3696 *J. Phys. Chem. A* **2003,** *107,* 3696−3703

Kinetics and Thermochemistry for the Gas-Phase Keto−Enol Tautomerism of Phenol ↔ 2,4-Cyclohexadienone

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Received: May 21, 2002; In Final Form: February 17, 2003

Isomerization of phenol is considered an important step in the metabolism of aromatic compounds and it may be the first step of phenol decomposition in thermal reaction systems. Ideal gas thermochemical properties, $\Delta H^\circ_{f,298}$, S°_{298}, and $C_p^\circ(T)$ (300 ≤ T/K ≤ 1500) for two keto forms of phenol (**1**), 2,4-cyclohexadienone (**2**), and 2,5-cyclohexadienone (**3**), are calculated in this study. $\Delta H^\circ_{f,298}$(**2**) is computed as −4.4 ± 2.4 kcal/mol at CBS-QB3 level and isodesmic reactions are utilized to minimize the systematic calculation errors. $\Delta H^\circ_{f,298}$(**3**) = −6.0 ± 2.4 kcal/mol is obtained from the total energy difference between **2** and **3**. The two keto tautomers are less stable than their enol form, phenol, $\Delta\Delta H^\circ_{f,298}$(**1↔2**) = −18.6 and $\Delta\Delta H^\circ_{f,298}$(**1↔3**) = −17.0 kcal/mol, respectively. The rate constant through transition state **4** for the tautomerization of phenol to 2,4-cyclohexadienone is obtained as $8.06 \times 10^{12} \exp(-69.4 \text{ kcal mol}^{-1}/RT)\ \text{s}^{-1}$. The equilibrium constants are computed as 7.15×10^{-14} and 2.16×10^{-13} at 298 K for reactions **1** ↔ **2** and **1** ↔ **3**, respectively. Kinetic parameters for the unimolecular isomerization and decomposition of **2** are also determined. IRC analysis on the transition state indicates that decomposition occurs by cleavage of the weak bond between allylic carbon and carbonyl carbon (73.1 kcal/mol, doubly allylic) to *cis*-1,3-butadienyl-4-ketene. ΔH_{rxn} of these paths are estimated. $\Delta H^\circ_{f,298}$ of *cis*- and *trans*-1,3-butadienyl-4-ketenes are determined as 24.5 and 19.2 kcal/mol, respectively. $\Delta H^\circ_{f,298}$ of species **2** and **3** are also calculated at the CBS-Q//B3LYP/6-31G(d,p) level and compared with the CBS-QB3 results.

1. Introduction

Benzene and phenol are fundamental species in the combustion chemistry of aromatic compounds. Addition of the hydroxyl radical to benzene forms a hydroxyl−cyclohexadienyl (C_6H_6O) radical, which can either dissociate to phenol plus H, or back to benzene + OH (Figure 1). The overall reaction to phenol is thermoneutral, and the barrier to hydrogen elimination is close to the initial energy of hydroxyl radical plus benzene. This reaction system is at equilibrium under combustion or high-temperature conditions and the thermal reaction rate is, therefore, controlled by the reactant concentrations. As hydroxyl is a dominant radical species under normal fuel lean combustion, the reaction serves as a conversion process for the aromatics to the corresponding phenol. Phenol is demonstrated precursor of dibenzo-*p*-dioxins and dibenzofurans in thermal processes, especially incineration.[1,2]

Phenol can also be formed from electrophilic addition of ^{3}O atoms to the benzene ring, followed by spin flip and then a 1,2-hydrogen shift (either order) resulting in 2,4-cyclohexadienone, this keto product can be photolyzed to butadienyl ketene by near-UV light[3] or can undergo intramolecular isomerization to phenol.

The addition of ^{3}O atoms to the benzene ring has been studied by Hodgson et al.[4] on the triplet surface. They performed CBS-QB3 energy calculations on adducts, isomers, and transition states on the basis of B3LYP/6-311G(d,p) optimized geometries, with RRKM methods for kinetics of the chemical activation benzene + ^{3}O reaction. They discuss a number of products for the C_6H_6O reaction on the triplet surface, where C_6H_6O reacts to phenoxy + H (E_a = 4.9 kcal/mol) is the dominant product at low temperature. Conversion to the singlet surface is considered to be not important due to the low barrier to phenoxy + H atom.

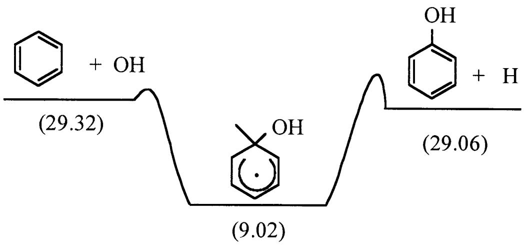

Figure 1. Pathway for benzene + OH to phenol + H ($\Delta H^\circ_{f,298}$ in kcal/mol).

Several researchers have investigated the pyrolysis of phenol experimentally. Lovell et al.,[5] as well as Manion and Louw,[6] used flow reactors at 1 atm and temperatures up to 1100 K. They considered the initial step as bond dissociation of phenoxy−H followed by the phenoxy radical decay to cyclopentadiene radical and CO. Horn et al.[7] and Cypres and Bettens[8] indicate that the hydroxyl H atom first undergoes a migration to form the 2,4-cylcohexadienone, which then decays into cyclopentadiene and CO. Horn et al. used shock tube experiments between 1450 and 1650 K at ∼2.5 bar and applied atomic and molecular resonance absorption spectroscopy to monitor time-dependent H and CO concentrations. Cypres and Bettens performed thermal cracking experiments on ^{14}C- and ^{3}H-labeled phenol between 938 and 1138 K at 1 atm; products were

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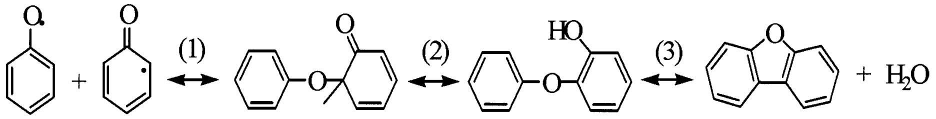

Figure 2. Example of formation of dibenzofuran via keto−enol reaction.

measured by weight analysis and radio-chromatography. Horn et al.[7] report that their experimental data can be satisfactorily modeled, when the dominant initiation step of the phenol pyrolysis is the molecular channel, phenol → C_5H_6 + CO, and when the rate of radical channel (phenol → phenoxy + H) does not exceed 15% of the molecular channel. Dissociation reactions of the phenol cation were recently studied by mass spectrometry experiments and by theoretical methods,[9] with a number of routes to CO elimination discussed.

