

Determination of the rate of $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ ($\text{M} = \text{N}_2, \text{Ar}, \text{H}_2\text{O}$) from ignition of syngas at practical conditions

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Abstract

In H_2 and H_2/CO oxidation, the $\text{H} + \text{O}_2 + \text{M}$ termination step is one of the most important reactions at elevated pressures. With the recent, increased interest in synthetic fuels, an accurate assessment of its rate coefficient becomes increasingly important, especially for real fuel/air mixtures. Ignition delay times in shock-tube experiments at the conditions selected in this study are only sensitive to the rates of the title reaction and the branching reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$, the rate of which is known to a high level of accuracy. The rate coefficient of the title reaction for $\text{M} = \text{N}_2, \text{Ar}$, and H_2O was determined by adjusting its value in a detailed chemical kinetics model to match ignition delay times for $\text{H}_2/\text{CO}/\text{O}_2/\text{N}_2$, $\text{H}_2/\text{CO}/\text{O}_2/\text{Ar}$, and $\text{H}_2/\text{CO}/\text{O}_2/\text{N}_2/\text{H}_2\text{O}$ mixtures with fuel/air equivalence ratios of $\phi = 0.5, 0.9$, and 1.0 . The rate of $\text{H} + \text{O}_2 + \text{N}_2 = \text{HO}_2 + \text{N}_2$ was measured to be $2.7 (-0.7/+0.8) \times 10^{15} \text{ cm}^6/\text{mol}^2 \text{ s}$ for $T = 916\text{--}1265 \text{ K}$ and $P = 1\text{--}17 \text{ atm}$. The present determination agrees well with the recent study of Bates et al. [R.W. Bates, D.M. Golden, R.K. Hanson, C.T. Bowman, *Phys. Chem. Chem. Phys.* 3 (2001) 2337–2342], whose rate expressions are suggested herein for modeling the falloff regime. The rate of $\text{H} + \text{O}_2 + \text{Ar} = \text{HO}_2 + \text{Ar}$ was measured to be $1.9 \times 10^{15} \text{ cm}^6/\text{mol}^2 \text{ s}$ for $T = 932\text{--}965 \text{ K}$ and $P = 1.4 \text{ atm}$. The rate of $\text{H} + \text{O}_2 + \text{H}_2\text{O} = \text{HO}_2 + \text{H}_2\text{O}$ was measured to be $3.3 \times 10^{16} \text{ cm}^6/\text{mol}^2 \text{ s}$ for $T = 1071\text{--}1161 \text{ K}$ and $P = 1.3 \text{ atm}$. These are the first experimental measurements of the rates of the title reactions in practical combustion fuel/air mixtures.

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1. Introduction

Carbon monoxide and hydrogen are produced during coal-gasification along with possible H_2O and CO_2 , and together these gases are commonly referred to as synthesis gas, or syngas [1]. Syngas can be burned with air in gas turbines to produce electric power, and there is increasing interest in

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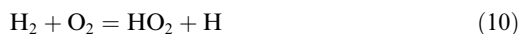
alternative fuels and related fuel flexibility issues in such systems [2]. The chemical kinetics of syngas blends are very important in practical devices due to the differences in flame speeds and autoignition behavior in comparison to traditional natural gas-based systems which operate at elevated pressures and utilize special combustor circuits to minimize emissions. In recent shock-tube studies of CO/H₂/O₂/N₂ ignition at gas turbine conditions [3–5], the termination reaction:



was identified as the controlling reaction for ignition delay times for a variety of pressures and temperatures. The title reaction is also responsible for the well-known second-explosion limit behavior in hydrogen oxidation at lower temperatures and higher pressures. The reaction numbering scheme is taken from the chemical kinetics model of Davis et al. [6].

There have been numerous experimental and theoretical studies of this reaction for a variety of specific collision partners. Thorough reviews of previous experimental and theoretical determinations of reaction (9) are provided elsewhere [7–11]. The results of these studies and their relevance to the current investigation will be discussed further in the results section. Some of the previous experimental studies utilized diluted mixtures with N₂ as the collision partner at pressures comparable to those of the current study, that is, pressures as high as 15 atm or more. However, the current study is the first to measure this reaction in practical combustion mixtures, i.e. undiluted fuel/air concentrations. Since the termination reaction (9) is so important in syngas–air and most other combustion systems, re-evaluation of its rate coefficient as new data and information become available is critical, particularly with respect to the efficiencies of the various collision partners.

