

A TENTATIVE DETAILED CHEMICAL SCHEME FOR THE OXIDATION OF BENZENE-AIR MIXTURES

Christophe Chevalier, Jürgen Warnatz
Institut für Technische Verbrennung, Universität Stuttgart
Pfaffenwaldring 12, 7000 Stuttgart 80, Germany

Keywords: Kinetics, numerical simulation, laminar flames and ignition of benzene.

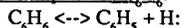
INTRODUCTION

The increasing use of unleaded gasoline in western countries in the last 20 years has forced oil companies to find substitutes for the alkyl-lead compounds, in order to supply high-octane fuels. Among aromatic hydrocarbons, which are well known to have a high octane number, benzene is a preferred compound (up to 5% or more in liquid commercial fuels). Unfortunately, it has a pronounced propensity to form soot during its combustion (1). Nevertheless, a rather limited number of works on detailed chemical schemes has been published yet. Early studies considered the low temperature ignition of aromatic hydrocarbons in static reactors (2-9), where a major step is the addition of molecular oxygen to a phenyl radical, leading to a bridging peroxy radical which, according to Benson (10), is very unlikely to be formed at temperatures above 700 K. More recently shock tube (11) and flow reactor (12-15) experiments have pointed out the most important pathways at higher temperatures. It appears that a phenyl radical and O_2 react to form a phenoxy radical and an O atom. However, no detailed reaction mechanism for the oxidation of benzene in flames and for its auto-ignition over a wide range of conditions has been published yet. Based on a review of the rate coefficients proposed for each elementary reaction, a detailed chemical scheme is presented and discussed here. Numerical simulations of premixed laminar flames, and calculations of auto-ignition delay times are compared with experiments, in order to check the validity of the mechanism.

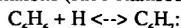
REACTION MECHANISM

The reaction mechanism presented here is based on a high temperature gas phase mechanism, which has been developed recently (16) for saturated and unsaturated hydrocarbons up to C_4 . However, due to lack of space, this work (including several hundreds of literature references) cannot be presented here. Most of rate coefficients of the reactions involving C_6H_6 follow the recommendations of the CEC evaluation group (17). The reverse reaction rates have been calculated using the equilibrium constants (reactions characterized by " \leftrightarrow "). Irreversible steps are denoted by " \rightarrow ". Reactions directly related to the oxidation of benzene are discussed here, and summarized in table 1. The complete detailed mechanism contains 57 species and 475 elementary reactions.

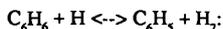
1) Consumption of C_6H_6 :



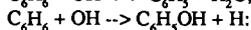
Due to the size of the benzene molecule, a fall-off behavior appears only for very low pressures; thus, at 1 bar, the high pressure rate coefficient may be used (18). This has been confirmed by RRKM calculations (Rice-Ramsberger-Kassel-Marcus theory).



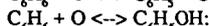
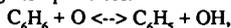
Measurements for this recombination reaction have only been carried out at low temperatures ($T < 1000$ K). The C_6H_7 radical may be one of the possible starting points for an opening of the cycle, but no rate coefficient is available for this step.



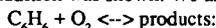
Due to the scatter in the experimental data at high temperatures, it is difficult to evaluate the rate coefficient. Since this abstraction channel is necessary for a mechanism describing combustion in flames, the value of Fujii and Asaba has been taken (19).



At high temperatures, the H-abstraction seems to be the dominant channel. The displacement reaction is probably not an elementary process (proceeding via a $\text{C}_6\text{H}_6\text{OH}$ species), but cannot be neglected at high temperatures.



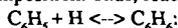
Experiments have been carried out up to 1000 K. Moreover, no clear separation between abstraction and addition was shown. We assumed the same reaction rate for both channels.



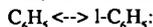
No data was found for this reaction, which may play an important role for the ignition.

2) Consumption of C_6H_5 :

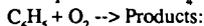
Most of the reactions concerning the phenyl radical have been studied in relation with the thermal decomposition. Thus, reactions with other radicals are not well known.



The reverse of this recombination reaction has been discussed above.