Keto−enol tautomerization has been a subject of study for numerous species containing of −C(=O)− and −Si(=O)− groups, as well as the amino-imino tautomerization between C=N− and C−NH− groups. The tautomerization plays a fundamental role in the mechanism of a number of organic synthesis, biochemical processes, and enzymatic mechanisms.[10]

There are a number of thermodynamic analysis on keto−enol interconversion for −C=O− or −Si=O− groups containing species in both gas and liquid phases, although the study for gas-phase is limited to the equilibrium of the two forms. Thermochemisty for the simple system of acetaldehyde shows vinyl alcohol is 11.2 kcal/mol higher in enthalpy than acetaldehyde.[11] Perez et al. studied 10 acetyl derivatives (CH_3COX, X = H, OH, CH_3, OCH_3, NH_2, $N(CH_3)_2$, OCHO, F, Cl, and Br) and report the keto forms are 13−30 kcal/mol more stable than the enol using density functional B3LYP/6-31G(d,p) analysis.[10] Phenol is, however, an exception because of its aromaticity or rather the loss of aromaticity in the keto form; phenol is more stable than its tautomers, 2,4-cyclohexadienone and 2,5-cyclohexadienone. In contrast, Kresge shows that anthrone (keto form) is measured to be more stable than 9-anthrol (enol form) due to the reduced resonance energy of isolated benzene rings.[12]

Keto tautomers of phenol, although energetically unfavorable, are frequently invoked as reactive intermediates: examples are the photo-Fries rearrangement, the Kolbe−Schmitt and Reimer−Tiemann reactions, electrophilic substitutions of phenol, and the oxidative metabolism of aromatic compounds ("NIH-shift").[13] In many of these reactions the enolization of the carbonyl compound is the rate-determining step.

Figure 2 illustrates how the keto form and the keto−enol conversion may play an important role in pathways from phenol to dibenzofurans and dibenzo-*p*-dioxins.[2,14]

The keto form of phenol has been detected as a transient intermediate.[15,16] Capponi et al. generated cyclohexa-2,4-dieneone by flash photolysis and observed the kinetics of cyclohexa-2,4-dieneone → phenol, in acidic and neutral aqueous solutions.[15] They estimated the equilibrium constant is about $10^{13\pm1}$. The gas-phase $\Delta H^\circ_{f,298}$ of 2,4- and 2,5-cyclohexadienones have been studied by Shiner et al.[17] in 1986 using the following equation:

$$\Delta H^\circ_{f,298}(\text{dienone}) - \Delta H^\circ_{f,298}(\text{phenol}) = \Delta H^\circ_{\text{acid }298}(\text{phenol}) - \Delta H^\circ_{\text{acid }298}(\text{dienone}) \quad \text{(E1)}$$

The $\Delta H^\circ_{\text{acid }298}$ of 2,4- and 2,5-cyclohexadienones are measured as 344 ± 3 and 340 ± 2 kcal/mol after their exposure to a series of bases with a range of proton affinities. Acidity and the enthalpy of formation of phenol are 349.8 and −23.04 kcal/mol; thus $\Delta H^\circ_{f,298}$ of 2,4- and 2,5-cyclohexadienones were determined to be −17 ± 3 and −13 ± 3 kcal/mol, respectively.

Ab initio 6-31G(d) basis set calculations have been carried out by Gadosy and McClelland in 1996.[18] Geometries of phenol and 2,4- and 2,5-cyclohexadienones were optimized at the RHF level of theory, and single point energies were calculated at the HF and MP2 levels. The relative energies between 2,4-cyclohexadienone and 2,5-cyclohexadienone versus phenol were reported as 17.33 (MP2) and 16.88 (MP2) kcal/mol, respectively. The equilibrium constant for phenol ↔ 2,4-cyclohexadienone is then estimated as 1.98×10^{-13} at 298 K. Santoro and Louw recently report the $\Delta H^\circ_{f,298}$ of 2,4- and 2,5-cyclohexadienones calculated at the B3LYP/6-31G(d,p) level using isodesmic reactions,[19] which lead to enthalpy values of −7.3 and −8.0 kcal/mol for these two dienones. They also use simple group additivity but the values yielded are 6 kcal/mol higher due to the underestimation of conjugation and specific structure effects. Relative energies of the phenol ion and its isomers were calculated recently by Le et al.[9] at B3LYP/6-311++G(d,p) and CASPT2(7,8)/6-31G(d,p) levels; the energies of 2,4-cyclohexadienone ion and 2,5-cyclohexadienone ion were reported as 34.89 and 31.79 kcal/mol above that of the phenol ion.

The relative energies and the rate of isomerization of phenol to its keto form are important to understanding the initial step(s) in phenol pyrolysis and in step 2 of the reaction path to dibenzofuran formation (Figure 2). A summary of available literature data for the $\Delta H^\circ_{f,298}$ of two keto forms of phenol is presented in Table 1. We report the $\Delta H^\circ_{f,298}$, S°_{298}, and $C_p^\circ(T)$'s ($300 \leq T/\text{K} \leq 1500$) for phenol (**1**), 2,4-cyclohexadienone (**2**), 2,5-cyclohexadienone (**3**), and the transition state (**4**) of the intramolecular H-transfer of phenol to 2,4-cyclohexadienone in this work and parameters for further reaction of **2**. The keto−enol isomerization and the subsequent barriers to reaction of the ketone structure are the second focus of this study. The goal is an attempt to identify the major unimolecular dissociation channel of phenol, and to allow estimation of the rate constant of step 3 in Figure 2 for the formation of dibenzo-*p*-dioxins and dibenzofurans.

