Ethylene Ignition and Detonation Chemistry, Part 1: Detailed Modeling and Experimental Comparison

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A numerical investigation is reported on the chemical kinetics of C_2H_4 ignition and detonation in oxygen-diluent mixtures. Conditions addressed cover initial (postshock) temperatures between 1000 and 2500 K, pressures between 0.5 and 100 bar and equivalence ratios between 0.5 and 2. Attention is paid to histories of species concentrations and temperature, to autoignition times, and to subsequent heat release that is relevant to detonation structure. A detailed mechanism is proposed consisting of 148 reversible elementary reactions among 34 chemical species. This mechanism is shown to provide good agreement with most ignition times measured in shock tubes and with burning-velocity measurements available in the literature. The results provide a basis for developing simplified descriptions that can be used in multidimensional detonation studies for applications to propulsion devices.

Introduction

ETHYLENE is a fuel of interest for a variety of propulsion applications, such as in pulse-detonation engines (PDEs). Although it is a fairly reactive gaseous hydrocarbon that is not, by itself, a very practical fuel, it is a significant constituent of certain practical fuels and an important decomposition product of many liquid fuels, such as JP-10, a prime candidate for a PDE fuel in airbreathing propulsion. Whereas the burning velocities, autoignition rates, and detonability of ethylene are less than those of acetylene, they are greater than those of most hydrocarbon fuels, including the more practical liquid fuels. Ethylene, therefore, facilitates the ignition, flame propagation, and detonation of liquid fuels, whence it can be considered for use in various ways to enhance performance of airbreathing engines. It is, moreover, a model gaseous fuel that has been selected for fundamental scientific experimental and computational studies of soot formation, autoignition, and PDE wave dynamics. Because there are poorly understood aspects of ethylene chemistry, which need to be clarified for these applications, the present study is directed toward contributing to improved knowledge of ethylene chemistry in relationship to combustion.

In the last several decades many researchers[1-16] investigated the kinetics of ethylene oxidation in shock tubes; the results are summarized in Table 1. Correlations of ignition delay times with oxygen concentration and temperature were obtained from fits to experimental results as given in Table 1, where the fit parameters reported are those of the authors when possible, although most were derived by us. Note that when attempts were made to calculate measured ignition delays from detailed reaction mechanisms available in the literature, reasonable agreements were achieved for methane and heptane but not for ethylene, and therefore "additional work is required in modeling ethylene ignition."[15] The present paper proposes a detailed ethylene reaction mechanism that is developed by extending our previous mechanisms for other hydrocarbons through methods that include sensitivity and reaction-path analyses. This mechanism yields good predictions of most of the measured ig-

nition times and also reasonable agreement with burning-velocity measurements in the literature.

Detailed Mechanism

Many previous studies have addressed detailed kinetic modeling of ethylene oxidation.[13,17-19] Much of this work includes pyrolysis of pure ethylene as well, with buildup of larger molecules, leading to appreciable complexity in fuel chemistry. Although this is important for processes leading to soot formation, for example, such chemistry is too slow to be relevant to the rapid ignition considered in the present study, which is restricted to equivalence ratios less than about two or three. This limitation of the present work affords a significant simplification of the detailed chemistry and also substantially reduces uncertainties in predictions associated with unknown elementary rate parameters. Improved confidence is thereby obtained in the results, which can be applied not only to ignition but also to flames with equivalence ratios not greater than about 2.5, at rates of strain representative of many applications. The range of conditions addressed here, namely, initial temperatures between 1000 and 2500 K, pressures between 0.5 and 100 bar, and equivalence ratios between 0.5 and 2, has been selected to include the anticipated range of interest in practical applications, although limited available data preclude testing the mechanism over this entire range, especially above 10 bar. The new detailed mechanism introduced is an extension of our previous flame chemistry for methane, ethane, and acetylene.[20-24] It consists of 148 reversible elementary reactions among 34 species, C_2H_4, C_2H_3, C_2H_2, CH_2CO, CH_2CHO, C_2H_4O, O_2, H_2, H_2O, HO_2, H_2O_2, $HCCO$, CH_4, CH_3, CH_2O, CHO, H, OH, O, CO, CO_2, CH_3O, CH_2OH, C_2H_6, C_2H_5, C_2H, singlet and triplet CH_2, CH, C_3H_7, C_3H_6, C_3H_5, C_3H_4, and C_3H_3.

The relevant reactions and rates are the same as those of our previous work,[20] with the exception of the new steps and revised rates listed in Table 2 (see Refs. 13, 19, and 22–33). Differences from other mechanisms in the literature have been discussed previously.[20-24] A few of the entries in Table 2 have no influence on ethylene ignition and are given here only for the purpose of providing a complete up-date of the previous listing.[20] These include the new entries 1 and 2 that were needed for methane ignition,[26] the revised entries 38, 39, and 40 that were needed for acetylene ignition,[24] and the typographical rate-parameter corrections in entries 28 and 36. They also include entries 26, 27, and 29 which are the same as given earlier[20] and are listed here only to provide an accessible falloff reference. Entry 24 is a small change with no measurable influences, an update based on newer information,[34] for simplicity still taking temperature-independent third-body efficiencies for the species in the applications addressed, whereas entry 25 now introduces falloff with rate parameters the same as those of GRI 3.0, the latest version of the well-known mechanism of the Gas

