

BENZENE/TOLUENE OXIDATION MODELS: STUDIES BASED ON FLOW-REACTOR AND  
LAMINAR FLAME SPEED DATA

K. Brezinsky, F.N. Egolfopoulos, J.L. Emdee, C.K. Law and I. Glassman  
Department of Mechanical and Aerospace Engineering  
Princeton University  
Princeton, N.J. 08544

**Introduction**

Aromatic hydrocarbons are expected to remain significant components of gasolines and jet fuels because they offer many advantages such as a high energy density (Goodger and Vere, 1985) and a high knock rating (ASTM Special Technical Publication No. 225, 1958). In working towards a comprehensive understanding of aromatic combustion, the high temperature oxidation mechanism of toluene has been studied extensively at Princeton (Euchner, 1980, Venkat et al., 1983, Brezinsky et al., 1984, Brezinsky, 1986, Litzinger, 1986, Brezinsky et al., 1990). The mechanistic details that evolved in those studies have indicated that at temperatures near 1000 K and 1 atmosphere pressure the early time oxidation characteristics are dominated by side chain chemistry followed by aromatics ring attack. The reactions of the small molecule fragments of the aromatic ring, for the most part, occur later in the reaction sequence; therefore a modest sized model, based largely on the mechanisms given by Brezinsky (1986) for the oxidation of toluene near 1200 K. This model captures the early time chemistry and the essential details of the later time small molecule reactions for both toluene and benzene at flow reactor conditions. The success of this model in predicting flow reactor species profiles, as will be briefly described in the succeeding paragraphs, led to the application of the model to the calculation of laminar flame speeds. The results of these calculations will be described.

**Experimental Data for Model Verification**

The toluene oxidation data of Brezinsky et al. (1984) and the benzene oxidation data of Lovell et al. (1989) were used to verify the toluene model and its benzene sub-mechanism. These data were from Princeton flow reactor experiments and include lean and rich equivalence ratios ( $\phi$ ) with initial temperatures from 1100 K to 1190 K. The experimental details are described in the individual papers.

Slight adjustments were made to the data presented in the above two references to reflect recent calibration of the flow reactor rotameters and velocity profile. The effect of these recent changes is to give reaction times which are approximately 15-20% shorter than given in the original papers. It should be noted that the velocity profile in the reactor tube is still under investigation. Further details regarding the reduction of the experimental data can be found in Emdee (1991).

**Description and Analysis of the Model**

The model consists of 68 reactions forming a benzene sub-model and 62 additional reactions for the toluene model. A complete description of the model and associated thermodynamic properties of the chemical species is available (Emdee et al., 1991; Emdee, 1991). Since benzene is a key intermediate in the oxidation of toluene, the benzene sub-model results will be considered before the toluene model is discussed.

**Comparison of the Benzene Oxidation Model and Experimental Data**

The flow reactor experiments approximate an adiabatic, constant

pressure, reaction system in which hydrodynamic and diffusional transport effects are small compared to changes brought about by chemical reaction. Thus, to make a comparison between the experimental data and the kinetic model, the reaction system was numerically treated as a time-dependent, adiabatic, constant pressure, homogenous mixture using CHEMKIN (Kee et al., 1980). Since mixing of the fuel and oxygen in the diffuser section of the flow reactor shortens the time for initial consumption of the fuel, the experimentally derived reaction time is only relative. Thus the comparison between experiment and model was made after shifting the experimental data in time so that the experimental fuel concentration at 50% of the measured consumption matched the model prediction. The time shift was constant for each experimental condition.

The experimental data and model results for benzene are compared in Fig. 1. Intermediate species profiles are shown for the  $\phi = 0.91$  case only; further results for other conditions can be found in Emdee (1991).