Chemical reaction in shock-heated syngas/air mixtures at the conditions of this study begins in the first few microseconds with the generation of O- and H-atoms through two primary initiation reactions:



These reactions quickly become insignificant as reactions (1)–(3) become the important sources of radical-species:



However, H-atom levels and therefore radical-species generation are strongly suppressed by the removal of H-atoms by reaction (9). As a result,

ignition delay times are highly sensitive to the relative rates of reactions (1) and (9). And because reactions (1) and (9) are two- and three-body-reactions, respectively, large increases in ignition delay times are observed with increased pressure [3,4]. In addition, real (undiluted) fuel/air mixtures are more sensitive to this transition, allowing for the rate of (9) to be determined at pressures and temperatures that are less extreme than required in more dilute experiments.

The current study employs ignition delay time data from new and previously reported [3–5] shock-tube ignition delay time measurements. Rate coefficient determinations were made for M = N₂ in CO/H₂/O₂/N₂ mixtures with CO/H₂ ratios ranging from 20/80 to 95/5, fuel/air equivalence ratios of $\phi = 0.5$ and 1.0, and temperatures and pressures ranging from 909 to 1265 K and 1.1 to 17.9 atm, respectively. Rate coefficient determinations were also made for M = Ar in seven CO/H₂/O₂/Ar mixtures from 932 to 965 K at 1.4 atm, and for M = H₂O in four CO/H₂/O₂/N₂/H₂O mixtures from 1071 to 1161 K at 1.3 atm. The rate of reaction (9) was determined by adjusting its value in the reaction mechanism to match calculated and measured ignition delay times. This is made possible by the fact that the rate of reaction (1) is known to within $\pm 15\%$ [6], and contributions from other competing reactions are much less significant.

2. Experimental details

The ignition delay time experiments were conducted in the authors' shock-tube facility described in Petersen et al. [12]. The stainless steel shock tube has a 3.5-m long driver section with a 7.62-cm inner diameter and a 10.7-m long driven section with a 16.2-cm inner diameter. All experiments were performed behind reflected shock waves. Reaction progress was monitored using the emission from the hydroxyl radical $A^2\Sigma^+ \rightarrow X^2\Pi$ transition (i.e., OH* chemiluminescence) and five fast-response (<1 μs) PCB 311A pressure transducers. Further details are given elsewhere [12].

A list of new and previously reported [3–5] mixtures utilized in this study is shown in Table 1. All mixtures were pre-mixed in tanks using partial pressures before being fed into the driven section of the shock tube, with the exception of the mixtures containing water vapor. For the H₂O-containing mixtures (Table 1), the water was introduced directly into the driven section of the shock tube, and the premixed hydrogen–oxygen–nitrogen mixture was then added [5]. Since all mixtures were undiluted in “air” (with either N₂ or Ar as the diluent), the possibility of heat release and reaction behind incident-shock waves was monitored closely. Although no pre-reaction was

Table 1

Mixtures employed in the present study for the determination of k_9

Mixture	Fuel blend (CO/H ₂ , %)	X _{CO}	X _{H₂}	X _{O₂}	X _{N₂}	X _{Ar}	X _{H₂O}	ϕ
1 ^a	80/20	0.235	0.059	0.148	0.558	–	–	1.0
2 ^{b,c}	95/5	0.165	0.009	0.174	0.652	–	–	0.5
3 ^{b,c}	90/10	0.156	0.017	0.175	0.652	–	–	0.5
4 ^{b,c}	80/20	0.140	0.035	0.174	0.651	–	–	0.5
5 ^b	60/40	0.104	0.070	0.174	0.651	–	–	0.5
6 ^b	20/80	0.035	0.139	0.174	0.652	–	–	0.5
7 ^a	90/10	0.156	0.017	0.175	–	0.652	–	0.5
8 ^d	5/95	0.010	0.180	0.113	0.431	–	0.231	0.9

^a This study.^b Kalitan et al. [3].^c Kalitan et al. [4].^d Barrett et al. [5].

evident for the data presented herein and in the original studies, mixtures with hydrogen fuel content above 20% resulted in reaction behind the incident-shock wave for initial conditions producing elevated reflected-shock pressures. Mixtures with hydrogen fuel content above 20% were only studied at reflected-shock pressures of ~ 1 atm.

