p(T)$, from vibrational, translational, and external rotation contributions were calculated using statistical mechanics based on the vibration frequencies and structures. Hindered rotational contributions to $S^0(T)$ and $C_p(T)$ were calculated from the energy levels of the internal rotational potential calculated at the B3LYP/6-31G(d,p) level. The anomeric effect where the lone pair on oxygen is hyperconjugated with the antibonding orbital of adjacent C–C bonds is found to stabilize the *CHD*-OH in the lowest energy conformation. This hyperconjugation increases the barrier of the OH rotor and leads to a lower entropy value of *CHD*-OH from our previous estimation. Evaluations of data from the isodesmic reaction at each calculation level results in the enthalpy of formation of *CHD*-OH in a range of 10.76 [G3MP2//MP2(full)/6-31G(d)] to 9.92 [CBS-Q//B3LYP/6-31G(d,p)] kcal mol⁻¹ at 298 K. The reaction energy (ΔH_{r298}^0) of $\text{C}_6\text{H}_6 + \text{OH} \leftrightarrow \text{CHD-OH}$ (1) was determined to be $-18.38 \text{ kcal mol}^{-1}$ in good agreement with literature values that range from -19.9 ± 1.2 to $-16.5 \text{ kcal mol}^{-1}$. Entropy (S_{298}^0) of *CHD*-OH was estimated as $79.24 \text{ cal mol}^{-1} \text{ K}^{-1}$, $3.5 \text{ cal mol}^{-1} \text{ K}^{-1}$ lower than our previous value of $82.7 \text{ cal mol}^{-1} \text{ K}^{-1}$. The reaction entropy ΔS_{r298}^0 was calculated as $-29.01 \text{ cal mol}^{-1} \text{ K}^{-1}$ about $4.6 \text{ cal mol}^{-1} \text{ K}^{-1}$ higher than literature value of $-33.6 \pm 2.6 \text{ cal mol}^{-1} \text{ K}^{-1}$. The rate constant for *CHD*-OH adduct dissociation to $\text{C}_6\text{H}_6 + \text{OH}$ was calculated and compared to literature data.

Introduction

The atmospheric decomposition of benzene and other aromatics is primarily initiated through the addition of OH radical to the aromatic ring



The entropy and enthalpy of the benzene-OH adduct (hydroxycyclohexadienyl, *CHD*-OH) are needed to determine the equilibrium constant of reaction 1 and the dissociation rate constant of *CHD*-OH to benzene + OH. Lin, Kuo, and Lee (LKL)¹ estimated the entropy change $\Delta S_{r298}^0 = -33.6 \pm 2.6 \text{ cal mol}^{-1} \text{ K}^{-1}$ (e.u.), for reaction 1. Adopting $S_{298}^0(\text{C}_6\text{H}_6) = 64.37 \text{ e.u.}^2$ and $S_{298}^0(\text{OH}) = 43.88 \text{ e.u.}^3$, $S_{298}^0(\text{CHD-OH})$ was calculated as 74.65 e.u. This value is about 10 e.u. lower than the value we estimated using group additivity and near free rotor simulation that of hydroxycyclohexadienyl: $S_{298}^0(\text{CHD-OH}) = 84.11 \text{ e.u.}^4$

The well depth of benzene + OH addition was experimentally determined by LKL¹ to be $-19.9 \pm 1.2 \text{ kcal mol}^{-1}$. Witte et al.⁵ also reported an experimental value for OH + benzene addition: $-16.5 \text{ kcal mol}^{-1}$, which is about $3.5 \text{ kcal mol}^{-1}$

different from the value reported by LKL. A recent theoretical study by Tokmakov et al.⁶ determined the $\Delta H_{r298}^0 = -18.1 \pm 3 \text{ kcal mol}^{-1}$ and $\Delta S_{r298}^0 = -29.0 \text{ cal mol}^{-1} \text{ K}^{-1}$.

Bartolotti and Edney⁷ performed a series of density functional theory (DFT) based quantum mechanical calculations using the DMol computer program for the reactions of OH addition to toluene. The calculations were performed using Vosko–Wilk–Nusair local exchange correlation functional and extended basis set (3 s-like plus 2p-like functions for H, 4s + 4p + 2d for carbon, and 4s + 4p + 3d + 2f for oxygen). The reaction energies of OH addition to toluene were calculated to be -43.48 , -41.36 , and $-42.0 \text{ kcal mol}^{-1}$ for the ortho, meta, and para positions, respectively, more than 20 kcal mol^{-1} deeper than value of experiment or group additivity estimation. The well depths of the addition reactions were, however, calculated to be only 16.8 – $18.4 \text{ kcal mol}^{-1}$ by Andino et al.⁸ using the B3LYP/6-31G(d)//PM3(UHF) method. We predicted the well depth of OH addition to the aromatic ring to be ca. 19 kcal mol^{-1} using group additivity and the HBI method⁴ which is close to the values reported by Andino et al.⁸ In studies on toluene, Uc et al.⁹ analyzed the critical points of the potential energy surface and determined the rate-equilibrium relationships for the OH addition at the ortho, meta, para, and ipso positions using the Møller–Plesset perturbation theory and the B3LYP density functional theory. The reaction energies were -19.03 ,

