ANALYSIS OF AN ELEMENTARY REACTION MECHANISM FOR BENZENE OXIDATION IN SUPERCRITICAL WATER

JOANNA L. Dinaro,1 JACK B. Howard,1 WILLIAM H. Green,1 JEFFERSON W. Tester1
and JOSEPH W. Bozzielli2

1Department of Chemical Engineering and Energy Laboratory
Massachusetts Institute of Technology
Cambridge, MA 02139, USA
2Chemistry and Chemical Engineering Department
New Jersey Institute of Technology
Newark, NJ 07102, USA

A benzene supercritical water oxidation (SCWO) mechanism, based on published low-pressure benzene combustion mechanisms and submechanisms describing the oxidation of key intermediates, was developed and analyzed to determine the controlling reactions under SCWO conditions of 750–860 K, 139–278 bar, and equivalence ratios from 0.5 to 2.5. To adapt the combustion mechanisms to the lower temperature (<975 K) and higher pressure (>220 bar) conditions, new reaction pathways were added, and quantum Rice–Ramsperger–Kassel theory was used to calculate the rate coefficients and, hence, product selectivities for pressure-dependent reactions. The most important difference between the benzene oxidation mechanism for supercritical water conditions and those for combustion conditions is reactions in supercritical water involving C6H5OO predicted to be formed by C6H5 reacting with O2. Through the adjustment of the rate coefficients of two thermal decomposition pathways of C6H5OO, whose values are unknown, the model accurately predicts the measured benzene and phenol concentration profiles at 813 K, 246 bar, stoichiometric oxygen, and 3–7 s residence time and reproduces the finding that the carbon dioxide concentration exceeds that of carbon monoxide at all reaction conditions and levels of benzene conversion. Comparison of the model predictions to benzene SCWO data measured at several different conditions reveals that the model qualitatively explains the trends of the data and gives good quantitative agreement without further adjustment of rate coefficients.

Introduction

Supercritical water oxidation (SCWO) is a remediation process for treating aqueous organic wastes. When organic compounds and oxygen are brought together in water well above its critical point of 221 bar and 647 K, the organic is oxidized to carbon dioxide and water, heteroatoms are converted to their corresponding mineral acids and can be neutralized using a suitable base, and any nitrogen forms N2 or N2O [1]. The present working hypothesis maintains that SCWO proceeds by free-radical reactions and that the individual elementary reactions are similar to those which would take place in combustion at the temperature and pressure of SCWO. Furthermore, water, which serves as the reaction medium and participates in reactions both as a reactant and as a third-body collider, does not interfere with reaction events through solvation effects.

The free-radical reaction pathway hypothesis has received support by multiple attempts to model reactions using low-pressure combustion mechanisms adapted to SCWO conditions. Previous modeling efforts yielded kinetic mechanisms describing the oxidation of simple compounds such as hydrogen [2–7], carbon monoxide [3,5,6], methane [5,6,8,9], methanol [6,7,10–14], and phenol [15]. The model predictions have been compared, with varying degrees of success, to experimentally measured species concentration profiles.

An elementary reaction mechanism for benzene oxidation under supercritical water conditions was developed [16] based on a detailed kinetic mechanism for benzene oxidation under combustion conditions [17,18]. The present paper reports results obtained using this developed mechanism to identify reactions controlling benzene oxidation under supercritical water conditions. The model predictions are compared with benzene and phenol concentration profiles measured in our experimental investigation of benzene SCWO at 750–860 K and sub- to supercritical pressures (139–278 bar) under fuel-rich to fuel-lean conditions for reactor residence times of 3–7 s [19]. The details of these experiments are reported elsewhere [19], but briefly benzene SCWO was studied in an 11 mL Hastelloy C276 tubular plug-flow reactor. Temperature was controlled by immersing the reactor in a fluidized sand bath. Aqueous feed solutions of benzene and oxidant were
Adaptation of Benzene Oxidation Mechanisms from Combustion to Supercritical Water Conditions

The most obvious modification necessary to make low-pressure combustion mechanisms suitable for SCWO conditions is adjustment of reaction rate coefficients for the effect of pressure. Unimolecular rate coefficients are well known to depend on pressure to a power which is unity in the low-pressure limit, zero in the high-pressure limit, and fractional in the intermediate-pressure or fall-off region. The transitions to the low- and high-pressure limits occur at reaction-specific pressures.