2. Calculations

2.1. Geometries and the Transition State for Phenol → 2,4-Cyclohexadienone. The CBS-QB3[20] method in the Gaussian 98[21] program suite is used for all calculations. This method is chosen because it showed comparable accuracy with G3 or G3(MP2) methods.[22] The structures of phenol (**1**), 2,4-cyclohexadienone (**2**), 2,5-cyclohexadienone (**3**), the transition state of phenol to 2,4-cyclohexadienone (**4**), and all other species fully optimized at the B3LYP/6-311G(d,p) level of theory are given in Supporting Information table 1, along with the harmonic vibration frequencies and zero-point vibrational energy (ZPVE) computed at the same level. Total energies (Supporting Information table 2) are corrected by ZPVE's, which are scaled by 0.99. All calculations are performed on the singlet surface for the phenol−keto isomerization and the keto isomer dissociation. Thermal corrections (0−298 K) are calculated to estimate $\Delta H^\circ_{f,298}$ at 298 K.[23]

The $(\overline{\text{CCCCCC}})$=O structures for 2,4-cyclohexadienone and 2,5-cyclohexadienone are planar, which is in agreement with

TABLE 1: Literature Summary on Relative Energies and/or $\Delta H^\circ_{f,298}$ (kcal/mol) of Phenol and Its Two Keto Forms[a]

author	results	method
Capponi et al., 1986[15]	K_{eq}(2,4-cyclohexadienone (**2**)-phenol (**1**)) = $10^{13\pm1}$	flash photolysis expt
Shiner et al., 1986[17]	$\Delta H^\circ_{f,298}$(2,4-cyclohexadienone, **2**) = −17 ± 3 $\Delta H^\circ_{f,298}$(2,5-cyclohexadienone, **3**) = −13 ± 3	expt, and from $\Delta H^\circ_{acid\ 298}$
Gadosy and McClelland, 1996[18]	$\Delta\Delta H^\circ_{f,298}$(**2**-phenol) = 17.33 $\Delta\Delta H^\circ_{f,298}$(**3**-phenol) = 16.88	MP2/6-31G(d)
Santoro and Louw, 2001[19]	$\Delta H^\circ_{f,298}$(**2**) = −7.3 $\Delta H^\circ_{f,298}$(**3**) = −8.0	B3LYP/6-31G(d,p) with isodesmic reactions
Le et al., 2001[9]	$\Delta\Delta H^\circ_{f,298}$(**2**-phenol) = 17.45 $\Delta\Delta H^\circ_{f,298}$(**3**-phenol) = 16.49	B3LYP/6-311++G(d,p)(+ZPE)
this study	$\Delta H^\circ_{f,298}$(**2**) = −4.4 $\Delta H^\circ_{f,298}$(**3**) = −6.0 $\Delta\Delta H^\circ_{f,298}$(**2**-phenol) = 18.6 $\Delta\Delta H^\circ_{f,298}$(**3**-phenol) = 17.0	CBS-QB3 with isodesmic reactions

[a] ΔH°_f in kcal/mol.

TABLE 2: $\Delta H^\circ_{f,298}$ (kcal/mol) of Species 2, 3, 7, and 8 by (Isodesmic) Working Reactions

isodesmic reactions	CBS-QB3[a,b]	CBS-Q//B3LYP/6-31G(d,p)	uncertainty from reference species
2,4-cyclohexadienone (**2**) + cyclohexane → cyclohexanone + 1,3-cyclohexadiene	−4.6	−6.6	0.91
2,4-cyclohexadienone (**2**) + cyclopentane → cyclopentanone + 1,3-cyclohexadiene	−4.6	−6.7	0.71
2,4-cyclohexadienone (**2**) + 1-butene → vinyl methyl ketone + 1,3-cyclohexadiene	−4.1	−6.3	1.33
2,5-Cyclohexadienone (**3**) → 2,4-cyclohexadienone (**2**)	−6.0	−8.8	2.41
cis-1,3-butadienyl-4-ketene (**7**) + CH_4 → ketene + $CH_3CH{=}CHCH{=}CH_2$	24.5	25.5	0.61
trans-1,3-butadienyl-4-ketene (**8**) + CH_4 → ketene + $CH_3CH{=}CHCH{=}CH_2$	19.2	16.5	0.61

[a] Based on B3LYP/6-311G(d,p) geometries; [b] Recommended in this work.

the results calculated at RHF/6-31G(d) by Gadosy et al.[18] The cyclohexadiene ring in the transition state of phenol to 2,4-cyclohexadienone (**4**) is slightly strained where the CO bond (1.286 Å) is ca. 30° out plane with the C6 ring. The migrating H atom in **4** is 1.396 Å from the O it is leaving and 1.411 Å from the C it is approaching.

2.2.1. $\Delta H^\circ_{f,298}$ (by Isodesmic Reactions), S°_{298}, and $C_p^\circ(T)$ of Two Cyclohexadienones. The method of isodesmic reaction is used to calculate the $\Delta H^\circ_{f,298}$ of 2,4-cyclohexadienone (**2**). This method relies on the similarity of the bond environments in the reactants and products that leads to partial cancellation of systematic errors in the ab initio or density functional calculations. The basic requirement of an isodesmic reaction is that the number of each type of bond is conserved in the reaction. In addition to bond balance, we try to use working reactions with group balance for maximum cancellation of error, but most reactions in this study do not conserve group balance. Redfern et al. have shown that B3LYP calculations with homodesmic reactions result in accurate enthalpy data for hydrocarbons, whereas use of atomization reactions for the data leads to significant error.[24] Curtiss et al. and Raghavachari et al. also show that use of isodesmic reactions leads to more accurate enthalpies than use of atomization reactions with G3 calculation methods.[25,26]

As an example, $\Delta H^\circ_{f,298}$ of 2,4-cyclohexadienone (**2**) can be calculated from the following isodesmic reaction:

$$\text{2,4-cyclohexadienone} + \text{cyclohexane} \rightarrow \text{cyclohexanone} + \text{1,3-cyclohexadiene}$$

There are two C=O bonds, two C=C bonds, nine C−C bonds, and eighteen C−H bonds in both sides of above reaction. According to $\Delta H_{rxn,298} = \Sigma$(total energies)$_{298}$ of products − Σ(total energies)$_{298}$ of reactants = Σ(literature $\Delta H^\circ_{f,298}$ of products) − Σ(literature $\Delta H^\circ_{f,298}$ of reactants); the $\Delta H^\circ_{f,298}$ of 2,4-cyclohexadienone is obtained from the enthalpy change of the isodesmic reaction and the known $\Delta H^\circ_{f,298}$ of the reference species.

Total energies (Supporting Information table 2) of all species in the isodesmic reactions are computed at the CBS-QB3 level. The literature enthalpies of formation for reference species are given in Supporting Information table 3. Three CBS-QB3 $\Delta H^\circ_{f,298}$ values from three isodesmic reactions for **2** are listed in Table 2; and the arithmetic average is −4.4 kcal/mol. $\Delta H^\circ_{f,298}$(**3**) is determined as −6.0 kcal/mol from the energy difference between **2** and **3**.

