Pyrolysis and Oxidation of Phenol

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Pathways of aromatic fuel oxidation have revealed the importance of phenol chemistry and motivated this study to obtain the very first stable intermediate species profiles for the atmospheric pressure oxidation of phenol near 1170 K over a range of equivalence ratios, 0.64−1.73. Under these conditions, cyclopentadiene was found to be a major reaction intermediate. Other major species observed included carbon monoxide, carbon dioxide, acetylene, benzene, 1,3-butadiene, ethene, and methane. Minor species were allene, methylacetylene, propene, ethane, methylcyclopentadiene, and naphthalene. The reaction intermediates are consistent not only with the findings of a cyclopentadiene oxidation study previously performed in this laboratory but also with reactions in the postulated mechanism of phenol oxidation. A complementary study of phenol pyrolysis indicated that carbon monoxide, cyclopentadiene, and benzene were major reaction intermediates, also consistent with an earlier study of phenol pyrolysis in this laboratory. Carbon monoxide yield was once again found to exceed that of cyclopentadiene. However, trace species not detected in the prior study were observed and now shown to account for the difference in formation of carbon monoxide and cyclopentadiene. These data and the associated mechanistic analysis should be instrumental in the further validation of benzene oxidation models and will prove essential to the understanding of the whole of aromatics fuel chemistry.

I. Introduction

Recent analyses[1−4] of the pathways of aromatics oxidation reveal the critical role that both phenol and phenoxy radical play in the oxidation process. Nonetheless, only a few high-temperature phenol studies have been reported[5−9] and no gas-phase oxidation data are available in the archival literature. Therefore, the primary intent of the present investigation was the acquisition of experimental oxidation data over a range of stoichiometries as well as complementary phenol pyrolysis data. The data consist of intermediate species mole fractions as a function of reaction time obtained from atmospheric pressure flow reactor experiments near 1170 K. As in previous flow reactor studies of aromatic compounds,[10−12] the data are most useful when viewed in the context of reactions of importance in the development of a detailed chemical kinetic model.

II. Results and Discussion

The experimental conditions for the oxidation and pyrolysis experiments are given in Table 1,and a summary of the species mole fractions obtained is given in Table 2. These experiments were performed in an atmospheric pressure flow reactor that previously has been extensively described.[10−13] The species profiles, mole fractions with respect to reaction time, are presented within the context of the subsequent discussion.

The thermal decomposition of phenol examined through pyrolysis studies provides a subset of intermediate species that can be associated with the chemistry that occurs in the absence of oxidation. This subset of pyrolysis intermediates then can be used to infer the chemical changes due to oxygen addition. Accordingly, pyrolysis data are presented and discussed first as a prelude to and context for the presentation and analysis of the results of the oxidation experiments.

TABLE 1: Experimental Conditions for Phenol Experiments

equivalence ratio ϕ	temp (K)	residence time (ms)	fuel loading (ppm)
pyrolysis	1173	131	1004
1.73	1169	126	533
1.03	1169	127	538
0.64	1169	126	533

TABLE 2: Maximum Intermediate Species Mole Fractions Reached in Phenol Experiments[a]

species	pyrolysis (ppm)	$\phi = 1.73$ (ppm)	$\phi = 1.03$ (ppm)	$\phi = 0.64$ (ppm)
CO	134	434	616	1078
C_5H_6	93	41	36	28 @ $t = 70$
C_6H_6	18	14	19	30
C_2H_2	<10	38	57	112
1,3-C_4H_6		19	28	32 @ $t = 98$
CH_4	11	<10	14	26
C_3		<10	<10	14
$C_{10}H_8$	<10	11	<10	<10
$CH_3C_5H_5$	<10	<10	<10	<10
C_2H_4		<10	<10	23
C_2H_6				<10
CO_2		120	135	204

[a] Unless otherwise noted, maximum mole fraction corresponds to residence time $t_{max} \approx 130$ ms.

