

Article

Dual Fuel Reaction Mechanism 2.0 including NO_x Formation and Laminar Flame Speed Calculations Using Methane/Propane/*n*-Heptane Fuel Blends

Sebastian Schuh * D and Franz Winter

Institute of Chemical, Environmental and Bioscience Engineering, TU Wien, Getreidemarkt 9/166,

1060 Vienna, Austria; franz.winter@tuwien.ac.at

* Correspondence: sebastian.schuh@tuwien.ac.at

Received: 23 December 2019; Accepted: 30 January 2020; Published: 11 February 2020



Abstract: This study presents the further development of the TU Wien dual fuel mechanism, which was optimized for simulating ignition and combustion in a rapid compression expansion machine (RCEM) in dual fuel mode using diesel and natural gas at pressures higher than 60 bar at the start of injection. The mechanism is based on the Complete San Diego mechanism with *n*-heptane extension and was attuned to the RCEM measurements to achieve high agreement between experiments and simulation. This resulted in a specific application area. To obtain a mechanism for a wider parameter range, the Arrhenius parameter changes performed were analyzed and updated. Furthermore, the San Diego nitrogen sub-mechanism was added to consider NO_x formation. The ignition delay time-reducing effect of propane addition to methane was closely examined and improved. To investigate the propagation of the flame front, the laminar flame speed of methane–air mixtures was simulated and compared with measured values from literature. Deviations at stoichiometric and fuel-rich conditions were found and by further mechanism optimization reduced significantly. To be able to justify the parameter changes performed, the resulting reaction rate coefficients were compared with data from the National Institute of Standards and Technology chemical kinetics database.

Keywords: dual fuel combustion; methane–propane–*n*-heptane mixtures; ignition delay time; reaction kinetics; reaction rate coefficient; Arrhenius parameter; sensitivity analysis; NO_x; laminar flame speed

1. Introduction

In the Paris Climate Agreement, it was negotiated that measures have to be taken to keep global warming below 2 °C [1]. To achieve this, a significant reduction of greenhouse gases is required. Electrification in the mobile sector plays a major role in achieving this goal, but also in the field of conventional combustion technology, optimization of existing and development of highly efficient technologies and advanced fuels [2,3] can make an important contribution. For example, in the transport sector, the use of dual fuel engines instead of pure diesel engines offers the potential for emission savings [4]. In the dual fuel combustion process, a mixture of air and natural gas is compressed by the piston and ignited by injection of a diesel pilot. In this operation mode, low-calorie fuel gases such as biogas can be used [5]. For emission reasons, the gas content should be as large as possible in the combustion process. Due to the high global warming potential of methane [6], which is a major component of natural gas, it is essential in dual fuel combustion that methane is completely converted and not emitted unburned. The dual fuel combustion process is very complex and not yet understood in detail.

In [7], the dual fuel combustion process was investigated experimentally and by simulations. Since diesel and natural gas consist of a huge number of different hydrocarbons, the consideration of all species



in the simulation would lead to an unmanageable simulation time. Therefore, surrogate fuels were defined for the simulation. *n*-heptane is a common diesel substitute in dual fuel investigations [8–10] and was used as a surrogate. It is therefore well suited as diesel substitute, since with a cetane number (which describes the flammability of the fuel) of 56 [11], *n*-heptane is in the range of the diesel cetane number, which has to be 51 or higher according to the DIN EN590 standard of October 2009. In analogy to diesel fuel, it is necessary to define a substitute fuel for natural gas. A frequently used substitute fuel is methane [8,10]. To better reflect the methane number (which is a measure of the knock resistance) of natural gas, a mixture of methane and propane was defined as a surrogate. In [7], in the first step, the ignition delay times (IDTs) of homogeneous methane–propane–*n*-heptane mixtures were investigated with a rapid compression machine (RCM) and a shock tube (ST) at PCFC (Physico Chemical Fundamentals of Combustion), RWTH Aachen [12,13], followed by the comparison of the measured values with simulation results using various *n*-heptane mechanisms available in the literature. For the simulations in [7], as well as the actual study, the program LOGEresearch (Version LSv1.09, LOGE AB, Lund, Sweden) [14] was used. The simulation of the RCM measurements was performed with the module "rapid compression machine" in LOGEresearch at a specific fuel composition, fuel-air equivalence ratio, starting temperature, and starting pressure of the mixture before compression. The RCM facility effects describe the non-ideal behavior of the test facility and the machine-specific compression of the mixture. The effects are considered in the simulation by reading in the effective volume profile derived from the pressure profile of the associated non-reactive RCM measurement in which oxygen was replaced by an inert gas. Details on determining the effective volume curve are available in [12,15].