The error range of the calculated standard enthalpy of formation using the isodesmic reaction has been discussed by Zhu et al.[27] and is summarized here: The accumulative uncertainties from reference species are listed in Table 2 (see also Supporting Information table 3), and the mean absolute deviation of the CBS-QB3 energy (using atomization reactions) on G2/97 set is tested to be 1.08 kcal/mol,[22] so the final $\Delta H^\circ_{f,298}$ of **2** and **3** are −4.4 ± 2.4 and −6.0 ± 2.4 kcal/mol, respectively; These results are 3 and 2 kcal/mol higher than

TABLE 3: Ideal Gas-phase Thermodynamic Properties[a]

			$C_p°(T)$							
species	$\Delta H^\circ_{f,298}$	ΔH°_{298}	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K	note
phenol **1**, use in this work	−23.04	75.26	24.74	32.18	38.69	43.93	50.62	55.33	62.90	TRC[39]
phenol **1**	−23.10	75.10	24.80		38.70		50.70	55.50	62.70	Benson[40]
phenol **1**[b,c]		72.75	22.30	29.77	36.05	41.08	48.42	53.48	61.01	TVR
		2.89	1.91	2.09	2.09	2.02	1.81	1.62	1.33	IR
		75.64	24.21	31.86	38.14	43.10	50.23	55.10	62.34	total
2,4-cyclohexadienone (**2**)	−4.4	77.52	24.00	31.30	37.54	42.62	50.18	55.45	63.20	*c*
2,5-cyclohexadienone (**3**)	−6.0	74.48	23.80	31.09	37.34	42.45	50.06	55.37	63.18	*c*
$TS_{1\rightarrow 2}$ (**4**)	46.7	73.79	23.01	30.55	36.95	42.10	49.62	54.72	62.04	*c*
$TS_{2\rightarrow 7}$ (**5**)	67.8	76.02	23.96	31.13	37.13	41.95	49.08	54.07	61.49	*c*
$TS_{2\rightarrow 3}$ (**6**)	100.8	74.87	23.98	31.69	38.08	43.15	50.43	55.34	62.37	*c*
cis-1,3-butadienyl-4-ketene (**7**)[d]	24.5	84.29	27.53	34.03	39.55	44.06	50.90	55.81	63.27	*c*
trans-1,3-butadienyl-4-ketene (**8**)[d]	19.2	84.08	27.77	34.16	39.61	44.10	50.93	55.83	63.28	*c*

[a] $\Delta H^\circ_{f,\,298}$ in kcal/mol, ΔH°_{298} and $C_p°$(T) in cal/(mol K). [b] See the article by Zhu and Bozzelli[31] for examples of "SMCPS" program for TRV (translation, vibration, external rotation) and "ROTATOR" program for IR. IR signifies analysis of contributions to entropy and heat capacities from the internal rotation, phenoxy−OH in phenol (with IR the torsion frequency is excluded in corresponding vibrational analysis). [c] Calculated in this study. [d] First frequency is treated as vibration due to the high barrier for internal rotor.

the values by Santoro and Louw,[19] −7.3 and −8.0 kcal/mol, who used B3LYP/6-31G(d,p) calculation with isodesmic reactions. Le et al.[9] also report relative computation values (B3LYP/6-311++G(d,p) + ZPE) for **2** and **3** relative to phenol which, when used with the $\Delta H^\circ_{f,298}$ of −23 kcal/mol for phenol with neglect of the small (0.2 kcal/mol) differences in thermal energy, result in −5.55 and −6.49 kcal/mol, respectively. The calculation literature and our results are significantly higher than the experimental determined $\Delta H^\circ_{f,298}$ values of Shiner et al.[17] −17 ± 3 and −13 ± 3 kcal/mol for **2** and **3**. The ion bracketing experiments as reported by Shiner et al. is usually considered to be accurate to within several kcal/mol. The results of previous calculation studies and of this work suggest that there may be value in new experiments on these cyclohexadienones.

We determine $\Delta\Delta H^\circ_{f,298}(\mathbf{1}\leftrightarrow\mathbf{2}) = -18.6$ kcal/mol, which is close to the results calculated at the MP2/6-31G(d)//RHF/6-31G(d) level) by Gadosy et al.,[18] −17.33 kcal/mol. The trend we find is the same as that of Gadosy et al., Santoro and Louw, and Le et al., i.e., $\Delta H^\circ_{f,298}(\mathbf{1}) \ll \Delta H^\circ_{f,298}(\mathbf{3}) < \Delta H^\circ_{f,298}(\mathbf{2})$.

$\Delta H^\circ_{f,298}$ of all species except phenol in Table 3 are calculated from isodesmic reactions in Table 2.

2.2.2. Entropy and Heat Capacity. Contributions to S°_{298} and $C_p°(T)$ from translation, vibrations, and external rotation are calculated using the "SMCPS" program.[28] This program utilizes the rigid-rotor-harmonic-oscillator approximation from the frequencies along with moments of inertia on the basis of the optimized B3LYP/6-311G(d,p) structures.

The potential barrier of internal rotation about the phenyl−OH bond was calculated at the B3LYP/6-31G(d,p) level. A Fourier series was used to represent the potential calculated at discrete torsional angles.

$$V(\Phi) = a_0 + a_i \cos(i\Phi) + b_i \sin(i\Phi) \qquad i = 1, 2, 3, ... \tag{E2}$$

where values of the coefficients in (E2) are calculated to provide the true minima and maxima of the torsional potential. Solutions to (E2) are obtained using wave functions of the free rotor; partition functions are calculated from the energy levels. Further description on this method to calculate contributions from the internal rotors are reported by methods of Lay et al.[28−30] and in an article by Zhu and Bozzelli.[31] We assume no internal rotors in *cis*- and *trans*-1,3-butadienyl-4-ketene (the last two species in Table 3); the barriers for internal rotations in these two species are higher than 10 kcal/mol and the corresponding lowest torsion frequencies are treated as a vibration.

The calculated S°_{298} and $C_p°(T)$ of phenol in this study are in very good agreement with the literature of TRC and Benson; for entropy values are 75.64 versus 75.26 (TRC) and 75.10 (Benson). We use the TRC data in our calculations.