Recombination reactions exhibit the same pressure dependence as unimolecular reactions when only one reaction pathway is possible. When additional products can be formed by chemically activated pathways, a complex pressure and temperature dependence can result from the competition between the stabilization and the decomposition and/or isomerization pathways [26,27], and experimentally measured rate coefficients cannot be extrapolated directly to other temperatures and pressures. The computer programs CHEMACT [27] and CHEMDIS [28,29] implement the bimolecular Quantum Rice Ramsperger Kassel (QRRK) analysis of Dean [26] and allow the estimation of the pressure and temperature dependence of the rate coefficients for such reactions. Westmoreland et al. [30] and Dean [26] discussed the governing bimolecular and unimolecular QRRK equations and compared predicted and measured rate coefficients. In the present study, two important chemically activated reactions, between H and O2 and between phenyl (C6H5) and O2, were evaluated.

\[
H + O_2 \leftrightarrow HO_2^* \leftrightarrow OH + O
\]

The addition/elimination reaction between H and O2 is one of the most important chain-branching steps in low-pressure combustion. The addition/elimination pathway proceeds through the formation of the activated intermediate HO2*, which can be stabilized to HO2 or dissociate to OH and O. The relative importance of the two pathways depends on pressure and temperature, with the HO2-forming pathway favored at higher pressures.

Cobos et al. [31] studied the recombination reaction forming HO2 at 296 K and 1–200 bar and estimated the high-pressure rate coefficient for recombination by extrapolating measured fall-off curves. Westmoreland et al. [30] used this high-pressure rate coefficient in a bimolecular QRRK analysis of the reaction between H and O2. The rates of both the stabilization (to HO2) and addition/elimination (to OH and O) pathways were successfully predicted over wide ranges of temperature and pressure.

A bimolecular QRRK analysis similar to that of Westmoreland et al., conducted using CHEMACT with rate coefficients from Cobos et al. [31] and Baulch et al. [32], predicted HO2 to be the primary product of the reaction between H and O2 at 246 bar and 813 K (for which conditions the most complete set of benzene concentration data are available [19]) with a rate coefficient close to the high-pressure limit [31]. Further calculations reveal excellent agreement between the predicted and measured rate coefficients for the recombination reaction in the high- [31] and low-pressure limit [32] and the addition/elimination pathway [32].

\[
\text{C}_6\text{H}_5 + O_2 \leftrightarrow \text{Products}
\]

The identity and formation rates of products of the reaction between phenyl and oxygen are a focus of continuing study. In previous benzene oxidation mechanisms, the products were set to phenoxy (C6H5O) and O [17,18,20–23]. A semiglobal pathway was also included in some of these mechanisms [17,18,23]:

\[
\text{C}_6\text{H}_5 + O_2 \leftrightarrow 2\text{CO} + \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4
\]

Frank et al. [33] studied the reaction of phenyl with O2 between 900 and 1800 K and 1.3 to 2.5 bar...
and proposed two sets of products: (1) C6H4O2 and H and (2) p-benzoquinone (C6H4O2) and H. The second of these overall addition/elimination pathways was necessary to explain their observation of fast initial H production. Rate coefficients were measured for both pathways and were included in a mechanism by Tan and Frank [24].

Yu and Lin [34] performed a direct study on the reaction between C6H5 and O2 at 297–500 K and 20–80 Torr. The overall reactions leading to C6H5O and O or C6H5O2 and H proceed first through the formation of an energized C6H5OO radical (C6H5OO*), which can undergo stabilization, isomerization, and/or dissociation to new products. Yu and Lin measured the recombination rate coefficient for C6H5 + O2 by monitoring C6H5OO formation and found it to be pressure independent under their conditions. The sole reaction product was C6H5OO, consistent with their Rice–Ramsperger–Kassel–Marcus prediction that stabilization to C6H5OO dominates over addition/elimination to C6H5O and O or C6H5O2 and H below 1000 K and between 20 and 80 Torr.