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−17.13, −17.37, and −19.65 kcal mol^{−1} from PMP2/6-31G(d,p) and −20.91, −19.21, −19.83, and −19.47 kcal mol^{−1} from B3LYP/6-31G(d,p) for the ortho, meta, para, and ipso positions, respectively. Suh et al.¹⁰ reported the $\Delta H_{298}^0 = -17.56$, −16.04, −16.71, and −16.33 at B3LYP/6-31G(d,p) for the ortho, meta, para, and ipso positions, respectively. The experimental value for ΔH_{298}^0 of toluene + OH \leftrightarrow toluene-OH reported by Perry et al.¹¹ is -16.5 ± 5 kcal mol^{−1}.

The values of thermodynamic parameters are important for evaluating reaction paths and kinetic processes of benzene + OH reactions followed by the addition of O₂ in the atmosphere environment. Enthalpy and entropy values are essential in the determination of equilibrium constants (K_{eq}) and, consequently, the ratio of forward and reverse reaction constants (k_f/k_r). We therefore perform high level ab initio calculations to determine the $\Delta H_f^0(T)$, $S^0(T)$ and $C_p(T)$ ($100 \leq T/K \leq 5000$) values for *CHD*-OH.

Computational Method

All of the density functional and ab initio calculations were performed using the Gaussian 94 and Gaussian 98 program suites.¹² The geometry optimization, harmonic vibration frequencies and zero-point vibrational energies (ZPVE) were computed with the B3LYP/6-31G(d,p) and MP2(full)/6-31G(d) levels of theory. The G3(MP2)¹³ method and complete basis set (CBS-Q)^{14,15} model chemistry based on MP2(full)/6-31G(d) and B3LYP/6-31G(d,p) geometries were used for energy calculations.

We made two modifications in our CBS-Q calculations. First, the geometries were obtained at the B3LYP/6-31G(d,p) and MP2(full)/6-31G(d) levels instead of MP2(FC)/6-31G'. Second, the zero-point energies were obtained at the B3LYP/6-31G(d,p) and MP2(full)/6-31G(d) levels and scaled by 0.9806 and 0.9661, respectively, as recommended by Scott et al.¹⁶ These calculations are referred to as CBSQ/B3LYP/6-31G(d,p) and CBSQ//MP2/6-31G(d,p).

We also modified G3(MP2) theory using the geometries and the zero-point energies obtained at B3LYP/6-31G(d,p) and MP2(full)/6-31G(d) levels. These calculations are referred to as G3(MP2)//B3LYP/6-31G(d,p) and G3(MP2)//MP2(full)/6-31G(d). Two single-point energy calculations are carried out at the QCISD(T)/6-31G(d) and MP2/G3MP2large levels.

The standard composite G3,¹⁷ CBS-Q,^{14,15} and CBS-QB3¹⁸ methods were also performed in this work.

Entropies and heat capacities at temperature range from 100 to 5000 K were calculated using the rigid-rotor-harmonic-oscillator approximation based on scaled vibrational frequencies, molecular mass, and moments of inertia of the optimized B3LYP/6-31G(d, p) and MP2(full)/6-31G(d) structures. Contributions from hindered rotors to $S^0(T)$'s and $C_p(T)$'s were determined by direct integration over energy levels of the calculated intramolecular rotation potential energy curves.^{19,20} The number of optical isomers and spin degeneracy of unpaired electrons were also incorporated for calculation of $S^0(T)$'s and $C_p(T)$'s.

The potential energy as function of the dihedral angle is performed by varying the torsion angle in 30° intervals and allowing other parameters to be optimized. The minima and maxima conformers on the torsion potential are fully optimized at the B3LYP/6-31G(d,p) level. The geometries and harmonic vibrational frequencies were also calculated for all rotational conformers at the same level. A Fourier series was used to represent the potential calculated at discrete torsional angles:

$$V(\Phi) = a_0 + a_n \cos(n\Phi) + b_n \sin(n\Phi), \\ n = 1, 2, 3, \dots \quad (\text{F1})$$