We have also performed CBS-Q calculations based on geometry optimization with a smaller basis set, B3LYP/6-31G(d,p), than B3LYP/6-311G(d,p) in CBS-QB3 with the same isodesmic reactions to obtain the $\Delta H^\circ_{f,298}$ of 2,4- and 2,5-cyclohexadienones as −6.5 and −8.8 kcal/mol. Besides a larger basis set for structure calculation, the CBS-QB3 uses a CCSD(T) calculation[20] in place of a QCISD(T), and a modified extrapolation method[22] as improvement in the CBS-Q//B3LYP/6−31G(d,p) method. We have used the CBS-Q//B3LYP/6-31G(d,p) method for oxy-chloro-hydrocarbons with satisfactory results.[27,31−37] Here the CBS-Q//B3LYP/6-31G(d,p) results are 2.1 and 2.8 kcal/mol lower than the corresponding CBS-QB3 for **2** and **3**, and are within 1 kcal/mol of the B3LYP/6-31G(d,p) values of Santoro and Louw.[19] The CBS-QB3 results are recommended in this work because the method is considered to represent a small improvement over CBS-Q in accuracy,[20] it also offers improvement in the geometry optimization and frequency calculation steps.

2.3. K_{eq} of Phenol ↔ 2,4-Cyclohexadienone and Phenol ↔ 2,5-Cyclohexadienone. The gas-phase equilibrium constant for reaction at 298 K is calculated from

$$\Delta G° = \Delta H° - T\Delta S° = -RT \ln K_{eq} \tag{E3}$$

$$K_{eq,298}(\mathbf{1}\leftrightarrow\mathbf{2}) = \exp\left[\frac{(-4.4 + 23.0) \times 10^3 - 298(77.52 - 75.26)}{-1.987 \times 298}\right] = 7.15 \times 10^{-14}$$

This result is about one-third of the estimation of Gadosy and McClelland.,[18] 1.98×10^{-13}, and the measurement by Capponi et al.,[13] 1.86×10^{-13}, in aqueous phase. We consider this reasonable agreement. $K_{eq,298}(\mathbf{1}\leftrightarrow\mathbf{3})$ is 2.16×10^{-13}, which is 2% of the value by Capponi et al.,[13] 1.05×10^{-11}, in the aqueous phase.

2.4. Reaction Path: Phenol ↔ 2,4-Cyclohexadienone → Products. Figure 3 shows the potential energy diagram of this phenol-keto reaction.

2.4.1. Reaction Barrier and Preexponential A Factor for H-migration of Phenol. As previously noted, the energies of the reactants and products in the reaction and ΔH_{rxn} are

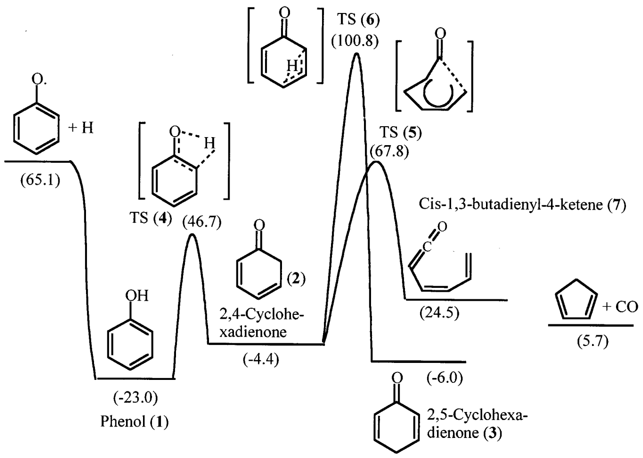

Figure 3. Potential energy diagram ($\Delta H^\circ_{f,298}$ in kcal/mol).

determined by use of several different isodesmic reactions and are reported as absolute, not relative values. ΔH_{rxn} is not just the difference in calculated energies plus ZPVE and thermal energies of the two isomers. The relative enthalpy of transition state, ($\Delta\Delta H^\circ_{f,298}$(**4**↔**1**)), is determined by ΔH_{rxn} of isodesmic reactions.

$$E_{af} = {}^{1}\!/_{2}\,\{[(\Delta H^\circ_{f,TS_4} - \Delta H^\circ_{f,_{phneol}}) + (\Delta H^\circ_{f,TS_4} - \Delta H^\circ_{f,2,4-cyclohexadienone})]627.51 + \Delta H^\circ_{rxn}\} + RT_m \quad (E4)$$

In the case of phenol isomerization to the 2,4 isomer

$$\Delta H^\circ_{rxn,298} = \Delta H^\circ_{f,298,2,4-cyclohexadienone'} - \Delta H^\circ_{f,298,phneol} = -4.4 - (-23.0) = 18.6\ \text{kcal/mol} \quad (E5)$$

E_{af} is then calculated as 69.4 kcal/mol from data in Table 3 when $T_m = 298$ K. We note that this barrier is close to that of the similar H atom transfer reaction of the phenol cation, which is reported at 66 kcal/mol.[9]

According to transition state theory, the Arrhenius A factor for unimolecular reaction is

$$A_{uni} = \frac{ekT}{h}\exp(\Delta S^{\ddagger}/R) \quad (E6)$$

where T is temperature in K, $R = 1.987$ cal/(mol K), and from Table 3 $\Delta S^{\ddagger} = S^\circ_{TS} - S^\circ_{phenol} = -1.47$ cal/(mol K) at 298 K, respectively. We calculate $A_{uni} = 8.06 \times 10^{12}$ s^{-1} at 298 K.

The Arrhenius rate constant expression is

$$k_{fwd}(1 \leftrightarrow 2) = A'T^n = 8.06 \times 10^{12} \exp(-69.4\ \text{kcal mol}^{-1}/RT)\ (\text{s}^{-1}\ \text{at 298 K}) \quad (E7)$$

2.4.2. Comparison of the Neutral and the Cation Reactions. Figure 8 in the article by Le et al.[9] show similar paths for the phenol cation isomerization and dissociation; it illustrates the similarity in the potential energy diagrams for reaction of the ion and neutral systems. We find a value of 69.4 for the barrier of the neutral hydrogen shift to form the 2, 4-cyclohexadienone, which is in reasonable agreement with the value of 66.5 (B3LYP/6-311++G(d,p) reported for this neutral system by Le et al. For the cation system Le et al. report a value of 66.0 in their B3 calculation and 69.5 at the CASPT2(7,8)/6-31G(d,p)+ZPE level. The overall values for this isomerization are nearly identical in the neutral and cation systems.

