Detailed Combustion Kinetics of Cyclopentadiene Studied in a Shock-Tube

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ABSTRACT: Mixtures of cyclopentadiene and oxygen diluted in argon were used to obtain ignition delay data in a single pulse shock-tube. The temperatures ranged from 1278–2110 K and the experimental pressures were between 2.43 and 12.45 atm. The fuel concentrations ranged from 0.5 to 2.5% and the oxygen concentrations were between 3.3 and 16.6%. A Semenov ignition delay expression was determined:

 $\tau = 10^{-12.5} \exp(+34500/\text{RT}) [C_5H_6]^{0.06} [O_2]^{-0.95} [Ar]^{0.29} \text{ sec}$

The concentrations are in mol/cc and the activation energy is in cal/mol. Gas-chromatographic analyses were run on samples quenched before the ignition. The kinetics of combustion of cyclopentadiene was modeled with a full scheme containing 439 elementary reactions and a reduced scheme containing 125 reactions. Both ignition delay times and product distribution served as modeling targets. The mechanism of combustion of cyclopentadiene is discussed in connection to the combustion of aromatic fuels. © 2001 John Wiley & Sons, Inc. Int J Chem Kinet 33: 491–508, 2001

INTRODUCTION

Although cyclopentadiene is a relatively uncommon hydrocarbon, it has been identified as an important transition species in the combustion of simple aromatics such as benzene and toluene. The oxidation of simple aromatics has been shown to possess a common reactive pathway [1–4]. The reaction of benzene is kinetically unfavored due to the resonance stabilization energy of the ring. As a consequence of the ring resistance, the side chain, if available, is subject to attack by preference, and is removed or displaced, yielding the phenyl radical ϕ •. The phenyl radical is known to react with molecular oxygen, forming the phenoxy radical and atomic oxygen:

$$\phi \bullet + O_2 \Longrightarrow \phi O \bullet + O \tag{30}$$

The phenoxy radical undergoes a ring contraction via unimolecular decomposition to yield carbon monoxide and cyclopentadienyl radical:

$$\phi O \bullet \rightleftharpoons C_5 H_5 + CO$$
 (31)

The mechanism by which the cyclopentadienyl radical is oxidized has been studied. A pyrolysis, and partial combustion study in a shock-tube was performed by Colket [1]. He reports a rate for the reaction $C_5H_6 \rightleftharpoons C_5H_5 + H$; $k = 2 \times 10^{15} \exp(-81,000/RT)$ \sec^{-1} . The only oxidation study in a plug flow reactor was made by Butler [2]. According to his proposed mechanism, the cyclopentadienyl radical ultimately undergoes ring cleavage and there is a transition to straight chain aliphatic chemistry, after which the chemistry is once again well understood. The formation of the cyclopentadienyl radical and its consumption involves the transition from cyclic to open chain

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chemistry. Thus, understanding the role of the cyclopentadienyl radical is crucial to linking these two chemical regimes, which have until now been connected only by global mechanisms. In addition, three articles connected with the subject of cyclopentadiene oxidation were published recently: Wang and Brezinsky [3], dealing with the decomposition of cyclopentadienone, Kern et al. [4], dealing with cyclopentadiene pyrolysis, and Zhang and Bozzelli [5], dealing with cyclopentadiene oxidation. The decomposition pattern of cyclopentadiene was studied separately [6,7], and the present study is devoted to its oxidation.

EXPERIMENTAL

Apparatus

The ignition delay time is defined as the time interval between the pressure rise caused by the reflected shock and the onset of pressure rise due to the ignition phenomenon. The ignition delay times are measured in a shock-tube, which serves as a millisecond homogeneous heater. The shock-tube is stainless steel, 54 mm in diameter, 4 m-long, and has the single pulse design. The driven section is 2.5-m long. Mylar diaphragms of different gauges are used and are burst by the driver gas pressure. The driver gas used is helium.

The sampling section, 0.25 m-long, contains three piezoelectric transducers. Two transducers, located 0.2 m apart, measure the shock velocity from which the temperature is calculated. A third piezoelectric gauge, located on the end plate, records the pressure history. The pressure-time traces are fed to a Nicolet dual trace digital oscilloscope.

Two traces of 4098 points each are recorded at 1- μ sec intervals. One trace is connected to the end-plate transducer and records the ignition delay time, while the other is connected to the other two transducers in parallel and records the shock speed.

Analytical Setup

In addition to the ignition delay times, it is also possible to determine the product distribution of stable species before ignition occurs. For this purpose, certain experiments are quenched right before the ignition and partially reacted gas is extracted from the shocktube in pre-evacuated glass bulbs. The gas is then injected into a HP 8900 series gas chromatograph equipped with a flame ionization detector and a methanizer.

The output of the ionization detector uses a Perkin-Elmer/Nelson Analytical PC Integrator card for gas chromatography. The unit performs instant area calculations of the peaks.

Handling of Mixtures

The cyclopentadiene (CPD) is not stable and dimerizes to $(C_5H_6)_2$. The di-cyclopentadiene used was Riedelde-Haen AG, 95% purity. To obtain the cyclopentadiene, the dimer was boiled in a flask under vacuum conditions, then the pumping was cut and the vapors were distilled through a preheated furnace at 780 K, as recommended by Butler [2], directly into the evacuated mixing tank. Oxygen Stores, 99% pure oxygen, was added on top, and the tank was pressurized to \sim 3.5 atm using Herzliva argon, 99% pure. All gas mixtures were prepared manometrically in stainless steel containers. To ensure thorough mixing of the gases, the mixtures were left in the containers for 48 h before use. The concentration of CPD was measured in the mixing tank during 6 weeks and was found to remain stable. The only impurities detected were $\sim 0.5\%$ CH₄ (originating from the argon) and a compound at the foot of the CPD peak whose concentration was <1% of the CPD concentration. We suppose it was either pentadiene or penteneyne, since we had no means of defining which.

Calculations

The reflected shock temperatures were calculated using standard conservation equations and the ideal gas equation of state, assuming frozen chemistry. Thermodynamic data for all species were taken from a recent compilation [8].

RESULTS

375 ignition delay experiments were performed with cyclopentadiene and oxygen mixtures diluted in argon. The seven different mixtures used are listed in Table I. The notation P_1 means initial pressure of the experiment, and P_5 and T_5 denote reflected shock pressure and temperature conditions. τ is the measured ignition delay time. The initial point of the jump was considered as time 0.

A multiregression statistical student-*t* program was used to evaluate the Semenov-type correlation of the experiments, and results for a confidence limit of 2σ , including 300 of our 375 experiments, are:

$$\tau = 10^{-12.5 \pm 0.5} \exp^{+}(34,500 \pm 800/RT)$$
$$[C_{5}H_{6}]^{0.06 \pm 0.05} [O_{2}]^{-0.95 \pm 0.06} [Ar]^{0.29 \pm 0.07} \sec$$

Exp No.	Symbol	[CPD]%	[O ₂]%	No. of Exp.	$P_1 \sim \text{Torr}$	P_5 atm.	$T_5 \mathrm{K}$	$ au$ μ sec
22					56	3.33	1497	84
37	+	2.5	16.6	88	56	4.29	1664	30
91					50	2.60	1303	468
96					74	2.69	1326	843
116	Δ	0.97	6.31	59	76	4.57	1807	29
139					73	3.23	1491	235
152					72	3.14	1504	600
159	0	1.01	3.29	40	75	4.91	1983	22
174					75	4.27	1779	64
239					73	4.39	1717	22
262	\diamond	1.00	12.95	51	79	3.14	1338	477
267					73	3.60	1518	88
289					74	4.29	1827	23
297	\diamond	0.52	6.98	52	74	3.02	1462	251
333					80	3.76	1597	80
339					76	3.46	1406	555
361		2.01	6.5	50	74	5.08	1800	25
374					77	4.31	1588	104
393					222	11.27	1725	42
396	∇	0.52	3.39	35	226	10.06	1585	111
406					223	8.43	1432	384

Table I Three Representative Ignition Delay Experiments from Each Mixture of CPD and Oxygen in Argon

The initial concentrations are given in mol/cc and the activation energy in cal/mol. This correlation is shown in Fig. 1. To get a better idea about the experimental error, a confidence limit of 3σ was calculated, which includes 370 of the 375 experiments. Here, the Semenov correlation is:

 $\tau = 10^{-12.4 \pm 0.3} \exp^+(34,400 \pm 600/RT)$ $[C_5H_6]^{0.08 \pm 0.04} [O_2]^{-0.98 \pm 0.04} [Ar]^{0.31 \pm 0.05} \text{ sec}$

Since in both cases the results obtained are very close to each other, they point out the quality of the data. For comparison purposes, the Semenov-type correlation of n-pentane is [9]:

$$\tau = 10^{-12.76} \exp(+34,610/RT)$$
$$[C_5H_{12}]^{0.29} [O_2]^{-1.10} [Ar]^{0.13} \sec(10,10)$$

In addition to the ignition delay time experiments, 18 shocks were performed for analytical purposes. The shocks were planned so that the ignition delay time would be longer than the time of arrival of the rarefaction wave, and the aerodynamic cooling of the gas occurs before the ignition starts. In this way, the concentration profiles of the mixture at temperatures before ignition were frozen. The gas was then removed to glass bulbs and analyzed for hydrocarbons with an FID detector, and a second sample from the same bulb was analyzed, after having been passed through the methanizer, for CO and CO₂ concentrations. Experiments were performed using a mixture of 1.0% CPD and 6.5% O₂ in argon. The shock-tube constant temperature dwell time was 400–600 μ sec, followed by a 2-msec cooling period.