The model prediction of the fuel decay was in good agreement with the experimental data for all three conditions considered. A fair match was achieved between the total  $C_4$  and  $C_2$  species. Lovell et al., did not make a distinction between the  $C_4$ 's and the  $C_2$ 's. However, they did indicate that the  $C_4$ 's were vinyl acetylene ( $C_4H_4$ ) and butadiene ( $C_4H_6$ ) in about a 3:1 ratio, and the  $C_2$ 's were "predominately acetylene and some ethylene". Because the present model can distinguish between species, the individual components of the  $C_4$ 's and  $C_2$ 's are also plotted in Fig. 1. The vinyl acetylene to butadiene ratio appears similar to the ratio indicated by Lovell et al., and the acetylene mole fraction is much larger than the ethylene mole fraction.

The mole fractions of phenoxy and cyclopentadienyl are included in the comparisons of phenol and cyclopentadiene because these species are resonantly stable and might be expected to build up to relatively high concentrations. If these radical species found a source of H in the sampling probe, they would have been detected as the stable parent species. Figure 1 shows that the inclusion of these radicals in the total phenol and cyclopentadiene profiles has a small effect on the former and a large effect on the latter.

Although good agreement between the predicted and experimental phenol profiles was achieved for the lean and near stoichiometric conditions, the model tended to underpredict the phenol mole fractions for rich conditions. The cyclopentadiene profiles were predicted with fair agreement by the total of the  $C_8H_8$  and  $C_5H_6$  concentrations for the lean and near stoichiometric conditions but was overpredicted by the rich condition. The overprediction of the cyclopentadiene coupled with the underprediction of the phenol for the rich case suggests that phenol is being consumed too quickly for this case. Carbon monoxide was underpredicted for all equivalence ratios considered which in part reflects the lack of a full sub-mechanism for small molecule chemistry.

#### Comparison of the Toluene Oxidation Model and the Experimental Data

The results of the calculations are shown in Figs. 2. The toluene model did very well at predicting the fuel consumption rate as well as the concentrations of many of the aromatic intermediates including benzene, benzaldehyde, ethylbenzene, benzyl alcohol and styrene for both lean and rich conditions. The concentrations of both phenol and cresol were however always underpredicted.

The figures show that the amounts of acetylene suggested by the model are at least a factor of two larger than the experimentally measured values.

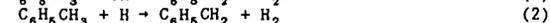
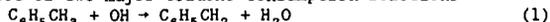
All of the acetylene comes from the  $C_4$  species which, although not shown, were underpredicted by the toluene model. Thus even though the  $C_2$ 's and  $C_4$ 's were predicted with fair agreement for the oxidation of benzene near 1100 K, the higher temperature ( $\approx 1190$  K) oxidation model of toluene suggests that the decomposition rate of the  $C_4$ 's to the  $C_2$ 's may not have the correct temperature dependence.

In contrast to the benzene oxidation model in which CO was underpredicted, the CO concentrations predicted by the toluene model matched well with the experimental data. The better CO prediction by the toluene model can be partially attributed to the greater understanding of side chain chemistry which dominates the early oxidation of toluene as compared to the limited understanding of ring chemistry which was important in the oxidation of benzene.

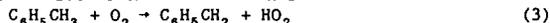
#### Summary of Flow Reactor Modeling

By constructing a kinetic model for the oxidation of toluene based on mechanistic and kinetic information from the literature and from thermochemical estimates, it was possible to reasonably model flow reactor oxidation experiments of benzene and toluene. The consumption rate of toluene and benzene for both lean and rich oxidation conditions is predicted quite well by the model as are many of the intermediates. The predictive capability of the model is a significant improvement over previously reported results (Bittker, 1987, 1988, 1991; Fujii and Asaba, 1973; McLain et al., 1979).

The inhibitory effect of two major toluene consumption reactions



was clearly indicated by a linear sensitivity analysis. Furthermore, the high sensitivity of the model results to the abstraction reaction:



has allowed for an estimate of this reaction rate constant with reasonable confidence.

The major shortcomings of the model were found to be the over prediction of acetylene and the under-prediction of phenol compounds. The acetylene profiles were not predicted correctly for the higher temperature toluene oxidation even though the lower temperature benzene sub-model predicted reasonable levels. With regard to the phenol formation, the temperature dependence of the decomposition rate of phenoxy was expected to be the source of error since phenol was predicted reasonably well in the lower temperature benzene sub-model.

