

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230545822>

Ignition Time Measurements for Methylcyclohexane- and Ethylcyclohexane-Air Mixtures at Elevated Pressures

ARTICLE *in* INTERNATIONAL JOURNAL OF CHEMICAL KINETICS · FEBRUARY 2009

Impact Factor: 1.52 · DOI: 10.1002/kin.20370

CITATIONS

40

READS

24

2 AUTHORS, INCLUDING:



[Matthew A. Oehlschlaeger](#)

Rensselaer Polytechnic Institute

77 PUBLICATIONS 1,610 CITATIONS

SEE PROFILE

Ignition Time Measurements for Methylcyclohexane- and Ethylcyclohexane-Air Mixtures at Elevated Pressures

JEREMY VANDEROVER, MATTHEW A. OEHLSCHLAEGER

Department of Mechanical, Aerospace, and Nuclear Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180

Received 18 May 2008; revised 12 June 2008; accepted 24 June 2008

DOI 10.1002/kin.20370

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The ignition of methylcyclohexane (MCH)/air and ethylcyclohexane (ECH)/air mixtures has been studied in a shock tube at temperatures and pressures ranging from 881 to 1319 K and 10.8 to 69.5 atm, respectively, for equivalence ratios of 0.25, 0.5, and 1.0. Endwall OH* emission and sidewall pressure measurements were used to determine ignition delay times. The influence of temperature, pressure, and equivalence ratio on ignition has been characterized. Negative temperature coefficient behavior was observed for temperatures below 1000 K. These measurements greatly extend the database of kinetic targets for MCH and provide, to our knowledge, the first ignition measurements for ECH. The combination of the MCH measurements with previous shock tube and rapid compression machine measurements provides kinetic targets over a large temperature range, 680–1650 K, for the validation of kinetic mechanisms. © 2008 Wiley Periodicals, Inc. *Int J Chem Kinet* 41: 82–91, 2009

INTRODUCTION

Because of their significant concentrations in practical fuels, cycloalkanes (naphthenes) have received recent interest from the combustion kinetics community. Commercial and military jet fuels consist of up to 20%

cycloalkanes by volume, and commercial diesel fuels consist of up to 35%–40% cycloalkanes by volume [1–4]. Furthermore, fuels derived from the Canadian oil-sands (currently recognized to be the second largest oil reserve in the world) exhibit high concentrations of cycloalkanes [1,4–7]. Because of their high concentrations in practical fuels, cycloalkanes have been included in surrogate mixtures for practical fuels [1–3,8–12] and kinetic mechanisms have been recently developed to describe their oxidation [13,14]. In several proposed surrogate mixtures for jet fuel, methylcyclohexane (MCH) has been chosen as the representative

Correspondence to: M. A. Oehlschlaeger; e-mail: oehlsma@rpi.edu.

Contract grant sponsor: U.S. Air Force Office of Scientific Research.

Contract grant number: FA9550-07-1-0114.
© 2008 Wiley Periodicals, Inc.

cycloalkane compound [2,3,8–11]. MCH itself is a significant component of commercial and military jet fuels (Jet A, JP-8) and makes up a very large fraction of the high-energy density missile fuel JP-9, which is a mixture of three high heating value hydrocarbons: MCH, exo-tetrahydrodicyclopentadiene (JP-10), and perhydronorbornadiene dimer [15]. Owing to the importance of MCH as a component of commercial and military liquid fuels and as a component of surrogate fuel mixtures, and the lack of a comprehensive experimental database of kinetic targets for MCH, the ignition characteristics of MCH have been chosen for study here. In addition, the ignition of ethylcyclohexane (ECH) has been investigated to determine the influence of the length of the alkyl side chain on the ignition of alkylcyclohexanes.

While, to our knowledge, there have been no previous kinetic measurements for ECH, there have been previous shock tube, rapid compression machine (RCM), flow reactor/tube, engine, and flame measurements for MCH. Hawthorn and Nixon conducted the first ignition delay time measurements for MCH in a shock tube [16]. They measured ignition delay times for temperatures ranging from 1200 to 1480 K, pressures from 0.6 to 1.7 atm, and equivalence ratios from 0.1 to 2.1, all with argon as the bath gas. More recently, Orme et al. [13] performed shock tube experiments in dilute argon mixtures (1200–2100 K, 1–4 atm, and $\Phi = 0.5$ –2.0) and developed a kinetic model for high-temperature MCH oxidation that predicts their experimental results well. Vasu et al. [17] have reported shock tube ignition delay times for MCH/O₂/argon mixtures at 1–3 atm and equivalence ratios of 0.5–2.0 and for stoichiometric MCH/air mixtures at 40–50 atm. Pitz et al. [14] have made RCM ignition measurements (700–1050 K, 10–20 atm, and $\Phi = 1.0$) and developed a kinetic model expanded from that published by Orme et al. [13] to include low-temperature peroxy chemistry responsible for the negative temperature coefficient (NTC) behavior observed in their RCM experiments. Tanaka et al. [18] also studied MCH oxidation in an RCM for one lean ($\Phi = 0.4$) experimental condition (827 K and 41 atm). MCH pyrolysis was studied by Garner and Petty [19] in a flow tube at 600–675 K and Brown and King [20] in a very low pressure pyrolysis reactor at 861–1218 K. Kaiser et al. [21] studied the oxidation and emissions of MCH in a single-cylinder engine. Zeppieri et al. [22] studied the oxidation and pyrolysis of MCH in a turbulent flow reactor from 1050 to 1200 K and Agosta et al. [11] studied lean MCH oxidation in a flow reactor at 750 K and 8 atm. McEnally and Pfefferle [23] studied MCH-doped CH₄/air atmospheric laminar flames. To our knowledge, only two kinetic mechanisms have been developed for MCH

oxidation, the high-temperature mechanism of Orme et al. [13] and the low- and high-temperature mechanisms of Pitz et al. [14].