As shown on the left side of Figure 1, the IDT is defined as the time between the point when the piston of the RCM reached its end position and the maximal pressure increase due to ignition of the mixture. The simulation of ST measurements was performed with the module "rapid compression machine" too, but with the difference that the temperature and pressure values reached in the ST after the shockwave reflection were used as starting values. The IDT is thus defined as the time difference between the simulation start and reaching the maximal pressure increase due to ignition as shown on the right of Figure 1. A device-specific pressure increase of 8%/ms was considered in the ST-simulation. The constant volume (CV) module of LOGEresearch was used to perform CV simulations at specified initial conditions, like pressure, temperature, and simulation time. The IDT definition is identical to that of the ST simulations.



Figure 1. Simulated pressure curve and ignition delay time (IDT)-definition for rapid compression machine (RCM) (**left**) and shock tube (ST) (**right**).

When comparing the simulation results using different *n*-heptane mechanisms in [7] over the entire parameter range considered, the most promising results were achieved with the Complete

San Diego mechanism with *n*-heptane extension [16]. The second step in [7] comprised the study of inhomogeneous mixtures. The investigation of the ignition of a diesel spray injected into air and a natural gas-air mixture experimentally as well as theoretically by computational fluid dynamics (CFD) simulations showed in part large deviations of the IDTs, which motivated the adaptation of the Complete San Diego reaction mechanism with *n*-heptane extension. By means of sensitivity and flow analyzes, reactions for the mechanism adaption were identified. The adapted mechanism is able to describe ignition phenomena in the context of natural gas-diesel dual fuel combustion. However, when considering the ignition properties of methane-propane mixtures, it could be established that the IDT-reducing effect of the propane addition to methane was overestimated. This was pointed out in [7], but a detailed treatment had to be postponed to follow-up investigations. Some changes made to the Arrhenius parameters are quite large, resulting in a specific application area of the mechanism. Due to the identified optimization potential in order to obtain a larger parameter range for the application, the mechanism was further developed. The present study deals with the detailed investigation of the kinetic-controlled ignition process focusing on homogenous fuel mixtures in order to avoid a superposition of the actual ignition properties of the mixture with the jet preparation and the non-uniform distribution of the fuel influencing the ignition process in the case of inhomogeneous mixtures. A total of 10 different homogeneous mixtures with various proportions of methane, propane and *n*-heptane in the pressure range 60 to 100 bar were investigated. An overview of the mixtures is given in Table 1. Details on the selection of the homogeneous mixtures used are available in [7].

Test Facility [−]	Fuel Composition				р	Т	Ref.	
	Mix	CH ₄ [mol%]	C ₃ H ₈ [mol%]	C ₇ H ₁₆ [mol%]	φ[-]	[bar]	[K]	
Rapid compression machine	1	100	0	0	0.526	100	906-941	[13]
	2	95	5	0	0.526	100	888-916	[13]
	3	90	10	0	0.526	100	803-898	[12]
	4	70	30	0	0.526	100	826-865	[13]
	5	92.68	4.88	2.44	0.594	60	701-877	[12]
	6	90.48	4.76	4.76	0.661	60	671–781	[12]
	7	92.68	4.88	2.44	0.594	100	709-817	[12]
	8	97.56	0	2.44	0.599	60	720-869	[12]
Shock tube	9	86.36	4.55	9.09	0.796	60	748–1187	[12]
	10	90.91	0	9.09	0.816	60	785-1284	[12]

Table 1. Overview of the homogeneous mixtures used for the optimization of the reaction mechanism including the respective proportion of methane, propane and *n*-heptane in the mixture, each in mol%, the fuel–air equivalence ratio ϕ , the pressure p in bar, and the temperature T in K.