#### Flame Modelling

The modelling of measured laminar flame speeds,  $S_{L1}$ , over a range of temperatures and pressures has been demonstrated to be an effective technique for developing and refining comprehensive chemical kinetic models (Egolfopoulos et al., 1991). For such modelling purposes, limited data from the measurement of laminar flame speeds of toluene and/or benzene are available in the literature (Garner et al., 1951, Gerstein et al., 1951, Wagner and Dugger, 1955, and Gibbs and Calcote, 1959). The encyclopedic work of Gibbs and Calcote (1959) contains flame speeds for benzene at atmospheric pressure over an equivalence ratio of 0.8 - 1.3. These values were obtained using a bunsen burner conical flame and shadowgraphs for definition of the flame surface. Fristrom and Westenberg (1965) have pointed out the complications in defining the flame surface by shadowgraphy and these complications would affect the magnitude of the flame velocities reported by

Gibbs and Calcote. Similarly, Law (1988) has emphasized the role that flame stretch can play in the determination of flame speeds and pointed out the substantial variation in measured values that can result if the flame speeds are not evaluated in the limit of zero stretch (Egolfopoulos et al. 1989). All the aromatics flame speeds reported in the literature are affected by stretch. In the absence of stretch free flame speeds for aromatics, the flame speed values for benzene measured by Gibbs and Calcote were used for comparison with model predictions since their measurement technique tended to minimize stretch effects:

$\phi$ =	.8	.9	1.0	1.1	1.2	1.3
$S_u$ =	39.4	45.6	47.6	44.8	40.2	35.6 (cm/sec)

The data on the flame speeds of toluene are much more limited than for benzene. The value commonly found in textbooks for a stoichiometric, one atmosphere flame, 38.8 cm/sec, is attributable to Wagner and Dugger (1955). For comparison with the Gibbs and Calcote measured value, the stoichiometric, one atmosphere benzene flame speed measured by Wagner and Dugger was 44.6 cm/sec.

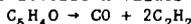
In order to model the reported flame speeds, the toluene model derived from flow reactor experiments was coupled to the PREMIX code (Kee et al., 1985). The calculated flame speeds for stoichiometric toluene/air and benzene/air mixtures were approximately 23 cm/sec - a value far beyond the range of error of the measured values. The low calculated flame speeds implied that the aromatics combustion process was not proceeding fast enough to the energy releasing, small molecule oxidation steps. The toluene model contained only a very basic sub-mechanism for the oxidation of species containing two or less carbon atoms in order to keep the number of reactions and species small. Therefore, the first attempt at altering the mechanism to obtain a higher flame speed consisted of replacing the abbreviated  $C_2$  oxidation scheme with a more complete, validated one (Egolfopoulos et al., 1991). The substitution of this  $C_2$  scheme led to a marginal increase of only 4 cm/sec.

A sensitivity analysis of the flame speed to each rate constant in the toluene model indicated that there was little sensitivity (less than 2%) to the alkyl side chain oxidation steps. Greater sensitivity (2% or more) was found for a subset of nine rate constants directly related to the oxidation of the aromatic ring and its fragments. The benzene flame calculations revealed a sensitivity to these same reactions. Of course, the greatest sensitivity of the flame speed was found to be for the  $CO + OH \rightarrow CO_2 + H$  reaction (11%) and for  $H + O_2 \rightarrow OH + H$  (21%). Since these latter two reactions have been extensively studied no further consideration was given to changing their rate constants. In view of the greater availability of benzene flame speed data and the sensitivity of both the toluene and benzene flame speeds to the same rate constants, the toluene mechanism was reduced, for ease of calculation and analysis, to a benzene mechanism by the removal of all the toluene related steps.