The results of the gas chromatographic analysis are shown in Figs. 2–8 for the species of methane, acetylene, ethylene, propyne, propylene, benzene, and CO. The final concentration values [species], in mole percent, on a logarithmic scale are drawn vs. 1/T. In Figs. 2–8, modeled concentration values are also shown as described in the following paragraphs. It should be mentioned that the data scatter in Figs. 2–8 is larger than usual. On the other hand, a scatter is encountered in the modeled results as well, suggesting that the velocity of the cooling process was not accurately defined (see computation).

THERMODYNAMICS

The basis for the modeling calculations is the knowledge of the rate equations for the different elementary





Figure 1 log $\beta = \log[\pi/[C_5H_6]^{0.06}[O_2]^{-0.95}[Ar]^{0.29}]$ vs. 1/*T* for the seven mixtures listed in Table I. Kinetic modeling calculation of the ignition delay time in the form of log β vs. 1/*T* for a mechanism of 439 reactions is shown by big black squares. The line drawn is a result of mean least square of the calculated points.

and non-elementary reactions; these, in turn, are dependent on the availability of the thermodynamics of the species involved.

In Table II, the thermodynamic properties at 298 K are listed for a number of key cyclopentadiene species involved in the modeling of this research. Most of these properties are not available from experimental data and our knowledge depends on estimated calculations. It is obvious from this table that the data present serious problems concerning the cyclopentadienyl radical C_5H_5 , cyclopentadienone C_5H_4O , and the 2,4-cyclopentadiene 1-oxy radical C_5H_5O . The data presented by Emdee [11], Bozzelli [5], and Burcat [8], were calculated using Benson's [10] group additivity method. Kern et al. [4] data are based on kinetic evidence and Wang and Brezinsky [3], Melius [12], and Karni et al. [13] are based on *ab-initio* calculations made with Gaussian [14] programs.

For the cyclopentadienyl radical, the group theory calculations of Emdee et al. [11] and Zhang and Bozzelli [5] give heat of formation values that are too small. Wang [3] calculated $\Delta_f H_{298}$ smaller than Karni's [13] and entropy based on an assumed rotation of the



Figure 2 Rate of formation of methane vs. 1/T obtained from gas chromatographic analysis (open circles) compared to the full model formation of methane (filled circles). The mixture used was 1.0% CPD and 6.5% O₂.



Figure 3 Rate of formation of acetylene vs. 1/T obtained from gas chromatographic analysis (open circles) compared to the full model formation of acetylene (filled circles). The mixture used was 1.0% CPD and 6.5% O₂.



10000/T, K⁻¹

Figure 4 Rate of formation of ethylene vs. 1/T obtained from gas chromatographic analysis (open circles) compared to the full model formation of ethylene (filled circles). The mixture used was 1.0% CPD and 6.5% O₂.



Figure 6 Rate of formation of propene vs. 1/T obtained from gas chromatographic analysis (open circles) compared to the full model formation of propene (filled circles). The mixture used was 1.0% CPD and 6.5% O₂.



Figure 5 Rate of formation of propyne vs. 1/T obtained from gas chromatographic analysis (open triangles) compared to the full model formation of propyne (filled triangles). The mixture used was 1.0% CPD and 6.5% O₂.



Figure 7 Rate of formation of benzene vs. 1/T obtained from gas chromatographic analysis (open circles) compared to the full model formation of benzene (filled circles). The mixture used was 1.0% CPD and 6.5% O₂.



Figure 8 Rate of formation of CO vs. 1/T obtained from gas chromatographic analysis (open circles) compared to the full model formation of CO (filled circles). The mixture used was 1.0% CPD and 6.5% O₂.

stabilized apex of the radical, which was calculated as an external rotor. This procedure provided an entropy value that is far too high. Kern et al. [4], on the other hand, calculated a $\Delta_f H_{298}$ value larger than Karni et al. [13], leaving Karni's values in the middle. Based on the fact that Karni's data fit the kinetic model presented here better, it was decided to give preference to Karni's values over the others.

The data about cyclopentadienone are especially controversial, as can be seen in Table II. The discrepancy in the proposed enthalpies of formation spread from Liebman's estimation [15] of -8.0 ± 8.0 kcal/ mol to Wang and Brezinsky's [3] calculated value of 13.2 kcal/mol. Since the group additivity values for cyclopentadienone are based on estimations and not on experimental evidence, and the Gaussian data are calculated using the G2 method, which is superior to the others in estimating the heats of formation, Wang's [3] values were preferred. Thus, new thermodynamic properties were calculated using the vibrations and rotational constants of this species as calculated by Wang [3], to which a few of the experimental vibrational values found in the literature [16] were added. The new, more accurate NASA polynomial for cyclopentadienone was calculated (see Table III) and used in this computation.

In Table II, the $2,4-C_5H_4$ -cyclo-OH radical shows that Karni's calculation corresponds well with the rest of the calculations and only the enthalpy of formation is too high. Therefore, this value was corrected with Wang's value, which is based on the Gaussian G2 method. Since Karni [13] did not calculate the 2,4cyclopentadiene-1-oxy radical, this isomer was taken also from Wang's data [3]. All of the thermodynamic data necessary for the modeling program were taken from a database [8] in which the cyclopentadiene and derived radicals were calculated by Karni et al. [13] and corrected as explained previously.

COMPUTATIONS

Modeling of the kinetic process of the oxidation of cyclopentadiene was achieved using the CHEMKIN [17] program. In the model, a large matrix of 69 species connected by a very large number of elementary chemical reactions, interact step by step in time. The ignition delay time is simulated as a jump in temperature. The initial point of the jump was taken when the jump of one step was equal to or surpassed 130 K. Eighteen points were calculated in order to include all the variations of concentrations, pressure, and temperature of the experiments. The kinetic scheme containing 439 reactions was gathered in the following way: The first 175 reactions were taken from a scheme for methane prepared at GRI [18]. 133 reactions were taken from Westbrook et al. [19,20]. This was basically the C₃ model. Westbrook has species defined as C₃H₄ without a positive identification of allene or pro pyne. In this study, this species was considered to be propyne ($CH_3C \equiv CH$). In addition, seven reactions of allene $(CH_2 = C = CH_2)$ were added [21], and the benzene formation reactions were taken from Frenklach et al. [22]. A few reactions were taken from Bittker [23]. Bittker's reaction rate for $C_5H_6 + O_2 \rightleftharpoons$ C_5H_5O + OH was found to give bad correlations in our kinetic scheme. The main scheme for cyclopentadiene oxidation was published by Emdee et al. [11] and Egalfopoulos et al. [24], but the decomposition reactions of cyclopentadiene [6] had to be changed in order to fit in with the experimental oxidation evidence. In addition, the oxidation reactions had also to be changed to fit the present data. Figure 1 shows the comparison of the calculated ignition delay points for our different mixtures vs. the experimental correlation, using big black squares. The experimental and calculated points coincide.

To calculate the product concentrations in order to compare those with the gas-chromatographic experiments, it was necessary to calculate the contribution of the cooling period to the species concentrations.