(A) Phenol Pyrolysis. As expected in view of prior studies,[6,8,14,15] major reaction intermediates found in the phenol pyrolysis experiments were carbon monoxide and cyclopenta-

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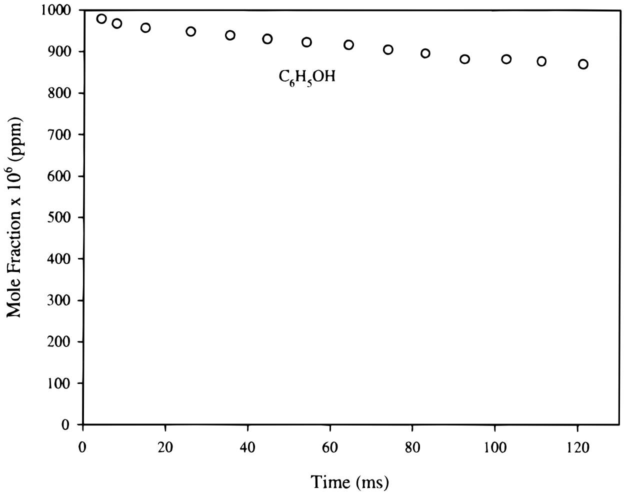

Figure 1. Profile reconstructed by summing the carbon contained in all other observed species, subtracting the sum from the initially known carbon loading, and dividing by the number of carbons per molecule of phenol.[13] Note that this technique precludes an independent determination of a carbon balance.

diene. Minor species observed included benzene, acetylene, naphthalene, methane, and methylcyclopentadiene.

C_6H_5OH Consumption. The phenol decay profile is shown in Figure 1. The destruction of phenol will most likely occur initially via the thermal decomposition

$$C_6H_5OH \rightarrow C_6H_5O^\bullet + H \qquad (1)$$

A rate constant for the reverse reaction was determined by He et al.[7] to be 2.5×10^{14} cm^3 mol^{-1} s^{-1}. This value is consistent with earlier observations[16] that rates of recombinations involving resonance-stabilized radicals seem to be especially large.

A recent high-temperature shock-tube study of phenol pyrolysis[17] addressed another possibility for phenol destruction. Horn and Frank[17] measured, through optical techniques, H atom and CO concentrations as a function of time. To model the time profiles of these species, it was necessary for the researchers to hypothesize that phenol underwent a direct molecular elimination:

$$C_6H_5OH \rightarrow CO + C_5H_6 \qquad (2)$$

With the inclusion of this step, their pyrolysis model predicted very well the measured CO profiles. H atom profiles were also well predicted by the inclusion of subsequent reactions of C_5H_6. The inclusion of reaction 2 in a model of phenol pyrolysis would be consistent with the benzene oxidation modeling effort of Zhang and McKinnon[18] who also postulated the importance of this step. Shandross et al.,[2] however, found that there was no basis for including this step in any model of benzene oxidation, and their analysis has left the significance of this reaction still uncertain. Flow reactor data cannot resolve this uncertainty, since, as will be discussed below, either decomposition reaction 1 or reaction 2 leads ultimately to the same detectable stable species, CO and C_5H_6.

Following initiation, phenol consumption most likely proceeds via reactions with the H atom:

$$C_6H_5OH + H \rightarrow C_6H_5O^\bullet + H_2 \qquad (3)$$

$$C_6H_5OH + H \rightarrow C_6H_6 + OH \qquad (4)$$

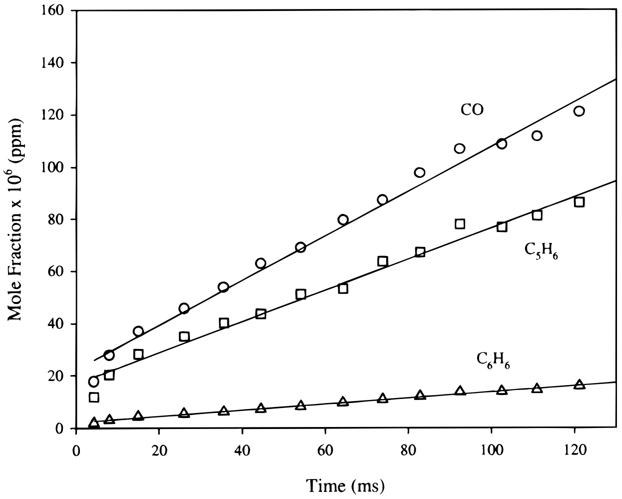

Figure 2. Carbon monoxide, cyclopentadiene, and benzene profiles from the pyrolysis of phenol at 1173 K.