The methods used to measure ignition delay time (τ_{ign}) are defined in previous references by the authors [13,14] and in the original ignition studies [3–5]. Reaction progress was monitored from the endwall location using both endwall pressure traces and OH* emission traces. It has been shown that endwall measurements of ignition time are more reliable than sidewall measurements for undiluted fuel/air mixtures with significant energy release [15–17], although sidewall measurements were also monitored [3–5]. For all tests, time-zero was indicated by the step pressure rise due to the arrival of the shock wave at the end wall. Ignition was indicated by the onset of OH* emission for tests with weak-to-moderately strong ignition pressure increases. These measurements were in agreement with ignition times identified from pressure traces using the method defined previously by the authors as the intersection of a line tangent to the steepest slope of the pressure rise with the initial (zero-time) pressure. For a small number of test cases, extremely strong ignition and/or detonations were observed. These typically occurred for the lowest-temperature experiments (~ 950 K or below), and ignition was defined in terms of the endwall pressure ‘spike’ [3–5]. Test temperatures behind the reflected-shock wave were calculated from the incident-shock speed utilizing the standard 1D shock-tube relations and the Sandia thermodynamic database [18].

Table 2 contains a full list of ignition delay time data, experimental conditions, and rate coefficients from new and previously published experiments. Note that only the ignition data from sources [3–5] that were sensitive to reaction (1) were utilized; data above the first explosion limit

where reaction (4) is dominant were not utilized herein.

3. Results

3.1. Methodology for rate coefficient determination for $M = N_2$

Kinetics modeling in the current study was performed using the Chemkin Collection [19] software package and the reaction mechanism and thermodynamic database developed for H₂/CO combustion by Davis et al. [6] It has been shown that this mechanism exhibits very good agreement with the ignition data utilized herein, especially at higher temperatures.

Calculated ignition times herein were determined using two techniques: the OH* reaction mechanism developed by Hall and Petersen [13,20] was added to the Davis et al. mechanism to determine the calculated time of the onset of OH* generation. These reactions have no effect on the reaction kinetics of other species. Calculated pressure profiles were also used to determine ignition times as described above for measured pressure traces. There was excellent agreement between the two calculated ignition times, except in the case of extremely strong ignition and/or detonations as discussed above. In such cases, only calculated pressure traces were used. In every other case, any difference between the two determinations was included in the uncertainty analysis for k_9 .

Each rate coefficient was determined by adjusting the overall value of k_9 in the Davis et al. mechanism to match calculated τ_{ign} to measured τ_{ign} . Figure 1 is a reaction sensitivity plot for atomic hydrogen for the stoichiometric case (mixture 1) at 933 K, 1.16 atm that demonstrates that the competition between reaction (1) and reaction (9) dominates the removal of H-atoms prior to ignition. Table 3 shows an example of the changes in calculated τ_{ign} due to adjustments in k_9 for

Table 2
Ignition delay time measurements utilized in the present study and the resulting k_9 values