Results and Discussion

The optimized geometries, vibrational frequencies and moments of inertia calculated at B3LYP/6-31G(d, p) and MP2(full)/6-31G(d) levels for *CHD*-OH are listed in Table 1. The DFT and MP2 optimized structures of *CHD*-OH both show a slightly longer bond length of 1.419 Å (1.417 Å) for C4–C3 and C5–C4 bonds and a lightly shorter bond length of 1.367 Å (1.343 Å) for C3–C1 and C6–C5 bonds whereas compared to the C–C bond length of 1.396 Å (1.395 Å) in benzene. The torsion frequency is omitted in calculation of entropy $S^0(T)$ and heat capacities $C_p(T)$; we replace its contributions with that from internal rotation analysis (discussed below). The torsion frequencies (396.55 cm^{−1} in MP2 and 377.77 cm^{−1} in B3LYP) are identified by examining the vibrational motion using Gauss View 2.1.²¹ Total energies calculated at various levels are listed in Table 2 along with zero-point vibrational energies (ZPVE) and thermal corrections to 298.15K (HT₂₉₈). Isodesmic reaction enthalpies ($\Delta H_{rxn,298}^0$), enthalpies of formation ($\Delta H_{f,298}^0$) and the uncertainties of reference species from literature that are used to determined $\Delta H_{f,298}^0$ of the *CHD*-OH adduct are listed in Table 3. $\Delta H_f^0(T)$, $S^0(T)$ and $C_p(T)$'s calculation results at temperature range from 100 to 5000 K are summarized in Table 4. TVR, represent the sum of the contributions from translations, external rotations and vibrations for $S^0(T)$ and $C_p(T)$'s. I.R., represent the contributions from internal rotations for $S^0(T)$ and $C_p(T)$'s.

Entropy. The rotation potential energies as function of the dihedral angle of $\angle H_{14}O_{13}C_2H_8$ are shown in Figure 1. One conformer (anti) lies ca. 3.6 kcal mol^{−1} below all other structures. The internal rotation barriers calculated from the differences between the total energy of each conformer and anti conformer are shown as circle points (in Figure 1). The total energies where the ZPVE and the thermal correction to 298 K (HT₂₉₈) included, are shown as triangles. The OH group torsion frequency in each rotational conformer is omitted in calculation of ZPVE and HT₂₉₈. Sum of $\Delta ZPVE$ (ZPVE difference between anti conformer and other conformers) and ΔHT_{298} (HT₂₉₈ difference between anti conformer and other conformers) are 0.11 (for eclipse-H conformer), 0.16 (for gauche conformer), and 0.12 kcal mol^{−1} (for eclipse-C conformer). Rotation barrier includes ZPVE and HT results in higher S^0 and C_p ; the differences are within 0.15 e.u. at temperature range from 100 to 5000 K.

Table 5 lists the dipole moments and energy difference of the conformers at the B3LYP/6-31G(d,p) level, where the maximum barrier calculated is 3.43 kcal mol^{−1}. A comparable barrier to rotation about the C–O bond in *iso*-propyl alcohol, (CH₃)₂CH–OH, was calculated to be 1.15 kcal mol^{−1}.²² This implies that the lone pair on the oxygen in *CHD*-OH is hyperconjugated with the antibonding orbital of adjacent C–C bonds, to an extent of about 2 kcal mol^{−1}. The highest dipole moment corresponds to the most stable conformer (anti) with the hyperconjugation. The maxima in the dipole moment also suggests that this conformer is withdrawing the most electrons from the ring, relative to the other conformers. Figure 2 shows the molecular orbital for the anti-conformer $\angle H_{14}O_{13}C_2H_8 = 180^\circ$ (Figure 2, parts a and b) and eclipse conformer $\angle H_{14}O_{13}C_2H_8 = 261.3^\circ$ (Figure 2, parts c and d). Comparison of the highest occupied orbitals (HOMO) in these two conformers (Figure 2, parts a and c) shows that more electrons are in the ring HOMO for the anti than in the eclipse conformer. An interaction between the H₁₄ atom of hydroxyl group and the C₆ p orbital is also observed. The HOMO-2 of the anti-conformer

TABLE 1: Geometric Parameters, Vibration Frequencies (cm^{-1}), and Moments of Inertia (amu Bohr^2)