He et al.[7] determined the rate constants $k_{(3)} = 1.15 \times 10^{14}$ exp$(-6240/T)$ cm^3 mol^{-1} s^{-1} and $k_{(4)} = 2.21 \times 10^{13}$ exp$(-3990/T)$ cm^3 mol^{-1} s^{-1}. Their results indicate that displacement is favored over abstraction for $T \leq 1360$ K, which has important implications for aromatics oxidation. Overall reaction progress is hindered by displacement, since it results in the unoxidized product benzene.[7] OH produced in the displacement reaction will abstract H from phenol to form water:

$$C_6H_5OH + OH \rightarrow C_6H_5O^\bullet + H_2O \qquad (5)$$

He et al.[7] found the rate constant for reaction of OH with phenol to be 6×10^{12} cm^3 mol^{-1} s^{-1} at 1032 K. The authors concluded that this result must correspond to abstraction of the phenolic H, since the previously determined[19,20] rate constant for attack on the ring is a factor of 10 smaller.

CO and C_5H_6. The phenoxy radical produced through reactions 1, 3, and 5 decomposes unimolecularly to CO and the cyclopentadienyl radical:[8,14,21]

$$C_6H_5O^\bullet \rightarrow CO + C_5H_5^\bullet \qquad (6)$$

The parent species cyclopentadiene is derived via reaction of the radical $C_5H_5^\bullet$ with a hydrogen donor, e.g., the initial fuel:

$$C_5H_5^\bullet + C_6H_5OH \rightarrow C_5H_6 + C_6H_5O^\bullet \qquad (7)$$

Phenoxy decomposition, reaction 6, when combined with reactions such as reaction 7, would lead in flow reactor experiments to the same observable products of CO and C_5H_6 as does the direct product from phenol (reaction 2).

Carbon monoxide and cyclopentadiene profiles are shown in Figure 2. Both the CO and C_5H_6 profiles are linear in time. Also, the CO yield exceeds the C_5H_6 yield by a factor of roughly 1.4. These observations are consistent with those of Lovell et al.[8] who found that over a range of experimental conditions the rate of CO formation was always significantly greater than that of C_5H_6. However, reactions 1 and 3−7 taken alone predict nearly equal rates of formation for CO and cyclopentadiene. Lovell suggested the occurrence of a reaction that would remove C_5 species from the system without an equivalent restriction of CO production. Naphthalene and indene, presumably derived from two cyclopentadienyl radicals, were observed by Lovell, but their yields were too small to constitute a major sink for $C_5H_5^\bullet$. Thermal decomposition of C_5 species was ruled out, since the expected $C_5H_5^\bullet$ pyrolysis products (methane, C_3's, and

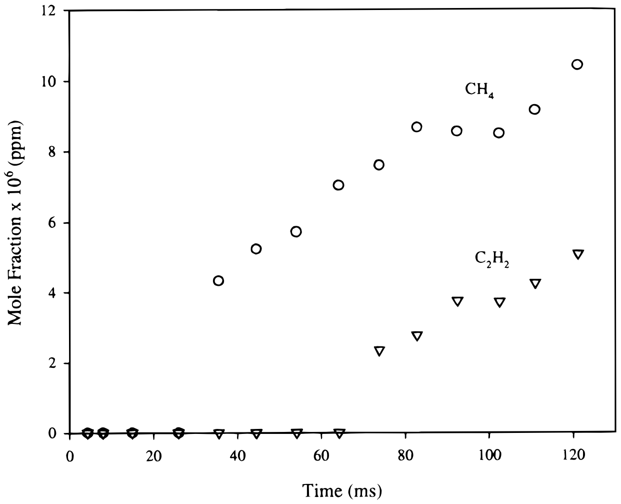

Figure 3. Methane and acetylene profiles from the pyrolysis of phenol at 1173 K.

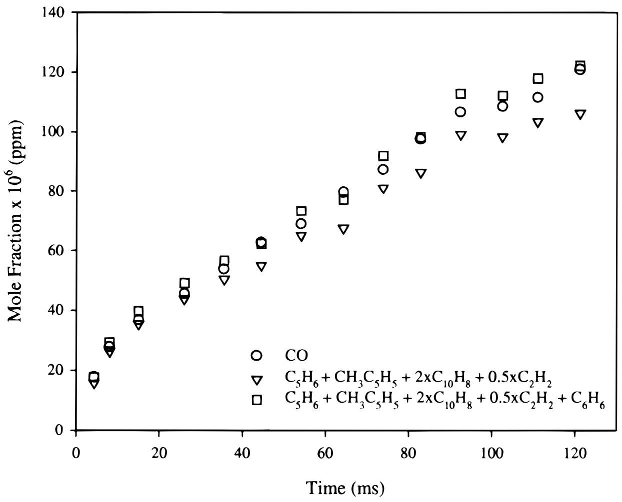

Figure 4. Comparison of carbon monoxide and sum of C_5H_5 derivatives from the pyrolysis of phenol at 1173 K.