Species	Property	Emdee	Bozzelli	Kiefer	Wang	Karni	Melius	NIST ^a
C ₅ H ₆ Cyclopentadiene 2,4	$\Delta_{f}H_{298}\ S_{298}\ { m Cp}_{298}$	32.0 64.46 16.67	31.26 65.5 18.23	32.0 64.0	32.3	32.09 65.6 18.03	31.58 ± 2.15	33.2-31.89 65.6 18.01
C ₅ H ₅ Cyclopentadienyl radical	$\Delta_{f} H_{298} \ S_{298} \ { m Cp}_{298}$	54.31 62.41 17.34	57.17 63.58 17.86	65.3 67.0	62.0 76.68 17.87	63.6 66.87 18.32	64.57	
C ₅ H ₄ O Cyclopentadiene-1- one	$\Delta_{f} H_{298} \ S_{298} \ { m Cp}_{298}$	4.15 67.13 18.33	7.40 66.71 19.5		13.2 69.36 19.13	- 1.59 66.57 19.6		
C ₅ H ₄ OH 1-OH-2,4 cyclopen- tadien-1-yl radical	$\Delta_{f} H_{298} \ S_{298} \ { m Cp}_{298}$	12.35 74.27 22.17	16.88 75.23 21.68		15.9	20.9 74.16 22.9		
C₅H₅O 1-oxy-2,4 cyclopen- tadien radical	$\Delta_{f} H_{298} \ S_{298} \ { m Cp}_{298}$	43.35 71.38 21.13	42.94 72.73 20.60		52.8			
C ₄ H ₅ CH ₂ =CHCH=CH* Butadiene radical	$\Delta_{f} H_{298} \ S_{298} \ { m Cp}_{298}$	80.21 69.81 19.71	83.99 69.05 19.06			82.5 68.9 18.5		
C ₄ H ₆ 1-3 butadiene	$\Delta_{f} H_{298} \ S_{298} \ { m Cp}_{298}$	26.34 66.62 22.36	26.08 66.61 19.23			26.5 68.3 18.75	trans- 24.69 ± 2.29 cis- 27.01 ± 2.4	26.0 ± 0.2 19.08
C_3H_5 CH_2 — $C*H$ — CH_2 Symmetric radical	$\Delta_{f} H_{298} \ S_{298} \ { m Cp}_{298}$			39.1 61.9		39.1 61.9 15.7	38.7 ± 4.19	

 $\textbf{Table II} \quad \text{Thermodynamic Properties of Some Key Species in kcal/mol} \ (\Delta_{f}H_{298}) \text{ and cal/mol} \ K(S \text{ and } Cp)$

^a Reference [34].

Table III Experimental and Calculated Vibrations and Rotation Constants of C₅H₄O Cyclopentadienone and Calculated NASA Polynomials of Thermochemical Properties

Wang ^a		$\mathbf{A}=0.$	273		$\mathbf{B}=0.$	131		$\mathbf{C}=0.0$)88		
				F	Rotation con	nstants cm ⁻	-1				
1068	1136	1332	1678	1724	1727	1789	1870				
		458		632			822				
Jacox E	xperimenta	ıl ^ь									
1084	1084	1147	1295	1342	1539	1605	1708	3151	3160	3191	3192
194	418	445	620	641	697	729	787	847	864	897	963
Wang M	/IP2(full)/6	-31G(d) ^a									
1084	1087	1123	1293	1342	1571	1643	1782	3161	3171	3204	3206
209	448	449	640	645	714	729	830	839	943	945	949
Wang E	B3LYP/6-31	lG(d) ^a									

Values printed in bold characters were selected for thermodynamic calculations.

^a Reference [3].

^b Reference [16].

C5H4O CY CPD-ONE T 8/99C 5.H 4.O 1. 0.G 200.00 6000.00 B 80.08616

1.00806824E+01	1.61143465E-02-	-5.83314509E-06 9.46759320E-10-	-5.68972206E-14	2
1.94364771E+03-2	2.94521623E+01	2.64576497E-01 3.348738273-02	1.67738470E - 06	3
-2.96207455E-08	1.54431476E-11	5.11159287E+03 2.35409513E+01	6.4245999E+03	4

1

The cooling period was approximated as a straight line with the inclination taken from the experimental oscillogram. For each experiment a specific rate of cooling was obtained. The spread obtained for the calculated points is probably caused by the imperfection of the previous approximation.

Generally, it was found that the calculated CH_4 concentrations shown in Fig. 2 are lower than the amount of CH₄ found, probably because of the CH₄ existing as impurity in our initial mixture. The calculations match very well the acetylene experiments (Fig. 3) and the ethylene found at high temperatures, but predict higher concentrations at lower temperatures (Fig. 4). The propyne is well predicted at low temperatures, but is underpredicted at high temperatures (Fig. 5). Propylene is predicted with an almost constant concentration for all temperatures, while the experimental points show a very high scatter around the calculated points (Fig. 6). Benzene is well predicted (Fig. 7), and CO shows a prediction on the higher side of the experimental scatter (Fig. 8). The calculated product distribution at 1350 K is shown in Fig. 9.

A big effort in the kinetic community has been made to reduce the size of the kinetic schemes [25] and specifically the size of the combustion kinetic schemes. To achieve this goal, sensitivity analyses were performed on all the reactions in the scheme in order to find the unimportant reactions and remove them from the model. Our method of reducing the rate of each reaction to almost zero and checking its effect on the calculated ignition delay obtained (Table IV) provides a criterion which is more sensitive than usual. In order to show the values of this method, a second sensitivity analysis was conducted by diminishing each rate by a factor of 5 (Table V). This is usually the classical way used by many researchers. The order of the most sensitive reactions is identical in both cases. As stated in previous publications [26,27], the first method is more sensitive and has a larger sensitivity index scale. The sensitivity index is: $S = \tau m / \tau n$ where τn is the standard ignition delay including all the reactions, as stated, and τm is the ignition delay with changes introduced to the *m*th reaction. Thus, to show a change the index is either

Table IVSensitivity Analysis for Stoichiometric Mixtures of Ignition Delay Time at Different Temperatures Whenthe Reactions Are Deleted (Full Model)

			S	
		Tempe	rature, K	
Reaction	1325	1500	1730	2000
$H + O_2 \rightleftharpoons O + OH$	2.72*	8.21*	25.1*	6.45*
$C_5H_5 + O_2 \rightleftharpoons C_5H_4O + OH$	3.19*	1.50*	1.03	
$C_5H_5 + HO_2 \Longrightarrow C_5H_5O + OH$	1.54*	1.32*	1.05	
$C_5H_6 + O_2 \rightleftharpoons C_5H_5H + HO_2$	1.38*	1.11	1.03	1.004
$CHO + O_2 \Longrightarrow HO_2 + CO$	1.15*	1.06	0.93	0.94*
$C_5H_5 + O \Longrightarrow C_5H_5O$	1.13*	1.09	1.02	
$C_3H_3 + C_3H_3 \Longrightarrow C_6H_5-c + H$	1.11	1.64*	2.57*	1.37*
$C_6H_5 \rightleftharpoons C_6H_5-c$	1.11	1.66*	2.41*	1.35*
$C_6H_5 + O_2 \rightleftharpoons C_6H_5O + O$	1.07	1.28*	1.06	1.07
$C_6H_5O \Longrightarrow CO + C_5H_5$	1.07	1.23	1.03	
$O + C_2H_2 \Longrightarrow H + C_2HO$	1.05	1.10	1.10	1.08
$C_2H_2 + C_2H \Longrightarrow C_4H_3$	_	_	1.28*	1.18*
$C_3H_5 + C_2H_2 \Longrightarrow C_5H_6 + H$	1.002	0.997	0.97	0.93*
$C_5H_6 + H \Longrightarrow C_5H_5 + H_2$	0.997	0.96	0.75*	0.70*
$C_4H_3 + C_2H_2 \Longrightarrow C_6H_5$	0.994	0.88*	0.72*	1.10*
$C_2H_2 + C_2H_2 \Longrightarrow C_4H_3 + H$	0.990	0.89*	0.69*	0.94*
$C_5H_6 + C_3H_3 \Longrightarrow C_5H_5 + C_3H_4$	0.98	0.84*	0.81*	0.97*
$C_5H_6 + C_3H_3 \Longrightarrow C_5H_5 + C_3H_4$	0.98	0.84*	0.81*	0.97*
$CHO + M \Longrightarrow H + CO + M$	0.94*	1.01	1.18*	1.24*
$OH + HO_2 \Longrightarrow O_2 + H_2O$	0.94*	0.94	0.94	0.98
$C_2H_2 + C_3H_3 \Longrightarrow H_5C_5$	0.91*	0.72*	0.70*	1.06
$C_5H_5 \Longrightarrow H_5C_5$	0.91*	0.72*	0.70*	1.06
$C_5H_5 + O \Longrightarrow C_5H_4O + H$	0.89*	0.92*	0.99	_
$C_5H_6 + M \rightleftharpoons C_5H_5 + H + M$	0.91*	1.16	3.03*	8.02*

* These reactions belong to the 12 most sensitive reactions also in the reduced model.