2. Materials and Methods

The mechanism presented in [7] is based on the Complete San Diego mechanism with *n*-heptane extension [16]. As this base mechanism has been expanded since the work presented in [7] and now consists of 303 reactions instead of 301, the most recent sub-mechanism files were downloaded from the San Diego mechanism database (Complete San Diego mechanism CK_2016-12-14, Heptane Chemistry CK_2015-03-01). In addition, the nitrogen sub-mechanism (Nitrogen Chemistry CK_2018-07-23) has been added in order to be able to calculate the formation of NO_x during combustion. The compound mechanism (MechA) consists of 344 reactions and considers 75 species.

The further development process is explained in the following and is shown graphically in Figure 2. First, the Arrhenius parameter changes made in [7] were transferred to the mechanism MechA. Second, a re-evaluation of the Arrhenius parameter changes was made. In the third step, the overestimation of the IDT-reducing effect of the propane addition to methane was investigated. In the fourth step, the laminar flame speed of methane–air mixtures was simulated and compared with experimental values taken from the literature. Derived from this comparison, the final adaptation of the mechanism was performed. It should be noted that during the whole optimization process the

thermodynamic and transport data remained unchanged and therefore correspond to the original data files of the Complete San Diego mechanism.



Figure 2. Schematic representation of the mechanism development process presented in the actual study.

2.1. Update of Arrhenius Parameters Adaption

At first, the IDTs were calculated using the compound mechanism MechA (Complete San Diego mechanism, *n*-heptane, and nitrogen sub-mechanism). In the next step, the parameter changes made in [7] were transferred to the compound mechanism resulting in MechB. A comparison of the simulated IDTs using MechA and MechB is shown in Figure 3.



Figure 3. Experimental data (symbols) [12,13] versus model prediction (lines) using the mechanism MechA (solid lines) and MechB (dashed lines). The respective content of methane, propane, and *n*-heptane is given in mol% and corresponds to the values in Table 1.

In the mechanism presented in [7], the Arrhenius parameters of eight reactions were adjusted, including three methane reactions and five reactions of the *n*-heptane sub-mechanism. The main target of the adaption was to reduce the difference between the pressure curve (and derived therefrom the point of ignition) measured in a RCEM, operated in dual fuel mode with diesel and natural gas, and the corresponding CFD simulation results. The current study concentrates on the kinetically controlled ignition processes, especially in homogeneous mixtures, in order to exclude influences on the ignition due to inhomogeneities in the fuel–air mixture caused by diesel spray injection. As can be seen in

2.1.1. Update of Methane Reaction Adaption

The methane reactions used for the adjustment in MechB are listed in Table 2. The largest change of the Arrhenius parameters was made in reaction 42. Reaction 44 and 45 were adapted only slightly to fine-tune the mechanism. To compare the reaction rate coefficients before and after adaption with an as large as possible number of reference data from literature, the NIST (National Institute of Standards and Technology) chemical kinetics database [17] was accessed. For reaction 42, 84 database entries [18–90] over the temperature range 178 to 3000 K were used. In the case of reaction 44 and 45, six [68,72,89,91–93] and three [68,72,94] entries, respectively, in the temperature range 300 to 2500 K were available. Using the reference data, the reaction rate coefficients for each data set in the specified temperature interval were calculated with a temperature resolution of 1 K. With these data points, a nonlinear fit based on the extended Arrhenius approach (1):

$$k = A \cdot T^{\beta} \cdot e^{\frac{-E_A}{R \cdot T}} \tag{1}$$

with the reaction rate coefficient k, the pre-exponential factor A, the temperature exponent β , the activation energy E_A , the temperature T, and the universal gas constant R, was performed with the program Origin (OriginPro 2017, OriginLab Corporation, Northampton, MA, USA) [95], where Equation (1) has been used in the rewritten form (2):

$$k^* = \log(k) = A^* + \log\left[\left(\frac{1000}{x}\right)^{\beta}\right] - \frac{E_A \cdot x}{1000 \cdot \ln(10) \cdot R}$$
(2)

with $x = \frac{1000}{T}$ and $A^* = log(A)$ for the fitting procedure.

Table 2. Overview of methane reactions used for the adjustment in MechB.