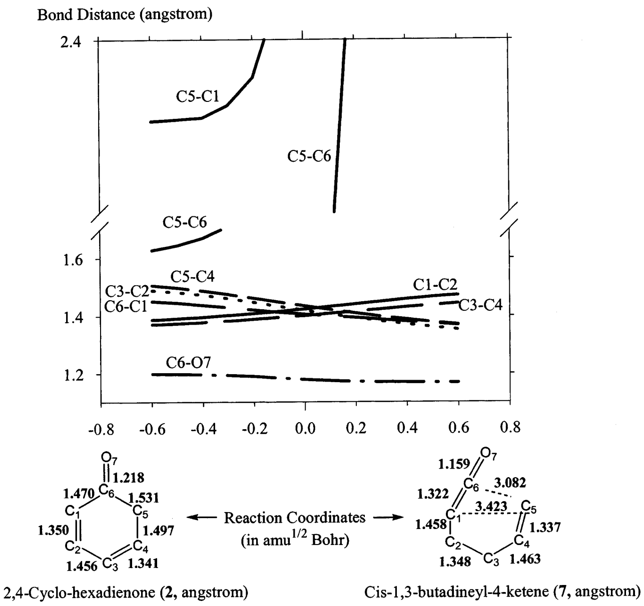

Figure 4. Intrinsic reaction coordinates (IRCs) around $TS_{2\rightarrow7}$ (**5**) at the B3LYP/6-31G(d,p) level of theory.

One major difference between the ion and neutral systems, which controls the kinetics, is the barrier for ring opening to form a ketene structure. This barrier is significantly lower in the cation system, ca. 8 kcal/mol versus 73.1 kcal/mol in our neutral system. This suggests that the missing electron in the ion significantly weakens the bond between allylic carbon and carbonyl carbon. This difference in barriers controls the kinetic to final phenol or phenol cation decomposition products. In the neutral system the controlling rate constant to the ring opening and further reaction to cyclopentadiene + CO is the ring-opening step, whereas in the ion reaction system it is the hydrogen transfer from the phenol structure that forms the 1,4-cyclohexadienone. We illustrate this further below and in the section of detailed mechanism analysis.

The enthalpy of the stable ketene structure (**7**) after ring opening in our neutral system is 47.5 kcal/mol higher than the phenol, whereas this structure in the cation system is ca. 30 kcal/mol higher in enthalpy than the phenol cation. Le et al.[9] also calculate and postulate that this noncyclic ketene structure in the ion system readily undergoes intramolecular reaction, ring closure, to form cyclopentadiene + CO, which is the product indicated by Horn et al.[7]

2.4.3. Further Reactions of 2,4-Cyclohexadienone. The 2,4-cyclohexadienone (**2**) has a weak carbon−carbon single bond adjacent to the carbonyl group due to resonance stabilization of the radical formed in cleaving it. Cleavage results in a diradical structure, *cis*-O=C$^\bullet$−C=C−C=C−C$^\bullet$ (initial structure). The electrons in this diradical are delocalized to cis-O=C$\cdots$C$\cdots$C$\cdots$C$\cdots$C$\cdots$C. The structure can rearrange to a stable ketene molecule, *cis*-O=C=C−C=C−C=C (**7**). The ring structure in the 2,4-cyclohexadienone (**2**) is only partially delocalized because of the sp^3 carbon. Calculation of a transition state (**5**) for ring opening between the allylic carbon and carbonyl group, to *cis*-1,3-butadienyl-4-ketene (**7**) shows that bond cleavage requires only 73.1 kcal/mol of energy.

The IRC (intrinsic reaction coordinate) analysis on TS **5** shown in Figure 4 confirms this C−C bond cleavage and not formation of a five-membered-ring structure. An IRC is defined as the minimum energy path connecting the reactant to the product via the TS. The IRC calculation follows the path both forward and backward from the TS while optimizing the

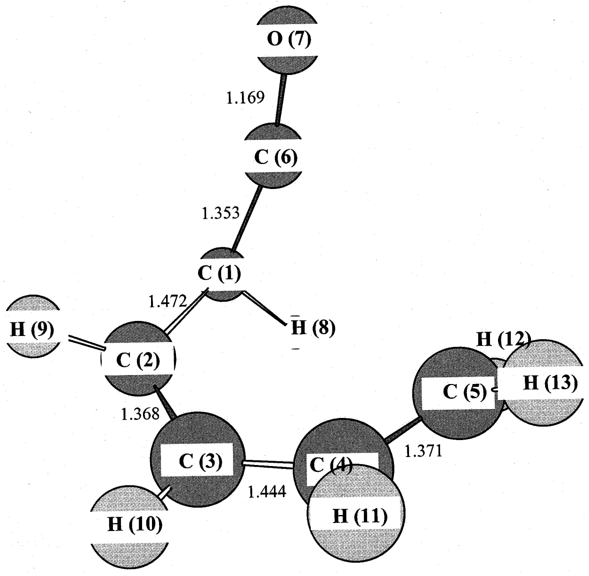

Figure 5. Geometry of the last (sixth) point of IRC analysis of TS **5** (distances in angstroms). Note the ketene and butadiene structures are almost completely formed.

geometry of the system at each point along the path. The point ($x = 0$) in Figure 4 corresponds to the TS of 2,4-cyclohexadienone (**2**) → *cis*-1,3-butadienyl-4-ketene (**7**) as it approaches the products (right) and reactant (left). We calculated six points for each of the reactant and the product directions with a step size of 0.1 amu$^{1/2}$ × Bohr (0.6819×10^{-21} g$^{1/2}$×cm). In Figure 4, when $r(C_5{-}C_6)$ increases from 1.63 to 3.09 Å, the $r(C_5{-}C_1)$ increases from 2.35 to 3.03 Å, showing bond cleavage and no cyclopentadiene formation in this step. Three single bonds on the cyclohexadiene ring, $r(C_1{-}C_6)$, $r(C_2{-}C_3)$, $r(C_5{-}C_4)$, and the C−O bond also decrease in length, and two double bonds, $r(C_1{=}C_2)$ and $r(C_3{=}C_4)$ both increase. We interpret these trends in bond length changes as a strong indication that the *cis*-1,3-butadienyl-4-ketene conformer is forming, while the $C_5{-}C_6$ bond is cleaving. Figure 5 illustrates the molecular structure at the last step (sixth point) toward ring-opening products in the IRC; it clearly shows the structure is very close to the *cis*-1,3-butadienyl-4-ketene. This pathway is also reported in that of the phenol cation dissociation.[9]

With an excess energy of over 43 kcal/mol relative to the bond fission TS **5**, *cis*-1,3-butadienyl-4-ketene may undergo isomerization to a more stable *trans*-1,3-butadienyl-4-ketene (**8**) or unimolecular reaction to cyclopentadiene + CO. Optimization of *cis*- and *trans*-1,3-butadienyl-4-ketenes in the CBS-QB3 calculations result in $\Delta H^\circ_{f,298}$ of 24.5 and 19.2 kcal/mol, respectively. Le et al. report a barrier of 23 to 24 kcal/mol for the ketene ion ring-opening product to undergo ring closure to CO + cyclopentadiene cation. This ring closure barrier to CO formation is ca. 23 kcal/mol below the ring-opening transition state energy and the reaction could readily occur in the neutral system. Ring opening would, however, need to be the dominant reaction for cyclopentadiene + CO to be the dominant products.