	S Temperature, K						
Reaction	1325	1500	1730	2000			
$H + O_2 \rightleftharpoons O + OH$	1.32*	2.40*	2.77*	1.95*			
$C_5H_5 + O_2 \rightleftharpoons C_5H_4O + OH$	1.81*	1.32*	1.02	_			
$C_5H_5 + HO_2 \Longrightarrow C_5H_5O + OH$	1.30*	1.21*	1.04				
$C_5H_6 + O_2 \rightleftharpoons C_5H_5H + HO_2$	1.23*	1.08	1.02	1.003			
$CHO + O_2 \rightleftharpoons HO_2 + CO$	1.08*	1.03	0.95*	0.96*			
$C_5H_5 + O \rightleftharpoons C_5H_5O$	1.07*	1.05	1.01				
$C_3H_3 + C_3H_3 \Longrightarrow C_6H_5-c + H$	1.06	1.27*	1.32	1.19*			
$C_6H_5 \Longrightarrow C_6H_5$ -c	1.02	1.07	1.08*	1.08*			
$C_6H_5 + O_2 \rightleftharpoons C_6H_5O + O$	1.04	1.18*	1.05				
$C_6H_5O \Longrightarrow CO + C_5H_5$	1.03	1.10*	1.01				
$O + C_2H_2 \rightleftharpoons H + C_2HO$	1.04	1.07	1.07	1.06			
$C_2H_2 + C_2H \Longrightarrow C_4H_3$		1.002	1.16*	1.10*			
$C_3H_5 + C_2H_2 \Longrightarrow C_5H_6 + H$	1.002	_	0.97	0.94*			
$C_5H_6 + H \rightleftharpoons C_5H_5 + H_2$	_	0.97	0.84*	0.80*			
$C_4H_3 + C_2H_2 \rightleftharpoons C_6H_5$	0.997	0.96*	0.95*				
$C_2H_2 + C_2H_2 \Longrightarrow C_4H_3 + H$	0.992	0.92*	0.78*	0.95*			
$C_4H_5 + M \Longrightarrow C_4H_4 + H + M$	0.98*	0.995	_				
$C_5H_6 + C_3H_3 \Longrightarrow C_5H_5 + C_3H_4$	0.96*	0.86*	0.85*	0.97*			
$CHO + M \Longrightarrow H + CO + M$	0.96*	_	1.11*	1.13*			
$OH + HO_2 \Longrightarrow O_2 + H_2O$	0.94*	0.95*	0.96*	0.98*			
$C_2H_2 + C_3H_3 \Longrightarrow H_5C_5$	0.989	0.982	0.994				
$C_5H_5 \Longrightarrow H_5C_5$		0.997	0.997				
$C_5H_5 + O \rightleftharpoons C_5H_4O + H$	0.92*	0.94*	0.99	_			
$C_5H_6 + M \rightleftharpoons C_5H_5 + H + M$	0.93*	1.07*	1.71*	1.99*			

Table V Sensitivity Analysis for a Mixture of 1% CPD 6.5% O_2 and 92.5% Ar at 3.5 Bars at Change of A-factor (A/5) Reactions (for Stoichiometric Mixtures) (Full Model)

* These reactions belong to the 12 most sensitive reactions also in the reduced model.

S > 1 or 1 > S > 0. This sensitivity method shows clearly which main reaction has secondary path bypasses and which does not. This information is not available when the reaction is divided by a small factor.

The sensitivity test was repeated twice. First, we checked the sensitivity to the ignition delay, and then the sensitivity to the product distribution concentration. This sensitivity (of the product distribution concentrations) was calculated by dividing each reaction rate by a factor of 5 only. Table VI shows a list of the ten most important reactions that influence the cyclopentadiene decay, and some of the products calculated at stoichiometric conditions, with the full model at 1288 K, the highest temperature achieved for product distribution before ignition. Thus, a multitude of parameters were tested: for the ignition delay, mixtures with stoichiometric, lean and rich concentrations were checked; and for the products of the oxidation process, all detected species were checked at stoichiometric conditions.

Each of the 439 reactions underwent the previously described sensitivity treatment, and we recorded which reactions show sensitivity between 0.99 > S > 1.01. These reactions have been removed. The smallest set that still can imitate the experimental ignition-delays includes 125 reactions. These reactions are shown in Table VII. In this table, the rate used for each reaction is listed. In the reference column, the origin of the reaction is listed as well as the original preexponent and activation energy, if these were changed. The group of 12 most sensitive reactions (marked with an *) is the same for the full and reduced models (compare Tables IV and VIII).

The sensitivity test was again repeated for the reduced model to check if it remains the same. Then the process was repeated again by dividing the reaction rates by 5 instead of removing them completely. The ignition delay calculated values for the reduced mechanism are within 5% of the results of the full mechanism except at the lean concentration limit (see Discussion and Figs. 10 and 11).

Component	Reaction	Sensitivity
C ₅ H ₆	$C_4H_5 \rightleftharpoons C_2H_3 + C_2H_2$	0.95
	$CHO + O_2 \Longrightarrow HO_2 + CO$	0.95
	$C_2H_3 + O_2 \rightleftharpoons CHO + CH_2O$	0.96
	$C_5H_5O \rightleftharpoons C_4H_5 + CO$	0.96
	$C_5H_5 + OH \Longrightarrow C_5H_4OH + H$	0.97
	$C_5H_6 + C_3H_3 \Longrightarrow C_5H_5 + C_3H_4$	1.09
	$C_5H_5 + O \Longrightarrow C_5H_5O$	1.10
	$C_5H_5 + HO_2 \rightleftharpoons C_5H_5O + OH$	1.11
	$C_5H_6 + OH \Longrightarrow C_5H_5 + H_2O$	1.19
	$C_5H_6 + O_2 \rightleftharpoons C_5H_5 + HO_2$	1.42
СО	$C_5H_6 + O_2 \rightleftharpoons C_5H_5 + HO_2$	0.19
	$C_5H_5 + O_2 \rightleftharpoons C_5H_4O + OH$	0.44
	$C_5H_5 + HO_2 \rightleftharpoons C_5H_5O + OH$	0.47
	$C_5H_5O \Longrightarrow C_4H_5 + CO$	0.55
	$C_3H_5 + C_5H_5 \Longrightarrow C_5H_6 + C_3H_4$	0.79
	$C_4H_5 \rightleftharpoons C_2H_3 + C_2H_2$	0.82
	$C_2H_3 + O_2 \rightleftharpoons CHO + CH_2O$	0.86
	$C_3H_4 + OH \rightleftharpoons C_3H_3 + H_2O$	1.06
	$C_4H_5 + M \rightleftharpoons C_4H_4 + H + M$	1.07
	$C_{5}H_{5} + O \Longrightarrow C_{5}H_{4}O + H$	1.08
C_2H_2	$C_5H_6 + O_2 \rightleftharpoons C_5H_5 + HO_2$	0.63
	$C_5H_5O \Longrightarrow C_4H_5 + CO$	0.67
	$C_5H_5 + O_2 \rightleftharpoons C_5H_4O + OH$	0.73
	$C_5H_5 + HO_2 \rightleftharpoons C_5H_5O + OH$	0.74
	$C_4H_5 \rightleftharpoons C_2H_3 + C_2H_2$	0.76
	$C_5H_6 + C_3H_3 \Longrightarrow C_5H_5 + C_3H_4$	0.79
	$C_5H_6 + OH \rightleftharpoons C_5H_5 + H_2O$	0.83
	$C_5H_5 + OH \Longrightarrow C_5H_4OH + H$	0.93
	$C_5H_6 + H \rightleftharpoons C_5H_5 + H_2$	1.10
	$H_4C_3 + OH \rightleftharpoons C_3H_3 + H_2O$	1.26
	$C_2H_2 + C_3H_3 \Longrightarrow H_5C_5$	1.33
	$C_3H_4 + OH \Longrightarrow C_3H_3 + H_2O$	1.40
C_6H_6	$C_5H_6 + O_2 \rightleftharpoons C_5H_5 + HO_2$	0.22
	$C_2H_2 + C_4H_5 \Longrightarrow C_6H_6 + H$	0.43
	$C_5H_5O \Longrightarrow C_4H_5 + CO$	0.44
	$C_5H_5 + HO_2 \rightleftharpoons C_5H_5O + OH$	0.45
	$C_5H_5 + O_2 \rightleftharpoons C_5H_4O + OH$	0.72
	$C_4H_5 + M \rightleftharpoons C_4H_4 + H + M$	1.12
	$C_4H_5 + O_2 \rightleftharpoons C_4H_4 + HO_2$	1.14
	$C_6H_6 + OH \Longrightarrow C_6H_5 + H_2O$	1.16
	$C_4H_5 \rightleftharpoons C_2H_3 + C_2H_2$	1.57
	$C_65H_5 + O_2 \rightleftharpoons C_6H_5O + O$	1.73