<i>CHD-OH</i>								
bond length	DFT	MP2	bond angle	DFT	MP2	dihedral angle	DFT	MP2
C2–C1 (=C6–C2)	1.5032	1.4964	$\angle\text{C3C1C2}$ (= $\angle\text{C5C6C2}$)	122.51	122.63	$\angle\text{C4C3C1C2}$ $\angle\text{C5C4C3C1}$	359.34 0.95	357.67 1.72
C3–C1 (=C6–C5)	1.3672	1.3433	$\angle\text{C4C3C1}$ (= $\angle\text{C6C5C4}$)	121.17	121.17	$\angle\text{C6C5C4C3}$ $\angle\text{H7C1C2C3}$	359.05 178.50	358.28 177.05
C4–C3 (=C5–C4)	1.4186	1.4166	$\angle\text{C5C4C3}$ $\angle\text{C6C2C1}$	119.77 112.9	119.54 112.8	(= $\angle\text{H11C6C2C5}$) $\angle\text{H8C2C1C3}$	122.27	125.66
H7–C1 (=H11–C6)	1.0864	1.0861	$\angle\text{H7C1C2}$ (= $\angle\text{H11C6C2}$)	116.35	116.11	$\angle\text{H9C3C1C2}$ (= $\angle\text{H12C5C6C2}$)	178.87	178.28
H8–C2	1.1025	1.0994	$\angle\text{H8C2C1}$	109.35	109.90	$\angle\text{H10C4C3}$	179.81	180.05
H9–C3 (=H12–C5)	1.0871	1.0868	$\angle\text{H9C3C1}$ (= $\angle\text{H12C5C6}$)	119.73	119.97	$\angle\text{O13C2C1C3}$ $\angle\text{H14O13C2C1}$	234.51 63.36	238.24 62.83
H10–C4	1.0850	1.0842	$\angle\text{H10C4C3}$	120.11	120.22			
O13–C2	1.4481	1.4468	$\angle\text{O13C2C1}$	111.23	110.58			
H14–O13	0.9683	0.9748	$\angle\text{H14O13C2}$	106.06	105.29			
moments of inertia			frequencies					
B3LYP			106.05, 284.70, 399.57, 441.61, 533.57, 582.96, 620.36, 705.58, 756.80,					
373.36, 686.22, 976.29			808.55, 864.18, 952.59, 965.85, 976.27, 997.09, 1028.77, 1033.54,					
			1127.66, 1170.07, 1195.37, 1229.80, 1318.43, 1361.06, 1398.41, 1417.21,					
			1459.06, 1555.51, 1608.84, 2974.31, 3171.75, 3174.61, 3194.69, 3195.55,					
			3209.65, 3781.19					
MP2			101.38, 294.57, 392.67, 471.29, 543.43, 589.67, 633.71, 707.48, 816.02,					
374.51, 668.30, 952.45			826.39, 913.40, 993.15, 1021.63, 1023.39, 1032.19, 1066.08, 1084.31,					
			1111.33, 1210.76, 1242.31, 1272.23, 1310.49, 1399.34, 1436.38, 1451.56,					
			1498.41, 1641.99, 1681.08, 3073.03, 3236.00, 3238.49, 3258.77, 3259.81,					
			3275.18, 3734.65					

TABLE 2: Total Energies, Zero-Point Energies (ZPVE, unscaled), and Thermal Corrections to Enthalpies at 298 K (HT_{298})

	G3	CBS-Q	CBS-QB3	B3LYP/6-31G(d,p)		MP2(full)/6-31G(d)	
				G3MP2	CBS-Q	G3MP2	CBS-Q
CHD-OH	-307.7670691	-307.4623050	-307.4611397	-307.4979771	-307.4618662	-307.4960666	-307.4592737
ZPVE ^a	0.1207060	0.1201150	0.1135450	0.113861		0.116731	
HT_{298} ^b	0.0068170	0.0068450	0.0070480	0.0070600		0.0069190	
cyclohexadienyl	-232.5816929	-232.3191406	-232.3180365	-232.3542966	-232.3179022	-232.3522901	-232.3156649
ZPVE ^c	0.1148320	0.1141680	0.1082950	0.108793		0.111782	
HT_{298}	0.0058830	0.0059030	0.0060170	0.0059980		0.0059300	
CCC	-118.9885855	-118.8494082	-118.8503662	-118.8765738	-118.8486660	-118.8752160	-118.8473865
ZPVE ^c	0.1105820	0.1100240	0.1029850	0.103698		0.10682	
HT_{298}	0.0053070	0.0053160	0.0054920	0.0054730		0.0053720	
C ₂ COH	-194.1759136	-193.9940491	-193.9954847	-194.0224138	-193.9937353	-194.0214412	-193.9928037
ZPVE ^c	0.1159520	0.1154340	0.1076990	0.1082580		0.1110400	
HT_{298}	0.0061320	0.0061530	0.0063660	0.0063550		0.0062310	

^a In the calculation of reaction enthalpies, ZPVE are scaled by 0.8929, 0.91844, 0.99, 0.9661, and 0.9806 for G3, CBS-Q, CBS-QB3, and MP2(full)/6-31G(d) and B3LYP/6-31G(d,p) levels, respectively. ^b Thermal corrections are calculated as follows for $T = 298.15$ K: $H_{\text{T}}^0 - H_0^0 = H_{\text{trans}}(T) + H_{\text{rot}}(T) + \Delta H_{\text{vib}}(T) + RT$; $H_{\text{trans}}(T) = (3/2)RT$, $H_{\text{rot}}(T) = (3/2)RT$, $\Delta H_{\text{vib}}(T) = N_{\text{A}}h\sum v_i/(\exp(hv_i/kT) - 1)$, where N_{A} is the Avogadro constant, h is the Planck constant, k is the Boltzmann constant, and v_i is vibrational frequency. The frequencies are not scaled in calculation of the vibration component of the thermal contribution to enthalpy.

(Figure 2b) shows delocalization between the oxygen lone pair with the C₁–C₂ and C₆–C₂ antibonding orbitals. The entropy contribution from the hindered internal rotation is determined to be 1.75 e.u. at 298 K.