2.5. Hydrogen Atom Transfer, Conversion of 2,4-Cyclohexadienone to the 2,5 Isomer. The 2,4-cyclohexadienone can have one of the H atoms on C(sp^3) migrate (TS **6**) to the carbon para to carbonyl-carbon, resulting in 2,5-cyclohexadienone. The forward reaction barrier of this H migration is calculated to be 105.3 kcal/mol, which is 33 kcal/mol higher than the barrier for the carbon−carbonyl carbon bond cleavage reaction (see Figure 3).

2.6. Detailed Mechanism Analysis: Comparison of Phenol Isomerization → 2,4-Cyclohexadienone and Ring-Opening Dissociation versus Phenol → Phenoxy + H. The high-pressure limit forward rate constant of phenol dissociating to phenoxy + H is estimated as $2.67 \times 10^{16} \exp(-88.8 \text{ kcal mol}^{-1}/RT)$ s^{-1} in the temperature range 1074−1162 K.[5] The isomerization of phenol to 2,4-cyclohexadienone has a lower energy of activation, but it is also a tighter transition state (lower A factor) relative to the PhO−H bond cleavage.

To evaluate the competition between the lower energy isomerization and the PhO−H bond cleavage where there is a higher preexponential factor, we evaluate the kinetics and pathways in the initial decomposition of phenol by assembling a small detailed kinetic model as described below. Rate constants for the different reaction paths (see data in Table 4) are incorporated into a multichannel unimolecular quantum Rice−Ramsperger−Kassel (QRRK) theory for $k(E)$, where master equation analysis is used for falloff analysis.[28] The data needed for input to this calculation are shown in the Supporting Information Table 5. The results from the calculation are shown in Figure 6. At 1 atm (Figure 6a), the 2,4-cyclohexadienone path dominates the phenol → phenoxy + H path at 1000−2400 K. Decomposition/isomerization rate constants versus pressure at 1000 K (Figure 6b), show the isomerization to 2,4-cyclohexadienone dominates the radical path at all pressures.

An elementary reaction mechanism is constructed using rate constants from the output of QRRK-master equation analysis; this small mechanism is listed in Table 5. We assume that reaction 2 (phenoxy + H) and reaction 4 (ring-opening) in Table 5 are nonreversible, whereas isomerization reactions 1 and 3 are reversible in this mechanism analysis. The CHEMKIN II mechanism integrator is used to model reaction conditions of 1% (volume) phenol in 1 atm N_2 and 1000 K.

Predictions of the products relative to the initial phenol concentration are plotted versus reaction time (10^{-9}−10^5 s) in Figure 7. The phenol concentration remains at 0.01 up to approximately 1000 s reaction time and decreases at longer times. The isomerization of phenol to 2,4-cyclohexadienone is favored by a factor of 50 over dissociation to phenoxy + H at early times. At 0.1 s the 2,4-cyclohexadienone reaches a quasi equilibrium at near 0.000 002 mole fraction), and the ratio for phenol to its keto isomer remains near constant at 5000. The ring-opening dissociation from 2,4-cyclohexadienone parallels the phenoxy + H channel, at near the 1% level in this time period. Loss of 2,4-cyclohexadienone becomes significant at longer times and dissociation of phenol to phenoxy + H continues to dominate the product ratio.

Overall isomerization occurs faster than phenol dissociation, and reverse isomerization is faster than forward isomerization and faster than dissociation of the cyclohexadienone. The lower energy isomer − phenol dominates over the dienone and phenol dissociation is dominant at longer times. We note that under combustion conditions where a radical pool is established the controlling reaction processes may be different. The PhO−H bond in phenol is only 86 kcal/mol, which is weak relative to hydrocarbons, and the phenoxy radical has a resonance form (keto structure radical site on the ring). Reaction of this keto form of phenoxy radical with HO_2 can lead to a cyclohexadienone via an exothermic disproportionation reaction. The overall phenol − keto equilibria may occur on a more rapid time scale in a combustion system with an existing radical pool; but the kinetic details depend on the specific conditions − concentrations, reaction time, temperature, etc. The detailed studies of the kinetics of these processes are, however, not a target of this manuscript.

2.7. Implications for Formation of Dibenzofuran and

TABLE 4: High-Pressure Limit Rate Constants as Input Parameters for QRRK-Master Equation Calculation of Phenol Dissociation (in N_2)[a–c]

	reaction	A (s^{-1})	n	E_a (kcal/mol)
k_1[d]	phenol (**1**) → 2,4-cyclohexadienone (**2**)	8.95×10^{10}	0.639	69.8
k_{-1}	2,4-cyclohexadienone (**2**) → phenol (**1**)	7.24×10^{9}	0.863	51.1
k_2	phenol (**1**) → phenoxy radical + H	7.63×10^{14}	0	86.9
k_3	2,4-cyclohexadienone (**2**) → 2,5-cyclohexadienone (**3**)	7.77×10^{8}	1.289	105.1
k_4	2,4-cyclohexadienone (**2**) → *cis*-1,3-butadienyl-4-ketene (**8**)	2.27×10^{11}	0.557	72.6