Mixture	P (atm)	T (K)	τ_{ign} (μs)	$k_9 \times 10^{-15}$ ($\text{cm}^6/\text{mol}^2 \text{ s}$)	Systematic uncertainty	Mixture	P (atm)	T (K)	τ_{ign} (μs)	$k_9 \times 10^{-15}$ ($\text{cm}^6/\text{mol}^2 \text{ s}$)	Systematic uncertainty
1 ^a	1.19	909	1945	2.30	(−24%, +23%)	3 ^c	15.7	1221	72	2.60	(−21%, +21%)
1 ^a	1.17	912	1215	2.15		3 ^c	17.1	1265	24.6	2.20	
1 ^a	1.16	933	1001	2.75		4 ^b	1.22	934	1233	2.70	
1 ^a	1.11	939	783	2.80		4 ^b	1.19	936	1123	2.70	
1 ^a	1.21	942	840	2.85		4 ^b	1.18	938	959	2.60	
1 ^a	1.21	947	618	2.65		4 ^b	1.22	957	599	2.60	
1 ^a	1.16	933	1001	2.75		4 ^c	2.64	980	864	2.30	
2 ^b	1.2	968	1365	2.75		4 ^c	2.64	992	856	2.65	
2 ^c	2.25	977	1538	2.10		4 ^c	2.61	1007	700	3.05	
2 ^c	2.25	1005	873	2.45		4 ^c	2.58	1011	443	3.00	
2 ^c	2.15	1010	780	2.55		4 ^c	2.59	1025	389	3.20	
2 ^c	2.15	1034	453	2.50		4 ^c	2.47	1026	263	2.85	
2 ^c	2.07	1039	363	2.10		4 ^c	14.5	1080	1153	2.70	
2 ^c	12.7	1110	1185	3.20		4 ^c	14.9	1114	638	3.00	
2 ^c	14.6	1114	806	2.45		4 ^c	14.9	1139	364	3.00	
2 ^c	14.0	1121	758	2.60	(−31%, +37%)	4 ^c	17.9	1182	136	2.65	(−27%, +26%)
2 ^c	13.6	1142	708	3.35		5 ^b	1.14	933	1471	3.25	
2 ^c	14.8	1144	740	3.50		5 ^b	1.12	948	600	3.00	
2 ^c	13.9	1151	435	2.70		5 ^b	1.17	973	301	2.55	
2 ^c	13.5	1163	266	2.40		6 ^b	1.11	916	2932	3.10	
3 ^b	1.22	960	1176	2.95		6 ^b	1.07	936	2011	3.60	
3 ^b	1.16	964	1067	3.00		6 ^b	1.15	954	462	3.30	
3 ^c	2.65	981	2284	2.45		6 ^b	1.11	957	311	2.50	
3 ^c	2.64	991	1117	2.40		6 ^b	1.07	960	327	2.70	
3 ^c	2.56	1016	582	2.75		7 ^a	1.39	932	1169	1.50	
3 ^c	2.15	1018	497	3.00		7 ^a	1.39	941	1080	1.80	
3 ^c	2.59	1026	434	2.80		7 ^a	1.39	941	1088	1.80	
3 ^c	2.49	1048	236	2.60		7 ^a	1.44	956	878	2.15	
3 ^c	14.3	1063	1695	2.30		7 ^a	1.46	956	898	2.10	
3 ^c	13.6	1090	842	2.20		7 ^a	1.37	959	760	2.00	
3 ^c	13.3	1117	644	2.80		7 ^a	1.46	965	629	1.75	
3 ^c	15.2	1123	546	2.55		8 ^d	1.37	1071	362	32.0	(−27%, +26%)
3 ^c	11.9	1126	472	2.75		8 ^d	1.37	1097	183	32.0	
3 ^c	14.3	1139	395	2.70		8 ^d	1.33	1116	140	33.0	
3 ^c	14.7	1158	272	2.70		8 ^d	1.23	1161	90	35.0	
3 ^c	13.2	1159	265	2.85							

Each point was chosen because of its high sensitivity to the rate of reaction (9).

^a This study.
^b Kalitan et al. [3].
^c Kalitan et al. [4].
^d Barrett et al. [5].

Table 3

Ignition delay time sensitivity to k_{9a} and k_{9f}

Mixture (CO/H ₂ , %)	<i>P</i> (atm)	<i>T</i> (K)	Calculated τ_{ign} (μs) for $k_{9a} \times 10^{-15} \text{ cm}^6/\text{mol}^2 \text{ s} =$			$(\tau_{\text{ign},k=3.2})/(\tau_{\text{ign},k=2.2})$
			2.2	2.7	3.2	
1 (80/20)	1.16	933	642	951	1734	2.7
2 (95/5)	13.9	1151	292	430	560	1.9
3 (90/10)	2.64	991	752	2028	4428	5.9
3 (90/10)	2.49	1048	178	230	308	1.7
3 (90/10)	14.3	1063	1620	2070	2484	1.5
3 (90/10)	15.7	1221	42	73	108	2.6
6 (20/80)	1.11	916	596	1012	4104	6.9
6 (20/80)	1.07	960	266	308	366	1.4