The anti conformer has minimum energy and was used to determine S_{298}^0 (external-rotation) = 27.02 e.u. from the B3LYP moments of inertia (26.97 e.u. from MP2). The symmetry

number of the adduct is assigned as 1 (in 180° rotation, the H atom and OH group on the sp³ carbon are reversed). The S_{298}^0 contribution from vibration is determined to be 9.86 e.u. from B3LYP frequencies (9.24 e.u. from MP2), where DFT and MP2 frequencies are scaled by 1.0015 and 1.0228, respectively, as recommended by Scott et al.¹⁵ The torsion frequency, 377.77 cm^{-1} in B3LYP (396.55 cm^{-1} in MP2), is excluded. Translation

TABLE 3: Isodesmic Reaction Enthalpies, Enthalpies of Formation of *CHD*-OH and Reaction Enthalpies of Reaction 1 at Various Calculation Levels^a

level of theory	G3	CBS-Q	CBS-QB3	//B3LYP/6-31G(d,p)		//MP2(full)/6-31G(d)		avg.
				G3MP2	CBS-Q	G3MP2	CBS-Q	
	11.25	13.16	13.23	10.67	12.60	9.93	11.68	
	-1.22	-0.93	-0.96	-1.36	-0.69	-1.54	-1.13	
	10.03	12.23	12.27	9.31	11.91	8.39	10.55	
	49.81	47.91	47.83	50.39	48.46	51.13	49.38	49.27
	10.45	10.15	10.19	10.58	9.92	10.76	10.36	10.34
	-18.32	-18.62	-18.59	-18.19	-18.85	-18.01	-18.41	-18.38

^a Literature data: $\Delta H_{f,298}^0$ of $(C_3H_8) = -25.02 \pm 0.12$ kcal/mol (ref 30); $(C_2COH) = -65.07 \pm 0.22$ kcal/mol (ref 31); $(1,4\text{-cyclohexadiene}) = 25.04 \pm 0.14$ kcal/mol (ref 32 and ref 33).

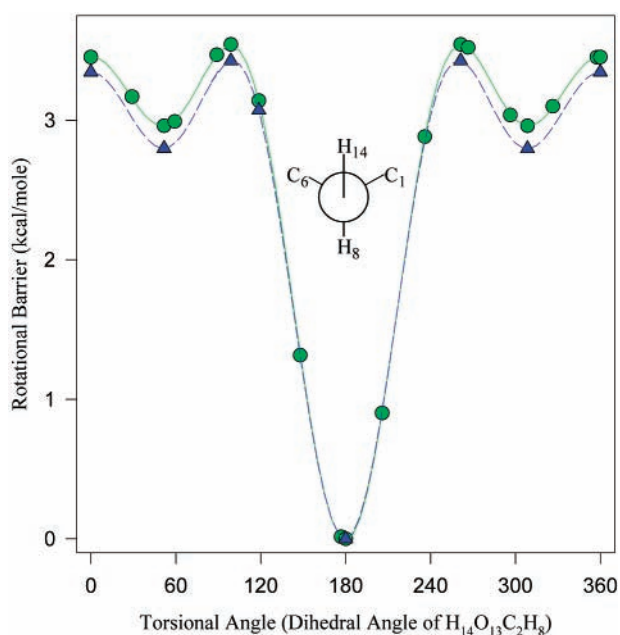


Figure 1. Potential barriers for internal rotations about -OH group in *CHD*-OH. Points are calculated values at B3LYP/6-31G(d) level of theory (triangles: include zero-point vibration energy (ZPVE) and thermal correction to 298 K (HT₂₉₈); circles: omit calculation of ZPVE and HT₂₉₈). Lines are results of Fourier expansion equation, F1.

contribution to entropy, S_{298}^0 (translation), is calculated to be 39.57 e.u. The optical isomer number is assigned as 1, as the structure is symmetric about the C(C2)(H)(OH) carbon. The degeneracy of electronic spin is assigned as 2, which contributes $R \ln 2 = 1.38$ e.u. for $S^0(\text{spin})$. S_{298}^0 (*CHD*-OH) is therefore determined as

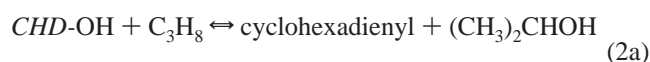
$$\begin{aligned}
 S_{298}^0(\text{CHD-OH}) &= S^0(\text{translation}) + S^0(\text{external-rotation}) + S^0(\text{vibration}) + \\
 &\quad S^0(\text{hindered-internal-rotation}) + S^0(\text{electron-spin}) \\
 &= 39.567 + 26.993 + 9.551 + 1.750 + 1.377 \\
 &= 79.24 \text{ (e.u.)}
 \end{aligned}$$

S_{298}^0 (*CHD*-OH) = 79.24 e.u. is 4.6 e.u. higher than estimated by LKL and about 4.9 e.u. lower than our previous estimate, which was obtained using the group additivity method

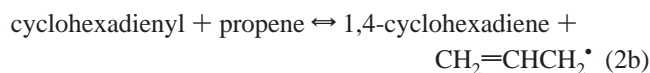
with the assumption that the number of optical isomer (OI) equals to 2. This assumption is not appropriate because the molecular orbital calculations indicate that the two carbons that are adjacent to the C(C2)(H)(OH) group are identical. The remaining difference from our use of group additivity and the current method on the determination of S_{298}^0 (*CHD*-OH) is about 3.5 e.u. (GA is higher). This difference of 3.5 e.u. is due to the high barrier for the internal rotor. The barrier we calculated is 3.43 kcal mol⁻¹ higher than the value of 1.1 kcal mol⁻¹ in typical alcohols.²³

The ΔS_{r298}^0 of reaction 1 is determined to be -29.01 e.u., which is ca. 4.4 e.u. different from the value reported by LKL: -33.4 ± 2.5 e.u. This difference represents about a factor of $\exp(4.4 \text{ cal mol}^{-1}/R) = 9.2$ in the Arrhenius preexponential factor of the reverse (dissociation) of the adduct to OH + benzene.