Reaction Number	Reaction Equation
42	$CH_4 + OH \leftrightarrow H_2O + CH_3$
44	$CH_4 + O_2 \leftrightarrow CH_3 + HO_2$
45	$CH_4 + HO_2 \leftrightarrow CH_3 + H_2O_2$

The effect of adjusting the Arrhenius parameters on the reaction rate coefficients is shown in Figures 4–6. In addition to the reaction rate coefficients, the graphs also show the fit function as well as the 95% prediction band in green and the 95% confidence band in red of the fit function. The confidence band is mostly so narrow that it is usually covered by the fit curve. The data from the NIST database are represented as black open circles. Due to the plot density with a temperature resolution of 1 K, the NIST data points usually appear as black lines.



Figure 4. Comparison of the reaction rate coefficient of reaction 42 ($CH_4 + OH \leftrightarrow H_2O + CH_3$) of MechA to MechC as well as the fitted rate coefficient using reference data from the NIST (National Institute of Standards and Technology) database.



Figure 5. Comparison of the reaction rate coefficient of reaction 44 ($CH_4 + O_2 \leftrightarrow CH_3 + HO_2$) of MechA to MechC as well as the fitted rate coefficient using reference data from the NIST database.



Figure 6. Comparison of the reaction rate coefficient of reaction 45 ($CH_4 + HO_2 \leftrightarrow CH_3 + H_2O_2$) of MechA to MechC as well as the fitted rate coefficient using reference data from the NIST database.

As can be seen in Figure 4, at temperatures in excess of approximately 400 K, the reaction rate coefficient of reaction 42 in MechB lies within the 95% prediction band of the fit function, but below all reference data. This was due to the fact that the target in [7] was to optimized the mechanism for a specific parameter range. However, since the focus of the current study is on developing a mechanism for a larger parameter range, the parameter adjustments carried out in [7] were revised so that for temperatures higher than 300 K the resulting temperature-dependent reaction rate coefficient of reaction 42 in the resulting mechanism MechC is within the range of reference data. In the case of reaction 44 and 45, only minor adjustments were made for fine-tuning, with the pre-exponential factors *A* remaining unchanged, the temperature exponent β being increased and decreased from 0 to 0.02 and -0.05, respectively, and the activation energy E_A being reduced by 7.7% and 6.7%, respectively, compared to the original parameters of the San Diego mechanism.

2.1.2. Update of *n*-heptane Mechanism Adaption

Due to the difference between the measured and calculated IDT for mixtures containing about 9 mol% *n*-heptane (mix 9 and 10 in Table 1), a sensitivity analysis was performed with LOGEresearch using mix 9 to determine the most influential reactions to total reactivity. The starting point of the sensitivity analysis is found in Equation (3):

$$\frac{\partial Y}{\partial t} = P(Y, u, T) + \omega(Y, T)$$
(3)

where *Y* is the n-dimensional vector of the mass fractions of the n species considered by the mechanism, *T* is the temperature, *u* the velocity field, *P* represents the spatial differential operator, and ω the chemical source term. In the course of the analysis, the influence of a small perturbation of the reaction rate coefficient on the concentration of a selected species is investigated. A detailed mathematical description can be found in [96,97]. All species considered by the mechanism, as well as the temperature, can be selected as an analysis target in LOGEresearch. Since the IDT- and temperature-sensitivity are correlated as shown by Ji et al. [98], the temperature was chosen as the analysis target in this study. For the sensitivity analysis, MechA was used to avoid any influence from the Arrhenius parameter adjustments made. As an example, Figure 7 shows the time-dependent sensitivity curve of reaction

274 ($C_7H_{16} + OH \leftrightarrow H_2O + n - C_7H_{15}$). In addition, the pressure curve and the first derivative of the pressure curve is shown. When searching for the maximum positive or negative sensitivity value, only the range of values between the simulation start and ignition (maximum of first derivative of pressure curve) of the mixture was considered. In the diagram, this range is highlighted in blue. The temperature-dependent course of the maximal sensitivity values can be seen in Figure 8 for the 16 most sensitive reactions.



Figure 7. Simulated time-dependent sensitivity towards temperature of the reaction 274 (C_7H_{16} + OH \leftrightarrow H₂O + *n*-C₇H₁₅) and the pressure profile in the area of ignition calculated at 800 K and 60 bar, using mix 9 from Table 1.



Figure 8. Reaction sensitivity towards temperature simulated with mix 9 from Table 1.

