Kinetics of 1,2-Dimethylbenzene Oxidation and Ignition: Experimental and Detailed Chemical Kinetic Modeling

Sandro Gaïl[1], Philippe Dagaut[1], Gráinne Black[2], John M. Simmie[2]
[1]Centre National de la Recherche Scientifique
1c, Avenue de la Recherche Scientifique
45071 Orléans Cedex 2, France

[2]Combustion Chemistry Centre
National University of Ireland, Galway, Ireland

1 Introduction

The isomers of dimethylbenzene (DMB) represent an important fraction of presently distributed commercial gasoline (c.a. 14% in wt.). They are also present in Diesel and jet fuels. Nevertheless, the oxidation and pyrolysis of these fuels are far from being understood [1] due to limited kinetic data. Emdee [2] proposed a reaction scheme for the oxidation of DMBs based on atmospheric flow reactor experiments performed over the temperature range 1093 to 1199 K. Gregory and Jackson [3] investigated the chemistry leading to the formation in engines exhaust of aromatic hydrocarbons from deuterium-labeled isomeric DMBs. Roubaud [4] studied the auto-ignition delays of DMBs in a rapid compression machine in the low-temperature oxidation regime ($5 < P$ / bar < 25, 600-900 K). More recently, the ignition of DMBs was studied in a shock tube and a reaction mechanism proposed [5]. The present study has two main objectives: (i) to obtain new experimental kinetic results for the oxidation of 1,2-DMB at 1 atm using a jet-stirred reactor (JSR) over a wide range of equivalence ratio and temperature, (ii) to obtain new experimental kinetic results for the ignition of 1,2-DMB at 1 atm using a shock tube (ST) over a wide range of equivalence ratio and temperature, and (iii) to further validate a detailed chemical kinetic reaction mechanism, already successfully used to simulate benzene, toluene, n-propyl-benzene, 1,3-DMB, and 1,4-DMB [6,7] oxidation and combustion, against the present experimental results.

2 Experimental set-up

The JSR experimental set-up is that used previously [6,7]. The reactor consisted of a fused silica sphere of 40 mm diameter (30.5 cc), equipped with 4 nozzles of 1 mm I.D. for the admission of the gases achieving the stirring. A nitrogen flow of 100 L/h was used to dilute the fuel and avoid its pyrolysis before admission in the reactor. The reactants were diluted by nitrogen and mixed at the entrance of the injectors. High purity reactants were used: oxygen was 99.995% pure and 1,2-DMB was 99% pure. Furthermore, 1,2-DMB was sonically degassed before use. A piston pump (Shimadzu LC-10AD VP) was used to deliver the fuel to an atomizer-vaporizer assembly maintained at 120°C. A good thermal homogeneity along the whole vertical axis of the reactor was observed for each experiment by thermocouple measurements (0.1 mm Pt-Pt/Rh 10% wires located inside a thin-wall silica tube). The reacting mixtures were sampled via a low-pressure fused-silica sonic probe. The samples (30 Torr ca. 4 kPa) taken at steady temperature and residence time were analyzed on-line by a GC-MS or FID and off-line after collection and storage in 1 L Pyrex bulbs. The low vapor-pressure compounds were analyzed on-line whereas permanent gases and high vapor-pressure species were analyzed off-line. All the products were analyzed by a chromatographic peak identified. The detection of aromatics (benzene, toluene, 1,2-DMB) from the on-line and off-line analyses was used to calibrate the measurements performed on-line. These