Table 1 Summary of shock-tube experiments on ethylene–oxygen ignition

Number	Experiment reference	Incident or reflected shock	Equivalence ratio ϕ	Argon mole fraction, %	Pressure range, bar	Temperature range, K	Ignition-time correlation t_i $[O2] = \Lambda c^{E/RT}$, s mol/cm^3		Detection method
							$-\log_{10} A$	E, kJ/mol	
1	Mullaney[1]	Incident	0.5	61.5 N$_2$	0.1–0.5	1100–1300	13.00	61.21	Pulsed-light schlieren
2	Gay et al.[2]	Incident	0.3–4.0	96.7–99.0	0.2–0.4	1400–2300	14.23	96.74	Onset of CH* emission
3	Homer and	Incident	0.50	96.5	0.4–0.8	1505–2325	13.19	73.71	Infrared emision, 10% of
4	Kistiakowsky[3]		1.50	98.5			13.47	74.52	maximum ([CO] + [CO$_2$])
5	White[4]	Incident	0.0075	0.0	1.0	1000–2000	11.98	74.16	Interferometry
6			0.15	95.8			13.30	80.75	
7	Drummond[5]	Reflected	1.00	92.0	1.5	1094–1452	14.76	128.87	OH absorption maximum
8			1.00	84.0	1.8	1129–1396	15.34	147.16	
9			1.50	85.0	1.6	1097–1289	15.15	143.00	
10			1.50	94.0	1.8	1173–1626	15.29	135.52	
11			2.00	95.0	1.3	1239–1580	15.20	132.19	
12	Baker and	Reflected	1.00	96.0	3.0	1112–1556	16.09	167.94	OH emission maximum
13	Skinner[6]		1.00	99.0	12.0	1176–1531	16.54	185.40	
14			2.00	95.0–98.8	3.0	1100–1800	14.63	132.19	
15			0.13	93.8	3.0	1058–1418	16.36	172.93	
16			0.50	93.0	3.0	1080–1440	16.48	174.60	
17			0.50	98.3	3.0	1104–1551	15.44	144.66	
18	Suzuki et al.	Reflected	0.46	70.0	1.7–2.4	1089–1320	17.16	182.08	OH absorption; maximum
19			0.75	70.0	1.8–2.3	1082–1241	18.06	204.52	rate of change
20			1.09	70.0	1.9–2.4	1069–1223	16.63	172.93	
21			2.63	70.0	2.3–3.2	1089–1300	16.15	162.12	
22	Yoshizawa and	Incident	0.05	0.0	0.2–10	950–1250	13.81	94.53	Visible emission; OH
23	Kawada[8]		1.00	99.0	0.1–10	1250–2000	15.54	120.97	threshold
24	Hidaka et al.[9]	Reflected	3.00	98.0	2.5–3.1	1769–2077	14.67	120.55	CH* emission onset
25			3.00	98.0	4.3–5.1	1629–1846	14.58	119.72	
26			1.50	97.0	1.9–3.2	1480–2081	14.34	112.24	
27			1.00	96.0	1.8–3.2	1443–1897	14.38	112.24	
28	Jachimowski[10]	Incident	0.50	93.0	1.2–1.6	1800–2301	13.27	71.17	0.37-μm emission spike
29			1.00	92.0	1.2–1.7	1815–2339	12.94	57.28	
30			1.50	91.0	1.3–1.7	1868–2311	13.10	57.28	
31	Bhaskaran and Srinivasa[11]	Reflected	0.5, 1, 3	0.0	5.0	900–1400	15.55	159.63	Pressure rise
32	Hidaka et al.[12]	Incident	1.00	98.0	0.3–0.4	1555–2128	14.17	90.62	Laser schlieren
33			0.33	95.0	0.2–0.4	1383–1984	13.69	79.90	
34	Hidaka et al.[13]	Reflected	0.50	99.3	1.6–2.1	1361–1616	14.61	111.41	Onset of 4.2-μm CO$_2$
35			1.00	98.0	1.5–2.2	1267–1637	15.27	139.68	emission
36			2.00	97.5	1.7–2.4	1357–1692	15.86	158.80	
37			0.50	96.5	1.5–2.3	1258–1678	14.84	124.80	
38	Brown and	Incident	1.00	96.0	1.3–3.0	1276–2211	14.06	98.94	Onset of CH* emission
39	Thomas,[14]			75.0	1.4–3.4	1102–1771	14.37	118.06	
40				97.2 N$_2$	2.3–4.9	1073–1565	15.82	131.36	
41	Colket and	Reflected	0.50	95.1	6.2	1127–1308	15.64	151.31	Onset of OH emission
42	Spadaccini[15]		0.75	96.5	6.7	1182–1350	15.81	154.64	
43			1.00	97.2	7.2	1380–1414	13.21	88.96	
44	Hanson (2000)	Reflected	1.00	96.2	1.0	1440–1745	13.98	103.09	CH* emission maximum
45				99.2		1573–1783	13.84	94.88	

Research Institute, to correct hydrogen–oxygen predictions above 10 atm (Ref. 30), but does not affect any of our other results, aside from lengthening predicted acetylene ignition times[24] slightly, below 1200 K at pressures above 50 atm. Entries 12–23, 32, and 33, which are relevant in the present system, were needed for the fuel chemistry in ethane flames and have been discussed previously,[22,23] the earlier[21] reasoning concerning entries 32 and 33 no longer applying after the typographical corrections in entry 28 and 36; all of these rate constants came from earlier literature.