The goal of the experimental work presented here is to provide a comprehensive data set for MCH and ECH ignitions at a range of pressures, equivalence ratios, and in an oxidizer mixture (air) relevant to jet fuel combustion in aero-engines and gasoline and diesel combustion in premixed lean to stoichiometric internal combustion engines such as homogeneous charge compression ignition (HCCI) engines. Ignition delay times have been measured, and their dependence on temperature, pressure, and equivalence ratio has been characterized for MCH/air and ECH/air mixtures. Experiments have been performed at temperatures ranging from 881 to 1319 K, pressures ranging from 10.8 to 69.5 atm, and equivalence ratios of 0.25, 0.5, and 1.0. The MCH experimental results have been compared to previous shock tube and RCM measurements and the predictions of the recently published kinetic mechanisms of Orme et al. [13] and Pitz et al. [14]. The MCH results presented here greatly extend the database of kinetic targets, particularly to lean conditions, and the ECH results are, to our knowledge, the first ignition measurements for this compound.

EXPERIMENTAL METHOD

Ignition times were measured in the RPI high-pressure shock tube facility previously described by Daley et al. [24]. The stainless steel facility is 5.7 cm in diameter and has a 4.11-m driven section and a 2.59-m driver section. The driven section is evacuated with a turbomolecular pump capable of ultimate pressures of 2×10^{-6} Torr; however, for these experiments typical ultimate pressures were 1×10^{-5} Torr. Polycarbonate diaphragms (0.51 and 1.52 mm thick) were burst via strain-induced failure by filling the driver section with helium. The incident shock velocity was measured with five piezoelectric pressure transducers spaced over the last meter of the shock tube. Time intervals for incident shock passage were determined using the five pressure transducers and four 120 MHz countertimes, from which four incident shock velocities were determined. The incident shock velocities were linearly extrapolated to the shock tube endwall to determine shock conditions at the test location. In addition, another piezoelectric pressure transducer located 2 cm from the endwall in the sidewall of the shock tube was used for quantitative pressure measurements. The incident and reflected shock conditions were determined using the normal shock relations, the measured incident shock velocity, the measured initial temperature

and pressure, and thermodynamic data for the species in the reactant mixture. Thermodynamic data for the species in the reactant mixtures were taken from the Burcat and Ruscic database [25] and for ECH from the Texas A&M Thermodynamics Research Center database [26]. Fuel/air mixtures (air is defined as pure O_2 and N_2 at a 21%/79% molar ratio) were made in an external mixing vessel with an internal magnetically powered vane stirrer. Mixtures were made using degassed methylcyclohexane (99+% purity) and ethylcyclohexane (99+% purity), introduced by vaporization into the mixing vessel, and oxygen (99.995% purity) and nitrogen (99.995% purity), introduced from high-pressure cylinders. Mixtures were made manometrically, with pressures measured using a high-accuracy pressure manometer and diaphragm pressure gauge, and allowed to mix for 2 h prior to experiments.

The shock tube and mixing vessel can be heated with an electronically controlled electrical resistance heating system (not previously described) that allows for the uniform heating of the shock tube and mixing vessel to specified temperatures from 25–150°C. The heating system allows for kinetic measurements for low vapor pressure hydrocarbons, which cannot be studied at room temperatures. The system consists of silicon heaters that uniformly cover the shock tube and mixing vessel and provide up to 0.775 W/cm². The current supplied to the heaters is controlled by two zone heater controllers, which monitor the output of type-K thermocouples spaced along the exterior walls of the shock tube and mixing vessel. The controllers control six independent heating zones along the shock tube driven section (4.11 m long) and four independent heating zones along the cylindrical mixing vessel (0.76 m long). The gas manifold, which allows gases to be introduced into the mixing vessel, is heated with fiberglass heating rope. The shock tube and mixing vessel are insulated with 2.5 cm thick mineral wool insulation and the gas manifold tubing is insulated with 1.1 cm thick silicon foam rubber insulation. Thermocouple measurements (type-K) are made at locations along the shock tube, mixing vessel, and gas manifold. In addition, the shock tube temperature profiles are regularly measured by translating a thermocouple along the inner wall of the shock tube to ensure uniformity prior to performing experiments. An example temperature profile, at a wall temperature (70°C) used for the current ECH experiments, is shown in Fig. 1. The heating system easily provides uniformity within the thermocouple uncertainty ($\pm 2.2^\circ\text{C}$). The axial uniformity of the shock tube temperature is important because a nonuniform temperature profile will cause an increased uncertainties in the shock conditions. Because of the vapor pressure of the two compounds studied here,

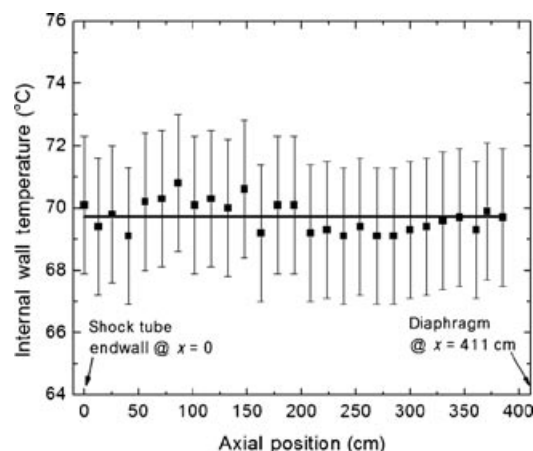


Figure 1 Typical heated shock tube inner wall temperature profile (driven section).

the measurements for MCH were performed without heating (room temperature shock tube) and the measurements for ECH were made with the shock tube both heated (70°C) and unheated (room temperature), depending on the equivalence ratio. ECH ignition time measurements made for the same condition with the shock tube both heated and unheated agree.

For the MCH experiments performed in the unheated room temperature shock tube, the uncertainty in the initial reflected shock temperature and pressure is estimated at approximately 1% and 1.5%, respectively. The condition uncertainties are primarily due to uncertainty in the measured incident shock velocity (estimated at 0.1%–0.5%). For the ECH experiments in the heated shock tube, the uncertainty in initial reflected shock temperature and pressure is estimated at approximately 1.5% and 2%, respectively. The increased uncertainty in reflected shock conditions in the heated shock tube is caused by uncertainty in the increased uncertainty in the initial temperature measured with the type-K thermocouples ($\pm 2.2^\circ\text{C}$). In the room temperature experiments the initial temperature is measured with a mercury thermometer (uncertainty of $\pm 0.5^\circ\text{C}$).

