

# An experimental study of benzene oxidation at fuel-lean and stoichiometric equivalence ratio conditions

Yan Chai and Lisa D. Pfefferle\*

Yale University, Department of Chemical Engineering, New Haven, CT 06520-8286, USA

(Received 17 January 1997; revised 16 July 1997)

Benzene oxidation at two equivalence ratios ( $\phi = 0.19$  and  $1.02$ ) was studied in a well-mixed reactor with a 50 ms mean residence time at 350 torr and 900–1300K. The temperature for 20% benzene conversion is shifted to approximately 90K higher temperatures for the stoichiometric condition as compared to the lean condition. Acetylene ( $C_2H_2$ ) was the major hydrocarbon intermediate for both stoichiometries. Phenol ( $C_6H_5OH$ ) and acrolein ( $C_3H_4O$ ) reach significant concentrations for the lean condition, while at the stoichiometric condition  $C_4H_4$  is more than twice as abundant compared to the lean case, and phenol and acrolein are minor intermediates. The predominant radical species for both conditions is cyclopentadienyl ( $C_5H_5$ ). Cyclopentadienonyl ( $C_5H_5O$ ) and phenoxy ( $C_6H_5O$ ) are the next most abundant radical species detected in the lean condition. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: benzene oxidation; kinetics; well-mixed reactor)

## INTRODUCTION

Understanding the mechanisms for benzene oxidation is necessary for better characterizing the net production of larger aromatic combustion byproducts and controlling their hazardous emissions. Benzene oxidation has been studied both experimentally and theoretically by a number of investigators<sup>1–7</sup>. Chemical kinetic modeling has become an important tool in the analysis of experimental data from complex combustion reacting systems with many unknowns such as benzene oxidation. The global steps of benzene oxidation have been studied by many investigators, especially at high temperatures ( $> 1600K$ ). The detailed oxidation mechanism, however, is not well understood, particularly at fuel-lean conditions and moderate temperatures (900–1300K).

At these conditions many hydrocarbon and oxygenated intermediate species are produced even at very low conversions including a large array of higher hydrocarbons. Published models give qualitative agreement with many experimental measurements; however, agreement for some intermediate species is poor. One example of this is dramatic overpredictions of phenoxy radical and phenol, especially when the models are modified to include the higher phenyl +  $O_2$  rate measured by Frank *et al.*<sup>8</sup> In addition, published models are not useable outside at the conditions of temperature and stoichiometry they were tested for. This indicates the significant uncertainty that still

exists in benzene oxidation mechanisms both with respect to new reaction channels and rate constants. Detailed experimental data including radical species measurements over a wide range of stoichiometries is important for the development and testing of benzene oxidation mechanisms.

Aromatic hydrocarbon oxidation has been studied extensively in the Princeton Flow Reactor at temperatures up to 1200K. Detailed kinetic modeling studies of benzene oxidation<sup>9,10</sup> showed reasonable agreement with the concentration profiles of major species from Princeton's results at atmospheric pressure and a temperature near 1100K for the stoichiometric equivalence ratio condition. However, the experimental data only cover a narrow temperature range (1100–1190K) and lack direct measurements of minor products, especially oxygenated species and radical species. In addition, the model of Emdee *et al.*<sup>9</sup> uses the lower phenyl +  $O_2$  rate which was consistent with the literature before the elementary reaction measurements of Frank *et al.*<sup>8</sup>. The previous work in this laboratory<sup>7</sup> on benzene oxidation presented another approach to the problem with the experimental advantage of using experimental technique which simultaneously measures both stable and radical species at the ppm level concentration. However, some of the intermediate species were not measured at that time due to equipment limitations and only one stoichiometry was studied. The current study is an extension of that work on benzene oxidation which includes data on a wider range of stable and radical intermediate species at both fuel lean and near stoichiometric conditions.

Due to the large number of unknowns in both pathways and rate constants, model testing requires as many

\* Corresponding author

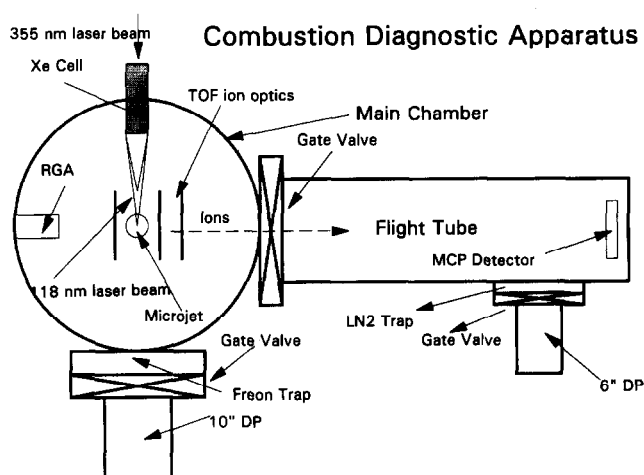
intermediate measurements as possible. An on-line, sensitive and fast detection technique is essential for this purpose. With a vacuum-UV photoionization time-of-flight mass spectrometer (VUV-TOF-MS) and a electron impact quadrupole residual gas analyzer (RGA) that allow simultaneous measurement of stable and radical intermediates in ppm concentrations, we studied benzene oxidation with a well-mixed reactor at fuel-lean ( $\phi = 0.19$ ) and near stoichiometric ( $\phi = 1.02$ ) conditions in the temperature range 900–1300K and 350 torr pressure. The results are presented and discussed in this paper. Differences in product and intermediate profiles for these two stoichiometries provide a useful database for testing models of benzene oxidation at moderate temperatures.