Based on the differences between the measured and calculated IDTs and the course of sensitivities, the changes in Arrhenius parameters made to the *n*-heptane sub-mechanism were re-evaluated. As a result, instead of five *n*-heptane reactions, the number of reactions used for adaption could be reduced to one lumped reaction (reaction 302 in Figure 8), which considers the branching decomposition

 $n-C_7$ -OQOOH \leftrightarrow OH + CH₂O + CO + C₂H₄ + $n-C_3$ H₇. The change made in this reaction is a reduction of the activation energy by about 1%. A comparison of the reaction rate coefficients of reaction 302 in its original state (MechA), with the parameter changes transferred from [7] (MechB) and after revision of the parameter changes (MechC) is shown in Figure 9. Because this reaction is not included in the NIST database, no comparison with literature data is apparent.



Figure 9. Comparison of the reaction rate coefficient of reaction $302 (n-C_7-OQOOH \leftrightarrow OH + CH_2O + CO + C_2H_4 + n-C_3H_7)$ of MechA to MechC.

2.2. Investigating the Influence of Propane Addition

In Figure 3, amongst others, the IDT of a methane–air mixture without propane addition and a propane admixture of 5, 10, and 30 mol% is shown. It can be observed that the deviation between measured and calculated IDTs increases with increasing propane concentration, suggesting that the IDT-reducing effect of the propane addition is overestimated by the mechanism. In order to determine which reactions have a significant effect on IDT in a methane–propane–air mixture, a sensitivity analysis towards temperature was performed with MechA. For the analysis, mix 4 in Table 1 with a propane content of 30 mol% was used. The left side of Figure 10 shows the temperature-dependent progressions of the 10 most sensitive reactions. For the sake of completeness, the measured IDTs and the values calculated with MechA for methane–propane mixtures with 0, 5, 10, and 30 mol% propane content (mix 1 to 4 in Table 1) are shown on the right-hand side of Figure 10.



Figure 10. Sensitivity towards temperature simulated with MechA and mix 4 from Table 1 (left); measured IDTs (symbols) and simulated values (lines) using MechA for different methane–propane mixtures (right). The content of methane and propane is given in mol% and corresponds to mix 1 to 4 in Table 1.

Based on the course of the reaction sensitivities and the temperature-dependent deviation between measured and calculated IDTs for the various methane–propane mixtures, five reactions were selected for the mechanism adaptation. Figure 11 shows an extract of the propane oxidation scheme derived from MechA. The five reactions selected for adaptation, including the OH- and HO₂-radical attack on propane, the oxygen addition on the propyl and hydroperoxyalkyl radical as well as the decomposition of carbonylhydroperoxide, are marked in red. In addition to the corresponding reaction numbers, the species with which the educts react are indicated. All reactions used for the adaption process are summarized in Table 3.



Figure 11. Extract from the propane oxidation scheme derived from MechA. Reactions with modified Arrhenius parameters to improve the calculation of the propane influence on the IDT are labeled in red.

Reaction Number	Reaction Equation
235	$C_3H_8 + OH \leftrightarrow n-C_3H_7 + H_2O$
238	$C_3H_8 + HO_2 \leftrightarrow n - C_3H_7 + H_2O_2$
244	$n-C_3H_7 + O_2 \leftrightarrow C_3H_6 + HO_2$
247	$C_{3}H_{6}OOH + O_{2} \leftrightarrow OC_{3}H_{5}OOH + OH$
248	$OC_3H_5OOH \leftrightarrow CH_2CHO + CH_2O + OH$

Table 3. Overview of the reactions used to adjust the calculation of the propane influence on the IDT.

As described in the previous chapter, reference data from the NIST chemical kinetics database were used, if available, to evaluate the effect of changes in the Arrhenius parameters on the reaction rate coefficients. In the case of reaction 235, six entries [39,79,99–102] were available in the temperature range 250 to 1220 K. For reaction 238, two entries [103,104] could be found in the database for temperature values between 300 and 2500 K. However, for adjusting the Arrhenius parameters of reaction 238, the parameters used in the AramcoMech 3.0 [105] mechanism served as template. In total, nine sources [18,73,103,106–111] were available for comparison purposes for reaction 244 between 296 and 2000 K. No reference data were included in the NIST database for reactions 247 and 248, which is why a graphical comparison with reference data is missing. Therefore, care was taken not to make too large changes to the parameters. The pre-exponential factors and the temperature exponents of the reaction 247 and 248 remained unchanged, the absolute values of the activation energy were increased by 7.1% and 9.3%, respectively. Figures 12–16 shows the temperature-dependent course of the reaction rate coefficients before (MechA) and after parameter adjustment (MechD).