Ignition time determinations were made using end-wall electronically excited OH (OH^*) emission around 306 nm and sidewall pressure measurements made at a location 2 cm from the endwall. OH^* emission was observed through a UV-fused silica optic located in the center of the shock tube endwall, using a silicon photodetector and a UG-5 Schott glass filter. Ignition times were defined as the time period between arrival and reflection of the shock wave at the endwall and the onset of ignition at the endwall. The shock arrival at the endwall was determined from the passage of the

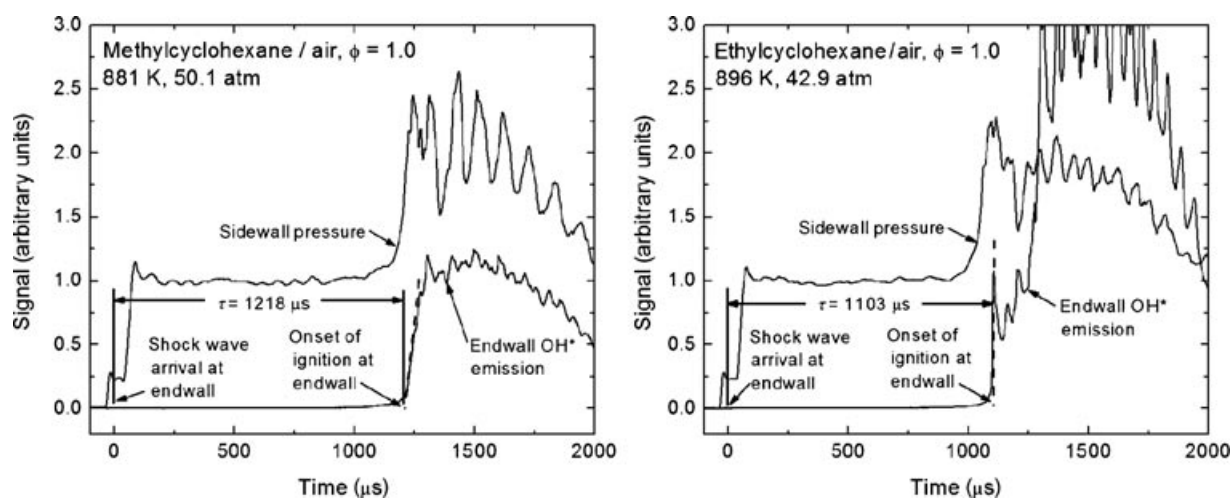


Figure 2 Example ignition time measurements: methylcyclohexane/air (left) and ethylcyclohexane/air (right).

shock wave at the last sidewall pressure transducer located 2 cm from the endwall and the incident shock velocity. The onset of ignition was defined by extrapolating the maximum slope in the endwall OH* emission signal to the baseline. A 1-MHz data acquisition system was used to record the pressure and emission signals. Example ignition time determinations can be found in Fig. 2 for MCH and ECH for relatively long ignition times. The two pressure traces show relatively little variation from the initial reflected shock condition, over the induction period prior to ignition, indicating that the shock tube is well behaved. The measured variation in pressure over the test time is +2 to +4%/ms from the initial reflected shock condition due to nonideal gasdynamic effects. Assuming isentropic compression of the test gases following the reflected shock passage, shown to be valid [27,28], the resulting variation in temperature is approximately +0.5 to +1%/ms. This is a relatively small variation in temperature during the induction period prior to ignition and was taken into account in the estimation of ignition time uncertainty given in the next section.

RESULTS, MODELING, AND DISCUSSION

Measurements of ignition times for MCH/air and ECH/air mixtures were made at a range of equivalence ratios ($\Phi = 0.25, 0.5$, and 1.0), pressures (10.8–69.5 atm), and temperatures (881–1319 K). The ignition time results are shown in Figs. 3 and 4 and given in Tables I and II. The measured ignition times have estimated uncertainties of $\pm 15\%$ based on uncertainties in reflected shock conditions (temperature, pressure, and mixture composition), variation in reflected shock

temperature and pressure due to nonideal gasdynamic compression, and uncertainties in determining ignition times from the measured OH* emission and pressure signals. The ignition time measurements show Arrhenius exponential dependence on inverse temperature at high temperatures and rollover at lower temperatures. This is clearly shown in the MCH 50 atm data for $\Phi = 1.0$. The rollover at low temperatures is the beginning of the NTC regime, which has also been observed for MCH by Vasu et al. [17] in shock tube measurements and Pitz et al. [14] in RCM measurements. The ignition time data also show an inverse dependence on pressure and equivalence ratio, for stoichiometric to lean mixtures (i.e., ignition time decreases with increasing pressure and equivalence ratio). The observations of inverse ignition time dependence on equivalence ratio and pressure are consistent with ignition measurements made for other compounds in air mixtures at elevated pressures, such as iso-octane [29], *n*-heptane [30], toluene [29], and cyclopentane and cyclohexane [24]. However, it should be pointed out that this observation is different from that observed in low-pressure highly diluted shock tube experiments, in which positive power-law dependence on equivalence ratio is often reported [31].

For other compounds, it has been shown that ignition times for fuel/air mixtures can be correlated using power-law dependence on reactant concentrations, or power-law dependence on pressure and equivalence ratio, and an exponential Arrhenius-dependence on inverse temperature [32]. Here, due to the low-temperature rollover in ignition time observed at the beginning of NTC, the data cannot be correlated using an exponential in inverse temperature. However, at temperatures greater than that where NTC behavior