Among the rate constants having the most effect on the flame speed a number are uncertain either because they are estimated rather than measured, measured over a narrow range of temperature, or have been determined in only one set of experiments. Therefore, sequentially for each uncertain rate constant, the value of A in the three parameter representation of the rate constant,  $k = AT^n \exp(E_a/RT)$ , was increased or decreased as indicated by the sensitivity analysis in order to "walk" the flame speed up into the 40 cm/sec range:

$C_6H_5O + H \rightarrow C_6H_5OH$  ; forward A decreased by 2.5 x; reverse increased 10x  
 $C_6H_5O \rightarrow C_6H_5 + CO$ ; forward A increased 10x  
 $C_6H_5 + O_2 \rightarrow C_6H_5O + O$ ; forward A increased 10x  
 $C_6H_5 + OH \rightarrow C_6H_5OH + H$ ; forward A increased 10x

The result of the above changes was a calculated flame speed of 41.6 cm/sec. A sensitivity analysis of this calculated flame speed indicated that changes in the rate constants of the three reactions of  $C_6H_5$  species would have a significant effect (2% or more) on the flame speed. A ten fold increase in the forward and reverse A values of



was sufficient to raise the stoichiometric flame speed to 43.8 cm/sec, a value lower than that measured by Gibbs and Calcote but within the range seemingly appropriate for benzene. The calculated flame speeds at other equivalence ratios were 31.2, 38.2, 48.7, and 50.1 cm/sec at  $\phi = 0.8, 0.9, 1.1$  and 1.2 respectively.

Species profiles calculated with the altered model for flow reactor conditions were significantly changed from those described earlier in this article. The changes were not surprising since the altered rate constants were the same ones shown by sensitivity analysis of the benzene decay profile to be significant during the flow reactor modelling efforts. In particular, the altered rate constants led to an order of magnitude decrease in initial benzene concentration within 60 msec, maximization of the phenol concentration within 30 msec and, CO production and almost complete consumption within 120 msec. These latter observations suggest how the toluene/benzene model might be made more comprehensive in order to predict both flow reactor and flame speed results.

The altered model in its ability to approximately match the measured benzene flame speeds has required a much more rapid production and oxidation of the energy releasing, small molecule hydrocarbon fragments. However, the flow reactor profiles indicate that alteration of the rate constants in the above extent and manner is not fully justified. It appears that a subset of toluene/benzene reactions is needed that would not drastically affect the calculated species profiles at flow reactor temperatures but would lead to an accelerated production of small hydrocarbons at flame temperatures. This conclusion has two implications; the temperature dependent parameters of the above mentioned altered rate constants reactions may require re-adjustment in a way already suggested by some of the inadequacies revealed during flow reactor modelling and, the addition of high activation energy pyrolysis reactions, such as aromatic ring rupture steps, not currently in the toluene/benzene mechanism may be necessary in order to provide H atoms to drive the overall reaction progress. Both of these approaches to creating a comprehensive toluene/benzene model are currently being pursued.

**Acknowledgement:** The support of this research by the Department of Energy, Office of Basic Energy Sciences, through Grant DE-FG02.86ER3554 is gratefully acknowledged.