The rate parameters for entry 31 are revised from the previous[20,23] values because of the inclusion of the additional channel in entry 3; for the previous flames it was sufficient to lump both channels into that of entry 31, but the greater degree of branching associated with entry 3 is important in properly decreasing predicted ethylene ignition times, so that it now becomes necessary to include these two channels separately. Similarly, inclusion of entry 7 as a possible initiation step led to the revision in entry 34, which previously had been taken to approximate the total ethylene decomposition rate, the products having been irrelevant.

The changes in entries 35 and 37 and additions in entries 8 and 9 were introduced in investigating acetylene ignition.[24] The first of

these revisions was made to achieve agreement with newer elementary rate data and the others to provide additional branching needed at the lowest of the temperatures considered, especially through entry 8. The present investigation encouraged increasing the prefactor for step 8 by a factor of two over that selected in the initial part of the acetylene study, to the upper edge of the uncertainty band, to achieve agreement of predictions with the most reliable recent shock-tube measurements of ethylene ignition times. This change also improved agreement of predictions with measured acetylene ignition times in the most recent, highest-pressure experiments.[24] Consistent with these revisions, the rate parameters for CH_2CHO decomposition, entry 10, were taken from Marinov and Malte[19] (also see Ref. 24).

Entry 4, from Hidaka et al.,[13] was added for completeness but had no noticeable effect on predictions; fuel–fuel interactions would arise only at higher equivalence ratios. Entry 5, on the other hand, was essential here (although negligible in our earlier studies[20–24]), being the dominant initiation step. The rate parameters for this step were taken from the most prevalent literature with some justification,[19] although Benson[35] has suggested that there may be a different path, with a lower barrier, which, therefore, may be faster.

Table 2 Changes to the detailed mechanism[20]

Number	Reaction		A^a	n^a	E^a	Reference
	Reactions that have been added					
1	$CH_4 + O_2 \rightleftharpoons CH_3 + HO_2$		3.98×10^{13}	0.00	238.0	25, 26
2	$CH_4 + HO_2 \rightleftharpoons CH_3 + H_2O_2$		9.03×10^{12}	0.00	103.0	25, 26
3	$C_2H_4 + O \rightleftharpoons CH_2CHO + H$		1.21×10^{06}	2.08	0.0	27
4	$2C_2H_4 \rightleftharpoons C_2H_3 + C_2H_5$		5.01×10^{14}	0.00	271.0	13
5	$C_2H_4 + O_2 \rightleftharpoons C_2H_3 + HO_2$		4.22×10^{13}	0.00	241.0	19
6	$C_2H_4 + HO_2 \rightleftharpoons C_2H_4O + OH$		2.23×10^{12}	0.00	71.9	27
7[b]	$C_2H_4 + M \rightleftharpoons C_2H_3 + H + M$		2.60×10^{17}	0.00	404.0	27
8	$C_2H_3 + O_2 \rightleftharpoons CH_2CHO + O$		7.00×10^{14}	-0.61	22.0	19, 24
9	$C_2H_3 + O_2 \rightleftharpoons C_2H_2 + HO_2$		5.19×10^{15}	-1.26	13.9	19, 24
10	$CH_2CHO \rightleftharpoons CH_2CO + H$		1.05×10^{37}	-7.19	186.0	19
11[c]	$C_2H_4O + HO_2 \rightleftharpoons CH_3 + CO + H_2O_2$		4.00×10^{12}	0.00	71.2	28
12	$CH_2CO + H \rightleftharpoons CH_3 + CO$		1.11×10^{07}	2.00	8.4	23, 25
13	$CH_2CO + O \rightleftharpoons {}_3\text{-}CH_2 + CO_2$		2.00×10^{13}	0.00	9.6	23, 25
14	$CH_2CO + O \rightleftharpoons HCCO + OH$		1.00×10^{13}	0.00	8.4	23, 25
15	$CH_2CO + OH \rightleftharpoons CH_2OH + CO$		1.02×10^{13}	0.00	0.0	23, 25
16	$CH_2CO + CH_3 \rightleftharpoons C_2H_5 + CO$		9.00×10^{10}	0.00	0.0	23, 25
17	$C_2H_2 + OH \rightleftharpoons CH_2CO + H$		1.90×10^{07}	1.70	4.2	23
18	$C_2H_2 + OH \rightleftharpoons C_2H + H_2O$		3.37×10^{06}	2.00	58.6	23
19	$C_2H + OH \rightleftharpoons HCCO + H$		2.00×10^{13}	0.00	0.0	23, 29
20	$C_2H + O \rightleftharpoons CO + CH$		1.02×10^{13}	0.00	0.0	23, 29
21	$C_2H + O_2 \rightleftharpoons HCCO + O$		6.02×10^{11}	0.00	0.0	23, 29
22	$C_2H + O_2 \rightleftharpoons CH + CO_2$		4.50×10^{15}	0.00	105.0	23, 29
23	$C_2H + O_2 \rightleftharpoons CHO + CO$		2.41×10^{12}	0.00	0.0	23, 29
	Reactions whose rates have been changed					
24[d]	$H + O_2 + M \rightleftharpoons HO_2 + M$		2.60×10^{19}	-1.20	0.0	30
25[ef]	$OH + OH + M \rightleftharpoons H_2O_2 + M$	k_0	2.30×10^{18}	-0.90	-7.1	30
		k_∞	7.40×10^{13}	-0.40	0.0	
26[f]	$CH_3 + H \rightleftharpoons CH_4$	k_0	6.26×10^{23}	-1.80	0.0	27
		k_∞	2.11×10^{14}	0.00	0.0	
27[f]	$2CH_3 \rightleftharpoons C_2H_6$	k_0	1.27×10^{41}	-7.00	11.6	31
		k_∞	1.81×10^{13}	0.00	0.0	
28	$C_2H_6 + OH \rightleftharpoons C_2H_5 + H_2O$		2.20×10^{7}	1.90	4.7	29
29[f]	$C_2H_6 \rightleftharpoons C_2H_5 + H$	k_0	4.90×10^{42}	-6.40	448.4	31
		k_∞	8.85×10^{20}	-1.20	427.7	
30[b]	$C_2H_5 \rightleftharpoons C_2H_4 + H$	k_0	1.00×10^{16}	0.00	126.0	32
		k_∞	1.30×10^{13}	0.00	167.0	
31	$C_2H_4 + O \rightleftharpoons CH_3 + CHO$		2.25×10^{06}	2.08	0.0	27
32	$C_2H_4 + H \rightleftharpoons C_2H_3 + H_2$		4.49×10^{07}	2.12	55.9	33
33	$C_2H_4 + OH \rightleftharpoons C_2H_3 + H_2O$		5.53×10^{05}	2.31	12.4	33
34[b]	$C_2H_4 + M \rightleftharpoons C_2H_2 + H_2 + M$		3.50×10^{16}	0.00	299.0	27
35[f]	$C_2H_3 + M \rightleftharpoons C_2H_2 + H + M$	k_0	1.51×10^{14}	0.10	137.0	24
		k_∞	6.38×10^{09}	1.00	157.0	
36	$C_2H_3 + H \rightleftharpoons C_2H_2 + H_2$		1.21×10^{13}	0.00	0.0	27
37	$C_2H_3 + O_2 \rightleftharpoons CH_2O + CHO$		1.70×10^{29}	-5.31	27.2	19, 24
38	$C_2H_2 + O_2 \rightleftharpoons CH_2O + CO$		4.60×10^{15}	-0.54	188.0	24
39	$HCCO + O_2 \rightleftharpoons 2CO + OH$		2.88×10^{7}	1.70	4.2	24
40	$HCCO + O_2 \rightleftharpoons CO_2 + CO + H$		1.40×10^{7}	1.70	4.2	24