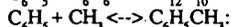
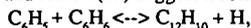


According to Braun-Unkoff et al. (20), who monitored H atoms, the opening of the cycle is the only possible decomposition, the pathways leading to $\text{C}_4\text{H}_3 + \text{C}_2\text{H}_2$, $\text{C}_6\text{H}_4 + \text{H}$, $\text{C}_4\text{H}_2 + \text{C}_2\text{H}_3$, or $\text{C}_4\text{H}_4 + \text{C}_2\text{H}$ either have a too high reaction enthalpy, or produce not enough H atoms. The linear $1\text{-C}_6\text{H}_5$ radical may then decompose either to $\text{C}_4\text{H}_3 + \text{C}_2\text{H}_2$ or to $1\text{-C}_6\text{H}_4 + \text{H}$, both reactions being pressure dependent.



This major oxidation step is unfortunately not well known. Venkat et al. (13) propose the formation of a phenoxy radical $\text{C}_6\text{H}_5\text{O} + \text{O}$, but no rate coefficient for this reaction has been measured.

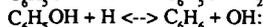
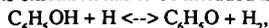
Fujii and Asaba (19) suggest a complex reaction, leading to $\text{C}_6\text{H}_4 + \text{H} + 2\text{CO}$.



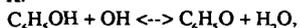
These reactions are not included in the mechanism at the moment, since they lead to biphenyl or toluene, which oxidation would require a much more complex mechanism.

3) Consumption of $\text{C}_6\text{H}_5\text{OH}$:

Phenol is formed in rather high amounts from benzene, by reaction with O and OH (see above), and its oxidation has to be included in the mechanism.



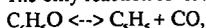
The only experiments available (21) show that the H-abstraction as well as the displacement reaction (the reverse one has been discussed earlier) both are possible at temperatures between 1000 and 1150 K.



This reaction has also been investigated by He and others (21), who do not supply information about the branching ratios.

4) Consumption of C_6H_5O :

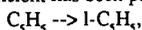
The only reaction reviewed by the CEC (17) has been proposed by Lin and Lin (22):



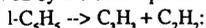
where the decomposition of the phenoxy leads to the formation of a cyclopentadienyl radical.

5) Consumption of C_3H_3 :

This species certainly reacts with radicals like O or OH, as suggested by Brezinsky (14), or with molecular oxygen (Venkat et al. (13)). However, the only pathway involving C_3H_3 for which a rate coefficient has been proposed (20) is reaction



followed by the decomposition



It seems that the lack of radical-radical routes for C_3H_3 is compensated by the semi-global reaction $C_6H_5 + O_2 \rightarrow C_4H_4 + H + 2CO$, since the more detailed scheme proposed by Venkat (13) might be summarized as: $C_6H_5 + O_2 \rightarrow C_6H_5O + O \rightarrow C_3H_3 + CO + O \rightarrow C_3H_3O + CO \rightarrow C_4H_4 + H + 2CO$.

RESULTS AND DISCUSSION

In order to check the mechanism, velocities of freely propagating premixed laminar flames as well as ignition delay times have been calculated, and compared with experiments, under non-sooting conditions (below the sooting limit: $\phi = 1.9$).

1) Laminar flames:

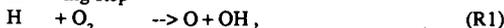
The solid line in Fig. 1 shows the burning velocities of benzene-air mixtures at 298 K and 1 bar, computed for benzene contents from 1.9% to 3.8% (equivalence ratios $\phi = 0.7$ to 1.4). The figure also shows experimental data (23) available for comparison. The maximum computed burning velocity (47.6 cm/s) occurs in stoichiometric mixtures, in agreement with experimental results. For rich mixtures, the computed values lie slightly above the measurements, but in view of the uncertainties in the experiments and in the kinetic data (see above), this difference cannot be considered being significant.

Fig. 2 shows the burning velocities of mixtures containing 1.5% to 5.0% benzene and 20.8% oxygen, diluted with nitrogen (equivalence ratios $\phi = 0.54$ to 1.80), $P = 1$ bar, $T_u = 298$ K, compared with experiments run under the same conditions (24). The maximum calculated speed (49.2 cm/s) is somewhat larger than the measured one (45.0 cm/s), and slightly shifted to lean mixtures ($\phi = 1.1$ instead of $\phi = 1.2$). Around stoichiometry, the computed velocities are found to be too fast (up to 9% discrepancy), but in rich mixtures, they are too slow (40% at most). Since the conditions of this experiment are very similar to those of the one presented first, this result is probably due to the reliability of the measuring techniques.