C_4's) were not observed. Ultimately, the addition reaction

$$C_6H_5O^\bullet + C_5H_5^\bullet \rightarrow C_6H_5OC_5H_5 \quad (8)$$

was proposed to explain the imbalance of CO and C_5H_6. It was postulated that the $C_6H_5OC_5H_5$ product would go unobserved, since large oxygenated aromatics (with low vapor pressures and high boiling points) are difficult to detect by sample trapping and batch analysis.

On the basis of the present experimental results, which differ somewhat from those of Lovell, an alternative analysis is given below for the observed difference in the rates of formation of carbon monoxide and cyclopentadiene.

C_5H_6 Decomposition. On the basis of the absence of methane and $C_{3,4}$ species, it was concluded in Lovell's study that the decomposition of C_5 species did not occur. However, acetylene, an expected product of cyclopentadiene pyrolysis,[15] was reportedly observed. In the present study, owing to improved analytic techniques, both acetylene and methane were detected and measured (Figure 3), suggesting that the decomposition of C_5 species did occur.

Acetylene and the allyl radical may be derived via H addition to cyclopentadiene followed by ring opening and decomposition of the resultant linear $C_5H_7^\bullet$ radical:[22]

$$H + C_5H_6 \rightarrow c\text{-}C_5H_7^\bullet \quad (9)$$

$$c\text{-}C_5H_7^\bullet \rightarrow n\text{-}C_5H_7^\bullet \quad (10)$$

$$n\text{-}C_5H_7^\bullet \rightarrow C_2H_2 + H_2C{=}CH{-}CH_2^\bullet \quad (11)$$

Subsequent reaction of allyl may yield acetylene and the methyl radical:[23]

$$H_2C{=}CH{-}CH_2^\bullet \rightarrow C_2H_2 + CH_3 \quad (12)$$

in which the methyl reacts in part to form methane. Admittedly, reaction 12 is energetically less favored than the decomposition of allyl to allene and H. However, no allene was observed among the reaction products and the above reaction steps for the production of acetylene and methane are consistent with the data. Nevertheless, reactions 9−12 are still a speculative explanation for the data and remain to be demonstrated.

C_6H_6. Benzene yield is shown in Figure 2. Consistent with the observations of Lovell et al.,[8] the profile is linear in time. As stated earlier, benzene may be formed directly from phenol via displacement of OH by an H atom, although there appears to be few pathways for the production of H and consequently very little H atom available for the displacement reaction. Trace methylcyclopentadiene (<2 ppm) observed in the present study suggests an additional benzene formation route. Methylcyclopentadiene and its radical are likely formed by reactions of $C_5H_5^\bullet$ and CH_3:

$$C_5H_5^\bullet + CH_3 \rightarrow CH_3C_5H_4^\bullet + H \quad (13)$$

$$C_5H_5^\bullet + CH_3 \rightarrow CH_3C_5H_5 \rightarrow CH_3C_5H_4^\bullet + H \quad (14)$$

The methylcyclopentadienyl radical can lead to the formation of benzene through isomerization and hydrogen loss:[24−26]

$$CH_3C_5H_4^\bullet \rightarrow C_6H_6 + H \quad (15)$$

Therefore, some fraction of the observed benzene may in fact be derived via $C_5H_5^\bullet$ rather than from phenol directly. This route is consistent with the observations of Butler[15] who found benzene to be a major product in the pyrolysis of cyclopentadiene at similar temperatures.

CO/C_5H_5 Balance. The above discussion implies a balance between CO and the sum of $C_5H_5^\bullet$ derivatives. Derivatives of $C_5H_5^\bullet$ include C_5H_6, $CH_3C_5H_5$, naphthalene, acetylene, and some fraction of the total benzene. Naphthalene, derived from two $C_5H_5^\bullet$ radicals, is counted twice in the tally. Acetylene is weighted by a factor of one-half, since the thermal decomposition of a single C_5 ring will yield two C_2H_2 molecules.