Correspondence to: dagaut@cnrs-orleans.fr

species were used as internal standards in the on-line analyses whereas relative response coefficients were derived from the injection of pure compounds (external standards) on both analytical systems. The present experiments were performed at steady state, at a constant mean residence time of 0.1 s. The reactants were flowing continuously in the reactor, varying stepwise the temperature of the gases inside the JSR. A high degree of dilution (0.1% vol. of fuel) was used for reducing temperature gradients in the JSR and heat release. Therefore, no flame occurred in the JSR and the temperature was constant within +/- 5 K along the vertical axis of the JSR. Several gas chromatographs (GC), equipped with capillary columns were used for stable species measurements. Compound identifications were made through GC/MS analyses of the samples. A good repeatability of the measurements and a reasonably good carbon balance (100±10%) were obtained in this series of experiments. Ignition delay measurements were carried out in a shock tube consisting of a test section measuring 6.22 m in length, with an internal diameter of 10.24 cm, and a barrel-shaped driver section measuring 53 cm in length. The two sections were separated by a polycarbonate diaphragm, which burst when forced into contact with a cross-shaped cutter due to the build up of sufficient pressure in the driver section. The driver gas used was helium (99.99% pure; BOC). Four pressure transducers located along the length of the tube were used to determine the velocity of the incident shock wave. The velocity at the endwall was determined through linear extrapolation of this data, so as to take attenuation of the shock wave into account. This value was then used to calculate the temperature and pressure of the mixture behind the reflected shock wave using the equilibrium program Gaseq [8]. The pressure at the endwall was monitored by means of a pressure transducer set into the endplate. Light emission from CH* at 431 nm was detected through a fused silica window embedded in the endplate using a photodetector (Thorlabs Inc. PDA55-EC). The ignition delay time was defined as the interval between the jump in pressure due to the arrival of the shock wave at the endwall and the maximum rate of rise of the emission signal. The shock tube was validated before and after performing this work by comparison of ignition delay values for n-heptane mixtures to those obtained previously [9,10]. The 1,2-DMB (99+ % pure) was supplied by Aldrich and the oxygen (99.5 % pure) and argon (99.9 % pure) by BOC. The 1,2-DMB was degassed through a series of freeze-thaw cycles, after which no more gas was observed to escape on thawing of the solid. Mixtures were made up using the method of partial pressure. A series of experiments were carried out at each equivalence ratio with an essentially constant reflected shock pressure of 1 atm +/- 2.6 %. Only delays between 50 and 1300 μs are reported, as this represents the optimal range of reliable measurements in our particular shock tube [11]. The vapor pressure of 1,2-DMB is relatively low – 4.89 torr at 20°C. To avoid the problem of condensation, mixtures were made up using only 1.5 torr of 1,2-DMB. A period of 15 minutes was allowed to elapse before addition of the oxygen, during which time the pressure due to 1,2-DMB remained constant, implying that at this pressure the vapor was not condensing. Battin-Leclerc et al. [5] also draw attention to the low volatility of DMBs and to problems relating to condensation and absorption in their shock tube measurements of ignition delay. They hypothesize that the larger scatter they observe for the DMBs over that for benzene or toluene [12,13] may be due to these effects.

3 Kinetic modeling

The ignition delays were simulated using the Senkin code [14]. For the JSR computations, we used the PSR computer code [15] that computes species concentrations from the balance between the net rate of production of each species by chemical reactions and the difference between the input and output flow rates of species. These rates are computed from the kinetic reaction mechanism and the rate constants of the elementary reactions calculated at the experimental temperature, using the modified Arrhenius equation. The reaction mechanism used here has a strong hierarchical structure. The reaction mechanism used here consisted of 1359 reversible reactions involving 189 species. This mechanism, including references and thermochemical data, is available from the authors. The rate constants for reverse reactions are computed from the corresponding forward rate constants and the appropriate equilibrium constants, $K_c = k_{forward} / k_{reverse}$ calculated using thermochemical data.