## EXPERIMENTAL APPROACH

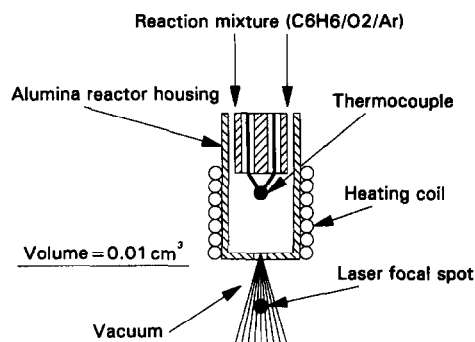
The VUV-TOF-MS apparatus and microjet reactor developed in this laboratory are similar to those described in previous studies<sup>7,11</sup>. Briefly, the system consists of a microjet reactor, a residual gas analyzer and time-of-flight mass spectrometers. *Figure 1* shows a schematic diagram of this combustion diagnostic apparatus. The major differences of this technique over other combustion diagnostic systems is that stable and radical species are simultaneously measured with ppm sensitivity. Therefore it avoids the prior separations used in most GC-MS technique. The detection technique for this system is fast enough (on the order of microseconds), so many parent ions can be detected prior to dissociation. The temperature, mean residence time and pressure can be varied in a wide range for this system which allows us to directly measure the concentration profiles of many hydrocarbon oxidation and pyrolysis at various experimental conditions.

The miniature reactor (shown in *Figure 2*) which approaches a well-mixed reactor at a range of flow conditions, termed a microjet reactor, is formed by inserting a 0.155 cm OD alumina tube into a 0.160 cm ID one end closed, alumina tube with a roughly 80  $\mu\text{m}$  diameter nozzle at its end. The inner tube is inserted to within 0.550 cm of the end of the outer tube, leaving a 0.011  $\text{cm}^3$  chamber that serves as the well-mixed reactor. The outer tube functions both as the reactor and as the nozzle for ejection of reaction species into the vacuum chamber. Under the conditions of this study the reactor behaves as a well-stirred reactor. The benzene diffusion time scale is of the order 100 times faster than the flow time for the range of conditions where benzene conversion was observed. The reactor was used for methane oxidation and both conversion and species versus temperature profiles were well predicted using a well-mixed reactor model along with a detailed methane oxidation mechanism.

The reaction chamber is resistively heated to the desired temperature by a tantalum heating coil. The heating-up process is very fast due to the small size of the reactor. Temperature is measured using a 0.0762 mm diameter uncoated type K thermocouple through the inner tube. The magnitude of reactor temperature rise due to the chemical reaction is negligible in our case due to the low mass flow rate and very diluted fuel in the reactor. Gas versus thermocouple temperature was checked using pneumatic thermometry (a technique described in Prada-Silva *et al.*<sup>12</sup>) A correction of up to 5% is required at temperatures above 1400K. The temperature inside the reactor can be varied from 300 to 1800K. The limitations on temperature are imposed by the softening point of alumina (2030K) and the propensity of the microjet orifice to clog with carbon



**Figure 1** Diagram of experimental apparatus (not to scale). The microjet reactor exhausts at the arrow perpendicular to the plane of the figure. The species emanating from the microjet are ionized by the VUV radiation and are extracted perpendicular to the jet. TOF stand for the time-of-flight mass spectrometer. MCP stands for microchannel plate



**Figure 2** Cross-section of microjet reactor

deposits at temperatures higher than 1800K and fuel-rich conditions. The reactor pressure was measured by a pressure gauge mounted outside the vacuum chamber, 30 cm from the microjet reactor. The error compared to the reactor pressure was estimated to be less than 2 torr by this arrangement. Premixed sample gases were delivered to the reactor via a mass flow controller. Reactor orifice sizes were chosen to control the gas mixture flow rate through the reactor and to maintain the high vacuum in the sampling chamber. There are two ways to estimate the residence time of this reactor: one is to keep the pressure constant by varying the flow rate when the temperature is changed. Another is to maintain a constant flow rate by varying the pressure as the reactor temperature changes during the experiment. The residence time here was obtained in a constant pressure mode with the flow rate measured for each temperature point. Then residence time is calculated by dividing the reactor flow volume by the volumetric flow rate of the reacting mixture to the reactor. Since the residence time estimated by the method above changes slightly for different temperature ( $\pm 3$  ms for our temperature range), so the residence time given here is the average residence time for the temperature range studied. The mass flux was varied by no more than a factor of 1.10 at the temperature range under which our experiments were conducted. This effect can be easily accounted for in model calculations and does

not affect the qualitative analysis of reaction pathways. The microjet reactor is especially attractive for studying combustion reactions since it quenches species within 1–2 ms of their ejection through a rapid decrease in density and temperature. This reactor/sampling technique is similar to the molecular beam probing method employed in other combustion studies<sup>13</sup>. The cooling during the gas expansion from the microjet reactor orifice into the high vacuum chamber ( $3 \times 10^{-5}$  torr) is sufficient to quench reactions and allow detection of hydrocarbon radicals.