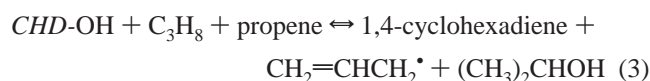
Enthalpy of Formation and Equilibrium Constant. Enthalpy of formation of the *CHD*-OH adduct is determined by the isodesmic reaction 2a



The value of ΔH_{f298}^0 (cyclohexadienyl) = 49.27 kcal/mol used in the isodesmic reaction 2a is calculated from the average values of G3, CBS-Q, CBS-QB3, G3(MP2)//B3LYP/6-31G(d,p), CBSQ//B3LYP/6-31G(d,p), G3(MP2)//MP2(full)/6-31G(d), and CBSQ//MP2(full)/6-31G(d) along with isodesmic reaction 2b and bond dissociation enthalpies of ΔH_{298}^0 of $(C=CC-H) = 88.12$ kcal/mol. Values are illustrated in Table 3



The sum of reactions 2a and 2b is reaction 3 and, because the calculations for species in reactions 2a and 2b are at the same levels the actual reaction used for determining ΔH_{f298}^0 (*CHD*-OH) is reaction 3



ΔH_{f298}^0 values for (*CHD*-OH) are calculated as 10.45, 10.15, 10.19, 10.58, 9.92, 10.76, and 10.36 kcal mol⁻¹ at the G3, CBS-

TABLE 4: Ideal Gas-Phase Thermodynamic Properties of $CHD-OH - \Delta H_f^0(T),^a S^0(T),^b$ and $C_p(T)^b$ ($100 \leq T/K \leq 5000$)^c

T (K)	$S^{0,c,e,f}$ (TVR)	$C_p^{c,e,f}$ (TVR)	S^0 (I. R.) ^d	C_p (I. R.) ^d	$H_T^0 - H_{298}^{0,f,g}$	$H_T^0 - H_{298}^0$ $OC(s)^{g,h}$	$H_T^0 - H_{298}^0$ $OH_{2(g)}^{g,h}$	$H_T^0 - H_{298}^0$ $OO_{2(g)}^{g,h}$	$\Delta H_f^0(T)^i$	$S^0(T)$	$C_p(T)$
100	60.83	10.61	0.10	0.40	-3.28	-0.24	-1.27	-1.38	13.65	60.93	11.02
200	69.69	16.28	0.78	1.76	-1.96	-0.16	-0.66	-0.69	12.05	70.47	18.05
298.1	77.49	23.90	1.75	3.11	0.00	0	0	0	10.39	79.24	27.00
300	77.63	24.05	1.77	3.13	0.04	0.00	0.01	0.01	10.36	79.40	27.17
400	85.55	31.85	2.76	3.61	2.85	0.25	0.71	0.72	8.90	88.31	35.46
500	93.31	38.51	3.55	3.40	6.37	0.57	1.41	1.46	7.70	96.86	41.91
600	100.76	43.89	4.13	2.98	10.50	0.95	2.11	2.21	6.74	104.90	46.87
700	107.81	48.24	4.56	2.57	15.12	1.37	2.80	2.99	5.97	112.38	50.81
800	114.45	51.81	4.88	2.25	20.12	1.83	3.51	3.77	5.35	119.33	54.05
900	120.69	54.80	5.13	1.99	25.46	2.32	4.23	4.6	4.85	125.83	56.79
1000	126.57	57.34	5.33	1.80	31.07	2.82	4.94	5.43	4.50	131.90	59.14
1100	132.12	59.52	5.50	1.66	36.92	3.35	5.67	6.27	4.25	137.61	61.18
1200	137.35	61.40	5.64	1.54	42.96	3.88	6.40	7.11	4.08	142.99	62.94
1300	142.31	63.03	5.76	1.46	49.19	4.43	7.14	7.97	4.00	148.07	64.49
1400	147.02	64.45	5.86	1.39	55.56	4.99	7.90	8.84	3.95	152.88	65.84
1500	151.50	65.69	5.96	1.33	62.07	5.55	8.67	9.71	3.96	157.45	67.02
1600	155.76	66.78	6.04	1.29	68.70	6.12	9.45	10.58	4.00	161.80	68.06
1700	159.82	67.73	6.12	1.25	75.42	6.70	10.23	11.47	4.09	165.94	68.98
1800	163.71	68.57	6.19	1.22	82.24	7.28	11.03	12.35	4.20	169.90	69.79
1900	167.43	69.32	6.25	1.20	89.13	7.86	11.84	13.25	4.33	173.68	70.51
2000	170.99	69.98	6.31	1.17	96.10	8.44	12.65	14.15	4.48	177.30	71.15
2500	186.86	72.37	6.57	1.10	131.74	11.40	16.85	18.73	5.38	193.42	73.47
3000	200.17	73.80	6.76	1.07	168.31	14.41	21.21	23.45	6.27	206.94	74.87
3500	211.61	74.72	6.93	1.05	205.45	17.46	25.70	28.28	6.99	218.54	75.77
4000	221.62	75.34	7.07	1.03	242.98	20.55	30.32	33.20	7.38	228.69	76.37
4500	230.52	75.77	7.19	1.02	280.76	23.67	35.04	38.20	7.36	237.70	76.80
5000	238.51	76.09	7.30	1.02	318.73	26.85	39.87	43.26	6.88	245.81	77.11