## References

- ASTM Special Technical Publication No. 225; American Society of Testing Materials, Philadelphia, 1958.
- Bittker, D. A., Detailed Mechanism of Benzene Oxidation; NASA Tech. Memo. 100202, 1987.
- Bittker, D. A., Detailed Mechanism of Toluene Oxidation and Comparison with Benzene; NASA Tech. Memo. 100261, 1988.
- Bittker, D. A., *Combust. Sci. Technol.* 1991, in press.
- Brezinsky, K., Litzinger, T. A. and Glassman, I., *Int. J. Chem. Kinet.* 1984, 16, 1053.
- Brezinsky, K., *Prog. Energy Combust. Sci.* 1986, 12, 1.
- Brezinsky, K., Lovell, A. B. and Glassman, I., *Combust. Sci. Technol.* 1990, 70:1-3, 33.
- Egolfopoulos, F.N., Cho, P. and Law, C.K., *Combust. Flame* 1989, 76, 375.
- Egolfopoulos, F.N., Du, D.X. and Law, C.K., *Combust. Sci. Technol.* 1991, submitted.
- Emdee, J. L., An Experimental and Modeling Study of the High Temperature Oxidation of the Xylenes; Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, 1991.
- Emdee, J. L., Brezinsky K. and Glassman, I., *J. Phys. Chem.* 1991, submitted.
- Euchner, J. A.: M.S.E. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, 1980.
- Fristrom, R.M. and Westenberg, A.A., *Flame Structure*, 1965, McGraw-Hill.
- Fujii, N. and Asaba, T., *Fourteenth Symp. (Int.) Combust.*; The Combustion Institute, Pittsburgh, 1973, p.433.
- Garner, F.H., Long, R. and Ashforth, G.K., *Fuel* 1951, 30, 17.
- Gibbs, G.J. and Calcote, H.F., *J. Chem. Eng. Data*, 1959, 4, 226.
- Goodger, E. and Vere, R., *Aviation Fuels Technology*; MacMillan Publishers Ltd., London, 1985.
- Kee, R. J., Miller, J. A. and Jefferson, T. H., CHEMKIN: A General Purpose, Problem-Independent, Transportable, Fortran Chemical Kinetics Code Package; Sandia Nat. Lab. Report SAND80-8003, 1980.
- Kee, R. J., Grcar, J. F., Smooke, M. D., and Miller, J. A. PREMIX; A Fortran Program for Modeling Steady Laminar One-Dimensional Premixed Flames; Sandia Report SAND 85-8240 UC4, 1985.
- Kee, R. J., Rupley, F. M., and Miller, J. A. The Chemkin Thermodynamic Data Base; Sandia Nat. Lab. Report SAND87-8215, 1987.
- Law, C.K., *Twenty-Second Symp. (Int.) Combust.*; The Combustion Institute, Pittsburgh, 1988, 1381.
- Litzinger, T. A.: Ph.D. Thesis, Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, 1986.
- Litzinger, T. A., Brezinsky, K. and Glassman, I., *Combust. Flame* 1986, 63, 251.
- Lovell, A. B., Brezinsky, K. and Glassman, I., *Twenty-Second Symp. (Int.) Combust.*; The Combustion Institute, Pittsburgh, 1989, p.1063.
- McLain, A. G., Jachimowski, C. J. and Wilson, C. H., Chemical Kinetic Modeling of Benzene and Toluene Behind Shock Waves; NASA Tech. Paper 1472, 1979.
- Wagner, P. and Dugger, G.L., *J. Am. Chem. Soc.* 1955, 77, 227.
- Venkat, C., Brezinsky, K., and Glassman, I., *Nineteenth Symp. (Int.) Combust.*; The Combustion Institute, Pittsburgh, 1983, p.143.