The VUV-TOF-MS measures the reaction products with ionization potentials (IPs) below 10.5 eV by ionizing them with a single 118 nm photon (10.5 eV) and detecting the resulting ions by time-of-flight mass spectrometry. These include C3 and larger hydrocarbon species, except propane and butane which have higher IPs. The laser power for ionization was maintained low enough to minimize ion fragmentation for accurate measurements. The RGA is used to measure the major species  $C_2H_2$ , CO,  $CO_2$ ,  $O_2$ , benzene and argon in the sampling chamber with 70 eV electron impact ionization energy. Benzene is measured both with the VUV-TOF-MS and RGA to provide a cross-calibration. Water concentration cannot be measured directly with this system due to its condensation on the walls of the chamber, but can be calculated from an atom balance.

The RGA measurements were calibrated by flowing known-composition gas mixtures through the microjet reactor at room temperature. For VUV-TOF-MS measurements, the sensitivity was either directly measured (propylene and butene) or assumed to be the same as benzene. The two isomers of  $C_3H_4$  (allene and propyne) were assumed to have the same response as propylene. All C4 compounds detected were assumed to have identical response as butene. In addition, the oxygenated hydrocarbons were assumed to have the same sensitivities as the regular hydrocarbons with the same mass, and all radical species are assumed to be identical as benzene due to the difficulty of calibration measurement. All of the absolute concentrations are accurate to within a factor of 3, and repeated measurements agree to within 20–30%. A detailed description of the data analysis is presented in another paper from this research group<sup>7</sup>.

## RESULTS AND DISCUSSION

All results presented in this study are for two mixtures with different equivalence ratios. Both contain  $0.51 \pm 0.03$  mol.% benzene in argon, and enough oxygen to make the equivalence ratio either 0.19 or 1.02, respectively. For all the experiments the total reactor pressure is  $350 \pm 2$  torr and the mean residence time is  $50 \pm 3$  ms. The temperature is varied from 800 to 1300K, covering benzene conversion of up to 99%. The carbon material balance in the experiment was reasonable (within  $\pm 1\%$ ) for most of the temperature range covered. However, it degraded slightly at the highest temperature end to  $\pm 5\%$ .

Since the mass spectrometer only provides masses, we assigned the elemental formulas for each observed signal peak based on hydrocarbon or oxygenated hydrocarbon species produced in modeling studies or measured in our earlier GC-MS experiments. In particular, the assignments for the major oxygenated species are also consistent with the mass spectrometric measurements of benzene oxidation from Rotzoll<sup>14</sup> where product identification studies were made by comparing the results from oxidation of  $C_6H_6$  and  $C_6D_6$ . Table 1 lists the most plausible structures and maximum concentrations for each mass we detected for the

stoichiometric and lean conditions. Product profiles for each stoichiometry are discussed below.

Figure 3 shows the concentration profiles of  $C_2H_2$ , CO,  $CO_2$  and benzene from RGA measurements for both the lean and stoichiometric cases. CO and  $CO_2$  concentrations are divided by factors of 2 and 4, respectively. Acetylene ( $C_2H_2$ ) is the only significant C2 product detected with the RGA since its ionization potential (11.4 eV) is out of the range of VUV (10.5 eV) single photon energy. As we noted, the RGA can easily fragment many analytes with its 70 eV electron impact energy. Although we subtracted the contribution from the fragmentation of benzene in our data analysis,  $C_2H_2$  may still contain some minor errors resulting from the fragmentation of other larger hydrocarbon species. According to modeling studies<sup>9,10</sup>, ethylene ( $C_2H_4$ ) is another C2 species produced in benzene oxidation and its peak concentrations has been measured to be about half of the acetylene peak concentration in the Princeton Flow Reactor for the stoichiometric oxidation of benzene<sup>3</sup>. However, it cannot be measured with the RGA in our study due to its overlap with CO at mass 28. The influence from  $C_2H_4$  to CO measurement is small since the CO is the predominant species at this mass channel.

Note the temperature at which 20% benzene conversion occurs is shifted to approximately 90K higher temperatures for the stoichiometric condition. In addition, the slope of the benzene conversion profile versus temperature for the stoichiometric condition is shallower than for the lean case, demonstrating that apparent activation energy for benzene conversion is affected by the  $O_2$  concentration. This makes sense if different elementary reactions governing the fuel consumption are a function of stoichiometry or oxygen concentration and can be used to test model performance.

Figure 4(a,b) and Figure 5(a,b) (lean), and Figure 6(a,b) and Figure 7(a,b) (stoichiometric) present concentration profiles of the major hydrocarbon and oxygenated hydrocarbon products measured with the VUV-TOF-MS. Note that the concentration scales of several species in both figures are divided by factors of 5 or 4 in order to fit on the figure. As seen in Figure 4(a,b), in addition to major hydrocarbon intermediate  $C_2H_2$  measured by the RGA,  $C_2H_2O$ ,  $C_4H_4$ ,  $C_3H_4$ ,  $C_3H_4O$ ,  $C_5H_6$  and  $C_3H_2O$  are the significant intermediate species present with masses less than benzene for the lean case. From kinetic and thermodynamic arguments, the 42 and 56 amu species are likely to be predominately ketene ( $C_2H_2O$ ) and acrolein ( $C_3H_4O$ ) instead of propene ( $C_3H_6$ ) and butene ( $C_4H_8$ ). As noted in earlier studies, phenol ( $C_6H_5OH$ ) is the first hydrocarbon intermediate observed and the most abundant species in the higher mass range [see Figure 5(a,b)]. Other higher hydrocarbon or oxygenated species are also produced in ppm concentrations, especially cyclopentadienone ( $C_5H_4O$ ) and benzoquinones ( $C_6H_4O_2$ ).