The CO/C_5H_5 comparison is illustrated in Figure 4. Near-perfect agreement between the CO and C_5H_5 curves is obtained if all of the observed benzene is assumed to be formed via $CH_3C_5H_4^\bullet$, thus supporting the conjecture that very few H atoms are available for benzene formation by the displacement of OH from phenol. Nevertheless, more detailed reaction modeling must be undertaken in order to establish whether these deductions are valid for the conditions of the present study.

(B) Oxidation. Species profiles obtained from the oxidation of phenol near 1170 K are shown in Figures 5−13. Although no prior high-temperature phenol oxidation studies have been reported, the oxidation of cyclopentadiene[15] has been investigated in the Princeton atmospheric pressure flow reactor. Reaction intermediates observed in the phenol experiments were consistent with the findings of the cyclopentadiene study. Major

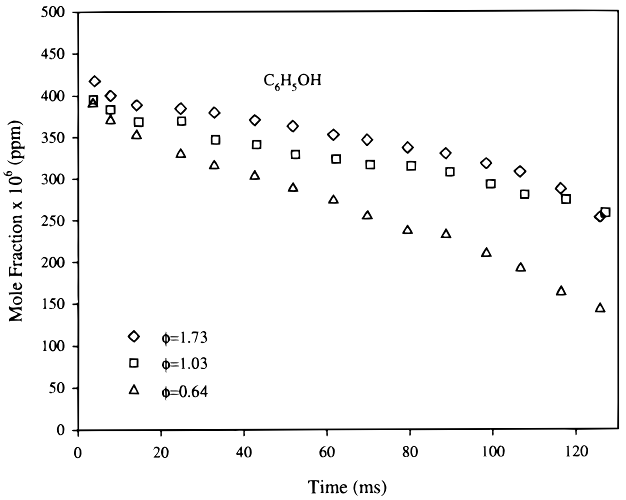

Figure 5. Reconstructed fuel decay profiles from the oxidation of phenol at 1169 K.

species included carbon monoxide, carbon dioxide, acetylene, cyclopentadiene, benzene, 1,3-butadiene, ethene, and methane. Minor species were allene, methylacetylene, propene, ethane, methylcyclopentadiene, and naphthalene.

C_6H_5OH Consumption. Phenol decay profiles for a range of equivalence ratios are shown in Figure 5. In addition to the phenol consumption reactions 1−5 discussed above, the reaction of phenol with molecular oxygen

$$C_6H_5OH + O_2 \rightarrow C_6H_5O^\bullet + HO_2 \tag{16}$$

must be considered. No measured rate for this reaction has been reported. However, a rate may be estimated by analogy with the reaction

$$C_6H_5CH_3 + O_2 \rightarrow C_6H_5CH_2^\bullet + HO_2 \tag{17}$$

since the phenolic O−H bond and the benzylic C−H bond are roughly equal in strength. In a flow reactor study of toluene oxidation, Emdee et al.[4] determined that the toluene profile predicted by their model was most sensitive to reaction 17. At that time, no direct determination of its rate was available in the literature. Therefore, the rate was initially estimated and then adjusted for a better fit to the experimental data to yield $A = 3.00 \times 10^{14}$ cm^3 mol^{-1} s^{-1} and $E_a = 41.4$ kcal/mol. To model the oxidation of phenol in supercritical water, Gopalan and Savage[27] estimated the rate of reaction 16 using Emdee's *A* factor for reaction 17. The activation energy was estimated from the heat of reaction plus a barrier of 1.31 kcal/mol (E_a for HO_2 + allyl radical → propene + O_2). A recent study conducted over the temperature range 673−793 K,[28] however, suggests that the preexponential of reaction 17 is actually a factor of 100 smaller, $\sim 2 \times 10^{12}$. However, an even more recent shock-tube study[29] conducted at higher temperatures, 1050−1400 K, supports very strongly the estimate of Emdee et al.[4] for the rate constant parameters of reaction 17. Clearly, rate coefficients for reactions 16 and 17 will require better evaluation before more definitive modeling of the oxidation of phenol and even toluene can be accomplished.