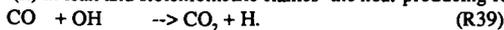
The pathways of the oxidation of C_6H_6 in a stoichiometric benzene/air flame and their relative importance are shown in Fig. 3. C_6H_6 is initially attacked by H, OH, and O radicals to form (i) benzyl radicals, which react with molecular oxygen as described above, (ii) phenol, which, after H-abstraction, leads to cyclopentadienyl radicals. Thus, it is clear that the mechanism leads to two parallel pathways, one being the phenyl route, the other the phenol route.

The sensitivity analysis in Fig. 4 shows the rate limiting reactions, for lean, stoichiometric, and rich mixtures. The sensitivities are obtained by a systematic variation of the preexponential factors of the rate constants. For the i^{th} reaction, the relative sensitivity $S_i = \Delta \ln v_u / \Delta \ln k_i$ denotes the change of the burning velocity with respect to a change of the preexponential factor.

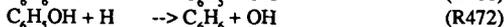
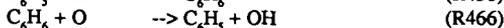
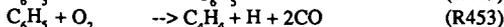
The sensitivity analysis for the reactions of the H_2 -CO- O_2 have been discussed earlier (25, 26). However, it is worth noting that the most sensitive reactions are (i) for all equivalence ratios the chain branching step



(ii) in lean and stoichiometric flames the heat-producing reaction



The reactions which are specific to the combustion of benzene are:



The decomposition of the linear $l-C_6H_5$ radical (produced in reaction R449) leads rapidly to the formation of H atoms; therefore, reaction R449 has a positive sensitivity in rich flames, where the molecular oxygen concentration is too low to oxidize all of the phenyl radicals through reaction R453. Reaction R453 directly produces H radicals, and has almost the same sensitivity under lean and under rich conditions. The recombination reaction R458 deprives reaction R1 of H atoms and reactions R449 and R453 of phenyl radicals; its sensitivity is strongly negative. In lean flames, the branching reaction R466 shows a positive sensitivity. The H-consuming reaction R472 has a negative sensitivity, because it competes with reaction R1.

These results point out that a deep insight into the reaction between phenyl and molecular oxygen is fundamental, because the whole mechanism depends on the route chosen.

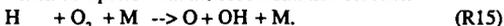
2) Ignition delay times:

Zero-dimensional simulations can be used to calculate ignition delay times of benzene-oxygen-argon mixtures in shock tubes. Fig. 5 shows calculated ignition delay times compared with experimental results of Burcat et al. (27), for stoichiometric mixtures containing 1.69% benzene, at pressures behind reflected shock between 2 and 3 bar, and at temperatures in the range 1286 to 1608 K. If a rather good agreement is observed at the highest temperatures (above 1450 K), an increasing discrepancy appears when decreasing the temperature.

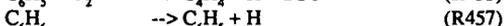
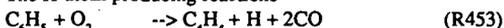
Sensitivity tests with respect to the OH concentration (Fig. 6) show the rate limiting reactions during the induction period at the lowest investigated temperature (1286 K). The main rate-limiting process here is the chain branching reaction, too.



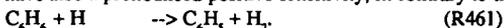
which competes with the recombination reaction



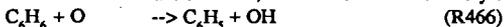
The H-atom producing reactions



have also a pronounced positive sensitivity, in contrary to the H-consuming reaction



Furthermore, the chain branching reaction R466 has a very high positive sensitivity and competes with the termination reaction R468, which has of course a very strongly negative sensitivity:

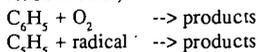


Further information about the relative importance of each channel is necessary to simulate correctly the ignition of benzene-oxygen mixtures.

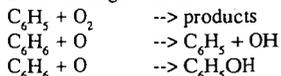
CONCLUSIONS

1- A review of the elementary reactions for the high temperature oxidation of benzene has been carried out, in order to evaluate the current kinetic and thermodynamic knowledge in this field.