Table VI Sensitivity of Reactions for Product Components Concentration at 1288 K When Decreasing the Pre-Exponential Factor A (A/5)

DISCUSSION

The Reduced Mechanism

In the past few years, the reduction of the kinetic schemes to a smaller number of elementary or nonelementary reactions [28] has been discussed. This stems from the need to incorporate chemical kinetic behavior into systems that are already overwhelmed with complex mathematical functions, such as Navier-Stokes flow functions, diffusion functions, thermal flux functions, etc. The introduction of a few hundred chemical elementary reactions into such systems is

No.	Reaction	Α	Ν	E_{a}	Ref.{Reaction No.}*,**
1	$C_5H_6 + H \rightleftharpoons C_5H_5 + H_2$	2.19×10^{9}	1.8	3000	11{23}
2	$C_5H_6 + CH_3 \rightleftharpoons C_5H_5 + CH_4$	$6.00 imes 10^{13}$	0	0	$6 A = 3 \cdot 10^{11}$
3	$C_5H_6 + C_3H_3 \rightleftharpoons C_5H_5 + C_3H_4$	$6.00 imes 10^{12}$	0	0	$6 A = 1 \cdot 10^{11}$
4	$C_5H_6 + C_3H_5 \Longrightarrow C_5H_5 + C_3H_6$	6.00×10^{12}	0	0	$6 A = 1 \cdot 10^{11}$
5	$C_5H_6 + C_2H_3 \rightleftharpoons C_5H_5 + C_2H_4$	6.00×10^{13}	0	0	11{25}
6	$C_5H_6 + C_4H_5 \rightleftharpoons C_5H_5 + C_4H_6$	6.00×10^{12}	0	0	$11{26} A = 6 \cdot 10^{12}$
7	$C_3H_5 + C_5H_5 \rightleftharpoons C_5H_6 + C_3H_4$	3.00×10^{12}	0	0	$35{44} A = 1 \cdot 10^{12}$
8	$C_5H_6 + O_2 \Longrightarrow C_5H_5 + HO_2$	4.00×10^{13}	0	30,000	$11\{20\} A = 3 \cdot 10^{13} = 25,000$
9	$C_5H_6 + HO_2 \Longrightarrow C_5H_5 + H_2O_2$	1.99×10^{13}	0	11,660	11{21}
10	$C_5H_5 + HO_2 \Longrightarrow C_5H_5O + OH$	1.50×10^{13}	0	0	$11\{18\} A = 3 \cdot 10^{13}$
11	$C_5H_6 + OH \Longrightarrow C_5H_5 + H_2O$	3.43×10^{9}	1.2	-447	$11\{22\} A = 3 \cdot 10^9$
12	$C_5H_5 + OH \Longrightarrow C_5H_4OH + H$	1.00×10^{13}	0	0	$11\{19\} A = 3 \cdot 10^{13}$
13	$C_5H_6 + O \Longrightarrow C_5H_5 + OH$	1.81×10^{14}	0	3080	11{24}
14	$C_5H_6 + M \rightleftharpoons C_5H_5 + H + M$	2.55×10^{85}	-18.4	126,255	4
15	$C_2H_2 + C_3H_3 \Longrightarrow H_5C_5$	1.00×10^{14}	0	0	$6A = 5 \cdot 10^{12}$
16	$C_5H_5 \Longrightarrow H_5C_5$	5.00×10^{14}	0	44,900	33{334}
17	$C_5H_5 + 0 \rightleftharpoons C_5H_5O$	1.00×10^{14}	0	0	23
18	$C_5H_5O \rightleftharpoons C_4H_5 + CO$	2.50×10^{11}	0	45,900	11{28}
19	$C_5H_5 + 0 \rightleftharpoons C_5H_4O + H$	5.00×10^{14}	0	0	$33{306} A = 7 \cdot 10^{13}$
20	$C_5H_4O \Longrightarrow C_4H_4 - c + CO$	6.20×10^{41}	-7.9	90,000	3, E = 98,700
21	$C_5H_4O \equiv CO + C_2H_2 + C_2H_2$	1.00×10^{16}	0	/8,000	11{30}
22	$C_5H_4OH \Longrightarrow C_4H_4 - c + CHO$	1.00×10^{10}	0	0	23
23	$C_5H_5O_2 = C_5H_4O + OH$	4.80×10^{12}	0	12,000	3, this study
24	$C_5H_4OH = C_5H_4O + H$	2.10×10^{14}	0	48,000	11{29}
25	$C_3H_5 + C_2H_2 = C_5H_6 + H$	2.95×10^{33}	-5.8	25,730	35{40}
26	$C_2H_2 + C_4H_5 = C_6H_6 + H$	2.80×10^{13}	2.9	1400	21{190}
27	$C_3H_3 + C_3H_3 = C_6H_5 - cn + H$	1.00×10^{13}	0	3000	21,3
28	$C_6H_5 \longleftarrow C_6H_5$ -cn	5.00×10^{14}	0	72,500	$55{550}$
29	$C_6 n_5 + n \leftarrow C_6 n_6$	3.00×10^{12}	0	0	$11{1} A = 2.5 \cdot 10^{12}$
30 21	$C_6H_5 + O_2 \longrightarrow CO_6H_5O + O$	2.09×10^{12}	0	/4/0	$11\{6\} A = 2 \cdot 10^{12}$
22	$C_6 n_5 O \longleftarrow CO + C_5 n_5$	2.31×10^{12}	0	45,900	11{/}
32 22	$C_6 n_5 O + n \leftarrow C_6 n_5 O n$	2.30×10^{13}	0	7010	11(0)
24	$C_6 n_5 OH + H \longrightarrow C_6 n_6 + OH$	2.21×10^{13}	0	/910	11(10)
34 35	$C_6 H_5 OH + OH \longleftarrow C_6 H_5 O + H_2 O$	0.00×10^{10}	0	5000	$11\{9\}$ 21(187)
35	$C_6 n_6 + n \longleftarrow C_6 n_5 + n_2$	5.00×10^{13}	2	60,000	21{10/}
30	$C_6\Pi_6 + O_2 \longrightarrow C_6\Pi_5 + \Pi O_2$	0.30×10 2.78 × 10 ¹⁴	0	/010	$11\{2\}$ $11\{4\}$
38	$C_6H_6 + O \longleftarrow C_6H_5O + H O$	2.78×10^{14}	0	4570	11(4)
30	$C_6\Pi_6 + O\Pi \longleftarrow C_6\Pi_5 + \Pi_2O$	2.11×10^{10} 1.52×10^{59}	-13.1	60 600	35(14)
40	$H_7C_5 \longleftarrow C_5H_7$	1.52×10^{59}	-13.1	60,000	35(14)
40	$\Pi_7 C_5 \longleftarrow C_5 \Pi_6 + \Pi$	$1.02 \times 10^{-1.02}$	0	00,100	55(15) 6 $A = 5 \cdot 10^{13}$
42	$C_{3}H_{5} + C_{3}H_{5} \leftarrow C_{6}H_{10}$	1.00×10^{13}	0	24 000	6
42	$C_{6}\Pi_{10} \longleftarrow C_{4}\Pi_{6} + C_{2}\Pi_{4}$	1.00×10^{-3} 3.98×10^{20}	-1	24,000 98 150	19/228
44	$C_4 H_6 \leftarrow C_2 H_3 + C_2 H_3$	1.00×10^{13}	0	0,150	19(220)
45	$C_4H_6 + OH C = C_2H_3 + CH_3CHO$	1.20×10^{12}	0	0	11{33}
46	$C_4H_5 + O_2 + C_4H_4 + HO_2$	3.98×10^{12}	07	0	11{33}
47	$C_4 + M \Longrightarrow C_4 + H + M$	2.98×10^{34}	-5	44 320	11{32}
48	$C_4H_4 - c \Longrightarrow C_4H_4$	1.00×10^{14}	0	42,000	3 estimate
49	$C_4 H_4 + H \Longrightarrow C_4 H_2 + H_2$	1.50×10^{15}	0	10.200	22{61}
50	C_{4} C_{4	1.00×10^{14}	Õ	45.000	19{89}
51	$C_2H_2 + C_2H \Longrightarrow C_4H_2$	1.00×10^{14}	Ő	.0,000	22{60}
	2 2 - 2 - 2 - 4 3	C 21 X 1016	0	05 000	10(1(1)