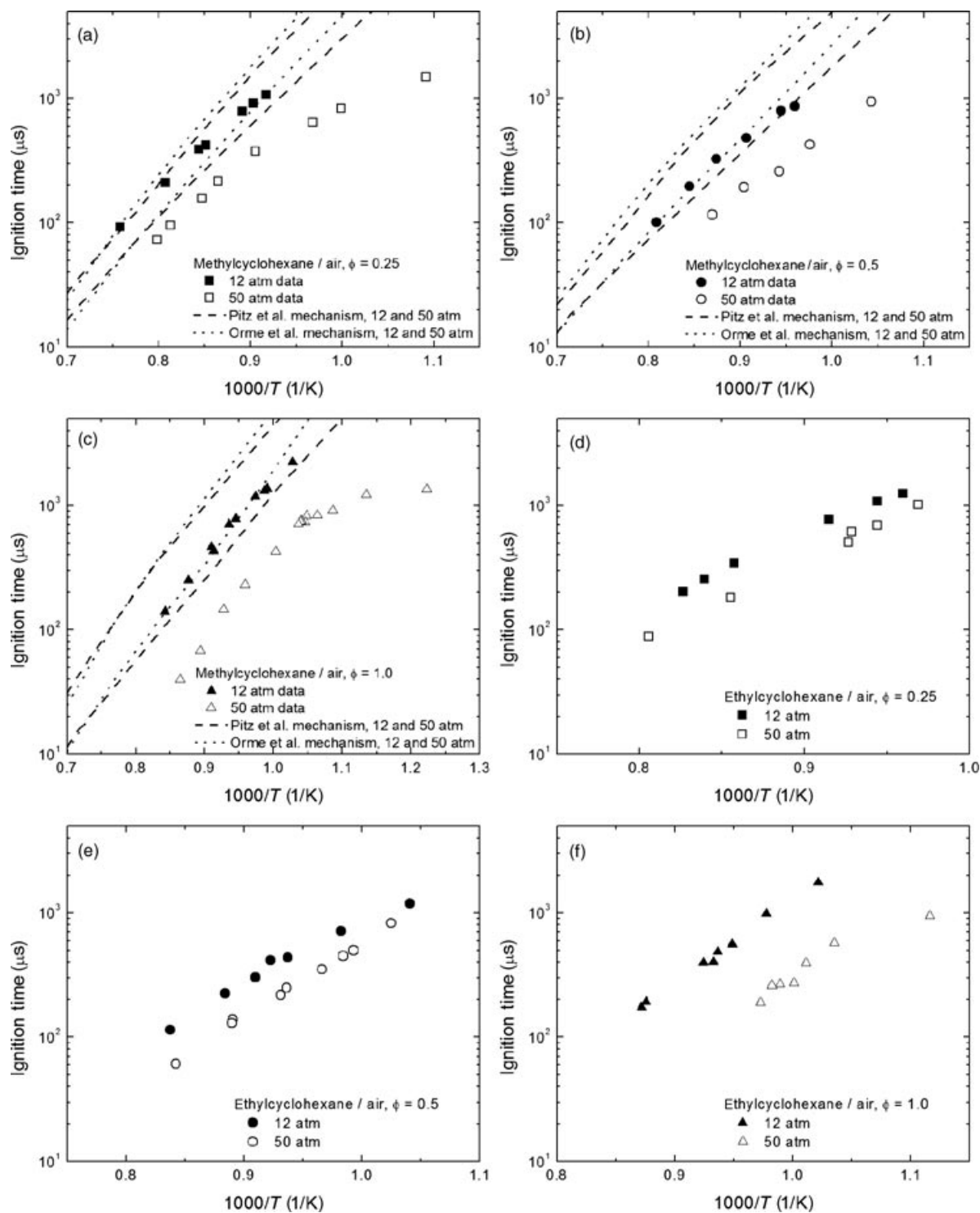


Figure 3 Ignition time measurements for methylcyclohexane/air (a, b, and c) and ethylcyclohexane/air (d, e, and f) mixtures with comparison to the predictions of the Pitz et al. [14] and Orme et al. [13] mechanisms for methylcyclohexane. Data scaled to 12 and 50 using power law pressure scaling parameters given in Table III to account for deviations in reflected shock pressure.

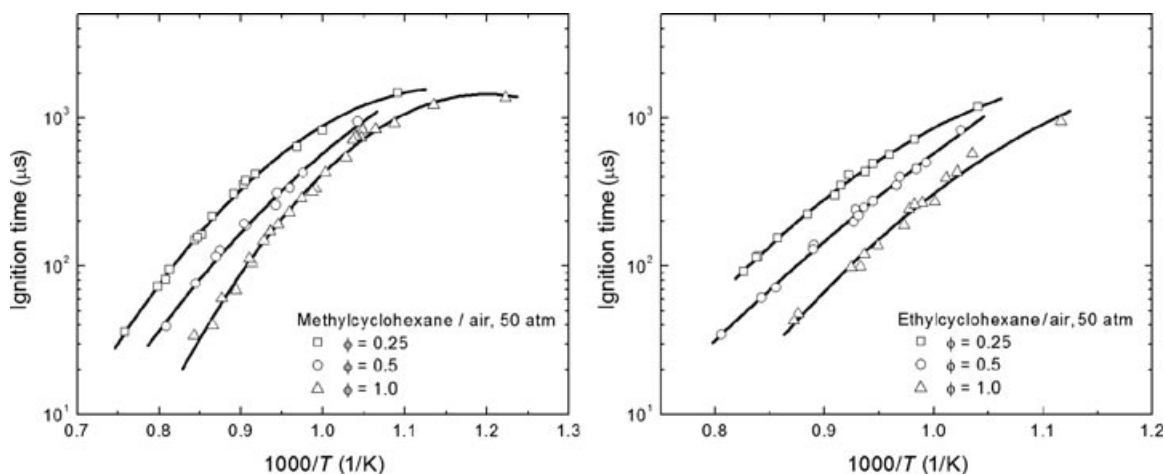


Figure 4 Ignition times for methylcyclohexane/air (left) and ethylcyclohexane/air (right) mixtures scaled to 50 atm, using power law pressure scaling parameters given in Table III.

begins the measurements for MCH and ECH have a common slope. The high-temperature activation energy is in the range of 31–33 kcal/mol for MCH and 28–30 kcal/mol for ECH, very similar to that observed for other hydrocarbons in the high-temperature regime under the conditions studied here [29,33–35].