For the stoichiometric condition [see Figure 6(a,b)], the most abundant intermediates with masses less than benzene following the highest concentration hydrocarbon intermediate,  $C_2H_2$ , measured with RGA are  $C_4H_4$ ,  $C_5H_6$ ,  $C_2H_2O/C_3H_6$  and  $C_4H_6$ . The concentration of  $C_4H_4$  is much higher ( $>90$  ppm) than for the lean condition; conversely phenol ( $C_6H_5OH$ ) and acrolein ( $C_3H_4O$ ), which are present at maximum concentrations of 38 and 24 ppm, respectively, in the lean condition, are present at only 7 and 6 ppm, respectively, at the stoichiometric condition. Cyclopentadiene ( $C_5H_6$ ) is over twice as abundant in the stoichiometric condition. Lower peak concentrations for intermediate

**Table 1** Hydrocarbons, radical and oxygenated species (> ppm) detected by mass spectroscopy in benzene oxidation with microjet reactor. The most plausible structure are listed for each mass, oxygenated species are more reasonable structures in lean case based on the modeling

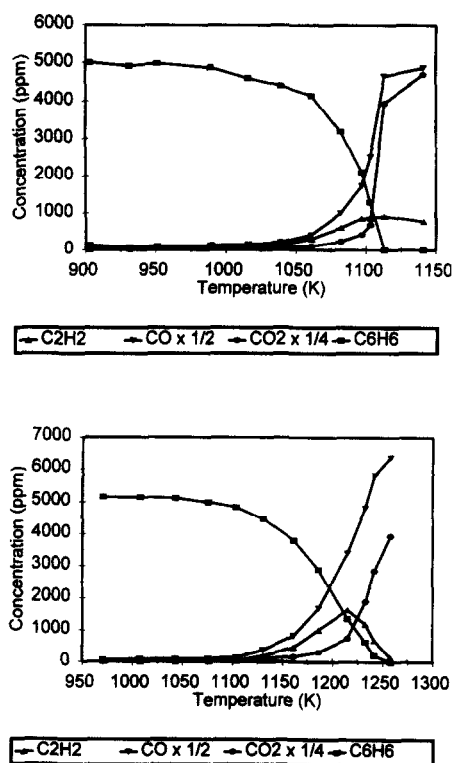
Mass (AMU)	Probable formula	Some possible structures	Peak concentration (ppm)	
			$\phi = 1.02$	$\phi = 0.19$
26	C <sub>2</sub> H <sub>2</sub>	Acetylene	1644	919
28	CO, C <sub>2</sub> H <sub>4</sub> <sup>a</sup>	Carbon monoxide, ethylene	13524	10582
40	C <sub>3</sub> H <sub>4</sub>	Allene, propyne	14	28
41	C <sub>2</sub> HÖ, C <sub>3</sub> H <sub>3</sub>	Ketyl radical, propenyl radical	5	4
42	C <sub>2</sub> H <sub>2</sub> O, C <sub>3</sub> H <sub>6</sub>	Ketene, propene	37	53
43	C <sub>2</sub> H <sub>3</sub> Ö	C–C=O	3	4
44	CO <sub>2</sub> , C <sub>2</sub> H <sub>4</sub> O <sup>b</sup>	Carbon dioxide, acetaldehyde	18987	20223
50	C <sub>4</sub> H <sub>2</sub>	Diacetylene	6	< 1
52	C <sub>4</sub> H <sub>4</sub>	Vinylacetylene	97	43
53	C <sub>3</sub> HÖ, C <sub>4</sub> H <sub>3</sub>	C=C=C=O, butadienyl	7	5
54	C <sub>3</sub> H <sub>2</sub> O, C <sub>4</sub> H <sub>6</sub>	C=C=C=O, butadiene	17	20
55	C <sub>3</sub> H <sub>3</sub> Ö	Acrolein radical	2	6
56	C <sub>3</sub> H <sub>4</sub> O	Acrolein	6	24
65	C <sub>5</sub> H <sub>5</sub>	Cyclopentadienyl	13	10
66	C <sub>5</sub> H <sub>6</sub>	Cyclopentadiene	42	21
67	C <sub>4</sub> H <sub>3</sub> Ö	Furan radical	5	4
68	C <sub>4</sub> H <sub>4</sub> O	Furan	4	9
70	C <sub>4</sub> H <sub>6</sub> O	Dihydrofuran	< 1	6
80	C <sub>5</sub> H <sub>4</sub> O, C <sub>6</sub> H <sub>8</sub>	Cyclopentadienone, hexadiene	6	10
81	C <sub>5</sub> H <sub>5</sub> O	Cyclopentenone radical	< 1	4
82	C <sub>5</sub> H <sub>6</sub> O	2-Cyclopenten-1-one	< 1	6
92	C <sub>7</sub> H <sub>8</sub>	Toluene	3	4
93	C <sub>6</sub> H <sub>5</sub> Ö	Phenoxy radical	2	5
95	C <sub>6</sub> H <sub>7</sub> Ö	Cyclohexenone radical	< 1	4
102	C <sub>8</sub> H <sub>6</sub>	Phenylacetylene	3	< 1
104	C <sub>8</sub> H <sub>8</sub>	Vinylbenzene	3	3
106	C <sub>7</sub> H <sub>6</sub> O, C <sub>8</sub> H <sub>10</sub>	Benzaldehyde, ethylbenzene	< 1	4
108	C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> , C <sub>7</sub> H <sub>8</sub> O <sup>b</sup>	Benzoquinone, methylphenol	2	6
110	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	Dihydroxybenzene, phenyl peroxide	< 1	4
116	C <sub>9</sub> H <sub>8</sub>	Indene	3	3
128	C <sub>10</sub> H <sub>8</sub>	Naphthalene	4	3
130	C <sub>10</sub> H <sub>10</sub>	Dihydronaphthalene	2	4
154	C <sub>12</sub> H <sub>10</sub>	Biphenyl	2	3