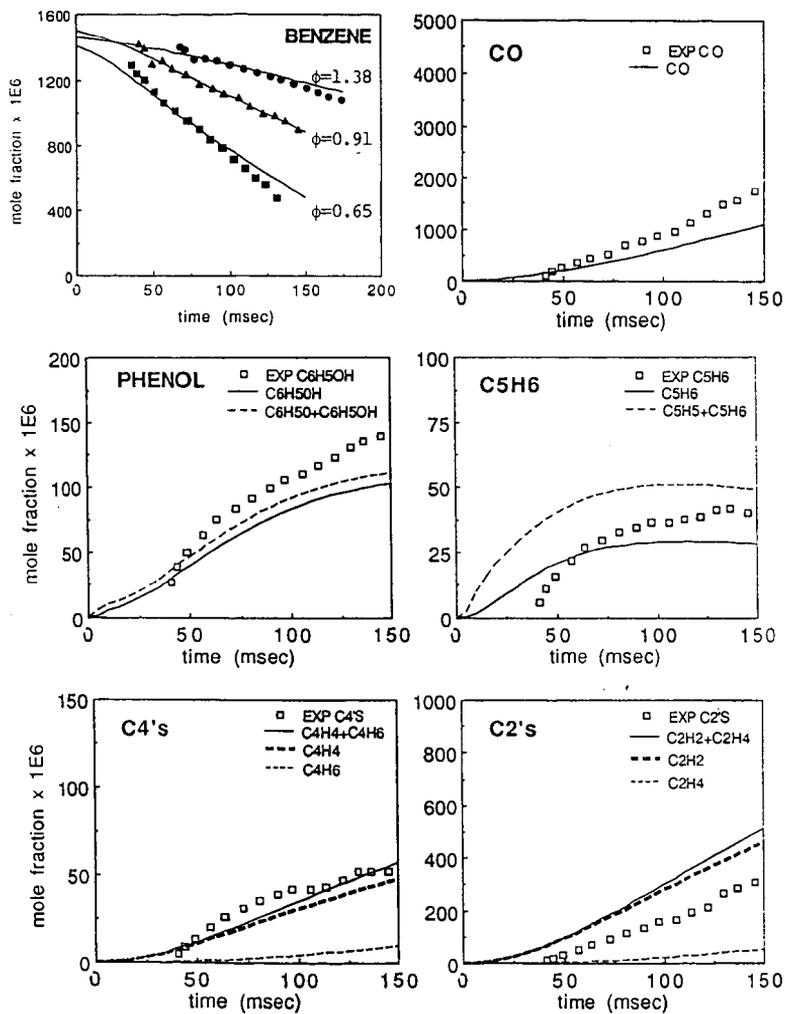


Fig. 1. Experimental (symbols) and model (lines) benzene decay profiles for three different equivalence ratios and intermediates experimental and model profiles for a  $\phi=0.91$  oxidation of benzene.

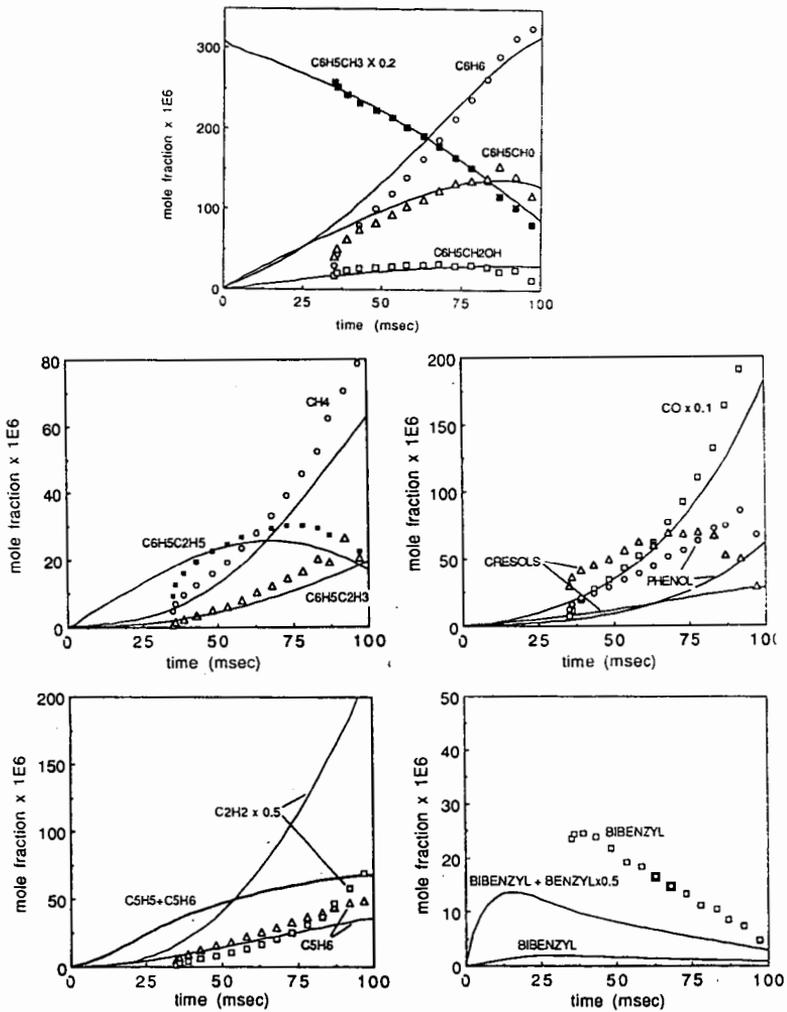


Fig. 2. Experimental (symbols) and model (lines) species profiles for a  $\phi=0.69$  oxidation of toluene.