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An updated reaction model for the high-temperature pyrolysis and oxidation of acetaldehyde

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ABSTRACT

Oxygenated biofuels such as fatty acid methyl esters or ethanol are incorporated in larger and larger amounts into conventional hydrocarbon fuels for use in internal combustion and jet engines. The use of these alternative fuels, along with new engine technology, results in an increased production of toxic pollutants among which aldehydes are the most abundant. The present study focuses on the kinetic modeling of acetaldehyde pyrolysis and oxidation. Based on new ignition delay-time measurements obtained in shock tube and the data from the literature, a comprehensive validation database was assembled. Available kinetic parameters for the most important chemical reactions are reviewed and an updated reaction model is proposed. The new reaction model enables reproducing most of the trends observed experimentally and constitutes an overall improvement as compared to standard detailed chemical models including Aramco 2.0, CaltechMech, and JetSurf.

1. Introduction

To face future fossil fuel shortage and increasingly stringent regulations, the addition of bio-fuels to conventional fossil fuels [1–6] is increasingly prevalent due to the reduction in CO_2 emissions either from exhaust measurements in some conditions [3,4] or from indirect emissions with well-to-wheel analysis [7]. Contrary to the beneficial impacts on CO_2 emissions, biofuels impact on emissions presents high variability depending on engine technologies, driving cycles or the blending levels considered. In the case of unregulated pollutants, bio-gasoline and bio-diesel combustion tends to induce an increase of a variety of carbonyl compounds, mainly aldehydes [8–14], which are being considered for specific regulations in some regions [15–17] due to their high toxicity [11,18,19]. Among aldehyde emissions from internal combustion engines, formaldehyde, acetaldehyde, and acrolein emissions are the highest carbonyl emissions [8,11,12,20]. Acetaldehyde has an important implication on urban atmospheric chemistry and air quality since it has been demonstrated as the primary precursor of peroxy acetyl nitrate (PAN). PAN has an important impact on tropospheric ozone and hydroxyl radical production [21,22].

Acetaldehyde have been extensively studied within the last century and a comprehensive review on the development of acetaldehyde decomposition mechanism has been recently made by Sivaramakrishnan et al. [23]. Nevertheless, most recent detailed reaction models have employed limited data sets for the validation of acetaldehyde kinetics. Aramco 2.0 [24] has been compared to flow reactor and shock tube data, see Supplemental material of [25]. CaltechMech [26] was validated against flame speed data. As for JetSurf, no specific validation is known to the authors but it was evaluated against flame structure data by Tao et al. [27]. Note that Aramco 1.3 was also employed by Tao et al. The most recent pyrolysis model for acetaldehyde developed by Sivaramakrishnan et al. [23] employs only two sets of experimental data from Vasiliou et al. [28,29] and Kern et al. [30].

The present study aims at developing an updated and accurate detailed reaction model to describe the kinetics of acetaldehyde pyrolysis and oxidation over a wide range of conditions. Given the large number of experimental data available in the literature, we focused only on the high-temperature conditions typically obtained in shock-tube. Comparisons with other combustion relevant data (jet-stirred reactor, flame speed and structure) are provided as Supplemental material. A comprehensive experimental data set, which covers wide ranges of compositions, conditions, and kinetics targets, has been assembled, based on the literature and new experimental work presently performed, to evaluate the predictive capabilities of the updated model and perform a comparison with selected state-of-the-art reaction models.

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Table 1

Compositions and conditions used during the experimental studies selected as a validation database. For mixture 12 and 13, the equivalence ratio is defined using the H_2 to O_2 ratio. For all mixtures, the diluent used was argon except for mixtures 25 for which Neon was used, and mixtures 26 to 28 for which krypton was used.

Mix	X_{CH3CHO}	X_i	X_{O2}	Φ	T_5 (K)	P_5(kPa)	Experimental target	Ref
1	0.005	–	0.025	0.50	1295–1537	328–392	OH^*, CH^*, CO_2^*	Present study
2	0.0086	–	0.0214	1.00	1370–1487	316–404	OH^*, CH^*, CO_2^*	Present study
3	0.0112	–	0.0187	1.50	1338–1580	306–358	OH^*, CH^*, CO_2^*	Present study
4	0.005	–	0.025	0.50	1313–1590	353	CO_2^*	[34]
5	0.01	–	0.0125	2.00	1362–1734	353	CO_2^*	[34]
6	0.01	–	0.025	1.00	1252–1475	505	CO_2^*	[34]
7	0.005	–	0.025	0.50	1274–1515	505	CO_2^*	[34]
8	0.01	–	0.05	0.50	1276–1530	505	CO_2^*	[34]
9	0.025	–	0.025	2.50	1485–1674	29–46	O_2	[35]
10	0.01	–	0.025	1.00	1404–1671	29–53	O_2	[35]
11	0.01	–	0.035	0.71	1396–1631	33–54	O_2	[35]
12		$X_{H2} = 0.01$	0.01	0.50	1252–1731	202	OH	[36]
13	0.001	$X_{H2} = 0.01$	0.01	0.50	1280–1677	148–227	OH	[36]
14	0.02	–	0.02	2.50	1400–1700	197–270	CO_2, Abs(216 nm)	[36]
15	0.02	–	0.05	1.00	1280–1620	173–258	CO_2	[36]
16	0.01	–	0.05	0.50	1300–1570	169–229	CO_2	[36]
17	0.04	–	0.03	3.33	1393–1560	224–272	Abs(3.39 µm), Em(4.68 µm)	[36]
18	0.05	–	–	∞	1013–1577	128–286	CH_3CHO, CO, CH_4, C_2H_6, C_2H_4, C_2H_2	[36]
19	0.04	–	–	∞	1329–1589	200–272	Abs(3.39 µm), Abs(200 nm), Em(4.68 µm)	[36]
20	0.01	–	–	∞	1278–1606	169–188	CH_3CHO	[37]
21	5.75E−06	–	–	∞	1400	143	H	[38]
22	6.39E−06	–	–	∞	1440	123	H	[38]
23	1.32E−06	–	–	∞	1600	133	H	[38]
24	2.62E−05	$X_{C2H5I} = 2.86E-6$	–	∞	1190	142	H	[38]
25	0.032	–	–	∞	1717	32	CH_3CHO, CO, CH_4, C_2H_4, C_2H_2	[30]
26	7.34E−07	–	–	∞	1601	25	H	[39]
27	1.19E−05	–	–	∞	1314	50	H	[39]
28	1.19E−04	$X_{C2H5I} = 1.06E-6$	–	∞	1085	35	H	[39]
29	0.001	–	–	∞	1447	162	CO	[40]
30	5.00E−05	–	–	∞	1494	151	CO	[40]