<sup>a</sup>Small contributor (< 1% of total)<sup>b</sup>Trace component (ppm level)

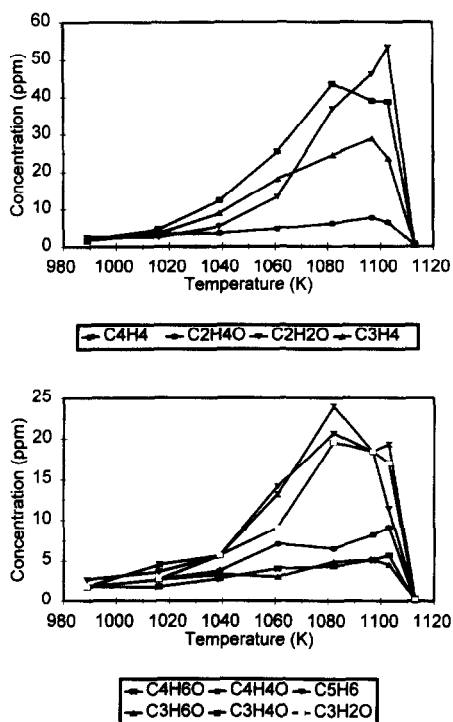
species would be expected for this case if the lower oxygen concentration slows the net benzene decomposition rate (the initial benzene concentration is equal for both cases) because formation of benzene decomposition products will be slowed more than their consumption rates which do not depend as strongly on the O<sub>2</sub> concentration. For the stoichiometric case, phenol (C<sub>6</sub>H<sub>5</sub>OH), naphthalene (C<sub>10</sub>H<sub>8</sub>) and C<sub>5</sub>H<sub>4</sub>O (and C<sub>6</sub>H<sub>8</sub>) are the most abundant higher hydrocarbons for the stoichiometric case [Figure 7(a,b)]. The naphthalene to phenol ratio increased dramatically (by approximately a factor of two) reflecting the slower C<sub>5</sub>H<sub>5</sub> consumption by O and HO<sub>2</sub> increasing the peak C<sub>5</sub>H<sub>5</sub> concentration. C<sub>5</sub>H<sub>5</sub> recombination has been proposed as an important route for naphthalene production<sup>15</sup>.

The concentration profiles and maximum concentrations listed in Table 1 for hydrocarbon intermediates and oxygenated species in both lean and stoichiometric conditions also exhibit a number of interesting features. The dramatic changes on peak concentration of phenol between the two stoichiometries are consistent with the faster

benzene consumption for the lean case and the higher O<sub>2</sub> concentration. The lower net benzene consumption rate for a fixed temperature and residence time in the stoichiometric case results in a dramatically reduced peak concentration of phenol. Phenol is formed through the reactions phenyl + O<sub>2</sub> = phenoxy + O and benzene + O = phenoxy + H (or to phenol directly). Both O<sub>2</sub> and O atom concentrations are significantly higher for the lean case. The reaction of benzene + O is a particularly important source of H atoms at low to moderate temperatures. Contrary to previous assumptions in the literature, Bajaj and Fontijn<sup>16</sup> have recently shown that the major reaction channel for benzene + O at our reaction conditions is phenoxy + H (not phenol directly) with a rate that makes this reaction competitive with phenyl + O<sub>2</sub> under many conditions. Phenoxy decomposition is slow (due mainly to C<sub>5</sub>H<sub>5</sub> + CO) and is not highly dependent on oxygen concentration. Thus the reduced peak phenol concentration coupled with a slower benzene decomposition rate suggests that for the conditions of this study, a large fraction of the benzene decomposition to smaller hydrocarbons proceeds through