Since the reaction between C6H5 and O2 proceeds through the formation of C6H5OO*, the rate coefficients for the addition/elimination pathways measured at the conditions of Frank et al. [33] or used in low-pressure mechanisms [17,18,20–24] are not applicable at SCW conditions. CHEMDIS was used to calculate the rate coefficients for stabilization (to C6H5OO) and addition/elimination (to C6H5O and O). The high-pressure rate coefficient for C6H5OO formation was taken from Yu and Lin [34], and the high-pressure rate coefficient for dissociation of C6H5OO* to C6H5O and O was estimated from microscopic reversibility and assuming the reverse reaction has a pre-exponential factor for diffusion-controlled reactions (A = 10^{12} cm^2 mol^-1 s^-1) and no energy barrier (E_a = 0). At 813 K and 246 bar, the calculated stabilization rate coefficient is two orders of magnitude larger than that for addition/elimination to C6H5O and O. A comparison between the predicted and measured [33] rate coefficients for the addition/elimination pathway at 2.3 bar and from 1000 to 1200 K showed agreement to within 10% to 20% (Table 1), indicating that the estimated value of k_a for C6H5OO* dissociation to C6H5O and O may not be a source of significant error.

Since C6H5OO was predicted to be the main reaction product of C6H5 and O2, bimolecular and unimolecular reactions of C6H5OO were also incorporated into the benzene SCW mechanism [16]. The rates of the unimolecular reaction were found to dominate at supercritical water conditions. The unimolecular decomposition reactions of C6H5OO tested in the SCW mechanism are

\[
C_6H_5OO \leftrightarrow C_6H_5O + O \quad (R2)
\]
\[
C_6H_5OO \leftrightarrow C_6H_5O_2 + H \quad (R3)
\]
\[
C_6H_5OO \leftrightarrow C_6H_5 + CO_2 \quad (R4)
\]

The rate coefficient of reaction R2 was calculated using QRRK analysis and the reverse rate constant by microscopic reversibility. Inclusion of reactions R3 and R4 was necessary, as will be shown below, to gain agreement between the predicted and experimental benzene concentration profile. However, reactions R3 and R4 are not elementary reactions, and rate coefficients for these overall steps were chosen so as to affect the radical pool to give the best fit between the mechanism predictions and the benzene concentration profile measured at 813 K, 246 bar, and residence times of 3–7 s. Their reverse rate coefficients were calculated by microscopic reversibility. Since the present rate coefficients for reactions R3 and R4 are semiempirical, any attempt to use them in other models should be pursued with caution. While the mechanisms by which reactions R3 and R4 take place have not been experimentally determined and likely involve never observed intermediates, theoretical calculations using density functional analysis show that reactions R3 and R4 involve one common isomerization path through a dioxetane cyclic intermediate. After this first isomerization, a path to C6H5O2 + H is present. A second series (unzipping process) is also present, along with another isomerization series. The rate-controlling step involves a 3,2,0 bicyclic (four plus five member ring) tight transition state. CO2 results from the unimolecular decomposition of this bicyclic [35–37].

Justification for the inclusion of reaction R3 comes from the detection of C6H5OO during benzene combustion at both fuel-rich and fuel-lean conditions at 900–1300 K [25], our observation of C6H5O2 in the oxidation of benzene under supercritical water conditions [16,19], and the incorporation of the overall reaction of C6H5 and O2 to C6H5O2 and H in the benzene combustion mechanism of Tan and Frank [24]. Since the reaction between C6H5 and O2 predominantly forms C6H5OO at 246 bar and 813 K, reaction R3 was used in place of the addition/elimination reaction suggested by Frank et al. [33] to

<table>
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<tr>
<th>T(K)</th>
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<tr>
<td>1000</td>
<td>1.2 × 10^{12}</td>
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<td>1100</td>
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<td>1200</td>
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account for C₆H₄O₂ production. Further reactions of C₆H₄O₂ were accounted for by incorporating a recent submechanism [38] by which C₆H₄O₂ is fully oxidized.

Reaction R4 is included to explain the very early appearance of CO₂ in benzene oxidation under supercritical water conditions [16]. The CO₂ yields exceeded those of CO at all conditions studied and for all conversions of benzene. Observations of CO₂ yields always exceeding those of CO were also reported in the SCWO of phenol [15,39] and substituted phenols [40–43], leading to speculation of pathways for CO₂ formation which do not involve CO. Additionally, in benzene combustion at 900–1300 K and at 350 Torr, Chai and Pfefferle [25] measured high amounts of CO₂ at low benzene conversions and postulated CO₂ production by routes other than the reaction of OH and CO. Carpenter [35], Barckholtz et al. [36] and our work [37] show that the reaction of C₆H₅ and O₂ leads to formation of C₅H₅ and CO₂. In the present study, since C₆H₅OO is the primary reaction product of C₆H₅ and O₂ at 246 bar and 813 K, reaction R4 was included in place of an addition/elimination reaction.