Mixture (CO/H ₂ , %)	<i>P</i> (atm)	<i>T</i> (K)	Calculated τ_{ign} (μs) for $k_{9f} \times 10^{-15} \text{ cm}^6/\text{mol}^2 \text{ s} =$			$(\tau_{\text{ign},k=40})/(\tau_{\text{ign},k=26})$
			26.0	33.0	40.0	
8 (5/95)	1.37	1071	235	420	1205	5.1
8 (5/95)	1.37	1097	148	194	294	2
8 (5/95)	1.33	1116	116	138	174	1.5
8 (5/95)	1.23	1161	80	86	96	1.1

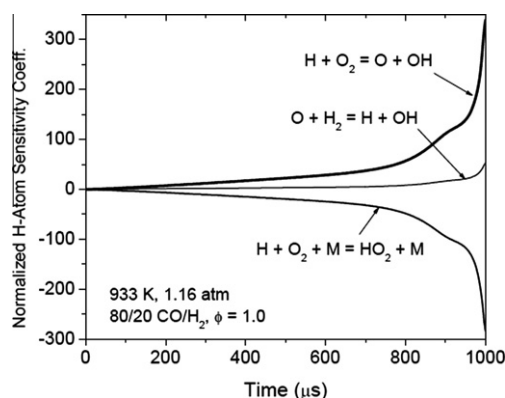


Fig. 1. Sensitivity of H-atom production to the rate coefficients of key reactions, calculated from Chemkin [19]. $\text{H} + \text{O}_2$ branching and termination compete with each other and dominate radical buildup. Calculation is for mixture 1 at 933 K, 1.16 atm.

$\text{M} = \text{N}_2$ for a variety of experiments. This calculation demonstrates the high sensitivity of τ_{ign} to the value of k_9 : changing k_9 from -20% to $+20\%$ resulted in τ_{ign} changing by factors of 1.4 to 7, depending on mixture conditions. Table 3 also demonstrates the large changes in τ_{ign} with temperature and pressure.

All of the results for k_9 and systematic uncertainties for some values are shown in Table 2. Systematic uncertainties in k_9 were determined by adjusting the rates of other reactions within uncertainty limits taken from Davis et al., and by adjusting the value of $\Delta H_{f298} = 3.0 \text{ kcal/mol}$ for HO_2 used by Davis et al. over the range 2.7–3.7 kcal/mol [21]. Table 4 shows this systematic

uncertainty determination for two experiments, A and B, both of which are also included in Table 3. Table 4 demonstrates the process of adjusting the rate of each reaction in the mechanism to each uncertainty limit and then readjusting k_9 in the mechanism to match calculated τ_{ign} to measured τ_{ign} . Asymmetric effects result from Davis et al. having optimized rates of various reactions within their uncertainty limits, moving some rate coefficients closer to one uncertainty limit and farther from the other. Note that the present study is not an attempt to optimize the Davis et al. mechanism based on the new ignition data. Rather, this study uses the data and the Davis et al. mechanism to determine k_9 for experiments showing particular sensitivity to its value.

Table 4 shows that the sensitivity of τ_{ign} to the value of k_9 shown in Table 3 does not tell the whole story; an accurate determination of k_9 also depends on the relative sensitivity of τ_{ign} to reaction (9) compared to other reactions. The experiment for which τ_{ign} had a higher sensitivity to k_9 in Table 3 actually had a higher percentage systematic uncertainty in Table 4. Discussion of competing reactions is presented later in the paper. Table 4 also lists random uncertainties in k_9 resulting from uncertainties in reflected-shock temperatures and pressures ($\pm 1\%$) and the accuracy of the determinations of experimental and calculated ignition times, by adjusting k_9 in the same fashion described above to account for these variations. Random uncertainties vary little between cases, and are shown only for cases A and B. Total uncertainty in the overall rate coefficient was determined by combining systematic and random uncertainties as independent sources