[a] Lennard-Jones parameters are $\sigma = 5.69$ Å and $\epsilon/k = 526.9$ K. [b] Reduced frequency sets (from CPFIT[43]): phenol (1026.3 $cm^{-1} \times 32.5$), 2,4-cyclohexadienone (518.6 $cm^{-1} \times 11.2$, 1283.3 $cm^{-1} \times 15.4$, 3073.0 $cm^{-1} \times 6.4$). [c] See Supporting Information tables 5−7 for the input and output format of QRRK-master equation calculation. [d] k_1, k_3, k_4 fitting with three-parameter modified Arrhenius equation over the temperature range 300−2000 K using THERMKIN (a canonical transition state calculation for the rate constant from the thermochemical data on the reactants and corresponding transition state).[28,41] An example for k_1 is shown in Supporting Information table 4. k_{-1} from k_1 and microscopic reversibility 〈MR〉. k_2 from k_{-2} and 〈MR〉, $k_{-2} = 2 \times 10^{14}$ from He et al.[42]

TABLE 5: Mechanism of Phenol Dissociation (1 atm N_2, 1000−2400 K)[a]

reaction	A (s^{-1})	n	E_a (kcal/mol)
phenol → phenoxy radical + H	1.25×10^{67}	−14.82	122.6
phenol ↔ 2,4-cyclohexadienone	2.82×10^{42}	−8.26	92.0
2,4-cyclohexadienone ↔ 2,5-cyclohexadienone	3.43×10^{119}	−31.21	166.4
2,4-cyclohexadienone → *cis*-1,3-butadienyl-4-ketene	7.89×10^{86}	−21.17	120.2

[a] From calculations shown in Supporting Information tables 5−7.

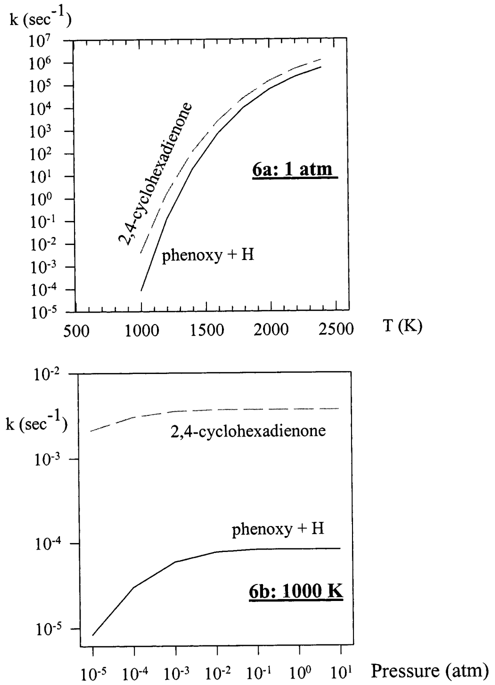

Figure 6. Calculated rate constants for two paths of phenol dissociation.

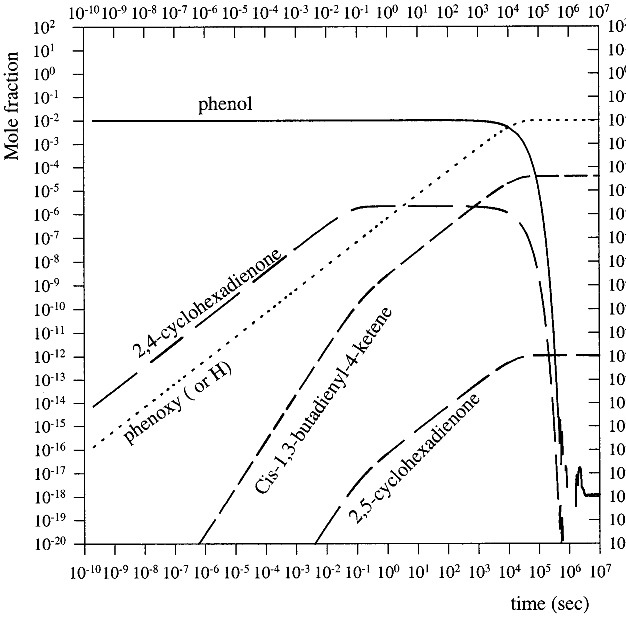

Figure 7. Products from dissociation of 1% phenol in 1 atm N_2 at 1000 K.

Dibenzodioxin from Association of Two Phenoxy Radicals. The calculated barrier for hydrogen transfer from ortho phenoxy cyclohexadienone to form a phenoxy phenol, reaction 2 in Figure 2, where the phenol is a precursor to formation of dibenzofuran or dibenzodioxin via H_2O elimination is determined to be 51 kcal/mol. This barrier will be affected somewhat by the oxygen ether link on the cyclohexadienone,[38] where a H atom is present in the cyclohexadienone in this study. The preexponential factor is relatively tight, 8×10^{12} at room temperature. This barrier is estimated to be ca. 10 kcal/mol lower than the bond cleavage reaction (−1) in Figure 2 and can occur by chemical activation reaction 1 in Figure 2.

3. Summary

Phenol can isomerize to 2,4-cyclohexadienone with a ΔH_{rxn} of 18.6 kcal/mol over a barrier of 69.4 kcal/mol, which is lower in energy than needed for phenoxy−H bond (86 kcal/mol) cleavage. The 2,4-cyclohexadienone can further dissociate via bond cleavage of a weak (73.1 kcal/mol) C−CO bond to ring opening, which forms *cis*-1,3-butadienyl-4-ketene. The cyclohexadienone isomer has a lower barrier for the reverse reaction, back to phenol, than to dissociation channels. The forward and reverse isomerizations of phenol to 2,4-cyclohexadienone are faster than the dissociation reactions and, in the absence of other radical reactions, can lead to equilibria. The reaction enthalpies for phenol to phenoxy + H versus phenol to *cis*-1,3-butadienyl-4-ketene (via 2,4-cyclohexadienone) are estimated to be near identical. Equilibria favor the phenol, and entropy favors phenol dissociation over ring opening. The 1,3-butadienyl-4-ketene has not previously been considered as a product. We look to future experimental studies for identification of this possible new product. Calculated values for $\Delta H^\circ_{f,298}$ on 2,4- and 2,5-cyclohexadienone are nearly 10 kcal/mol higher, −4.4 and −6.0 kcal/mol, respectively, than experimental data from ion transfer reactions.

Acknowledgment. We acknowledge the USEPA Northeast Regional Research Centers and the USEPA Research Center on Airborne Organics for the funding. We acknowledge Dr. Chad Sheng for the "SMCPS" computer code, Prof. Lev Krasnoperov for the "ROTATOR" computer code, and Dr. Chiung-Chu Chen for providing her unpublished data on benzene−OH adduct.

Supporting Information Available: Geometries and vibrational frequencies, total energies, enthalpies of formation, THERMKIN calculation example, formats for input and output files for QRRK−master equation calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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