Despite the observed low-temperature rollover in ignition times, power law scaling parameters for ignition time dependence on pressure, $\tau \propto P^n$, were determined by finding the values of n that provide a best fit second-order polynomial to the measurements for a given mixture; the pressure-scaling parameters are

Table I Measured Ignition Times for Methylcyclohexane/Air Mixtures

Mixture: 0.4977% MCH, 20.90% O ₂ , and 78.60% N ₂ ; $\Phi = 0.25$			Mixture: 0.9905% MCH, 20.80% O ₂ , and 78.21% N ₂ ; $\Phi = 0.5$			Mixture: 1.962% MCH, 20.60% O ₂ , and 78.21% N ₂ ; $\Phi = 1.0$		
T_5 (K)	P_5 (atm)	τ (μ s)	T_5 (K)	P_5 (atm)	τ (μ s)	T_5 (K)	P_5 (atm)	τ (μ s)
1090	14.0	963	1042	14.2	770	973	15.3	1746
1107	15.3	772	1059	12.5	775	1009	15.3	1080
1122	14.0	712	1103	13.1	453	1013	14.0	1122
1174	14.3	373	1144	12.5	318	1027	15.0	946
1185	12.5	377	1184	11.8	198	1058	12.7	740
1238	12.0	210	1236	11.0	107	1069	13.9	612
1319	12.7	89	959	51.4	923	1095	12.5	415
916	41.9	1664	1025	52.2	414	1099	16.4	340
1001	46.4	869	1061	50.8	256	1141	14.2	212
1033	44.9	686	1106	49.6	194	1187	13.6	124
1104	46.4	394	1150	47.4	120	818	41.8	1627
1156	45.0	232				881	50.1	1218
1180	40.4	180				920	54.4	840
1230	37.1	116				940	57.6	730
1252	41.9	82				954	49.5	834
						956	46.9	778
						961	49.2	770
						962	51.2	724
						965	53.4	665
						997	51.9	412
						1043	52.7	219
						1078	51.9	143
						1119	66.3	52
						1156	69.5	29

Table II Measured Ignition Times for Ethylcyclohexane/Air Mixtures

Mixture: 0.4358% ECH, 20.92% O ₂ , and 78.65% N ₂ ; $\Phi = 0.25$			Mixture: 0.8603% ECH, 20.83% O ₂ , and 78.31% N ₂ ; $\Phi = 0.5$			Mixture: 1.721% ECH, 20.65% O ₂ , and 77.63% N ₂ ; $\Phi = 1.0$		
T_5 (K)	P_5 (atm)	τ (μ s)]	T_5 (K)	P_5 (atm)	τ (μ s)	T_5 (K)	P_5 (atm)	τ (μ s)]
1042	12.2	1230	1032	10.8	1081	979	14.3	1478
1059	13.6	1004	1059	12.1	687	1023	15.1	788
1093	11.9	772	1077	14.0	551	1054	12.5	538
1166	12.2	338	1079	12.8	482	1068	11.3	518
1191	12.0	255	1169	12.8	174	1072	11.8	409
1210	11.6	205	1241	16.3	72	1082	12.6	379
961	48.2	1210	976	47.3	856	1142	13.1	177
1018	50.5	708	1007	43.4	546	1147	13.0	161
1067	45.1	461	1016	49.2	456	896	42.9	1103
1084	52.8	401	1035	44.7	376	966	45.1	634
1099	39.4	344	1068	48.2	255	989	44.0	447
1131	45.2	237	1074	47.2	227	999	42.8	317
1194	42.9	124	1123	49.8	139	1011	45.8	292
			1124	50.5	129	1018	43.9	296
			1187	51.5	60	1028	42.8	221

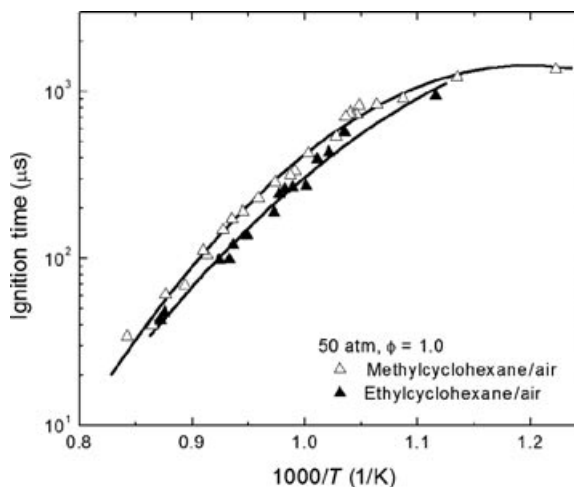
given in Table III. It was found that there is a decrease in pressure dependence with decreasing equivalence ratio for both MCH and ECH. This has previously been observed by Daley et al. [24] for cyclopentane/air and cyclohexane/air ignitions and Davidson et al. [29] for iso-octane/air and toluene/air ignitions. No dependence on temperature was observed for the power law pressure scaling factor, n . The correlated data scaled to a common pressure (50 atm), using the power law pressure scaling parameters given in Table III, are shown in Fig. 4. It should also be noted that the data in Fig. 3 are scaled to common pressures (12 and 50 atm), using the above pressure-scaling parameters to account for variations in the reflected shock pressure within a given data set.

The data for MCH and ECH at $\Phi = 1.0$ and 50 atm are compared in Fig. 5. The ignition times show similar temperature dependence; the ignition times for ECH are 20%–40% shorter than those for MCH, indicat-

ing that for alkylcyclohexanes the reactivity increases for larger alkyl side chains. Roubaud et al. [36] found similar results for alkylbenzenes in RCM experiments. They found ignition times decreased as the size of the alkyl side chain increased for toluene, ethylbenzene, and *n*-butylbenzene; this has also been observed in unpublished shock tube measurements of ignition delay times for toluene and ethylbenzene made by our group. The reduction in ignition time for increasing alkyl group size is presumably due to the greater number of H-atoms available for abstraction and, importantly, the addition of secondary C–H bonds, which

Table III Ignition Time Pressure-Scaling Parameters, $\tau \propto P^n$, Based on Regression of the Ignition Times to Second-Order Polynomials on the Logarithmic τ versus $1/T$ Axes; see Fig. 4

Compound	Φ	n
Methylcyclohexane	0.25	−0.66
Methylcyclohexane	0.5	−0.66
Methylcyclohexane	1.0	−0.99
Ethylcyclohexane	0.25	−0.55
Ethylcyclohexane	0.5	−0.65
Ethylcyclohexane	1.0	−0.98

**Figure 5** Comparison of ignition times for methylcyclohexane/air and ethylcyclohexane/air mixtures at $\Phi = 1.0$ and 50 atm; data scaled to 50 atm using power law pressure scaling parameters given in Table III.