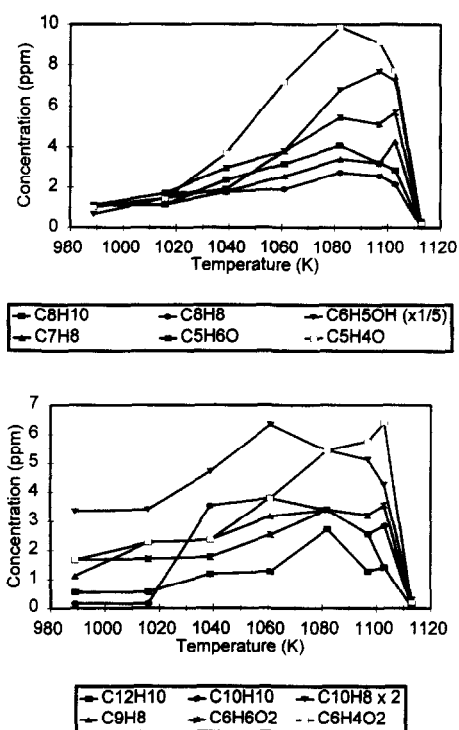


**Figure 3** RGA results of  $\text{C}_2\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{C}_6\text{H}_6$  from 0.51 mol.% benzene/argon mixture at a pressure of 350 torr and mean residence time of 50 ms. Top,  $\phi = 0.19$ ; bottom,  $\phi = 1.02$

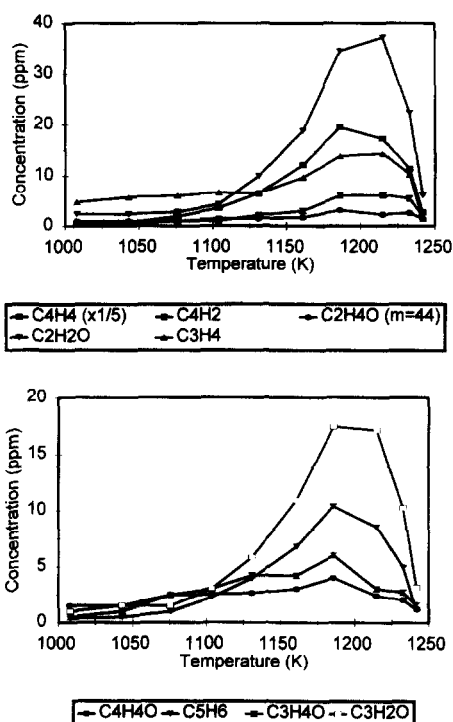


**Figure 4** VUV-TOF-MS results of major hydrocarbon and oxygenated hydrocarbon products with masses < benzene from benzene oxidation for 0.51 mol.% benzene/argon mixture with  $\phi = 0.19$  at a pressure of 350 torr and a mean residence time of 50 ms

the two reactions phenyl +  $\text{O}_2$  and benzene +  $\text{O}$ . Also of interest is the appearance of benzoquinone ( $\text{C}_6\text{H}_4\text{O}_2$ ) and  $\text{C}_6\text{H}_6\text{O}_2$ , especially for the lean condition. Both of these species reach three to four times higher concentrations for

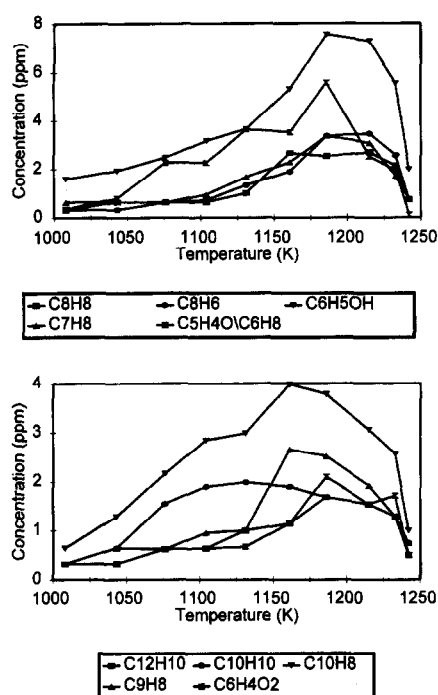


**Figure 5** VUV-TOF-MS results of major hydrocarbon and oxygenated hydrocarbon products with masses > benzene from benzene oxidation for 0.51 mol.% benzene/argon mixture with  $\phi = 0.19$  at a pressure of 350 torr and a mean residence time of 50 ms



**Figure 6** VUV-TOF-MS results of major hydrocarbon and oxygenated hydrocarbon products with masses < benzene from benzene oxidation for 0.51 mol.% benzene/argon mixture with  $\phi = 1.02$  at a pressure of 350 torr and a mean residence time of 50 ms

the lean versus the stoichiometric condition along with a five-times higher peak concentration of phenol for the lean versus stoichiometric condition. While the peak phenol concentration decreases dramatically as the equivalence



**Figure 7** VUV-TOF-MS results of major hydrocarbon and oxygenated hydrocarbon products with masses > benzene from benzene oxidation for 0.51 mol.% benzene/argon mixture with  $\phi = 1.02$  at a pressure of 350 torr and a mean residence time of 50 ms

ratio increases, the cyclopentadiene peak concentration increases with increasing equivalence ratio. This observation is interesting because cyclopentadiene is formed primarily through phenoxy decomposition, suggesting that either alternative phenoxy destruction pathways compete at lean conditions (possibly supported by higher  $C_6H_4O_2$  and  $C_6H_6O_2$  concentrations) and/or  $C_5H_6$  and  $C_5H_8$  destruction pathways are enhanced at lean conditions.