[a] Specific reaction-rate constant $k = AT^n e^{-E/RT}$, units mol, cm^3, s, K and kJ/mol.
[b] Chaperon efficiency: 1.0 for all species.
[c] See text for explanation.
[d] Chaperon efficiencies: O_2, 0.3; H_2O, 7.0; CO, 0.75; CO_2, 1.5; C_2H_6, 1.5; Ar, 0.5; others, 1.0.
[e] Chaperon efficiencies: H_2, 2.0; H_2O, 6.0; CH_4, 2.0; CO, 1.5; CO_2, 2.0; C_2H_6, 3.0; Ar, 0.7; others, 1.0.
[f] Falloff included as given in the cited reference.

If this were true, then it would be necessary to revise the rates of some of our dominant steps, such as entry 8, if we are to achieve agreement with measured ignition times.

Entry 30 is based on the measurements and calculations by Feng et al.[32] Reported rate expressions in helium are used here, even though the rate constants may be somewhat higher for the chaperons encountered under combustion conditions. Although direct measurements of rates at low temperatures and low pressures with nitrogen and ethane as inert are available, rate expressions that are applicable for the high temperatures encountered in combustion conditions, taking into consideration the important effects of falloff, are practically nonexistent. Moreover, with the rate parameters that can be found in the literature, there are wide differences in the rates under the conditions of interest. One study, based on theoretical extrapolations, results in rates nearly an order of magnitude higher

than ours and leads to predicted delay times that are much too large at low temperatures when used with our mechanism. In GRI 3.0, optimization following extrapolation resulted in rate parameters that depend on other selected values of rate parameters and that produce a rate nearly an order of magnitude lower than that from the parameters adopted here.

The rate for entry 30 is nearly two orders of magnitude greater than that of Hidaka et al.,[13] which is one order of magnitude below any other rates available in the literature and is attributed without comment to work reported by Hidaka at the Thirty-Second Japanese Combustion Symposium held in 1994. Although we were able to obtain reasonable agreements with many measured ignition times using Hidaka's full mechanism, when we employed Hidaka's rate for this step in our mechanism, we found ignition times that were clearly too short. It was this difficulty and the better agreement of
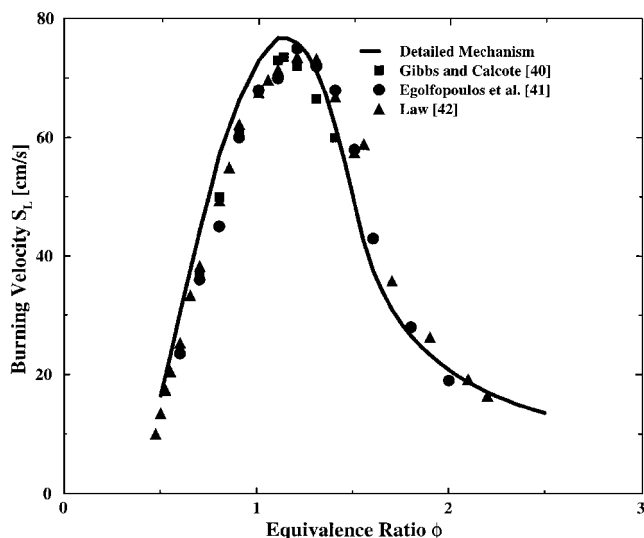
Fig. 1   Comparison of calculated and measured[37−39] laminar burning velocities of ethylene–air mixtures.

our rate for this step with the rest of the literature that led us to discard Hidaka's mechanism in favor of our own.