Comparison of Model Predictions and Measurements of Benzene Oxidation under Supercritical Water Conditions

The predictions of the benzene SCWO mechanism [16], developed by adapting the benzene combustion mechanism of Shandross et al. [17] and Shandross [18] for the present conditions (813 K, 246 bar, and fuel equivalence ratio, φ, of 1.0), are compared in Fig. 1 (solid line) against the experimental data (points). Also shown is the profile predicted by the original mechanism of Shandross et al. [17] and Shandross [18] (long-dashed line), which generally represents the predictions of low-pressure benzene combustion mechanisms at SCWO conditions. Dissociation reactions of C₆H₅OO to C₆H₅ and O₂, and H and C₅H₅ and CO₂ were necessary in the SCWO mechanism to improve the agreement between the predictions and the data. With their inclusion, the shape and position of the predicted benzene concentration profile agree with the experimental data. The absolute values of the rate coefficients of reactions R3 and R4 were found not to have significant effects on the model predictions as long as the ratio of k₁₄ to k₁₃ is equal to 0.4. If this ratio is larger or smaller than 0.4, the predicted benzene reaction rate is too slow or too fast, respectively. Without inclusion of reaction R3 or R4, the predicted benzene oxidation rate is too fast and the reaction delay is too small (short-dashed line). The induction time can be varied from 0 to a maximum of ~1 s by changing the rate coefficient of reaction R3. The dashed-and-dotted line represents the slowest benzene oxidation rate that can be achieved through adjustment of k₁₃ (without including reaction R4).

The net rates of formation or destruction of key species by the individual reactions in the mechanism were calculated to determine the controlling reactions at 813 K and 246 bar with stoichiometric oxygen. By comparing the net rates of all reactions involving a single species, the primary destruction and formation pathways were determined.

Benzene was found to react almost exclusively by reactions R5 and R6:

\[
C₆H₆ + OH \leftrightarrow C₆H₅OH + H \quad (R5)
\]

\[
C₆H₅ + OH \leftrightarrow C₅H₅ + H₂O \quad (R6)
\]

with reaction R6 accounting for over 97% of the oxidation rate of benzene at 813 K and 246 bar. The rate coefficient used for reaction R6 [32] is the same as that used by Shandross et al. [17] and Shandross [18]. Although reaction R5 is recognized to proceed by a chemically activated pathway [44], given the relative unimportance of reaction R5 the rate coefficient used [45] is the same as that used by Shandross et al. [17] and Shandross [18]. The destruction of phenyl radical (C₅H₅) formed by reaction R6 is completely accounted for by reaction R7.
which C5H5 from reaction R4 reacts primarily by the benzene SCWO mechanism, according to coefficients at 813 K and 246 bar were included in Bozzelli [47,48]. Reactions with the highest rate co-
to 1000 K using the data presented in Zhong and mechanism of Emdee et al. [21], in which the C5H5 in the Shandross mechanism were taken from the
tio of 0.4 for from the density functional analysis supports the ra-
and analysis of thermochemistry and the kinetics and O (reaction R2) can only be a minor channel,
reactions R3 and R4, the predicted C 6H5OH concent-
tration profile agrees with the experimental data. As stated previously, the rate coefficients of reactions R3 and R4 were chosen to optimize model-
data agreement for the benzene concentration pro-
file. Including reaction R3 with a higher rate constant than reaction R2 eliminates the rapid for-
mation of O and the subsequent overproduction of OH by reaction R9. Since reaction R3 generates H, OH formation proceeds through reactions R11, R12, and R13, and inclusion of reaction R3 alone cannot decrease the rate of benzene oxidation sufficiently to bring the model into agreement with the data. As discussed earlier, the reaction of H and O2 producing OH and O is not important at SCWO conditions. To gain model-data agreement, reaction R4 was included. The inclusion of reaction R4 slows the benzene oxidation rate, as C5H3 is relatively unreactive. Reaction R4 also provides a pathway for CO2 formation to account for the experimental observation that CO2 yields exceed those of CO for all measured residence times and reaction conditions [19]. Without reaction R4, the model incorrectly predicts that the CO2 concentration remains below that of CO for residence times less than 7 s. Even with reaction R4, the model underpredicts the concentrations of CO and CO2, reflecting inadequate chemistry for further oxidation of intermediate species. A large fraction of carbon remains as C5H1O2, C5H4O, C5H5, and H2CCCH are also significant.