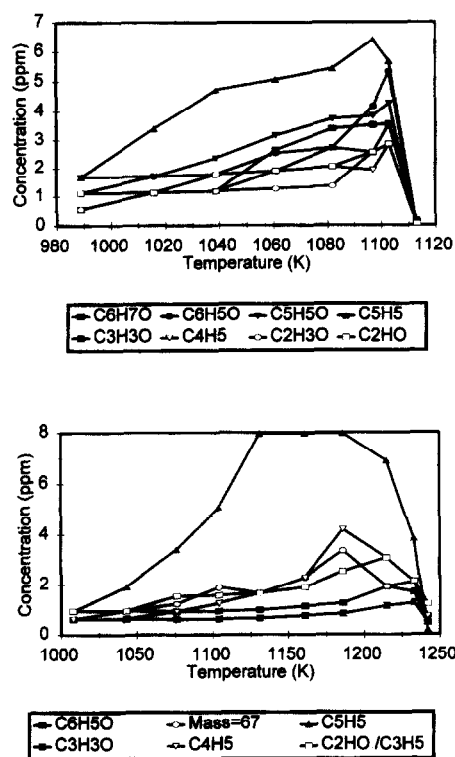
$C_5H_5 + HO_2$  is a major reaction pathway for cyclopentadienyl consumption at both lean and rich conditions<sup>17</sup>. Significantly lower  $C_5H_6$  peak concentrations as  $O_2$  is increased suggests that an additional channel for  $C_5H_5$  consumption is important at the lean condition. O atom concentrations are significantly higher for the lean versus stoichiometric conditions, and the work of Bozzelli<sup>17</sup> shows that the reaction channel of  $C_5H_5 + O$  is a competitive reaction at this stoichiometry and temperature range. The higher concentration of  $C_5H_4O$  detected for the lean case also supports this argument since  $C_5H_4O$  is likely formed from the  $C_5H_5$  oxidation reaction. It should also be noted, however, that at a fixed residence time, the temperature for an equivalent benzene conversion is shifted up in the stoichiometric case, with the magnitude of the temperature shift dependent on conversion. The temperature shift for 20% benzene conversion is approximately 90K.

In addition, the increase in the maximum  $C_4H_4$  concentration for the stoichiometric condition suggests the fact that the net  $C_4H_4$  production is affected by the presence of  $O_2$ . High  $O_2$  concentrations could conceivably increase  $C_4H_4$  via production through  $C_4H_5 + O_2$ ; however, decreases would result if  $C_4H_5 + O_2 \rightarrow$  smaller oxygenated species was important which would be consistent with proposed pathways for vinyl +  $O_2 \rightarrow HCO + H_2CO$  (see Slagle *et al.*<sup>18</sup>). The decrease in the net  $C_4H_4$  production with increasing  $O_2$  is also seen in Princeton data<sup>1</sup> where the undiluted  $\phi = 1$  (with higher  $O_2$  concentration) shows

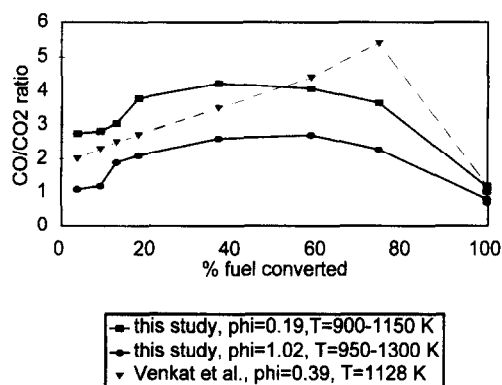
less  $C_4H_4$  when compared to  $C_5H_6$  than our diluted data at  $\phi = 1.02$  with lower  $O_2$  concentration. The absence of masses 70 (most likely  $C_4H_6O$ ), 81 ( $C_5H_5O$ ), 82 ( $C_5H_6O$ ) and 106 ( $C_7H_6O$ ) in detectable quantities at stoichiometric condition also indicate the important impact of oxygen in net formation of those compounds.

Many radical species are easily detected in these experiments and the peak concentrations are listed in Table 1 and major radical species profiles are shown in Figure 8. As expected for a resonantly stabilized species which could build to a relatively high concentration, the predominant radical for both conditions is the cyclopentadienyl ( $C_5H_5$ ). The importance of cyclopentadienyl was inferred by Venkat *et al.*<sup>1</sup> from cyclopentadiene concentrations, since it was not measured directly. The higher peak concentration of cyclopentadienyl ( $C_5H_5$ ) for the stoichiometric condition might explain the higher observed naphthalene and dihydronaphthalene concentrations, since naphthalene may be produced through the radical–radical recombination reaction of cyclopentadienyl to dihydronaphthalene<sup>15</sup>. Cyclopentadienonyl ( $C_5H_5O$ ) is the next most abundant radical for the lean case, but it is only present at the detection limit for the stoichiometric case. Phenoxy ( $C_6H_5O$ ), the key radical species in the initial aromatic ring-destruction step, reaches concentrations over 5 ppm in the lean case but is present at lower concentrations than butadienyl ( $C_5H_5$ ),  $C_4H_3O$  and  $C_2HO/C_3H_5$  in the stoichiometric case. Phenyl radical plays an important role in the benzene oxidation. We cannot detect it due to influence from the shoulder of strong benzene signal. It is likely present at ppm or lower concentrations from calculations.