The HO_2 attack in entry 6 is unimportant except at the lower temperatures, typically below 1500 K. There is an abstraction path, yielding $C_2H_3 + H_2O_2$, the rate of which is entirely negligible over this low-temperature range and which, therefore, is not included. The addition path in entry 6 to ethylene oxide is much faster, and it aids branching by releasing hydroxyl immediately, as well as by entry 11, because much of the H_2O_2 that is produced there breaks up into 2 OH. Of the various steps for consuming C_2H_4O (Ref. 28), entry 11 is the only significant one under these conditions, mainly because of the high HO_2 concentration, the reactions of which have been discussed.[36] Entry 11 describes an overall result, because the initial products are $C_2H_3O + H_2O_2$, but C_2H_3O isomerizes rapidly mainly to CH_3CO (Ref. 17), which in turn decomposes rapidly to $CH_3 + CO$ (Ref. 28). Without the net branching afforded by entries 6 and 11, predicted ignition times are much too long at the lowest temperatures addressed here (about 1000 K).

As a test of the detailed mechanism, laminar burning velocities of ethylene–air mixtures were calculated and compared with experiment. The results, shown in Fig. 1 (see Refs. 37–39), demonstrate agreement generally within experimental error, whereas GRI 3.0, for example, substantially overpredicts these burning velocities.[40] This helps to provide some confidence in use of the present detailed mechanism, at least at 1 bar. The theoretical curves seem shifted to slightly smaller equivalence ratios than the experiments, an effect shared by a number of other mechanisms as well[40] and one that deserves further investigation. In the second part of this paper, a short mechanism, involving only 38 irreversible elementary steps among 21 chemical species, is developed from the detailed mechanism that is considered here, for use in ignition and detonation. In the following section, further tests of the detailed mechanism and the short mechanism, namely, against shock-tube ignition-time data, are discussed.

Comparison with Ignition Experiments

There are a number of ways to evaluate how well the chemical mechanism describes ethylene induction and detonation processes. Although calculations of one-dimensional, steady detonation structures can be made, there are no good data that can be compared with such results, cellular structures being dominant. There are a number of measurements of detonation cell sizes, but their calculation requires solution of nonlinear time-dependent multidimensional partial differential equations, which is difficult. The many available shock-tube measurements of ignition times, as summarized

in Table 1, afford the best opportunity for testing the mechanisms. Such data cannot test the subsequent detonation heat release following induction. It is, however, less critical to make such tests because these later processes are more common to detonations of other fuels as well. We have addressed this later heat release for acetylene[24] and do not expect substantial differences for ethylene, for which the most important steps are the same. The most critical tests, therefore, are the ignition-time tests.

To obtain ignition times theoretically, histories of temperatures and species concentrations predicted by the detailed mechanism were computed using FlameMaster.[41] The calculations were performed for homogeneous, adiabatic, isobaric conditions. In analysis of shock-tube data, it is more conventional to employ isochoric instead of isobaric conditions. It is even better to employ the full one-dimensional time-dependent gasdynamic conservation equations behind the inert shock, but this is not often done because the associated computer programs are less readily available. Differences in results obtained by these different procedures are negligible until appreciable heat release occurs. In particular, results for ignition times do not differ significantly. Therefore, the ignition histories obtained from the present computations are quite representative of those for shock-tube experiments with the given mechanisms.

Figure 2 compares predicted ignition times with 15 sets of experimental results. The experimental data were obtained under different conditions by many research groups. In addition, different investigators employ different definitions of ignition times. Table 1 lists the criteria used by each investigator. When computed histories with the detailed mechanism were examined, ignition times corresponding to the different experimental criteria were determined, and these are employed for making comparisons. This type of experiment-by-experiment comparison provides a finer test than the more traditional approach of correlating all experiments on a single plot, disregarding the different ignition definitions.

For comparing predictions with experiments that measure infrared or ultraviolet emissions,[3,10] density changes,[4,12] and pressure changes[11] (entries 1, 3–6, and 28–33 of Table 1), ignition was defined as the point at which 20% of the total temperature increase has occurred. This selection was deemed most representative of density-change or pressure-change experiments because in certain cases the 50% point, for example, occurred much later, during slow continuing heat release. Also shown for comparison in some of the tests are predictions based on the criterion of attainment of an inflection point in the temperature history. These two criteria also were exercized for the aforementioned short mechanism, and the predicted ignition times were found to agree with those of the detailed mechanism very closely in most cases, with differences never reaching a factor of two. For experiments selecting the onset of CH (Refs. 2, 9, and 14) OH (Ref. 15), or CO_2 (Ref. 13) emissions (entries 2, 24–27, and 34–43 of Table 1), the maximum rate of increase of concentrations of these species was employed, in view of the uncertainty dependent on the sensitivity of the instrumentation. For experiments employing the maximum of OH (Refs. 5 and 6) or CH (Ref. 16) emission or absorption (entries 7–17 and 44–45 of Table 1), the calculated maximum concentrations were adopted. Although different definitions often produce approximately the same ignition times, there are instances in which differences of a factor of 10 occur.