Figure 2 demonstrates that with inclusion of re-
actions R3 and R4, the predicted C5H5OH concen-
tration profile agrees with the experimental data.

\[
\text{C}_3\text{H}_5 + \text{HO}_2 \leftrightarrow \text{C}_2\text{H}_3\text{O} + \text{OH} \quad (R8)
\]

C5H5O then undergoes ring-opening reactions, leading eventually to CO and CO2.

Since the oxidation of benzene proceeds mainly by reaction R6, the reaction delay (or induction time) and the subsequent rate of benzene reaction are determined by the rate of OH radical generation, which, in the present mechanism, is primarily by reaction R8.

If the global reactions R3 and R4 are not incor-
porated into the mechanism, reaction R2 is the dom-
inant C6H5OO destruction channel. With O formed by reaction R2, excess OH is generated directly by reaction R9

\[
\text{O} + \text{H}_2\text{O} \leftrightarrow \text{OH} + \text{OH} \quad (R9)
\]

and indirectly by the following series of reactions:

\[
\text{C}_6\text{H}_6 + \text{O} \leftrightarrow \text{C}_6\text{H}_5\text{O} + \text{H} \quad (R10)
\]

\[
\text{H} + \text{O}_2 \leftrightarrow \text{HO}_2 \quad (R11)
\]

\[
\text{HO}_2 + \text{HO}_2 \leftrightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad (R12)
\]

\[
\text{H}_2\text{O}_2 \leftrightarrow \text{OH} + \text{OH} \quad (R13)
\]

Reaction R6 proceeds much too quickly, and the present mechanism overpredicts the benzene oxidation rate.

The fate of C6H5OO is the most critical unknown. Comparisons with the data suggest that the radical-forming, chain-branching loss channel to C6H4O2 and O (reaction R2) can only be a minor channel, and analysis of thermochemistry and the kinetics from the density functional analysis supports the ratio of 0.4 for \(k_{f,3}/k_{f,4}\) under SCWO conditions [37].

The reactions and associated rate constants of cyclopentadienyl (C5H5) and cyclopentadiene (C5H6) in the Shandross mechanism were taken from the mechanism of Emdee et al. [21], in which the C5H5 submechanism was based on the outline presented by Brezinsky [46], and the abstraction of H from C6H6 by HO2, OH, H, and O was estimated from the analogous reactions with formaldehyde. In the SCWO-mechanism, we computed rate coefficients using CHEMDIS for the addition and combination reactions of C5H5 and C5H6 at 246 bar from 300 to 1000 K using the data presented in Zhong and Bozelli [47,48]. Reactions with the highest rate coefficients at 813 K and 246 bar were included in the benzene SCWO mechanism, according to which C5H5 from reaction R4 reacts primarily by reaction R8:

\[
\text{C}_6\text{H}_5 + \text{O} \leftrightarrow \text{C}_6\text{H}_5\text{O} \quad (R7)
\]
Without reactions R3 and R4, phenol is overpredicted by a factor of ~100. Phenol is initially formed by reaction R5, destroyed by reaction R14, and then reformed in reaction R15 in an equimolar exchange:

\[
\text{C}_6\text{H}_5\text{OH} + \text{CH}_2\text{CHCHCH}_2 \leftrightarrow \text{C}_6\text{H}_5\text{O} + \text{C}_2\text{H}_6
\]  \hspace{1cm} (R14)

\[
\text{C}_6\text{H}_5\text{O} + \text{C}_2\text{H}_6 \leftrightarrow \text{C}_6\text{H}_5\text{OH} + \text{C}_3\text{H}_5
\]  \hspace{1cm} (R15)