 Table VII
 The Reduced Kinetic Model for Cyclopentadiene Oxidation

(Continued)

Table VII	(Continued)
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No.	Reaction	Α	Ν	E_{a}	Ref.{Reaction No.}*.**
53	$C_3H_6 + O \Longrightarrow C_2H_4 + CH_2O$	$5.89 imes 10^{14}$	0	5000	19{114}
54	$C_3H_6 + OH \Longrightarrow C_3H_5 + H_2O$	3.98×10^{13}	0	0	19{134}
55	$C_3H_6 + OH \Longrightarrow CH_3 + CH_3CHO$	3.47×10^{12}	0	0	19{122}
56	$C_3H_6 + OH \Longrightarrow C_2H_5 + CH_2O$	$7.94 imes 10^{13}$	0	0	19{120}
57	$C_3H_5 + C_2H_2 \Longrightarrow H_7C_5$	3.42×10^{53}	-12.2	27,980	35{39}
58	$C_3H_5 + C_2H_2 \rightleftharpoons C_5H_7$	$8.38 imes 10^{31}$	-6.2	12,820	35{38}
59	$C_3H_5 + O_2 \Longrightarrow H_4C_3 + HO_2$	6.03×10^{12}	0	10,000	19{138}
60	$C_3H_5 + H \rightleftharpoons H_4C_3 + H_2$	$1.00 imes 10^{14}$	0	0	19{162}
61	$C_3H_5 \Longrightarrow H_4C_3 + H$	$3.98 imes10^{14}$	0	70,000	19{137}
62	$C_3H_4 + OH \Longrightarrow C_3H_3 + H_2O$	$4.00 imes10^{08}$	2	1000	21{193}
63	$C_3H_4 + H \rightleftharpoons C_3H_3 + H_2$	$5.00 imes10^{08}$	2	5000	21{192}
64	$C_3H_4 \Longrightarrow H_4C_3$	$2.00 imes 10^{14}$	0	62,000	36
65	$H_4C_3 + H \Longrightarrow CH_3 + C_2H_2$	$1.00 imes 10^{15}$	0	4000	21{195}
66	$H_4C_3 + H \Longrightarrow C_3H_3 + H_2$	$5.00 imes10^{08}$	2	5000	21{194}
67	$H_4C_3 + OH \Longrightarrow C_3H_3 + H_2O$	$2.00 imes10^{08}$	2	1000	21{196}
68	$H_4C_3 + OH \Longrightarrow CH_2O + C_2H_3$	1.00×10^{13}	0	0	19{147}
69	$H_4C_3 + OH \Longrightarrow CHO + C_2H_4$	1.00×10^{13}	0	0	19{148}
70	$C_2H_3 + O_2 \rightleftharpoons CHO + CH_2O$	$3.98 imes 10^{13}$	0	-240	19{171}
71	$C_2H_2 + CH_3 \rightleftharpoons C_3H_5$	$1.10 imes 10^{46}$	-9.4	35,410	35{35}
72	$C_2H + O_2 \rightleftharpoons CHO + CO$	$5.00 imes 10^{14}$	0	1500	18{169}
73	$C_2HO + O_2 \Longrightarrow OH + 2CO$	1.60×10^{13}	0	854	18{174}
74	$2C_2HO \Longrightarrow 2CO + C_2H_2$	1.00×10^{14}	0	0	18{175}
75	$C_2H_2O + OH \Longrightarrow CH; 2O + CHO$	$2.80 imes 10^{14}$	0	0	19{153}
76	$CH_3CHO + OH \Longrightarrow CH;3 + CO + H_2O$	1.00×10^{14}	0	0	2{183}
77	$CH_25 + CH_3 \Longrightarrow H + C_2H_4$	4.00×10^{14}	0	0	18{136}
78	$CH_2 + C_2H_2 \rightleftharpoons C_3H_3 + H$	1.20×10^{14}	0	6600	21{143}
79	$CH_2 + O_2 \rightleftharpoons CH_2O + O$	$5.00 imes 10^{14}$	0	9000	21{69}
80	$CH_2 + O_2 \Longrightarrow OH + CHO$	1.32×10^{14}	0	1500	18{133}
81	$CH_2 + O_2 \Longrightarrow CO_2 + H + H$	1.60×10^{13}	0	1000	21{68}
82	$CH_2 + O \Longrightarrow CO + H_2$	5.00×10^{14}	0	0	$21\{67\} A = 3 \cdot 10^{13}$
83	$CH_2(S) + C_2H_2 \rightleftharpoons C_3H_3 + H$	1.80×10^{15}	0	0	21{160}
84	$CH_2(S) + O_2 \Longrightarrow H + OH + CO$	2.80×10^{14}	0	0	18{142}
85	$CH_2(S) + O_2 \Longrightarrow CO + H_2O$	1.20×10^{14}	0	0	18{143}
86	$CH_3 + CHO \Longrightarrow CH_4 + CO$	2.65×10^{14}	0	0	18{158}
87	$CH_3 + O_2 \Longrightarrow O + CH_3O$	2.68×10^{14}	0	28,800	18{153}
88	$HO_2CO \Longrightarrow OH + CO_2$	1.50×10^{15}	0	23,600	18{118}
89	$2HO_2 \Longrightarrow O_2 + H_2O_2$	4.20×10^{15}	0	12,000	18{114}
90	$HO_2 + CH_3 \Longrightarrow OH + CH_3O$	2.00×10^{14}	0	0	18{117}
91	$HO_2 + CH_2O \Longrightarrow CHO + H_2O_2$	1.00×10^{13}	0	8000	18{119}
92	$OH + C_2H_2 \Longrightarrow H + C_2H_2O$	2.18×10^{-3}	4.5	-1000	18{106}
93	$OH + CH_4 \Longrightarrow CH_3 + H_2O$	1.00×10^{9}	1.6	3120	18{97}
94	$OH + CH_2 \Longrightarrow CH + H_2O$	1.13×10^{8}	2	3000	18{92}
95	$OH + CH_2 \Longrightarrow H + CH_2O$	2.00×10^{14}	0	0	18{91}
96	$2OH \Longrightarrow O + H_2O$	3.57×10^{5}	2.4	-2110	18{86}
97	$2OH(+M) \Longrightarrow H_2O_2(+M)$	7.40×10^{14}	-0.4	0	18{85}
98	$OH + H_2 \Longrightarrow H + H_2O$	2.16×10^{9}	1.5	3430	18{84}
99	$OH + CH_3 \Longrightarrow CH_2(S) + H_2$	2.50×10^{14}	0	0	18{96}
100	$OH + CH_3 \Longrightarrow CH_2 + H_2O$	5.60×10^{8}	1.6	5420	18{95}
101	$OH + CO \Longrightarrow H + CO_2$	4.76×10^{8}	1.2	70	18{98}
102	$OH + CH_2O \Longrightarrow CHO + H_2O$	3.43×10^{10}	1.2	-447	18{100}
103	$OH + C_2H_2 \Longrightarrow C_2H + H_2O$	3.37×10^{8}	2	14,000	18{108}
104	$OH + CHO \Longrightarrow H_2O + CO$	5.00×10^{14}	0	0	18{99}

(Continued)