The numbers of Table 1 are employed to identify the curves of Fig. 2, where ϕ is equivalence ratio, P pressure, X mole fraction, and T temperature. The data points are from experiments and curves from the calculations. For brevity, not all entries in Table 1 are present in Fig. 2, where only representative comparisons are shown, along with demonstrations of maximum disagreements. There is good agreement with experiments for curve 3 in Fig. 2; this curve also agreed with computed results based on maximum-heat release rate. The experimental ignition criterion based on the sum of CO and CO_2 concentrations (see Table 1) also corresponds closely to this criterion, according to the computed histories. On the other hand, for entry 5, despite the expectation of close correspondence between the theoretical and experimental ignition criteria in this case, the present chemistry is seen to overpredict ignition times

under these extremely fuel-lean conditions, whereas for acetylene, the measurements of the same investigator under quite similar conditions are underpredicted,[24] suggesting need for further work on the mechanisms if they are to provide high-temperature ignition-time predictions better than a factor of two in great excesses of oxygen.

Curves 7–13 indicate generally good predictions of OH maxima at stoichiometric conditions, but possible underprediction of ignition times for fuel-rich conditions at the lower temperatures. No experimental points are shown for curves 12 and 13 because the authors report only these correlations rather than individual data points. There are situations having computational ambiguities for OH maxima (as well as occasionally, for other criteria); there often are two local OH maxima, for example, and depending on conditions either the first or second may be larger. Two solid lines are shown for curve 11 corresponding to the two local OH maxima.

The first is seen to be closer to the criterion based on 20% temperature increase. The data for entry 11 tend to fall between the two maxima, which suggests that if the two maxima do really exist, then the data represent some sort of an average. The solid lines for curves 12 and 13 correspond to the second maximum, in these cases clearly the larger of the two, and they agree comparatively well 11.with the data. The other two curves shown for entry 13 demonstrate how strongly the ignition time can depend on the selected criterion; they demonstrate that the large OH maximum often occurs quite late, as has previously been remarked in the literature.[42]

Ignition times obtained using 20% temperature rise as the ignition criterion are seen in Fig. 2 to be slightly longer for curve 29 than the experimental results obtained by identifying the emission spike from the $CO + O \rightarrow CO_2$ reaction. This may be due to relatively early peaking of this reaction; the temperature criterion is
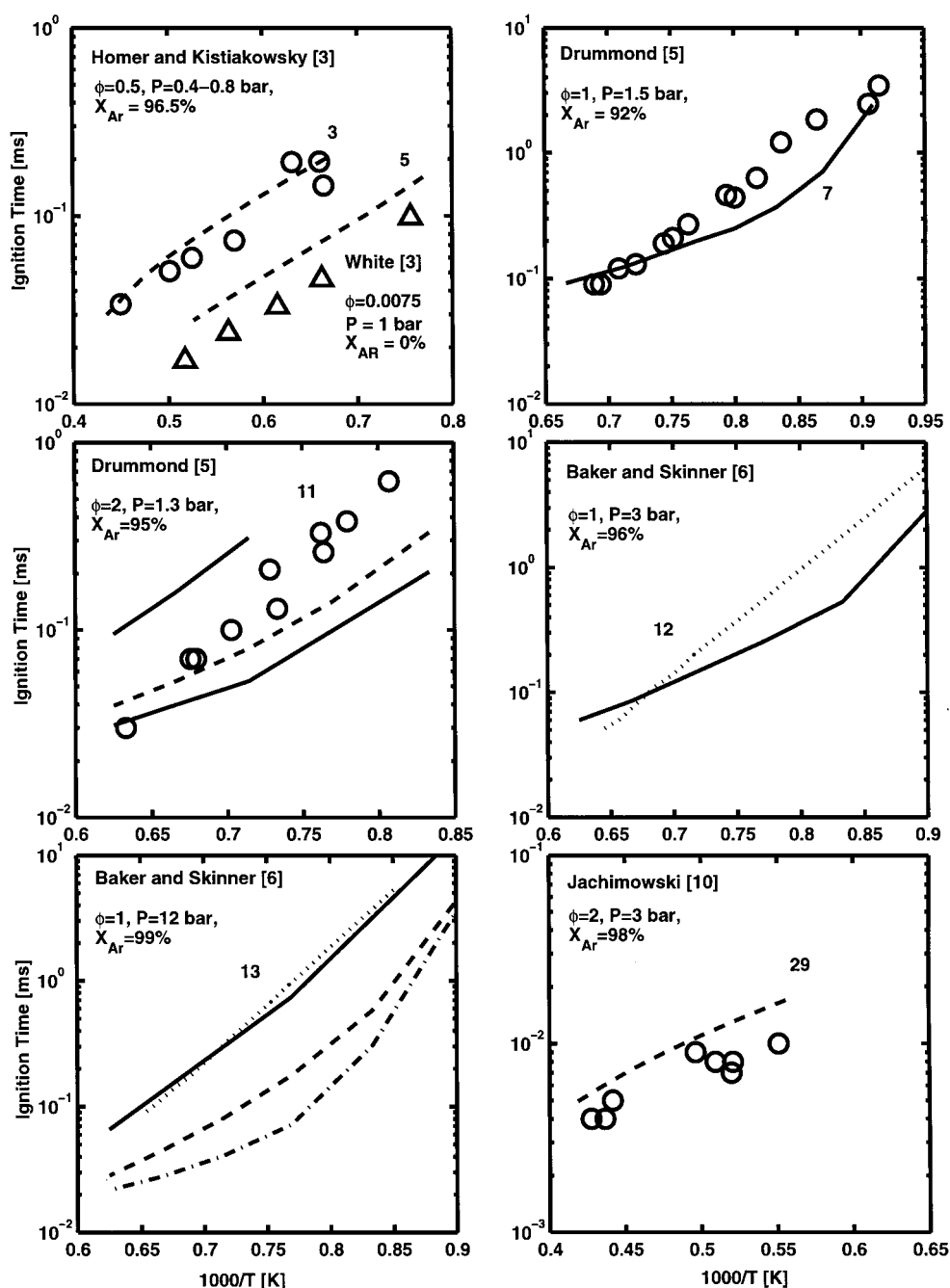