2. Experimental method and results

2.1. Experimental method

All gases were of research grade (Air Liquide). A mixture containing 2% by volume of acetaldehyde in argon was used to prepare the blends. Homogeneity of the mixtures was obtained by active mixing for one hour in a 9.25 liter vessel. Mixture compositions and experimental conditions are summarized in Table 1 (mixtures 1–3).

The shock-tube employed in the present study has been described in [31–33]. A three-section shock tube was employed to study the ignition of the acetaldehyde-oxygen-argon mixtures. The driver and driven sections have an inner diameter of 15.24 cm and respective lengths of 6.19 and 11.28 m. The test section is 2.44 m in length and has an inner diameter of 7.62 cm. A cookie-cutter (2.03 m in length with inner diameter of 7.62 cm) enables to transmit the shock wave from the driven to the test section. Before each experiment, the test section was vacuumed to a pressure equal or below 1 Pa. Nitrogen was used as the driver gas. The chemical dynamics of the mixtures was characterized using three simultaneous emission diagnostics: OH^*, CH^* and CO_2^*. Recording the signals of these three species is interesting for kinetic modeling because their precursors are different [31,33]. The time to emission peak, $\tau_{100\%}$, was used as a characteristic time of reaction for each species. The 1D shock theory along with the incident shock velocity were used to calculate the thermodynamic conditions behind the reflected shock wave. As in our previous studies, the uncertainties on the temperature and pressure behind the reflected shock are 1% whereas the uncertainty on $\tau_{100\%}$ is of 20%. Fig. 1 a) shows a typical example of emission profiles and pressure signals obtained during the present study.

2.2. Experimental results

The emission of OH^*, CH^* and CO_2^* has been used to characterize the auto-ignition in acetaldehyde-based mixtures. Experiments were performed behind reflected shock wave with the parameter ranges: $\Phi = 0.5–1.5$; $T_5 = 1295–1580$ K; and $P_5 = 306–392$ kPa. The tabulated results are given as a Supplemental material. As seen in Fig. 1 a), OH^* and CH^* peak at a similar time whereas CO_2^* peaks a few µs later. The delay-times obtained with the different species are on average within 12% to each other, which is well below the estimated 20% uncertainty of the experimental values.

Fig. 1 b) shows the time to OH^* peak measured at three different equivalence ratios. As previously observed for acrolein [33] and numerous other fuels [41–46], the ignition delay-time decreases with decreasing equivalence ratio in this high-temperature range. This decrease is generally attributed to the enhancement of the chain branching process induced by the increase of oxygen concentration [33]. The ratio of the delay-times for the rich and the lean mixtures is between 2 and 2.8 for temperatures up to 1500 K.

Based on the time to OH^* peak, the effective activation energy is 159 kJ/mol (P = 300–400 kPa) and is quantitatively consistent with the activation energy extracted from Dagaut's data [34] for acetaldehyde, 154 kJ/mol (P = 350–500 kPa). The activation energy for CH_3CHO-O_2-Ar mixtures is significantly higher than the activation energy obtained for acrolein-oxygen-argon mixtures [33], 126 kJ/mol (P = 170–420 kPa). It agrees with the value reported by Zhang et al. [45], 166 kJ/mol for butanal (P = 120–1000 kPa), but is lower than the values of Davidson et al. [46], 180 kJ/mol also for butanal (P = 130–180 kPa), and Yasunaga et al. [36], 177 kJ/mol for acetaldehyde (P = 170–270 kPa). In the present and previous studies [33,34,45,46], emission signals (OH^* and CO_2^*) were used to derive the activation energy, whereas in Yasunaga et al. [36], it was obtained from CO_2 profiles-based delay-time. Even though large discrepancies exist between the reported activation energies for various small and large n-alkanes [41,46,47,43], the activation energy measured in the present study and that reported by Dagaut et al. and Yasunaga et al. for