2- The calculation of premixed laminar flame velocities of benzene-air mixtures is in good agreement with experiments run at atmospheric pressure, over a wide range of equivalence ratios below the sooting limit. However, it would be helpful to get further data for some reactions (e.g. products, reaction rates):



3- The computed ignition delay times of stoichiometric benzene-oxygen mixtures diluted in argon were 1.5 to 5 times too short compared with shock tube experiments, depending on the temperature. According to sensitivity analyses, these results could certainly be improved by a better knowledge of the following reactions:



4- Based on these results, our preliminary mechanism will be improved in the near future. Calculated and measured species profiles in low pressure laminar flames will be compared, in order to obtain further information about the combustion processes in flames. Furthermore, ignition delay times at pressure ranging from 2 to 7 bar, in lean to rich mixtures will be computed in order to check the mechanism for auto-ignition.

ACKNOWLEDGEMENT

The authors are grateful to Dr. M. Braun-Unkloff and Dr. P. Frank for their interest and helpful discussions.

This research is financed by the commission of the European Communities within the frame of the Joule program, by the Swedish National Board for Technical Development, and by the Joint Research Committee of European automobile manufacturers (Fiat, Peugeot SA, Renault, Volkswagen, and Volvo) within the IDEA program.

REFERENCES

- (1) J.J. MacFarlane, F.H. Holderness, F.S.E. Witcher: *Comb. & Flame* 8, 215 (1964).
- (2) R. Fort, C.N. Hinshelwood: *Proc. Roy. Soc.*, A127, 218 (1930).
- (3) D.W. Newitt, J.H. Burgoyne: *Proc. Roy. Soc.*, A153, 448(1936).
- (4) J.H. Burgoyne: *Proc. Roy. Soc.*, A161, 48 (1937).
- (5) J.H. Burgoyne: *Proc. Roy. Soc.*, A171, 421 (1939).
- (6) J.H. Burgoyne: T.L. Tang, C.M. Newitt, *Proc. Roy. Soc.*, A174, 379 (1940).
- (7) J.H. Burgoyne: *Proc. Roy. Soc.*, A174, 395 (1940).
- (8) J.H. Burgoyne: *Proc. Roy. Soc.*, A175, 539 (1940).
- (9) R.G.W. Norrish, G.W. Taylor: *Proc. Roy. Soc.*, A234, 160 (1956).
- (10) S.W. Benson: *JACS* 87, 972 (1965).
- (11) C.R. Orr: 9th Symp. (Int.) Comb., 1034 (1963).
- (12) R.J. Santoro, I. Glassman: *Comb. Sci. Tech.* 19, 161 (1979).

- (13) C. Venkat, K. Brezinsky, I. Glassman: 19th Symp. (Int.) Comb., 143 (1982).
 (14) K. Brezinsky: Prog. Energy Combust. Sci., 12, 1 (1986).
 (15) A.B. Lovell, K. Brezinsky, I. Glassman: 22nd Symp. (Int.) Comb., 1063 (1988).
 (16) C. Chevalier, J. Warnatz: to be published in Prog. Energy Combust. Sci.
 (17) D.L. Baulch, T. Just, J.A. Kerr, M. Pilling, J. Troe, R.W. Walker, J. Warnatz: to be published in J. Phys. Chem. Ref. Data.
 (18) J. Troe, private communication.
 (19) N. Fujii, T. Asaba: J. Fac. of Eng. Univ. Tokyo (B) XXXIV, #1, 189 (1977).
 (20) M. Braun-Unkoff, P. Frank, Th. Just: 22nd Symp. (Int.) Comb, 1053 (1988).
 (21) Y.Z. He, W.G. Mallard, W. Tsang: J. Phys. Chem. 92, 2196 (1988).
 (22) C.Y. Lin, M.C. Lin: J. Phys. Chem. 90, 425 (1985).
 (23) G.J. Gibbs, H.F. Calcote: J. Chem. and Eng. Data 4, 226 (1959).
 (24) E.S. Goloniva, G.G. Fyodorov: 6th Symp. (Int.) Comb., 88 (1956).
 (25) J. Warnatz: 18th Symp. (Int.) Comb., 369 (1981).
 (26) U. Maas, J. Warnatz: Comb. & Flame 74, 53 (1988).
 (27) A. Burcat, C. Snyder, T. Brabbs: NASA Technical Memorandum 87312 (1986).