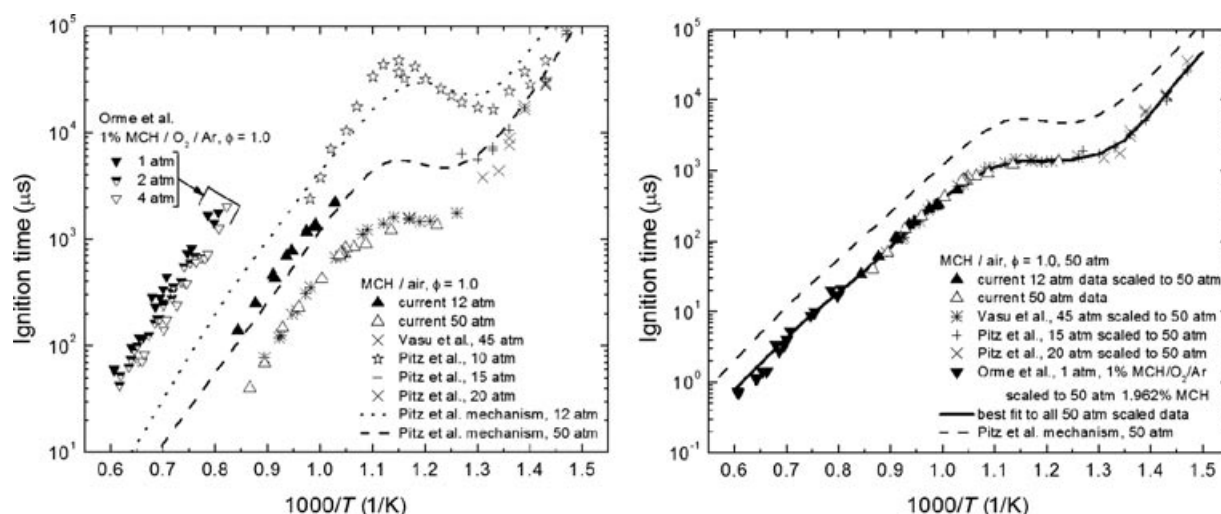


Figure 6 Current $\Phi = 1.0$ methylcyclohexane ignition time measurements with comparison to previous shock tube measurements of Vasu et al. [17] and Orme et al. [13] and rapid compression machine (RCM) measurements and mechanism predictions of Pitz et al. [14].

allow H-atom abstraction more readily than primary bonded H-atoms.

Comparisons of the current $\Phi = 1.0$ MCH data with the previous shock tube studies of Orme et al. [13] and Vasu et al. [17] and the rapid compression machine (RCM) study of Pitz et al. are made in Fig. 6. The graph on the left in Fig. 6 shows the raw data from these previous studies and the current study. The $\Phi = 1.0$ Orme et al. measurements were performed for 1% MCH/10.5% O_2 /Ar mixtures at 1, 2, and 4 atm and cover the temperature range of 1220–1650 K. The $\Phi = 1.0$ Vasu et al. measurements were performed for MCH/air mixtures (1.962% MCH/20.60% O_2/N_2) near 45 atm and cover the temperature range of 790–1120 K; the current study is in excellent agreement with the Vasu et al. measurements. Vasu et al. also made measurements for 1% MCH/10.5% O_2 /Ar mixtures at 1.3–2.9 atm and 1225–1560 K, which agree fairly well with the Orme et al. measurements made for the same mixture at similar conditions; for readability these results are not included in Fig. 6. Vasu et al. also developed a correlation for their high-temperature low-pressure results: $\tau = 7.5 \times 10^{-14} P[\text{atm}]^{-0.98} X_{\text{MCH}}^{-0.82} \Phi^{1.47} \exp(25,560/T [\text{K}])$. The RCM measurements of Pitz et al. were made for stoichiometric 1.962% MCH/20.60% O_2 /diluent mixtures at pressures of 10, 15, and 20 atm and temperatures ranging from 680 to 1020 K, using argon, nitrogen, and 50% Ar/50% N_2 mixtures as diluent gases.

Direct comparison of the Orme et al. and Pitz et al. data with the current data and Vasu et al. data is not particularly useful due to the wide range of experimental conditions investigated. However, the data can

be scaled to a common condition to provide useful comparison. Figure 6 (graph on right) shows a comparison of the $\Phi = 1.0$ data scaled to a common condition of 1.962% MCH (MCH concentration for stoichiometric in MCH/air mixture) and 50 atm. The data were scaled using $\tau \propto P^{-0.99}$, found in this study and in agreement with the Vasu et al. recommendation of $\tau \propto P^{-0.98}$ at lower pressures, and $\tau \propto X_{\text{MCH}}^{-0.82}$ (X_{MCH} is the MCH mole fraction), recommended by Vasu et al. These scaling parameters may vary at temperatures lower than those studied here where the chemistry shifts away from high- and moderate-temperature oxidation controlled by small molecule radical branching to low-temperature oxidation through peroxy compounds. However, with that caveat in mind, scaling the data using the above power-law parameters provides excellent agreement between the current data, the Orme et al. data, the Vasu et al. data, and the 15 and 20 atm Pitz data at the intersections and overlap in the data sets. The 10-atm data of Pitz et al. does not agree with the current study or Vasu et al. when scaled. This difference presumably represents a failure of the simple power law pressure dependence in the NTC regime. In combination these data sets provide kinetic targets for MCH over a large temperature range, 680–1650 K.