Fig. 2 Comparison of measured and predicted ignition times for 15 sets of experimental results; data points correspond to experiments, dotted lines to reported experimental correlations, solid curves to theoretical predictions based on the experimental criterion, dashed curves to predictions based on 20% of the total heat release, and chain curves to predictions based on temperature inflection.
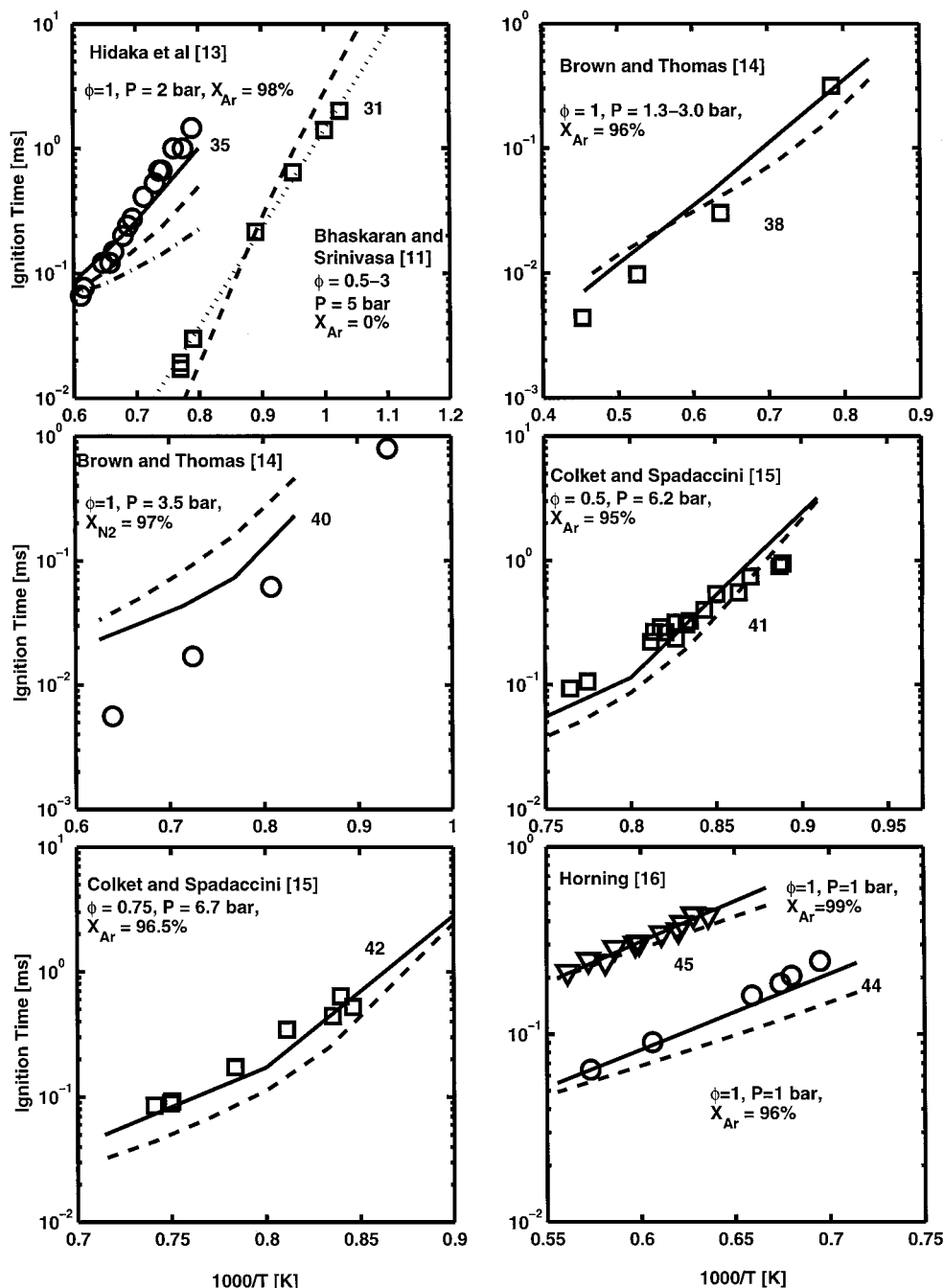
Fig. 2 Comparison of measured and predicted ignition times for 15 sets of experimental results; data points correspond to experiments, dotted lines to reported experimental correlations, solid curves to theoretical predictions based on the experimental criterion, dashed curves to predictions based on 20% of the total heat release, and chain curves to predictions based on temperature in flection (continued).

selected for the comparison here because of uncertainty concerning the exact origin of the emission spike and its coincidence with the maximum of the product of CO and O concentrations, which computationally is quite sensitive to uncertain chemical-kinetic details. There is reasonable agreement for curve 31, where both the data and the dotted-line correlation are shown. This agreement is favorable because these are the only experiments that correspond to the undiluted, high-pressure detonation conditions of greatest practical interest.