Table 1
 Benzene mechanism and rate constants in cm³, mol, s, K, and kJ.

Reaction	A	B	Ea	Ref.
414. C ₅ H ₅ → 1- C ₅ H ₅	1.000e+14	0.0	188.0	20
415. 1- C ₅ H ₅ → C ₃ H ₃ + C ₂ H ₂	1.000e+14	0.0	71.1	20
449. C ₆ H ₅ → 1- C ₆ H ₅	4.000e+13	0.0	305.0	17
450. 1- C ₆ H ₅ → C ₄ H ₃ + C ₂ H ₂	2.000e+62	-14.7	241.0	20
451. 1- C ₆ H ₅ ↔ 1- C ₆ H ₄ + H	2.500e+58	-13.8	208.0	20
453. C ₆ H ₅ + O ₂ → C ₄ H ₄ + H + 2CO	1.000e+12	0.0	8.4	19
455. C ₆ H ₅ O → C ₅ H ₅ + CO	2.500e+11	0.0	184.0	17
456. C ₆ H ₄ OH → C ₅ H ₅ + CO	2.500e+11	0.0	184.0	17
457. C ₆ H ₆ ↔ C ₆ H ₅ + H	4.410e+29	-3.9	489.9	18
459. C ₆ H ₆ ↔ C ₄ H ₄ + C ₂ H ₂	1.000e+15	0.0	450.0	17
461. C ₆ H ₆ + H ↔ C ₆ H ₅ + H ₂	7.900e+13	0.0	41.8	19
463. C ₆ H ₆ + OH ↔ C ₆ H ₅ + H ₂ O	1.630e+08	1.4	6.1	17
465. C ₆ H ₆ + OH → C ₆ H ₅ OH + H	1.320e+13	0.0	46.0	17
466. C ₆ H ₆ + O ↔ C ₆ H ₅ + OH	3.612e+01	3.7	4.5	17
468. C ₆ H ₆ + O ↔ C ₆ H ₅ OH	3.612e+01	3.7	4.5	17
470. C ₆ H ₅ OH + H ↔ C ₆ H ₅ O + H ₂	1.144e+14	0.0	51.9	17
472. C ₆ H ₅ OH + H → C ₆ H ₆ + OH	2.230e+13	0.0	33.2	17
473. C ₆ H ₅ OH + OH ↔ C ₆ H ₅ O + H ₂ O	3.000e+12	0.0	0.0	17
475. C ₆ H ₅ OH + OH ↔ C ₆ H ₄ OH + H ₂ O	3.000e+12	0.0	0.0	17

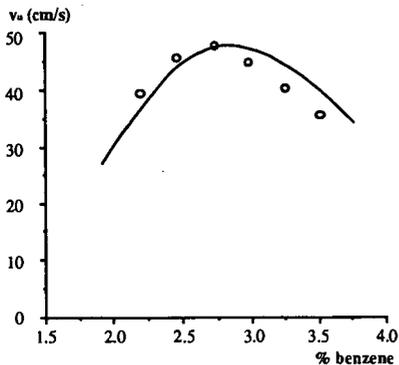


Fig. 1. Free flame velocities in benzene-air mixtures, $P = 1$ bar, $T_u = 298$ K. Points: measurements (23). Line: Calculation.

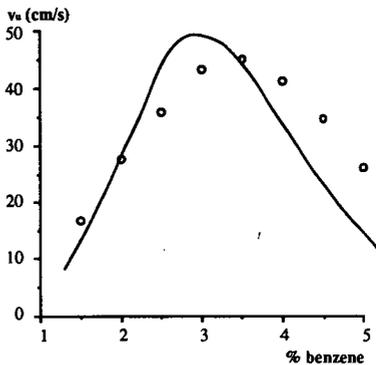


Fig. 2. Free flame velocities of benzene-20.8% oxygen-argon mixtures, $P = 1$ bar, $T_u = 298$ K. Points: measurements (24). Line: Calculation.