During the oxidation of hydrocarbons, CO is produced in substantial amounts. The subsequent oxidation of CO to  $CO_2$  is usually retarded until after the original fuel and the intermediate hydrocarbon species have all been consumed. Only at that time does the OH concentration rise to higher levels, rapidly converting the CO to  $CO_2$ . The CO/ $CO_2$  ratio as a function of conversion is illustrated in Figure 9 for our two stoichiometries and the undiluted  $\phi = 0.39$  case of Venkat *et al.*<sup>1</sup> (shown on the figure as a dashed line). The CO/ $CO_2$  ratio first increases with increasing benzene conversion in this low temperature range (800–1200K) and then decreases when conversion is further increased. Although we do not have a mechanistic explanation for this behavior, it is possible that a minority reaction channel to prompt  $CO_2$  exists at these conditions. Many investigations of phenol oxidation observed prompt  $CO_2$  formation (see for example Gopalan and Savage<sup>19</sup>, Manion and Louw<sup>20</sup>, and references therein). In addition, Buth *et al.*<sup>21</sup> also noted up to 15%  $CO_2$  from reaction of phenoxy + O at low pressure (mtorr range) and room temperature. This contribution might be higher for our case since at a significantly higher pressure this higher exothermicity reaction pathway could be more favored. In order to assess whether this early  $CO_2$  is an artifact of our experimental reactor configuration, the CO/ $CO_2$  ratio as a function of benzene conversion was calculated from published CO and  $CO_2$  profiles from benzene oxidation ( $\phi = 0.39$ , atmosphere pressure, temperature of 1128K, and a reaction time of 40–110 ms) in the Princeton Flow Reactor<sup>1</sup>. Although the reaction time (40–110 ms) in the Princeton experiments is different from ours (fixed at 50 ms) and the fuel in their experiment is undiluted so that the oxygen concentration is close to that of our lean case, the CO/ $CO_2$  ratios as a function of benzene conversion is similar to our lean case. The higher peak value



**Figure 8** VUV-TOF-MS results of major radical species from benzene oxidation for 0.51 mole% benzene/argon mixture at a pressure of 350 torr and a mean residence time of 50 ms. Top,  $\phi = 0.19$ ; bottom,  $\phi = 1.02$



**Figure 9** CO/CO<sub>2</sub> ratio versus benzene conversion

for the Princeton data may be explained by the differences in reactor geometries. The Princeton data are for a plug flow reactor and ours is for a nearly well-stirred reactor where the reactor concentrations are near the effluent level. Nonetheless, the important observation is the unexpectedly high amount of CO<sub>2</sub> at low conversions for both different reactor geometries with different surface to volume ratios. This suggests that the early CO<sub>2</sub> has a homogeneous rather than heterogeneous source.

Comparison of the intermediate species profiles during the benzene oxidation in the microjet reactor with Princeton's flow reactor system is instructive. Data are available in both studies for the stoichiometric equivalence ratio. The initial benzene and oxygen concentrations are, however, higher than our diluted case. The major species profiles (CO, CO<sub>2</sub>, C<sub>6</sub>H<sub>5</sub>OH, C<sub>5</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>4</sub>, C<sub>3</sub>s and C<sub>2</sub>s) show relatively quantitative agreement with our results;

however, there are still several obvious differences. First, the ratio of phenol/fuel converted from their experiments is higher than our result which is consistent with their higher O<sub>2</sub> concentration. Second, in our case the peak concentration of C<sub>4</sub>H<sub>4</sub> is over twice the peak concentration of C<sub>5</sub>H<sub>6</sub>. The peak concentration of C<sub>5</sub>H<sub>6</sub> is higher than the peak concentration of C<sub>4</sub>H<sub>4</sub> measured under the undiluted condition of the Princeton Flow Reactor. The differences observed in the C<sub>4</sub>H<sub>4</sub> and C<sub>5</sub>H<sub>6</sub> intermediates are consistent with the differences in the reactor and dilution because as noted above, an increase in O<sub>2</sub> concentration results in a increase of C<sub>5</sub>H<sub>6</sub> and a decrease of C<sub>4</sub>H<sub>4</sub> net production.

## CONCLUSION

The experimental technique used in this study has been demonstrated to be a useful approach for the analysis of benzene oxidation. Major and minor hydrocarbon, radical and oxygenated species are measured for the moderate temperature benzene oxidation. The major hydrocarbon intermediate for both the lean and the stoichiometric conditions is C<sub>2</sub>H<sub>2</sub>. The dramatic difference in the phenol concentration between the lean and stoichiometric conditions suggests the importance of the phenyl + O<sub>2</sub> reaction as a major pathway from C<sub>6</sub> to phenol and then smaller hydrocarbons at this temperature range. Changes in the O<sub>2</sub> concentration have a significant effect on the net production of C<sub>4</sub>H<sub>4</sub>, C<sub>5</sub>H<sub>6</sub> and phenol. Increased O<sub>2</sub> concentration increases the net formation of C<sub>5</sub>H<sub>6</sub> and decreases the net formation of C<sub>4</sub>H<sub>4</sub>. We also note that prompt CO<sub>2</sub> may play a role early in the benzene oxidation mechanism at this temperature range. The results from both fuel-lean and stoichiometric conditions provide the necessary database for further modeling of benzene oxidation at fuel-lean conditions.

## ACKNOWLEDGEMENTS

The authors appreciate useful discussions with Dr C.S. McEnally and financial support from the United States Environmental Protection Agency, grant R821206-01-0 and from NASA-Lewis grant NAG 3-996.

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