4 Results and discussion

Jet-stirred reactor conditions: Molecular species concentration profiles were obtained from the oxidation of 1,2-dimethylbenzene (1,2-DMB) in a JSR: O_2, CO, CO_2, CH_2O, CH_4, C_2H_2, C_2H_4, C_2H_6, allene, propyne, C_3H_6, acrolein,1,3-C_4H_6, vinylacetylene, 1,3-cyclopentadiene, benzaldehyde, benzene, styrene, toluene, ethylbenzene, 1,2-methyl-ethyl-benzene, 1,2-methylbenzaldehyde, 1,2-phthalaldehyde, dibenzyl, 1,2-methylstyrene, naphthalene, biphenyl, 2,2' dimethylbiphenyl, and 2,2' dimethylbibenzyl were measured by sonic probe sampling and GC analyses. The products detected here and their relative abundances agree with the experimental results obtained in a previous plug-flow reactor study [2]. The experimental results obtained in the present study for the oxidation of 1,2-DMB were compared to those obtained earlier [6,7] for the oxidation of 1,3-and 1,4-dimethylbenzene in similar conditions showing the kinetics of oxidation of 1,2-DMB is faster than that of the other isomers at atmospheric pressure. Figure 1 presents a comparison between the modeling and the experimental results obtained at 1 atm and φ=1. The experimental results show that besides CO and CO_2, the major intermediate products were formaldehyde (CH_2O), methane (CH_4), ethylene (C_2H_4), acetylene (C_2H_2), 1,3-cyclopentadiene (13CPD), benzene, toluene, styrene. As can be seen from Fig. 1, overall the model represents fairly well the experimental data. The reactivity of 1,2-DMB and the formation of CO, CO_2, toluene, benzene, methane, formaldehyde, ethane are well predicted by the model. However, it tends to over-predict the formation of acetylene (C_2H_2). Sensitivity and reaction path analyses, based on species reaction rate of production and rate of consumption, were used to elaborate the present scheme and interpret the results.

Shock-tube conditions: The ignition of 1,2-DMB-oxygen-argon mixtures were measured behind a reflected shock wave. The data ranged from φ =0.5 to 2. The ignition delays were measured following the CH* emission signal at 431 nm. The pressure behind the reflected shock wave, P_5 ranged from 0.966 to 1.068 atm and the temperature T_5 ranged from 1396 to 1826 K. As can be seen from Fig. 2, the model predicts very well the individual ignition delays in fuel-lean, stoichiometric and fuel-rich conditions. Furthermore, the computed overall activation energy fits well the experiments.

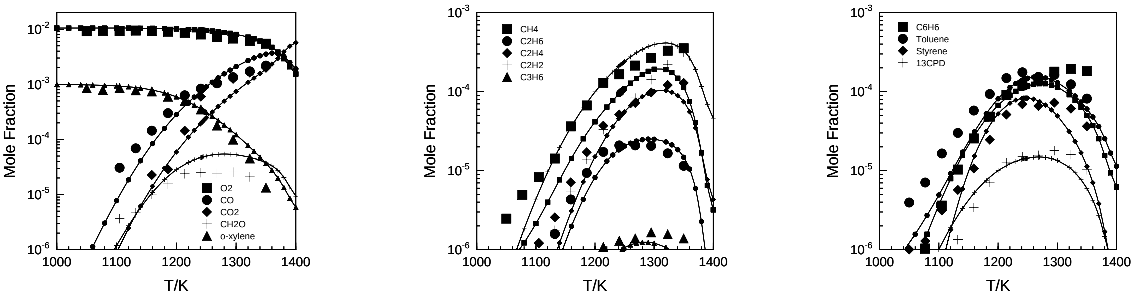

Figure 1. Oxidation of 1,2-DMB in a JSR at 1 atm and φ= 1.0 (1,2-DMB, 0.1% ; O_2, 1.05% ; N_2, 98.85% ; τ=0.1s. The data (symbols) are compared to computations (lines and small symbols).

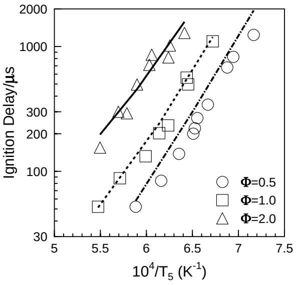

Figure 2 The ignition of 1,2-DMB/O_2/Ar mixtures behind a reflected shock wave at 1 atm and 0.5<φ<2. Initial conditions: 1,2-DMB, 0.375% ; at φ =0.5: O_2, 7.875% ; Ar, 91.75%; at φ =1: O_2, 3.937% ; Ar, 95.687%; at φ =2: O_2, 1.969% ; Ar, 97.65% (data: symbols, computations: lines).