Figure 12. Comparison of the reaction rate coefficient of reaction 235 ($C_3H_8 + OH \leftrightarrow n-C_3H_7 + H_2O$) of MechA and MechD as well as the fitted rate coefficient using reference data from the NIST database.



Figure 13. Comparison of the reaction rate coefficient of reaction 238 ($C_3H_8 + HO_2 \leftrightarrow n-C_3H_7 + H_2O_2$) of MechA, MechD and AramcoMech 3.0 as well as the fitted rate coefficient using reference data from the NIST database.



Figure 14. Comparison of the reaction rate coefficient of reaction 244 (n-C₃H₇ + O₂ \leftrightarrow C₃H₆ + HO₂) of MechA and MechD as well as the fitted rate coefficient using reference data from the NIST database.



Figure 15. Comparison of the reaction rate coefficient of reaction 247 ($C_3H_6OOH + O_2 \leftrightarrow OC_3H_5OOH + OH$) of MechA and MechD.



Figure 16. Comparison of the reaction rate coefficient of reaction 248 ($OC_3H_5OOH \leftrightarrow CH_2CHO + CH_2O + OH$) of MechA and MechD.

2.3. Laminar Flame Speed Calculation

After ignition by injection of a diesel pilot in dual fuel combustion, the flame front spreads into the surrounding natural gas–air mixture in the combustion chamber. To correctly reproduce the propagation velocity of this front, the mechanism must be able to correctly calculate the laminar flame speed. In order to assess the extent to which the mechanism can reproduce the laminar flame speed, a comparison was made between simulated laminar flame speed values of methane–air mixtures (since methane is the main component of natural gas) and measurements taken from the literature. The LOGEresearch module "Freely Propagating" was used to simulate the flame speed. In addition to the gas composition, temperature, pressure, and fuel–air equivalence ratio, the gridding settings must be defined for the flame speed calculation. The grid used consisted of 1000 points with a minimum discretization size of 10^{-9} m and a maximum discretization size of 5×10^{-2} m. In the simulation, the effect of thermal diffusion was taken into account; the influence of radiation effects was neglected. The experimental determined flame speed values were taken from the supplementary materials of the publication of Ranzi et al. [112]. The gas mixtures investigated include methane–air mixtures with a start temperature of 300 to 400 K in the pressure range of 10 to about 20 bar and a fuel–air equivalence ratio between 0.7 and 1.4. The comparison between measured and calculated laminar flame speeds is shown in Figure 17.



Figure 17. Measured laminar flame speeds (symbols) of methane–air mixtures [112] as function of the fuel–air equivalence ratio ϕ at different pressures and temperatures in comparison with simulated values (lines) using MechD.

For a fuel–air equivalence ratio of less than 0.9, the experimental values can be reproduced quite well by the simulation. When increasing the equivalence ratio, a deviation between the calculated and measured values is determinable, whereby the simulation underestimates the laminar flame speed. To improve the reproduction of the laminar flame speed, the "Freely Propagating" module from LOGEresearch was used to perform sensitivity analyses using MechD for detecting influential reactions to the flame speed. For each of the five parameter sets shown in Figure 17, a sensitivity analysis was performed and the 10 most sensitive reactions were filtered out. The reactions, which were among the 10 most sensitive reactions for all five investigated parameter sets, are shown in Figures 18 and 19.



Figure 18. Analysis of the most sensitive reactions regarding the laminar flame speed as function of the fuel–air equivalence ratio ϕ using a methane–air mixture at 300 K and 10.133 (**left**) and 20.265 bar (**right**).



Figure 19. Analysis of the most sensitive reactions regarding the laminar flame speed as function of the fuel–air equivalence ratio ϕ using a methane–air mixture at 300 (**left**), 360 (**middle**), and 400 K (**right**) and 10 bar.

Based on the sensitivity progressions and the detected deviations between measured and calculated laminar flame speed, reactions 1, 25, and 56 (listed in Table 4) were selected for the mechanism adjustment.