Table 4
Uncertainty analysis for k_{9a}

Reaction	Min. and max. Δk (%)	Δk_{9a} (%)	Δk_{9a} (%)
		Exp. (A)	Exp. (B)
<i>Systematic uncertainties</i>			
1. $H + O_2 = O + OH$	+15 −15	+26 −24	+15 −15
2. $O + H_2 = H + OH$	+10 −35	+2 −13	+2 −13
3. $OH + H_2 = H + H_2O$	+62 −4	+4 negl.	negl. negl.
11. $2OH(+M) = H_2O_2(+M)$	0 −55	0 negl.	0 −9
13. $HO_2 + H = OH + OH$	+90 −53	negl. negl.	+7 −6
14. $HO_2 + O = OH + O_2$	0 −75	0 negl.	0 +13
15a. $HO_2 + OH = O_2 + H_2O$	+144 −39	negl. negl.	−17 +7
22a. $CO + OH = CO_2 + H$	+44 0	negl. 0	+7 0
24. $CO + HO_2 = CO_2 + OH$	+100 −50	negl. negl.	+30 −15
$\Delta_f H_{298} HO_2$ =2.7 kcal/mol =3.7 kcal/mol		−4 +5	−4 +5
Total systematic uncertainty (%):		+26, −27	+38, −31
<i>Random uncertainties</i>			
$\Delta T = +1\%$, $\Delta P = -1\%$		+19	+15
$\Delta T = -1\%$, $\Delta P = +1\%$		−19	−15
Uncertainty in τ_{ign}		+/− 5	+/− 5
Total random uncertainty (%)		+/− 20	+/− 16

Exp. (A): 960 K, 1.07 atm, mixture 6.
Exp. (B): 1151 K, 13.9 atm, mixture 2.

Systematic uncertainties (Δk_{9a}) result from uncertainties in rate coefficients of other reactions and the HO_2 heat of formation. Random uncertainties (Δk_{9a}) come from uncertainties in the measurements of ignition time, T , and P .

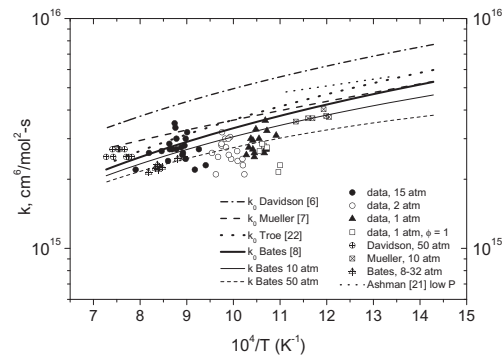
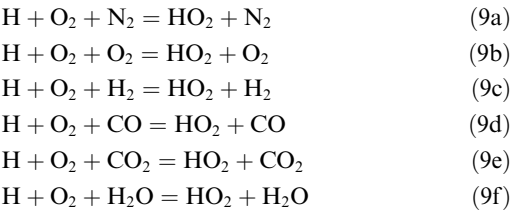


Fig. 2. Arrhenius plot for k_{9a} showing current data in comparison with results from the literature.

(square root of the sum of the squares) to determine total uncertainty for each point, and subsequently determining the limits on the overall rate coefficient that would fit through every point's uncertainty limits.

3.2. Sensitivities to various collision partners

Kinetics modeling was performed to examine the sensitivity of the determinations of k_9 for $M = N_2$ to the variation in mole fraction of different collision partners for different mixtures, conditions, and with respect to time in a given experiment. This was performed by replacing the overall reaction in the mechanism with rate coefficients for separate reactions for a variety of collision partners:



Collision efficiencies for reactions (9b)–(9f) relative to reaction (9a) were taken from Davis et al.

For each experiment, the value of k_{9a} (and therefore k_{9b-9f}) was adjusted until calculated τ_{ign} matched measured τ_{ign} , and reaction contribution factor plots and species reaction sensitivity plots were examined. From time zero until about $0.9\tau_{\text{ign}}$, the only collision partners of any significance are the constituents of the initial gas composition: N_2 , O_2 , H_2 , and CO . Shortly before ignition, around $0.95\tau_{\text{ign}}$, CO_2 and H_2O mole fractions rise above 0.005 and continue to increase rapidly. Therefore, over that short period, reactions (9e) and (9f) contribute from 1 to 10% to the overall rate of reaction (9). This is because the collision efficiencies of CO_2 and H_2O have been taken to be 2 and 12 times, respectively, that of N_2 . No other products of reaction have mole fractions large enough at any time prior to ignition to contribute to the overall rate of reaction (9). Results for k_{9a} using this technique varied less than 5% from the previous methodology, indicating that the determination of k_9 in these mixtures is indeed for $M = \text{N}_2$.