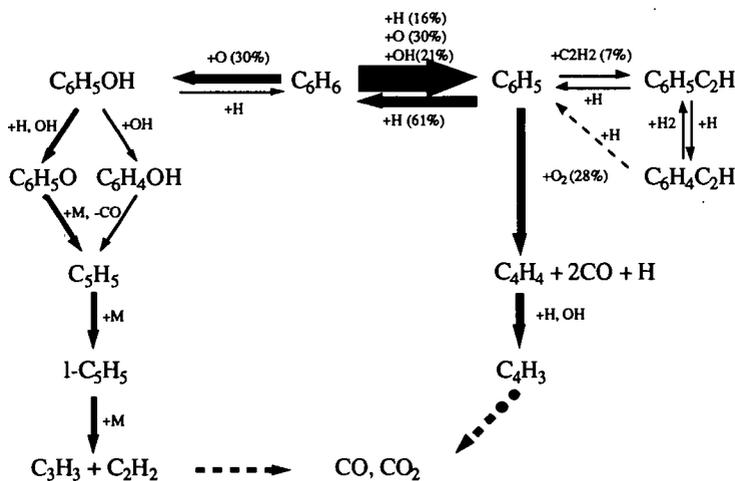


Fig. 3. Flow diagram for the oxidation of benzene in a stoichiometric flame, $P = 1$ bar, $T_u = 298$ K. The thickness of the arrows is proportional to the reaction rate integrated over the whole flame front

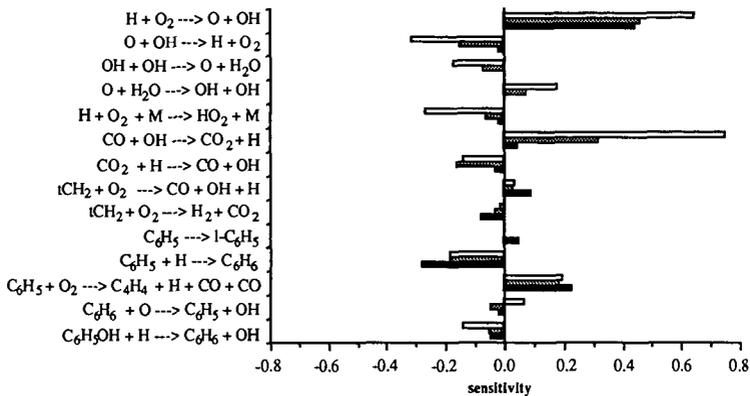


Fig. 4. Sensitivity analysis with respect to the laminar flame velocities in lean (white bars), stoichiometric (grey bars), and rich (black bars) benzene-air mixtures, $P = 1$ bar, $T_u = 298$ K.

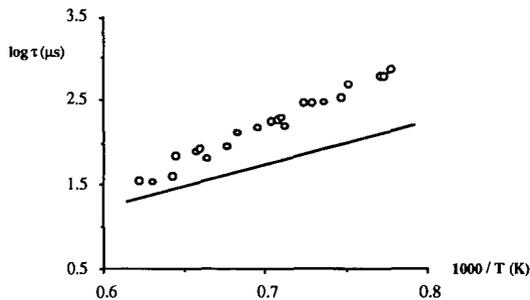


Fig. 5. Ignition delay times for stoichiometric benzene-oxygen-argon mixtures, $P = 2$ to 3 bar. Points: experimental values (27). Line: calculation.

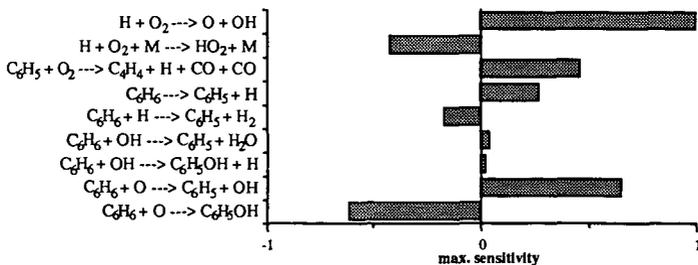


Fig. 6. Sensitivity test with respect to $[OH]$ concentration of a stoichiometric 1.69% benzene-12.675% O_2 mixtures diluted with argon, at $P = 2$ bar, $T_u = 1286$ K, and at $t = 30 \mu s$ ($\tau / 5$).