In addition to the comparison to previous experimental results, comparison is made with the two recently published kinetic mechanisms for MCH of Orme et al. [13] (190 species and 904 reactions) and Pitz et al. [14] (1001 species and 4436 reactions) in Figs. 3 and 6. Calculations were performed using CHEMKIN with a constant volume constraint. The Orme et al. mechanism was developed to describe the high-temperature oxidation of MCH and reproduces

their shock tube results well. The Pitz et al. mechanism was developed to describe both the low- and high-temperature oxidations of MCH and was developed by starting with a base set of reactions for C₁–C₆ chemistry from previous mechanisms of Pitz, Westbrook, and coworkers [5,37–39], adding the high-temperature MCH reactions from the Orme et al. mechanism, and adding low-temperature chemistry of MCH. The mechanism was subsequently compared to the Pitz et al. RCM data and modifications were made to the low-temperature MCH peroxy chemistry, based on the static reactor work on peroxy reactions of Walker and coworkers [40,41], to better predict the NTC behavior observed in the RCM experiments. The Orme et al. and Pitz et al. mechanisms provide the same results for temperatures greater than 1200 K. At lower temperatures, the low-temperature peroxy chemistry begins to play a role, which the Orme et al. mechanism does not contain. For all conditions both mechanisms over predict the measured ignition times. The Pitz et al. mechanism does a good job of predicting the temperature dependence throughout the large temperature range of the combined data sets in Fig. 6 (graph on right), capturing both the high-temperature activation energy and NTC behavior. However, the Pitz et al. predictions are a factor of three to five in excess of the measured ignition times.

Unfortunately, because of its large size we were unable to perform sensitivity analysis using the Pitz et al. mechanism. We did, however, perform sensitivity analysis using the Orme et al. mechanism for temperatures greater than 1000 K. The OH concentration, a marker of ignition and related to the ignition time sensitivity, showed sensitivity to many of the reactions that Orme et al. found ignition time sensitivity in their analysis at 1250 K and 1 atm. The sensitive reactions include many small molecule radical consumption and generation reactions including hydrogen peroxide decomposition, $\text{H}_2\text{O}_2 + \text{M} \leftrightarrow 2\text{OH} + \text{M}$, and reaction with molecular oxygen, $\text{H}_2\text{O}_2 + \text{O}_2 \leftrightarrow 2\text{HO}_2$, H-atom reactions with molecular oxygen, $\text{H} + \text{O}_2 \leftrightarrow \text{OH} + \text{O}$ and $\text{H} + \text{O}_2 + \text{M} \leftrightarrow \text{HO}_2 + \text{M}$, methyl recombination, $\text{CH}_3 + \text{CH}_3 + \text{M} \leftrightarrow \text{C}_2\text{H}_6 + \text{M}$, and others. Other reactions that show sensitivity are the H-atom abstraction reactions from MCH, with $\text{MCH} + \text{HO}_2 \leftrightarrow \text{C}_7\text{H}_{13} + \text{H}_2\text{O}_2$ having the largest sensitivity. The accurate temperature-dependence prediction but overprediction of ignition time by the Pitz et al. mechanism for all temperatures, perhaps, suggests that the MCH consumption reactions in the mechanism are too slow. Over most of the temperature range displayed in Fig. 6, H-atom abstraction is the primary means of MCH consumption with thermal decomposition playing a role at the highest temperatures. There have been no measure-

ments of H-atom abstraction rates from MCH, and the rate coefficients used in the Pitz et al. mechanism are based on rate coefficient estimation rules developed by Pitz, Westbrook, and coworkers [5,37–39]. We arbitrarily increased the rate coefficients for H-atom abstraction from MCH in the Pitz et al. mechanism by a factor of five and found that the mechanism gave somewhat better agreement; the overprediction in ignition time was reduced from a factor of approximately three to five to a factor of approximately 1.5–2.5. This adjustment is made without basis, and may be unreasonably large, but it does point out that the rates for H-atom abstraction are of importance and accurate measurement or quantum chemical calculation of these rates may provide improved predictions.

SUMMARY

Ignition times for MCH/air and ECH/air mixtures were measured in a shock tube at conditions of relevance to practical combustion devices: 10.8–69.5 atm, 881–1319 K, and equivalence ratios of 0.25, 0.5, and 1.0. The ignition time measurements show exponential dependence on inverse temperature at high temperatures and rollover characteristic of negative temperature coefficient behavior for temperatures less than 1000 K; the ignition results also show inverse dependence on equivalence ratio and pressure. The ignition times for ECH were shorter than those for MCH for all conditions studied, indicating that for increasing alkyl side chain length in alkylcyclohexanes reactivity increases, consistent with previous findings for alkylbenzenes. The data are in good agreement with the previous shock tube studies of Orme et al. [13] and Vasu et al. [17] and rapid compression machine study of Pitz et al. [14], when all of the data are scaled to a common condition using power law scaling parameters determined in this study and by Vasu et al. The combination of these data sets provides kinetic targets for MCH over a large temperature range (for $\Phi = 1.0$, 680–1650 K). Comparison of the MCH data to the kinetic mechanism of Pitz et al. indicates that their mechanism captures the temperature dependence of the ignition time measurements but predicts ignition times that are longer than measured by a factor of three to five. Analysis suggests that increasing the rate coefficients for H-atom abstraction reactions from MCH improves the prediction of ignition times and that improved rate parameters for these reactions would be helpful. The present data greatly extend the range of data available for MCH and provide, to our knowledge, the first ignition data for ECH. These data should prove useful for the validation of future kinetic mechanisms for cycloalkanes.

This work was supported by the U.S. Air Force Office of Scientific Research (Grant No. FA9550-07-1-0114) with Dr. Julian Tishkoff as technical monitor.