HO_2 chemistry plays a role under the conditions of the present study (1 atm, $T \approx 1170$ K). Thus, the relevant reaction with phenol is

$$C_6H_5OH + HO_2 \rightarrow C_6H_5O^\bullet + H_2O_2 \tag{18}$$

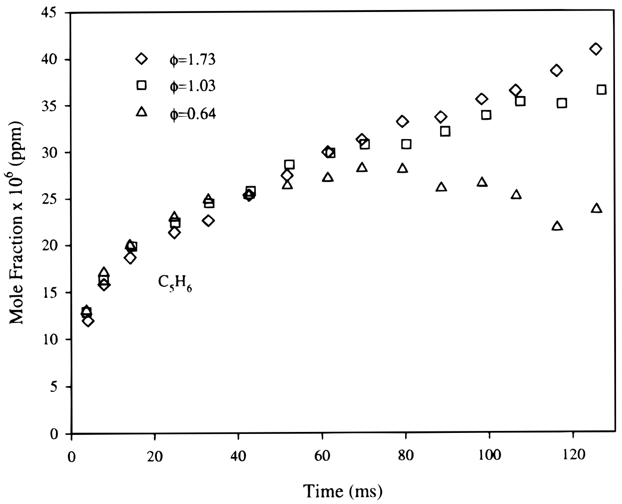

Figure 6. Cyclopentadiene profiles from the oxidation of phenol at 1169 K.

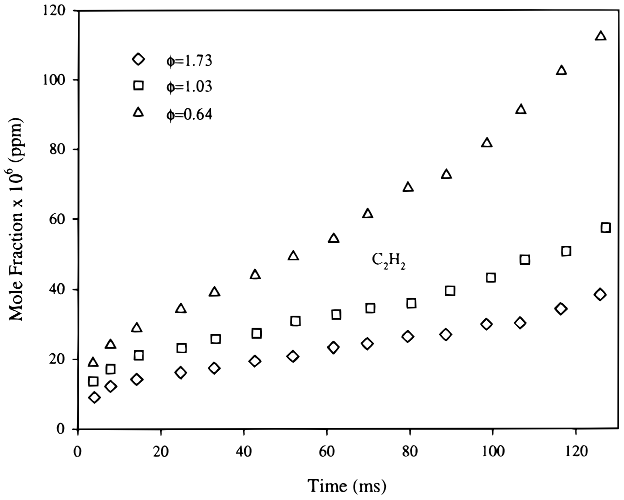

Figure 7. Acetylene profiles from the oxidation of phenol at 1169 K.

Gopalan and Savage estimated $k = 1.0 \times 10^{12} \exp[-10000 \text{ cal mol}^{-1}/(RT)]$ for reaction 18 based on the rate constant for abstraction of the aldehydic H from acetaldehyde ($CH_3CHO + HO_2$).

C_5H_6 Oxidation. Cyclopentadiene profiles are shown in Figure 6. The profiles exhibit the expected oxygen dependence with the most significant consumption of C_5H_6 observed at the leanest condition. Cyclopentadiene oxidation products including acetylene, 1,3-butadiene, methane, and C_3 species are shown in Figures 7−10. Yields of these species increase with decreasing equivalence ratio (more oxygen available). With the exception of 1,3-C_4H_6, the observed cyclopentadiene oxidation products do not undergo subsequent conversion on the time scale of these experiments.

The decomposition of C_5H_6 via H addition and subsequent ring opening was described above. In an oxidation system, addition of O and OH must be considered as well. Radical recombination reactions of $C_5H_5^\bullet$ with O and HO_2 are also expected to play a role in the conversion of the C_5 ring to noncyclic products. These reactions are detailed by Bozzelli et al.[22] and Butler.[15] Analogous reactions can be described for methylcyclopentadiene.