3.3. Comparison to other studies

There have been numerous studies of reaction (9a), including recent measurements of k_{9a} by Davidson et al. [7], Mueller et al. [8], Ashman and Haynes [22], and Bates et al. [9] at temperatures and pressures similar to those of the current study. Davidson et al. and Mueller et al. each presented detailed reviews of previous studies of reaction (9a) and recommended expressions for the low-pressure-limit rate coefficient $k_{9a,0}$ for expanded temperature ranges. Troe [23] recently performed a theoretical study of reaction (9a), and Bates et al. and Troe both present theoretical expressions for $k_{9a,0}$, the high-pressure-limit rate coefficient $k_{9a,\infty}$, and pressure falloff constants. Michael et al. [10] also recently measured k_{9a} at temperatures of 296–698 K and low-pressures and presented a graph of theoretical calculations of k_{9a} for a variety of pressures from 300 to 1500 K.

Figure 2 is an Arrhenius plot that shows the measurements of k_{9a} and expressions for $k_{9a,0}$ of these studies, and the results of k_{9a} of the current study. The scatter of the current results is consistent with the random uncertainties of k_{9a} due to uncertainties in temperature, pressure, and τ_{ign} shown in Table 4. Figure 2 also shows k_{9a} calculated from the expressions of Bates et al. for pressures of 10 and 50 atm. These curves are in excellent agreement with the results of the current study and fall within the uncertainty limits of the results of all the aforementioned recent studies. The average value for all the measurements of the current study is $k_{9a} = 2.7 \times 10^{15} \text{ cm}^6/\text{mol}^2 \text{ s}$. It should be noted that the graph of theoretical calculations of k_{9a} by Michael et al. are also in excellent agreement with the current study, but

their results cannot be translated accurately onto Fig. 2.

3.4. Rate coefficient determination for $M = \text{Ar}$

Rate coefficient determinations were also made for seven $\text{CO}/\text{H}_2/\text{O}_2/\text{Ar}$ ignition experiments from 932 to 965 K at 1.4 atm. Note that unlike most of the N_2 -based experiments, these data were not previously published, and are provided here for the first time. The results are shown in Table 2. Reactions (9b)–(9f) were included in the mechanism, and the rate of $k_{9\text{argon}}$ was adjusted to fit the ignition times. While there is no N_2 in these mixtures, a value of $k_{9a} = 2.7 \times 10^{15} \text{ cm}^6/\text{mol}^2 \text{ s}$ and the relative collision efficiencies for reactions (9b)–(9f) from Davis et al. were used to provide values of k_{9b-9f} in the mechanism. The average value for the seven $\text{CO}/\text{H}_2/\text{O}_2/\text{Ar}$ mixtures is $k_{9\text{argon}} = 1.9 \times 10^{15} \text{ cm}^6/\text{mol}^2 \text{ s}$. Hahn et al. [11] performed a high-pressure flow-cell study of reaction (9) for $M = \text{Ar}$ from 300 to 700 K, and performed detailed analysis presenting an expression for k for a wider range of temperatures and pressures. Their expression provides a low-pressure rate constant of $2.0 \times 10^{15} \text{ cm}^6/\text{mol}^2 \text{ s}$ at 950 K, which is in excellent agreement with the current study. The ratio of the average value of k_9 for argon mixtures to that of nitrogen mixtures for the current study is 0.69. This ratio can also be calculated from the results for $M = \text{N}_2$ and $M = \text{Ar}$ for each of the aforementioned studies [7–10,22] and varies from 0.56 to 0.7.