Rate coefficients for reactions R14 and R15 were kept at the values used by Shandross et al. [17] and Shandross [8]. Given that reactions R14 and R15 are the principal reactions involving both \(\text{C}_6\text{H}_5\text{O}\) and \(\text{C}_6\text{H}_5\text{OH}\) and that \(\text{C}_6\text{H}_5\text{OH}\) is minor compared with \(\text{C}_6\text{H}_5\) as a benzene decomposition product, \(\text{C}_6\text{H}_5\text{O}\) is also not a key intermediate in the SCWO mechanism. Without reaction R3, excess \(\text{C}_6\text{H}_5\text{O}\) is formed by reaction R2, leading to the overprediction of \(\text{C}_6\text{H}_5\text{OH}\). With all reactions which lead to \(\text{C}_6\text{H}_5\text{OH}\) formation in the SCWO mechanism involving \(\text{C}_6\text{H}_5\text{O}\) with the exception of reaction R5, and given that reaction R5 is not competitive with reaction R6 at these conditions, agreement between the experimental and predicted \(\text{C}_6\text{H}_5\text{OH}\) concentrations indicates that \(\text{C}_6\text{H}_5\text{O}\) concentration is now properly predicted as long as the \(\text{C}_6\text{H}_5\text{O}/\text{C}_6\text{H}_5\text{OH}\) chemistry is correctly represented.

To test the robustness of the mechanism, the model predictions were compared with benzene SCWO measurements over considerable ranges of reactor conditions [19]. No further adjustments were made to the mechanism. The rate constants of reactions R3 and R4 were treated as temperature independent. Benzene concentrations predicted by the model as a function of temperature at a given pressure, equivalence ratio, and residence time are compared with the experimental data in Fig. 3. Predicted benzene concentration profiles are compared with the data at equivalence ratios from 0.5 to 2.5 at a given temperature and pressure in Fig. 4 and over a range of water densities or pressures at a given temperature.
temperature and equivalence ratio in Fig. 5. The good agreement seen between predictions and experimental data in all cases is especially encouraging in view of the ranges of conditions covered.

Summary and Conclusions

A benzene SCWO mechanism was developed using published benzene combustion mechanisms and submechanisms describing the oxidation of key intermediates. To adapt the benzene combustion mechanism to the lower temperatures and higher pressures of SCWO, new reaction pathways were added and QRRK theory was used to calculate the rate coefficients and predict reaction products for pressure-dependent reactions. The most important difference between the benzene oxidation mechanism for supercritical water conditions and those for combustion conditions is reactions in supercritical water involving $C_6H_5OO$ predicted to be formed by $C_6H_5$ reacting with $O_2$. By adjusting the rate constants of two proposed, global thermal decomposition reactions of $C_6H_5OO$, the first forming $p$-benzoquinone and $H$ and the second forming cyclopentadienyl and $CO_2$, the model was fit to the benzene concentration profile measured during SCWO at 813 K, 246 bar, and 3–7 s residence time with stoichiometric oxygen. The resulting mechanism accurately reproduces the experimental benzene and phenol concentration profiles at these conditions and predicts well the benzene concentration profiles under SCWO conditions ranging from 750 to 850 K, 139 to 278 bar, and equivalence ratios from 0.5 to 2.5.

Acknowledgments

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The reaction of CO and OH proceeds through the formation of an activated HOCO intermediate. At high pressures, the stabilization pathway to HOCO dominates over the dissociation pathway to CO$_2$ + H (Fulle et al., 1996). Stabilized HOCO can then undergo reaction, including dissociation back to CO + OH or to CO$_2$ + H. As is the case with the cyclohexadienyl-OH adduct, reverse dissociation to products is favored over the CO$_2$ + H pathway.

**COMMENTS**

**Alexander Fridman, University of Illinois at Chicago, USA.** Standard mechanisms of C$_6$H$_6$ oxidation in gas phase cannot be used for oxidation in supercritical water. When looking for special new oxidation channels in supercritical water, it would probably be important to take into consideration ion formation and following ion-molecular reactions like H$_2$O$^+$ + H$_2$O $\rightarrow$ H$_3$O$^+$ + OH, and so on, leading to OH formation. Such reactions in supercritical conditions can be important when working at higher temperature limits.

**Author's Reply.** Ionic reactions were not considered because the supercritical water environment at our conditions (475–600 C, 250 bar) does not support ionic species due to the low dielectric constant of water. In addition, typical ionization potentials are 200 kcal/mol, whereas bond energies are about 100 kcal/mol. Because of the higher entropy of OH dissociation back to benzene relative to H, the dissociation of the cyclohexadienyl-OH adduct back to OH + benzene is not the order of 1 s at atmospheric temperature, but only about 3 $\mu$s at SCWO temperatures. A more important reaction of the cyclohexadienyl-OH adduct at SCWO conditions is H-atom elimination to phenol and a slightly lower (less than 2 kcal/mol) lower enthalpy for the dissociation. This reaction was taken into account by including the high pressure value of He et al. (1996) for the overall reaction.