C_6H_6. In the absence of oxygen, the benzene profile was found to be linear in time. As shown in Figure 11, the benzene profile is also linear under oxidation conditions; the slope (i.e.,

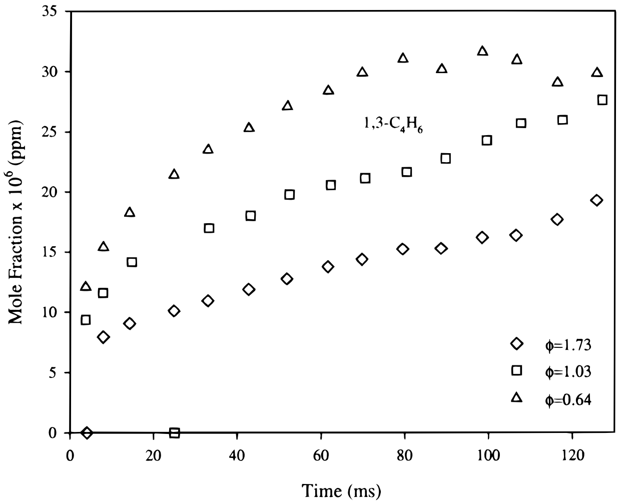

Figure 8. 1,3-Butadiene profiles from the oxidation of phenol at 1169 K.

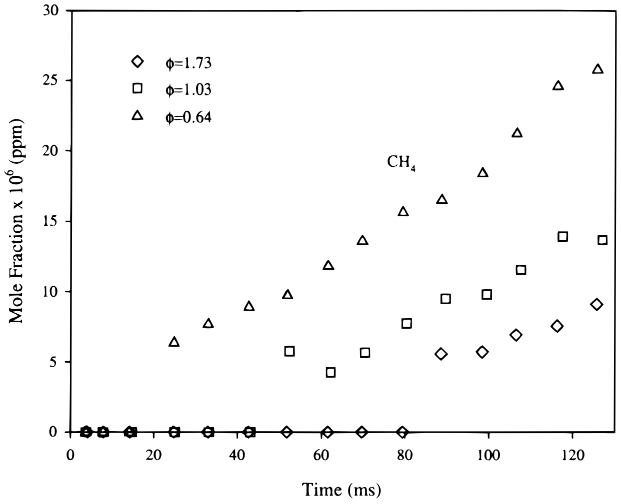

Figure 9. Methane profiles from the oxidation of phenol at 1169 K.

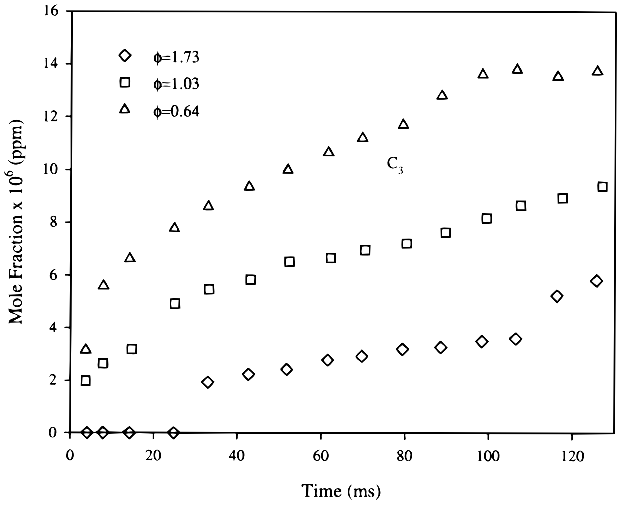

Figure 10. C_3 profiles from the oxidation of phenol at 1169 K. C_3 = propene + allene + methylacetylene.

the rate of benzene production) increases with decreasing equivalence ratio. Trace methylcyclopentadiene was observed, again suggestive of the formation of benzene via $CH_3C_5H_4^{\bullet}$.

CO and CO_2. CO and CO_2 profiles are shown in Figure 12. The CO_2 profiles are characterized by a rapid, early growth (i.e., prior to the first sampling point) followed by a period of near-zero growth that persists over most of the 126−127 ms reaction time. This observation is indicative of a rapid, early production of CO_2, which is terminated prior to the first sampling point.

The present data suggest that the chemistry in the initial region of the flow reactor is more rapid than would be expected for a

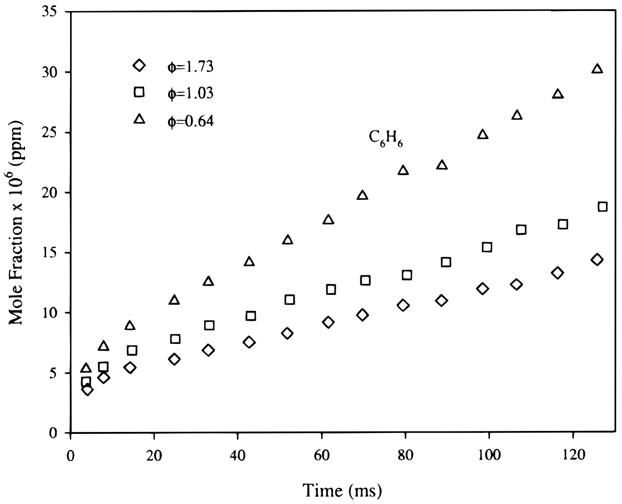

Figure 11. Benzene profiles from the oxidation of phenol at 1169 K.