3.5. Rate coefficient determination for $M = \text{H}_2\text{O}$

Measurements by Barrett et al. [5] demonstrate that ignition in practical syngas mixtures is significantly delayed when water vapor is present in the fuel/air mixture. This is a result of the much higher collision efficiency of H_2O for reaction (9), increasing the relative overall rate of the termination reaction compared to the branching reaction. Tables 1 and 2 show the conditions and results for four experiments for $\text{CO}/\text{H}_2/\text{O}_2/\text{N}_2/\text{H}_2\text{O}$ mixtures (with 22% water vapor), for which reaction (9f) is the dominant H-atom removal mechanism prior to ignition. It should be noted that there are small fractions of CO_2 (2.3%), CH_4 (0.9%), and Ar (0.2%) in the initial mixture compositions that are not listed in Table 1 due to space limitations, however they were included in the kinetics modeling. The rate of reaction (9f) was determined by adjusting its value in the reaction mechanism to fit τ_{ign} for these four experiments. A value of $k_{9a} = 2.7 \times 10^{15} \text{ cm}^6/\text{mol}^2 \text{ s}$ and the relative collision efficiencies for reactions (9b)–(9e) from Davis et al. were used to provide values of $k_{9a-k_{9e}}$ in the mechanism. Table 3 shows the changes in calculated τ_{ign} due to adjustments in k_{9f} for the four experiments.

This demonstrates the high sensitivity of τ_{ign} to the value of k_{9f} : changing k_{9f} from -20% to $+20\%$ resulted in τ_{ign} changing by a factor of 5.1 at the most sensitive conditions. It should be noted that changing the value used for k_{9a} in the mechanism by 20% would change the results for k_{9f} by approximately 5% in the opposite direction. The average value for the four experiments is $k_{9f} = 3.3 \times 10^{16} \text{ cm}^6/\text{mol}^2 \text{ s}$, resulting in a ratio of $k_{9f}/k_{9a} = 12.2$. This is in excellent agreement with the value $k_{9f}/k_{9a} = 12$ adopted by Davis et al. from the theoretical work of Troe [23], and the aforementioned experimental results of Ashman and Haynes ($k_{9f}/k_{9a} = 10.6$ from 750 to 900 K), Michael et al. ($k_{9f}/k_{9a} = 11.6$ at room temperature), and Bates et al. ($k_{9f}/k_{9a} = 10.3$ from 1082 to 1262 K, using the averages of their measured values of k_{9f} and k_{9a}).

4. Discussion

In summary, the rate of the reaction (9a) in $\text{CO}/\text{H}_2/\text{O}_2/\text{N}_2$ mixtures over the range of conditions in this study has been determined to be

$$k_{9a(\text{M}=\text{N}_2)} = 2.7(+0.8/-0.7) \times 10^{15} \text{ cm}^6/\text{mol}^2 \text{ s}$$

from the ignition of practical $\text{CO}/\text{H}_2/\text{O}_2/\text{N}_2$ shock-heated mixtures. No temperature or pressure dependence was observed within the scatter of the results.

Equivalent results in modeling the ignition of practical $\text{CO}/\text{H}_2/\text{O}_2/\text{N}_2$ mixtures can be achieved using the pressure-dependent expressions of Bates et al. [9] for k_{9a} and the relative collision efficiencies for (9b)–(9f) adopted by Davis et al. [6]. These curves are in excellent agreement with the results of the current study, and fall within the uncertainty limits of the results of all the aforementioned recent studies [7–10,22].

The rate coefficients for reaction (9) for $\text{M} = \text{Ar}$ and $\text{M} = \text{H}_2\text{O}$ were determined to be

$$k_{9\text{argon}} = 1.9 \times 10^{15} \text{ cm}^6/\text{mol}^2 \text{ s},$$

$$k_{9f(\text{M}=\text{H}_2\text{O})} = 3.3 \times 10^{16} \text{ cm}^6/\text{mol}^2 \text{ s}.$$

These are the first experimental measurements of the rates of the title reactions at practical combustion fuel/air mixtures.

From examination of Table 4 it can be seen that reaction (24)



helps to speed up ignition in low- H_2 , high- CO mixtures at higher pressures, as pointed out in the ignition sensitivity analysis of Kalitan et al. [3,4]. Future measurements of the rate of reaction (24) would help refine kinetics models of practical syngas combustion, although for the bulk of data points utilized herein for the determination of k_9 it was of negligible importance (Table 4).

It should also be noted that at even higher pressures and lower temperatures, ignition times are no longer sensitive to the relative values of k_1 and k_9 . This is demonstrated by the discrepancy between the current kinetics model and data as presented by Petersen et al. [24]. Further experiments are required to map out the transition between chain termination via reaction (9) and chain branching via the third explosion limit for syngas-type mixtures.

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