^a Units in kcal mol⁻¹; average values of that are calculated at various levels in this study and include statistical distribution of rotation conformers.

^b Units in cal mol⁻¹ K⁻¹. ^c The sum of contributions from translations, external rotations, and vibrations. ^d Contribution from internal rotations.

^e Symmetry and spin degeneracy of unpaired electrons are taken into account. ^f Based on B3LYP/6-31G(d,p) and MP2(full)/6-31G(d) levels. ^g $H_T^0 - H_{298}^0$: the difference between the enthalpy at temperature T and 298 K. ^h Reference 3. ⁱ $\Delta H_f^0(T) = \Delta H_f^0(298) + [H_T^0 - H_{298}^0](\text{compound}) - \sum [H_T^0 - H_{298}^0](\text{elements})$.

TABLE 5: Dipole Moments and Energy Difference of the Conformers at B3LYP/6-31G(d,p) Level

torsion angle $\angle H_{14}O_{13}C_2H_8$	dipole moments (Debye)	relative energies ^a ΔE (kcal mole ⁻¹)
-0.1	1.62	3.34
51.7	1.54	2.80
98.8	1.60	3.43
180.0	1.65	0.00
261.3	1.60	3.43
308.5	1.54	2.80
359.9	1.62	3.34

^a Relative energy were calculated as the difference in total energies + scaled (0.9806) zero-point vibrational energies + thermal correction to 298 K, where the corresponding torsional frequencies are excluded in the calculation of ZPVE and thermal correction.

Q, CBS-QB3, G3MP2//B3LYP/6-31G(d,p), CBS-Q//B3LYP/6-31G(d,p), G3MP2//MP2(full)/6-31G(d), and CBS-Q//MP2(full)/6-31G(d) levels of theory, respectively, see Table 3. The computed reaction energies of OH addition to benzene range from -18.01 (G3MP2//MP2(full)/6-31G(d)) to -18.85 (CBS-Q//B3LYP/6-31G(d,p)) kcal mol⁻¹; these can be compared to an estimated value of -19.13 kcal mol⁻¹ in our previous study.⁴ The values calculated in this work are also close to values determined by Perry et al.,¹¹ $\Delta H_{r298}^0 = -18.4 \pm 3$ kcal mol⁻¹, Lorenz et al.,²⁴ $\Delta H_{r298}^0 = -18.4 \pm 1.4$ kcal mol⁻¹, and a value reported by LKL, $\Delta H_{r298}^0 = -19.9 \pm 1.2$ kcal mol⁻¹.

Using $\Delta H_{r298}^0(1) = -18.38$ kcal mol⁻¹ and $\Delta S_{r298}^0(1) = -29.01$ e.u., the Gibbs energy change, ΔG_{r298}^0 for reaction 1 is determined to be -9.74 kcal mol⁻¹, which is 0.22 kcal mol⁻¹ different from LKLs value of -9.95 kcal mol⁻¹. The equilibrium constant calculated using these two sets of data are different by