BIBLIOGRAPHY

- Farrell, J. T.; Cernansky, N. P.; Dryer, F. L.; Friend, D. G.; Hergart, C. A.; Law, C. K.; McDavid, R.; Mueller, C. J.; Pitsch, H. SAE Paper 2007-01-0201. In SAE World Congress, Detroit, MI, 2007.
- Colket, M.; Edwards, T.; Williams, S.; Cernansky, N. P.; Miller, D. L.; Egolfopoulos, F. N.; Lindstedt, P.; Seshadri, K.; Dryer, F. L.; Law, C. K.; Friend, D. G.; Lenhert, D. B.; Pitsch, H.; Sarofim, A.; Smooke, M.; Tsang, W. AIAA-2007-0770. In 45th AIAA Aerospace Sciences Meeting and Exhibit, Reno, NV, 2007.
- Edwards, T.; Maurice, L. Q. J Propul Power 2001, 17, 461–466.
- Briker, Y.; Ring, Z.; Iacchelli, A.; McLean, N.; Rahimi, P. M.; Fairbridge, C.; Malhotra, R.; Coggiola, M. A.; Young, S. E. Energy Fuels 2001, 15, 23–37.
- Silke, E. J.; Pitz, W. J.; Westbrook, C. K.; Ribaucour, M. J Phys Chem A 2007, 111, 3761–3775.
- Guthrie, J.; Fowler, P.; Sabourin, R. Gasoline and diesel fuel survey; Environment Canada: Gatineau, Quebec, Canada, 2003; retrieved March 1, 2008, from: www.ec.gc.ca/cleanair-airpur/CAOL/OGEB/fuels/reports/fullreport/pdf/FullReport2003_e.pdf.
- Walsh, C. Canada's oil reserves 2nd only to Saudi Arabia; available at <http://www.rense.com/general37/petrol.htm>; Dow Jones Newswire, petroleumworld.com 5/6/2003.
- Violi, A.; Yan, S.; Eddings, E.; Sarofim, A. F.; Granata, S.; Faravelli, T.; Ranzi, E. Combust Sci Technol 2002, 174, 399–417.
- Schulz, W. D.; Heneghan, S. P.; Locklear, S. L.; Geiger, D. L.; Anderson, S. D. J Propul Power 1993, 9, 5–9.
- Wood, C. P. M.S. Thesis, Department of Mechanical Engineering, University of California, Irvine, CA, 1989.
- Agosta, A.; Lenhert, D. B.; Miller, D. L.; Cernansky, N. P. In Proceedings of the 3rd Joint Meeting of the U.S. Sections of the Combustion Institute, Chicago, IL, 2003.
- Pitz, W. J.; Cernansky, N. P.; Dryer, F. L.; Egolfopoulos, F. N.; Farrell, J. T.; Friend, D. G.; Pitsch, H. SAE Paper 2007-01-0175. In SAE World Congress, Detroit, MI, 2007.
- Orme, J. P.; Curran, H. J.; Simmie, J. M. J Phys Chem A 2006, 110, 114–131.
- Pitz, W. J.; Naik, C. V.; Ní Mhaoldúin, T.; Westbrook, C. K.; Curran, H. J.; Orme, J. P.; Simmie, J. M. Proc Combust Inst 2007, 31, 267–275.
- Bacha, J.; Barnes, F.; Franklin, M.; Gibbs, L.; Hemighaus, G.; Hogue, N.; Lesnini, D.; Lind, J.; Maybury, J.; Morris, J. Aviation Fuels; Technical Review, Chevron Products Company, 2000.
- Hawthorn, R. D.; Nixon, A. C. AIAA J 1966, 4, 513–520.
- Vasu, S.; Parikh, N. N.; Davidson, D. F.; Hanson, R. K. In Proceedings of the 5th Joint Meeting of the U.S. Sections of the Combustion Institute, San Diego, CA, 2007.
- Tanaka, S.; Ayala, F.; Keck, J. C.; Heywood, J. B. Combust Flame 2003, 132, 219–239.
- Garner, F. H.; Petty, D. S. Trans Faraday Soc 1951, 47, 877–896.
- Brown, T. C.; King, K. D. Int J Chem Kinet 1989, 21, 251–266.
- Kaiser, E. W.; Siegel, W. O.; Cotton, D. F.; Anderson, R. W. Environ Sci Technol 1992, 26, 1581–1586.
- Zeppieri, S.; Brezinsky, K.; Glassman, I. Combust Flame 1997, 108, 266–286.
- McEnally, C. S.; Pfefferle, L. D. Proc Combust Inst 2005, 30, 1425–1432.
- Daley, S. D.; Berkowitz, A. M.; Oehlschlaeger, M. A. Int J Chem Kinet, in press.
- Burcat, A.; Ruscic, B. Ideal gas thermochemical database with updates from active thermochemical tables; retrieved Sept. 15, 2007, from: <http://garfield.chem.elte.hu/burcat/burcat.html>.
- Thermodynamics Research Center. Selected Values of Properties of Chemical Compounds; Thermodynamics Research Center, Texas A&M University: College Station, TX, 1997.
- Oehlschlaeger, M. A.; Davidson, D. F.; Jeffries, J. B. Appl Optics 2005, 44, 6599–6605.
- Li, H.; Owens, Z. C.; Davidson, D. F.; Hanson, R. K. Int J Chem Kinet 2008, 40, 189–198.
- Davidson, D. F.; Gauthier, B. M.; Hanson, R. K. Proc Combust Inst 2005, 30, 1175–1182.
- Herzler, J.; Jerig, L.; Roth, P. Proc Combust Inst 2005, 30, 1147–1153.
- Oehlschlaeger, M. A.; Davidson, D. F.; Herbon, J. T.; Hanson, R. K. Int J Chem Kinet 2004, 36, 67–78.
- Davidson, D. F.; Hanson, R. K. Int J Chem Kinet 2004, 36, 510–523.
- Olchanski, E.; Burcat, A. Int J Chem Kinet 2006, 38, 703–713.
- Smith, J. M.; Simmie, J. M.; Curran, H. J. Int J Chem Kinet 2005, 37, 728–736.
- Herzler, J.; Fikri, M.; Hitzbleck, K.; Starke, R.; Schulz, C.; Roth, P.; Kalghatgi, G. T. Combust Flame 2007, 149, 25–31.
- Roubaud, A.; Minetti, R.; Sochet, L. R. Combust Flame 2000, 121, 535–541.
- Curran, H. J.; Gaffuri, P.; Pitz, W. J.; Westbrook, C. K. Combust Flame 2002, 129, 253–280.
- Curran, H. J.; Gaffuri, P.; Pitz, W. J.; Westbrook, C. K. Combust Flame 1998, 114, 149–177.
- Pitz, W. J.; Seiser, R.; Bozzelli, J. W.; Da Costa, I.; Fournet, R.; Billaud, F.; Battin-Leclerc, F.; Seshadri, K.; Westbrook, C. K. In Proceedings of the 2nd Joint Meeting of the U.S. Sections of the Combustion Institute, Oakland, CA, 2001.
- Gulati, S. K.; Walker, R. W. J Chem Soc, Faraday Trans 1989, 2, 1799–1812.
- Handford-Styring, S. M.; Walker, R. W. Phys Chem Chem Phys 2001, 3, 2043–2052.