No.	Reaction	Α	Ν	E_{a}	Ref.{Reaction No.}***
105	$OH + H_2 \rightleftharpoons O_2 + H_2O$	2.90×10^{14}	0	-500	18{87}
106	$OH + H_2O_2 \Longrightarrow HO_2 + H_2O$	$5.80 imes 10^{15}$	0	9560	18{88a}
107	$OH + C_2H_4 \Longrightarrow C_3H_3 + H_2$	3.60×10^{7}	2	2500	18{111}
108	$O + CH_3 \rightleftharpoons H + CH_2O$	$8.43 imes 10^{14}$	0	0	18{9}
109	$O + C_2 HO \Longrightarrow H + 2CO$	$1.00 imes 10^{15}$	0	0	18{28}
110	$O + C_2H_2 \Longrightarrow CO + CH_2$	1.02×10^{8}	2	1900	18{23}
111	$O + C_2H_2 \Longrightarrow H + C_2HO$	1.02×10^{8}	2	1900	18{21}
112	$O_2 + CH_2O \Longrightarrow HO_2 + CHO$	$1.00 imes 10^{15}$	0	40,000	18{32}
113	$CHO + O_2 \rightleftharpoons HO_2 + CO$	$7.60 imes 10^{13}$	0	400	18{166}
114	$CHO + H_2O \Longrightarrow H + CO + H_2O$	$2.24 imes 10^{19}$	-1	17,000	18{164}
115	$CHO + M \Longrightarrow H + CO + M$	1.45×10^{15}	0	19000	18{165}
116	$H + CH_3(+M) \Longrightarrow CH_4(+M)$	1.27×10^{17}	-0.6	383	18{52}
117	$H + CH_4 \rightleftharpoons CH_3 + H_2$	$6.60 imes 10^{9}$	1.6	10,840	18{53}
118	$H + C_2H_4(+M) \rightleftharpoons C_2H_5(+M)$	$1.08 imes 10^{13}$	0.5	1820	18{73}
119	$H + C_2H_2(+M) \rightleftharpoons C_2H_3(+M)$	$5.60 imes 10^{13}$	0	2400	18{71}
120	$H + CH_2O \Longrightarrow CHO + H_2$	$2.30 imes 10^{11}$	1.1	3275	18{58}
121	$H + CHO \Longrightarrow H_2 + CO$	$7.34 imes 10^{14}$	0	0	18{55}
122	$H + HO_2 \rightleftharpoons O_2 + H_2$	$2.80 imes10^{14}$	0	1068	18{45}
123	$H + HO_2 \Longrightarrow 2OH$	$1.34 imes 10^{15}$	0	635	18{46}
124	$H + O_2 + Ar \rightleftharpoons HO_2 + Ar$	$7.00 imes 10^{18}$	-0.8	0	18{37}
125	$H + O_2 \Longrightarrow O + OH$	$8.30 imes 10^{14}$	0	14,413	18{38}

Table VII (Continued)

* The kinetic reaction is given as $k = AT^n \exp(-E/RT)$. E is given in calories. A is given in moles/cc.

**A = is the original pre-exponential factor appearing in the given reference.

E = is the original activation energy mentioned in the given reference.

In addition to the above 125 reactions, the following reactions were used for the full mechanism:

129 reactions were taken from [18] 1–8, 10–20, 22, 24–27, 29–31, 33–36, 39–44, 47–51, 54 56–57, 59–70, 72, 74–83, 89, 90, 93–94, 101–105, 107, 109–110, 112–113, 115–116, 120–132, 134–135, 137–141, 144–152, 154–157, 159–163, 167–168, 170–172, 176–177.

109 reactions were taken from [19] 90–113, 115–119, 121, 131–133, 135–136, 139–146, 149, 163, 168, 174–227, 229–230, 232–238. 13 reactions were taken from [20] 298, 299, 301–303, 308–311, 316, 321, 323, 324.

8 reactions were taken from [11] 11-15, 23, 27, 35.

45 reactions were taken from [24] 48–52, 58, 68, 72–81, 87, 88, 91–93, 111, 118, 124, 125, 127, 131, 133, 136–151.

2 reactions were taken from [35] 28, 42.

13 reaction was taken from [37] 21.21; 25.5; 25.12; 25.15; 25.22; 26.7; 26.8; 26.12; 26.15; 26.19; 26.21; 26.24.

1 reaction from [38] 2.

2 reactions from [39] 1, 13.

1 reaction from [40] 88.

 H_5C_5 is the chain specie 1 pentene-3yne-5yl. C_4H_5 is $n-C_4H_5$ radical and C_4H_6 is 1, 3 butadiene.

difficult, thus, the constant demand to represent each kinetic system by a one line "reaction" or at most a very small number of "reactions." However, the implications of such drastic reduction are not well understood by everybody.

In our case, it is easy to show the implications by comparing the results as defined by the Semenov equation, which we found experimentally, and the correlation found by the modeling process. As shown in Figs. 10 and 11, the Semenov equation predicts a straight line, if one of the *xy* parameters is the fuel concentration. The Semenov equation has no way to "feel" if one tries concentrations inside or outside the ignition limit borders. This equation is good only within the experimental window and those who use it for extrapolation outside the experimental window cause serious errors. On the other hand, the modeling correlation has a U shape with distinct limits in the lean and rich zone concentrations, as predicted by the common combustion theory [29]. When reducing the number of reactions, as seen in Figs. 10 and 11, the distance between the limits becomes smaller (the U becomes narrower at the lean limit and the same at the rich limit). Representing a kinetic scheme by a single reaction rate actually means to represent it by a straight line, which will be at some angle to the Semenov correlation, somewhere inside the real U shaped curve. Also, Figs. 10 and 11 clearly show that experiment and calculation agree better at low temperature for the lean mixtures and at high temperatures for the rich mixtures. Although this effect may be obvious, to the best of our knowledge it has never been openly discussed or demonstrated.

It is clear from the 125 reactions of the concise kinetic scheme that in the process of erasing "unimportant reactions" the parallel kinetic paths are eliminated as well, and with them some important species are ignored. For example, butene (one of our detected species) is relatively "unimportant" for the ignition process of cyclopentadiene. It should be clear from that what are the implications when we extrapolate this behavior to a mechanism represented by a single reaction or even by four-five synthetic reactions [28]. On the other hand, it can be specified that if we are not interested in the species kinetics and do not care that butene is not represented in the scheme, we may represent adequately the "ignition delay" phe-

nomenon by using the 125 reactions' reduced mechanism.

The Complete Mechanism

In the introduction, the path by which the cyclopentadienyl radical is formed through oxidation of the benzene ring has been described through reactions (30) and (31). The last reaction is well known and has been described in the molecular form [27] as in the ionic form [30,31]. Cyclopentadiene disappears either by an H atom abstraction or by a series of reactions that open the ring. H abstraction is endothermic due to the low C—H bond energy of cyclopentadiene, 88.4 kcal/mole.

When performing a sensitivity analysis we may find that for the consumption of CPD, the most sensitive reactions are the same group of reactions that influence the reactant itself, as well as the ignition delay time. The only difference is that for the disap-

		Tempe	S erature, K	
Reaction	1325	1500	1730	2000
$H + O_2 \rightleftharpoons O + OH$	3.25*	9.36*	39*	15.3*
$C_5H_5 + O_2 \rightleftharpoons C_5H_4O + OH$	3.50*	1.58*	1.03	_
$C_5H_5 + HO_2 \Longrightarrow C_5H_5O + OH$	1.49*	1.31*	1.05	
$C_5H_6 + O_2 \rightleftharpoons C_5H_5H + HO_2$	1.37*	1.11	1.03	1.004
$CHO + O_2 \rightleftharpoons HO_2 + CO$	1.12*	_	0.88	0.94*
$C_{s}H_{s} + 0 \rightleftharpoons C_{s}H_{s}O$	1.13*	1.10	1.02	
$C_3H_3 + C_3H_3 \Longrightarrow C_6H_5-c + H$	1.11	1.67*	3.15*	1.40*
$C_6H_5 \Longrightarrow C_6H_5 - c$	1.11	1.70*	2.80*	1.37*
$C_6H_5 + O_2 \rightleftharpoons C_6H_5O + O$	1.08	1.37*	1.08	
$C_6H_5O \rightleftharpoons CO + C_5H_5$	1.08	1.24	1.03	_
$O + C_2H_2 \Longrightarrow H + C_2HO$	1.08	1.11	1.10	1.07
$C_2H_2 + C_2H \Longrightarrow C_4H_3$	_	1.003	1.27*	1.21*
$C_2H + O_2 \rightleftharpoons CHO + CO$	1.03	1.20	1.99*	1.5*
$C_3H_5 + C_2H_2 \Longrightarrow C_5H_6 + H$	_	0.993	0.95	0.92*
$C_5H_6 + H \rightleftharpoons C_5H_5 + H_2$	1.009	0.96	0.75*	0.71*
$C_4H_3 + C_2H_2 \Longrightarrow C_6H_5$		0.86*	0.69*	1.10*
$C_2H_2 + C_2H_2 \Longrightarrow C_4H_3 + H$	0.993	0.87*	0.66*	0.94*
$C_5H_6 + C_3H_3 \Longrightarrow C_5H_5 + C_3H_4$	0.97	0.80*	0.78*	0.97*
$CHO + M \rightleftharpoons H + CO + M$	0.95*	1.05	1.26	1.27*
$OH + HO_2 \rightleftharpoons O_2 + H_2O$	0.94*	0.94	0.95	0.98*
$C_2H_2 + C_3H_3 \Longrightarrow H_5C_5$	0.91*	0.70*	0.68*	1.06
$C_5H_5 \Longrightarrow H_5C_5$	0.91*	0.70*	0.68*	1.06
$C_5H_5 + O \rightleftharpoons C_5H_4O + H$	0.87*	0.90*	0.99	
$C_{H_{2}} + M \Longrightarrow C_{H_{2}} + H + M$	0 90*	1 1 5	3 18*	8 40*