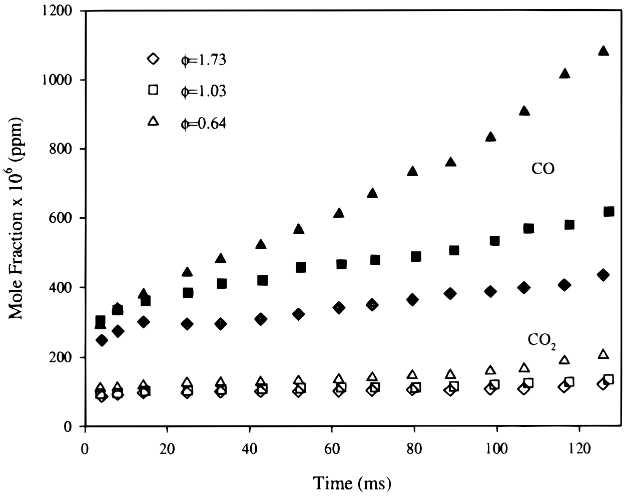

Figure 12. Carbon monoxide and carbon dioxide profiles from the oxidation of phenol at 1169 K.

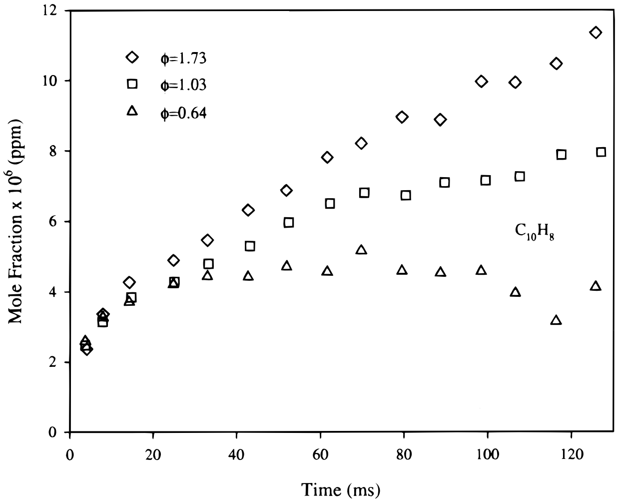

Figure 13. Naphthalene profiles from the oxidation of phenol at 1169 K.

uniform, zero-dimensional, chemically evolving mixture. The prevailing consequence of this effect is merely a shortening of the chemical induction time; modeling results[30] indicate that the postinduction chemistry is unaffected. Therefore, comparison of zero-dimensional model predictions with the present data may be made; a shift in time of the calculated species profiles will likely be required as has been performed in related studies [ref 4, for example].

III. Summary

The pyrolysis of phenol, previously studied in this laboratory,[8] has been extended. CO, cyclopentadiene, and benzene were major reaction intermediates, consistent with prior findings. Carbon monoxide yield was once again found to exceed that of C_5H_6. However, trace species not detected in the earlier study were observed and can be used to explain the difference in rates of formation of carbon monoxide and cyclopentadiene.

The very first data on the concentration of intermediates as a function of time from the oxidation of phenol have been obtained. Cyclopentadiene is a major reaction intermediate. Cyclopentadiene is most likely derived from its radical, formed via unimolecular decomposition of the phenoxy radical. Other reaction intermediates observed in the phenol oxidation experiments were consistent with the findings of a cyclopentadiene oxidation study[15] also performed in this laboratory. Major species included carbon monoxide, carbon dioxide, acetylene, benzene, 1,3-butadiene, ethene, and methane. Minor species were allene, methylacetylene, propene, ethane, methylcyclopentadiene, and naphthalene.

It is expected that these data will be instrumental in the validation of benzene oxidation models and will prove contributive to the understanding of the whole of aromatics chemistry.

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