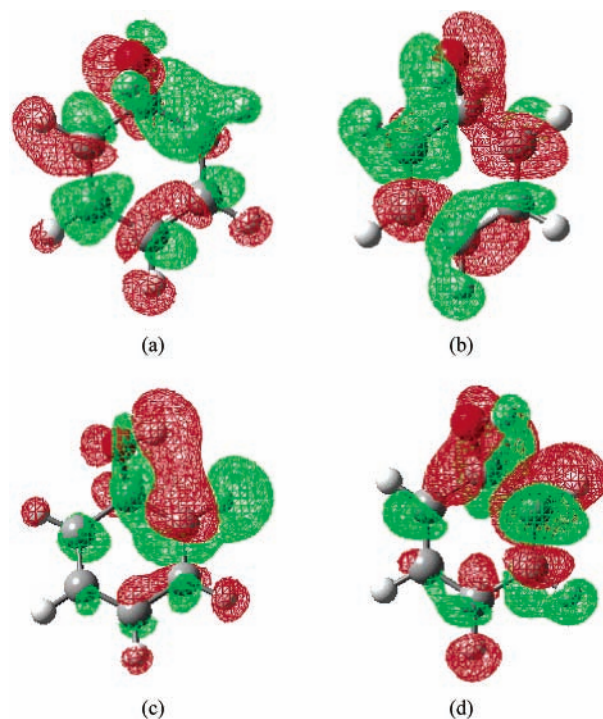


Figure 2. (a) Highest occupied molecular orbital (HOMO) for anti-conformer $\angle H_{14}O_{13}C_2H_8 = 180^\circ$, (b) HOMO-2 of anti-conformer ($\angle H_{14}O_{13}C_2H_8 = 180^\circ$), (c) HOMO for eclipse conformer ($\angle H_{14}O_{13}C_2H_8 = 180^\circ$), and (d) HOMO-2 of eclipse conformer ($\angle H_{14}O_{13}C_2H_8 = 261.3^\circ$). Based on B3LYP/6-31G(d,p) level. (Value of isosurface = 0.02 a.u.)

a factor of 1.44 at $T = 298$ K. Our theoretically derived equilibrium constant is in good agreement with the experimental data.

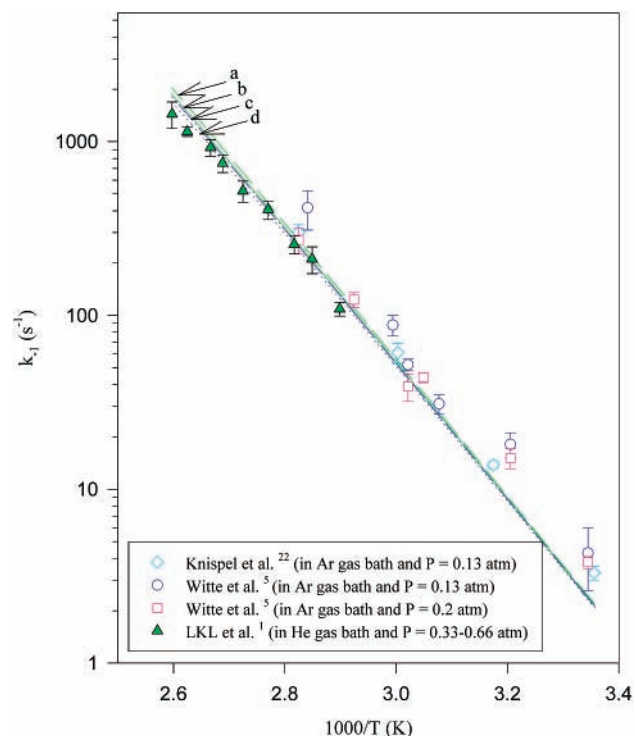


Figure 3. Comparison between our results (lines) with the experimental data for k_{-1} (symbols). Line a: He gas bath and $P = 0.66$ atm. Line b: He gas bath and $P = 0.33$ atm. Line c: Ar gas bath and $P = 0.20$ atm. Line d: Ar gas bath and $P = 0.13$ atm.

The reverse high-pressure rate constant of reaction 1, k_{-1} , is calculated to be $6.20 \times 10^{13} T^{-0.0041} \exp(-18.36 \text{ kcal}/RT) \text{ s}^{-1}$ for temperature from 298 to 385 K using $k_1 = 2.29 \times 10^{12} \exp(-0.68 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ as recommended by Baulch et al.²⁵ The rate constant k_{-1} as function of pressure and temperature is calculated using quantum Rice–Ramsperger–Kassel (QRRK) theory for $k(E)$ and master equation analysis for falloff.^{26,27} The rate constant k_{-1} is calculated to be $4.30 \times 10^{21} T^{-2.72} \exp(-19.84 \text{ kcal}/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at $298 \leq T \leq 385$ K and pressure = 1 atm. Comparison between our results with the experimental data is in good agreement and is shown in Figure 3; k_{-1} at 354 K = $2.55 \times 10^2 \text{ s}^{-1}$ (in Ar gas bath and $P = 0.131$ atm) and $2.68 \times 10^2 \text{ s}^{-1}$ (in Ar gas bath and $P = 0.197$ atm), compared to the data by Knispel et al.,²⁸ $k_{-1,354} = 3.01 \times 10^2 \text{ s}^{-1}$ (in Ar gas bath and $P = 0.131$ atm) and the data by Witte et al.,⁵ $k_{-1,354} = 2.72 \times 10^2 \text{ s}^{-1}$ (in Ar gas bath and $P = 0.197$ atm); k_{-1} at 375 K = $1.06 \times 10^3 \text{ s}^{-1}$ (in He gas bath and $P = 0.329 \sim 0.658$ atm), compared to the data by LKL, $k_{-1,375} = 9.25 \times 10^2 \text{ s}^{-1}$. We note that our results use the new value²⁹ of $\Delta H_{1298}^0(\text{OH}) = 8.96 \text{ kcal mol}^{-1}$ which is lower by $0.5 \text{ kcal mol}^{-1}$ than previous study and it results a factor of ca. 2 in equilibrium constants at 350 K.

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