Table VIII Sensitivity Analysis

Change of ignition delay time at different temperatures after deletion of reactions (for stoichiometric mixtures). Reduced model. * These belong to the 12 most sensitive reactions found for the full model.



Figure 9 General calculated product distribution at \sim 1350 K.

pearance of CPD reactant the oxidation reaction with OH is important, but not so much for the ignition delay sensitivity. The H + O_2 reaction, the most sensitive reaction in most combustion processes, is number one in our ignition delay sensitivity system at the high temperature end (1500–2000).

Emdee et al. [11] and Zhang and McKinnon [32] proposed a way to oxidize the C_5H_5 radical by the formation of C_5H_5O radical. The only path for the cyclic ketone in their system is identified through the formation of C_5H_4OH and its decomposition:

$$\bullet C_5 H_4 O H \Longrightarrow C_5 H_4 O + H$$
(24)

which subsequently decomposes according to Emdee et al. [11] to:

$$C_5H_4O \Longrightarrow 2C_2H_2 + CO$$
 (21)

The last reaction requires the breaking of three bonds; therefore, it must involve one or more thermally activated species in order to form the final product. Wang [3] shows that at high temperatures the decomposition of C_5H_4O leads primarily to cyclobutadiene C_4H_4 . He computed a pressure dependent rate coefficient for several steps for the decomposition of C_5H_4O . His parameters were used for the reaction:

$$C_5H_4O \Longrightarrow C_4H_4$$
-cy + CO (20)

The decomposition reaction of cyclobutadiene:

$$C_4H_4$$
-cy $\Longrightarrow 2C_2H_2$

was also used with the activation energy estimated by Wang [3]: 51 kcal/mol. In our system, an exothermic path was used for the direct formation of cyclopentadienone C_5H_4O :

$$C_5H_5 \bullet + O_2 \rightleftharpoons C_5H_4O + OH$$
(23)

and this step is shown to be the second most important in our model. It is also the second most important reaction for CO production (Table VI). The third most important reaction for ignition delays was:

$$C_5H_5 \bullet + HO_2 \Longrightarrow C_5H_5O \bullet + OH$$
 (10)



Figure 10 The influence of fuel on the ignition delay time τ for a constant concentration of oxygen of 6.5%, a pressure of 3.5 bars at T = 1350 K. The data obtained from the modeling of the 439 reaction mechanism are compared to the data obtained from the modeling of the 125 reaction mechanism and the Semenov equation.



Figure 11 The influence of fuel on the ignition delay time τ for a constant concentration of oxygen of 6.5%, a pressure of 3.5 bars at T = 1800 K. The data obtained from the modeling of the 439 reaction mechanism is compared to the data obtained from the modeling of the 125 reaction mechanism and the Semenov equation.

To enhance this ignition path through C_5H_4O , the rate of formation of C_5H_5O • had to be decreased by a factor of 5. Reaction (11) is also important for the formation of CO as the product distribution sensitivity shows (see Table VI).

Another reaction for the formation of cyclopentadienone C_5H_4O was included:

$$C_5H_5 \bullet + O \Longrightarrow C_5H_4O + H \tag{19}$$

The rate of the last reaction [33] was diminished by a factor of 2.

Another possible route would be through the formation of cyclopentadienyl-ol radical:

$$C_5H_5 \bullet + OH \Longrightarrow \bullet C_5H_4OH + H$$
 (12)

A similar step also proceeds via an energized complex, which is subject to QRRK/RRKM considerations:

$$C_5H_5 \bullet + O \Longrightarrow C_5H_5O \bullet$$
(17)

But this reaction was found only on the sixth place in our ignition study.

The direct oxidation of cyclopentadiene is the fourth most important reaction, but only at low temperatures:

$$C_5H_6 + O_2 \rightleftharpoons C_5H_5 \bullet + HO_2 \bullet$$
(8)

In addition to the chemical kinetic modeling studies, the chemistry of aromatic ring consumption is also important to the successful modeling of flame speeds and ignition delays. The main interest in the present study is the fact that CPD is an intermediate in the combustion kinetics of benzene, and indeed this connection is maintained even in the reduced mechanism through the reverse of reaction (31), reaction (30), and the reverse of reaction (26), which explains the appearance of benzene in the pre-ignition steps. The product sensitivity analysis (Table VI) shows that benzene is formed by preference from reactions of acetylene and butadienyl radical (26). The main source of butadienyl radical is the decomposition of $C_5H_5O_{\bullet}$ to butadienyl and CO (18).

In general, it is observed in modeling that before ignition the quantities of the parent molecule, CPD, are very small and the accumulated quantities of small hydrocarbon molecules, such as acetylene, are ten times higher than CPD. These molecules are consumed during the ignition step. This behavior is well known from other large fuel molecules and CPD is no exception. Thus, during the pre-ignition kinetics, the fuel molecule undergoes degradation by direct pyrolysis and by O attacks which produce, besides smaller hydrocarbon molecules, also CO.

Aside from the different tests previously described, the three new mechanisms that were recently published [3-5] were tested as is for their compliance with our data. Their set of thermodynamic data was used. As a result, we took reaction (14) C_5H_6 + $M \rightleftharpoons C_5H_5 + H + M$ from Kern et al. [4], and the reaction (20) $C_5H_4O \rightleftharpoons C_4H_4$ -c + CO from Wang [3]. Both Kern et al. [4] and Wang and Brezinsky [3] studies do not contain a full mechanism, but rather parts of it. Bozzelli's work [5], on the other hand, includes a full mechanism and more or less fits our experimental evidence for the ignition delay time and partially for the product distribution. A better fit can be achieved by changing the parameters of reactions with C_5H_4O and C_5H_5O . Even with these changes the concentration of allene turns out to be exaggerated by a factor of 5-10. Generally, above 1350 K, our computations fit well the experimental data, but between 1280-1350 K we also calculate noticeable amounts of C_5H_4O , which was not measured with our instrumentation. If the C_5H_4O formed will decompose, it will overproduce the small species' concentration.

The Bozzelli [5] mechanism contains many unknown and hard to detect peroxy compounds that were neither found nor proposed by other researchers. It also causes the calculations to end with relatively high concentrations of C_5 oxygenated compounds. If these compounds are given secondary decomposition paths, then the C_3 and C_2 molecules get out of proportion compared with experimental evidence.

CONCLUSIONS

A series of ignition delay and product distribution experiments were performed to determine the Semenov ignition delay parameters of cyclopentadiene oxidation and the experimental kinetics. A model of 439 reactions was assembled and eight sets of sensitivity analysis were performed. First, the full model was tested for compatibility of the calculated ignition delays with the experiments. That was performed by consecutively deleting each reaction rate, one at a time, and recording the changes in the ignition delay sensitivity index. Then the process was repeated by dividing the reaction rates by a factor of 5, twice, for the ignition delays and also for the product distribution concentrations. The order of the reactions in the two sets was identical, but the increased sensitivity of the first method was demonstrated.

After this process, the insensitive reactions were eliminated and a reduced set of 125 reactions was listed. The four sets of sensitivity analysis previously described were repeated on the reduced set to ascertain that the same order of sensitive reactions were obtained again.

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