The different slopes of the three different criteria shown for curve 35 demonstrate how strongly apparent activation energies can depend on the specific criterion selected. For these experiments, calculations based on the maximum rate of increase of CO_2 concentration seem to be in reasonable agreement with the observed onset of CO_2 emissions, although the latter depend more strongly on tempera-

ture. There are related difficulties in comparing with experiments based on the onset of CH emissions in curves 38 and 40. Computationally, a rapid but small CH increase occurs early, followed by a more gradual but larger increase appreciably later. The inflection selected for the solid curves 38 and 40 is the first, earlier one; although this leads to reasonably good agreement for curve 38, the predicted ignition times are still longer than experiment for curve 40, suggesting earlier experimental detection of CH emissions. It is, in general, difficult to compare accurately with experimental onset measurements because they tend to be instrument dependent.

There is good agreement between the calculated OH inflection and the measured onset in curves 41 and 42, as well as with the calculated and measured CH maxima in curves 44 and 45. These are favorable agreements because they correspond to the latest and likely most reliable experiments. The dashed curves for entries 38
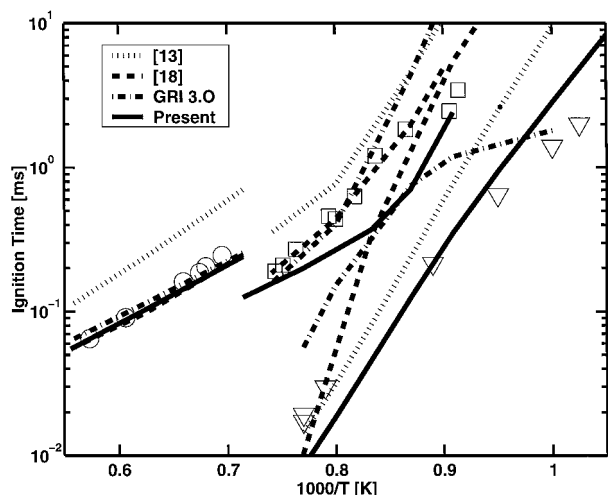
Fig. 3 Comparisons of ignition times predicted by the present mechanism, our transcription of the mechanism of Hidaka et al.,[13] an updated version of the mechanism of Dagaut et al.,[18] and GRI 3.0 with the data of entries 7 (squares), 31 (triangles), and 44 (circles) of Table 1.

and 41– 45 illustrate the differences that may be expected by using temperature-related criteria for ignition times.

The preceding comparisons demonstrate that the detailed mechanism developed here predicts ignition times that are in excellent agreement with recent high-temperature data (above 1500 K), whereas at lower temperatures, the ignition times are very sensitive to the choice of the ignition criterion. Agreements generally always lie within a factor of two for the ignition time when proper account is taken of the experimental ignition criterion employed.

Conclusions

This work has identified elementary chemistry that produces good agreement with much of the available experimental shock-tube ignition data of ethylene–oxygen-diluent systems. Very fuel-rich systems were excluded, thereby substantially reducing the complexity of the fuel chemistry that had to be addressed. Although much shorter than the other current detailed-chemistry mechanisms in the literature, the present mechanism appears to provide better agreement with most available burning-velocity and ignition-time measurements, as illustrated in Fig. 3. In generating the Fig. 3 comparison each of the detailed mechanisms were exercized with a well-defined ignition criterion corresponding to that of the experiment (CH maximum or OH maximum, or temperature inflection for pressure rise). These particular measurements have been selected because of the comparative unambiguity of the criterion. The next best agreements seem to be those of the current version of the mechanism of Dagaut et al.[18] (which contains more than 600 elementary steps), although note that the GRI mechanism was designed mainly for natural gas and is not recommended for ethylene, so that the quality of its performance here is in some sense fortuitous.

Limitations and uncertainties of the results need to be emphasized. There are some questions, already discussed, concerning selections for entries in Table 2, for example, entries 5 and 8, that deserve further investigation to reduce uncertainties. The mechanism tends to overpredict available measured ignition times for very lean conditions. Differences in this respect range to about a factor of two in ignition times. Differences in ignition times predicted by different criteria also typically differ by about a factor of two. Although the mechanism has been tested over nearly the entire temperature range from 1000 to 2500 K, tests were possible only in the lower part of the pressure range of interest, 0.5 to less than 10 bar. Although we have included falloff that we hope will provide reasonable results up to 100 bar, there is no experimental confirmation of any predictions at these higher pressures. For such conditions, the present results should be viewed merely as a proposal in need of testing.

To further improve ignition-time predictions using the detailed mechanism, it is helpful to develop a better understanding of the

chemistry during the induction period by examining the concentration histories under different conditions of temperature and pressure and seeking simplified descriptions. This task is addressed in part 2 of this paper, where the detailed mechanism described herein will be reduced further by applying steady-state and partial-equilibrium approximations, and analytical expressions for the induction period will be derived, ultimately leading to a two-step mechanism that can be used in multidimensional computational propulsion studies.

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