5 Conclusion

The first objective of this study was to obtain new kinetic results for the oxidation of 1,2-DMB. That was done studying the oxidation of 1,2-DMB in a JSR over the temperature range 950 to 1350 K, for equivalence ratios ranging from 0.5 to 1.5. Molecular species concentration profiles were obtained by probe sampling and GC analyses (GC-MS, GC-TCD and FID) for 30 species. The second objective of this work was to obtain new ignition delays for 1,2-DMB at 1 atm over a wide range of equivalence ratio and temperature. That was achieved using a shock tube for φ=0.5 to 2 at ca. 1 atm, over the temperature range 1396 to 1826 K. The third objective of this work was to validate a kinetic scheme over a wide range of conditions. That was achieved by modeling our new experiments with reasonable accuracy. Overall the proposed kinetic model represents well the data. The kinetic modeling allowed delineating the main routes involved in 1,2-DMB oxidation. Comparison with previous results obtained under similar conditions for the oxidation of 1,3- and 1,4-DMB [6,7] confirms the findings of Emdee [2]: the kinetics of oxidation of 1,2-DMB is faster than that of 1,3- and 1,4-DMB at 1 atm.

References

[1] Simmie, J.M. (2003). Detailed chemical kinetic models for the combustion of hydrocarbon fuels, Prog. Energ. Comb. Sci. 29, 599-634.

[2] Emdee, J. L. (1991). An experimental and modeling study of the high temperature oxidation of the xylenes. Ph.D. Thesis, Princeton University

[3] Gregory, D., Jackson, R.A. (1999). Mechanisms for the formation of exhaust hydrocarbons in a single cylinder spark-ignition engine, fueled with deuterium-labeled ortho-, meta- and para-xylene, Combust. Flame 118, 459-468.

[4] Roubaud, A., Minetti, R., Sochet L.-R. (2000). Oxidation and combustion of low alkylbenzenes at high pressure: comparative reactivity and auto-ignition, Combust. Flame 121, 535-541.

[5] Battin-Leclerc, F., Bounaceur, R., Belmekki, N., Glaude, P.A. (2006). Experimental and modeling study of the oxidation of xylenes, Int. J. Chem. Kinet. 38, 284-302.

[6] Gaïl, S., Dagaut, P. (2005). Experimental Kinetic Study of the Oxidation of *p*-Xylene in a JSR and Comprehensive Detailed Chemical Kinetic Modeling, Combust. Flame 141, 281-297.

[7] Gaïl, S. (2003). Etude cinétique de l'oxydation de composés aromatiques en relation avec la composition du gazole et de l'essence: Approche expérimentale et modélisation cinétique détaillée, Thesis, University of Orléans (in French).

[8] Morley, C., Gaseq version 0.76, http://www.gaseq.co.uk.

[9] Horning, D.C., Davidson, D.F., Hanson, R.K. (2002). Study of the high-temperature autoignition of n-alkane/O2/Ar Mixtures, J. Propulsion and Power 18, 363-371.

[10] Smith, J.M., Simmie, J.M., Curran, H.J. (2005). Autoignition of heptanes; experiments and modelling, Int. J. Chem. Kinet. 37, 728-736.

[11] Davidson, D.F., Hanson, R.K. (2004). Interpreting shock tube ignition data, Int. J. Chem. Kinet. 36, 510-523.

[12] Da Costa, I., Fournet, R., Billaud, F., Battin-Leclerc, F. (2003). Experimental and modeling study of the oxidation of benzene, Int. J. Chem. Kinet. 35, 503-524.

[13] Bounaceur, R., Da Costa, I., Fournet, R., Billaud, F., Battin-Leclerc, F. (2005). Experimental and modeling study of the oxidation of toluene, Int. J. Chem. Kinet. 37, 25-49.

[14] Lutz, A.E, Kee, R.J., Miller, J.A., 1988, "Senkin: A Fortran program for predicting homogeneous gas phase chemical kinetics with sensitivity analysis," Sandia Report No SAND87-8248, Sandia National Laboratories, Livermore, CA.

[15] Glarborg, P., Kee, R.J., Grcar, J.F., Miller, J.A, 1986, "PSR: A Fortran program for modeling well-stirred reactors," Sandia Report No. SAND86-8209, Sandia National Laboratories, Livermore, CA.