Reaction Number	Reaction Equation
1	$H + O_2 \leftrightarrow OH + O$
25	$CO + OH \leftrightarrow CO_2 + H$
56	$CH_3 + H (+M) \leftrightarrow CH_4 (+M)$

Table 4. Reactions selected for adjusting the laminar flame speed calculation.

In the case of reaction 56, not individual Arrhenius parameters were adapted, but the entire data set was changed to the dataset used in the mechanism AramcoMech 3.0, also including the third body collision coefficients and the LOW and TROE parameters. When adjusting the Arrhenius parameters of reaction 1 and 25, a comparison with reference data from the NIST database was made, with 68 entries [68,69,72,73,113–168] for reaction 1 and 83 entries [25,26,36,37,43,51,68,73–75,134,137,140,164,169–219] for reaction 25 available for this purpose in the temperature range 250 to 5500 K and 80 to 3150 K, respectively. Figures 20 and 21 show the reaction rate coefficients before (MechD) and after adaption (TU Wien dual fuel mechanism 2.0) and the reference data from the NIST database. For the adjustment of the Arrhenius parameters of reaction 25, the reaction rate coefficients used in the mechanism of Zsely et al. [220] and Varga et al. [221] served as guideline, therefore the corresponding rate coefficients are presented in Figure 21.



Figure 20. Comparison of the reaction rate coefficient of reaction 1 (H + $O_2 \leftrightarrow OH + O$) of MechA and TU Wien dual fuel mechanism 2.0 as well as the fitted rate coefficient using reference data from the NIST database.





Figure 21. Comparison of the reaction rate coefficient of reaction 25 (CO + OH \leftrightarrow CO₂ + H) of MechA, TU Wien dual fuel mechanism 2.0, Zsely et al. [220], Varga et al. [221] as well as the fitted rate coefficient using reference data from the NIST database.

3. Results and Discussion

In the course of the mechanism optimization process, in total the Arrhenius parameters of 12 reactions were adjusted. Table 5 provides an overview and a brief explanation why the respective reactions were used for the adaption process and which mechanism resulted from the individual adaptation steps.

Step	React.	Reaction Equation	Purpose	Mech.
1	42	$CH_4 + OH \leftrightarrow H_2O + CH_3$	Undate of	MachC
	44	$CH_4 + O_2 \leftrightarrow CH_3 + HO_2$	adjustments made	
	45	$CH_4 + HO_2 \leftrightarrow CH_3 + H_2O_2$		Meene
	302	$n-C_7-OQOOH \leftrightarrow OH + CH_2O + CO + C_2H_4 + n-C_3H_7$	шт [7]	
2	235	$C_3H_8 + OH \leftrightarrow n - C_3H_7 + H_2O$		MechD
	238	$C_3H_8 + HO_2 \leftrightarrow n - C_3H_7 + H_2O_2$	Commenting of an and a second	
	244	$n-C_3H_7 + O_2 \leftrightarrow C_3H_6 + HO_2$	Correcting propane	
	247	$C_3H_6OOH + O_2 \leftrightarrow OC_3H_5OOH + OH$	influence on ID1	
	248	$OC_3H_5OOH \leftrightarrow CH_2CHO + CH_2O + OH$		
3	1	$H + O_2 \leftrightarrow OH + O$	Correcting flame	TU Wien
	25	$CO + OH \leftrightarrow CO_2 + H$	contecting fidilite	dual fuel
	56	$CH_3 + H (+M) \leftrightarrow CH_4 (+M)$	speed calculation	mech. 2.0

Table 5. Overview of the reactions used for the mechanism adaption, the purpose of the adaptation and the resulting mechanism.

3.1. IDT Calculation with TU Wien Dual Fuel Mechanism 2.0

The comparison of the IDT simulated with the Complete San Diego mechanism with heptane and nitrogen extension (MechA) with the mechanism MechB, in which the Arrhenius parameter changes carried out in [7] were transferred, was already shown in Figure 3. In the following Figure 22, the comparison between the mechanism MechB and the final version TU Wien dual fuel mechanism 2.0 is presented, in which the parameter changes carried out in MechB were re-evaluated, the propane influence on the IDT was corrected and the flame speed calculation was adapted.



Figure 22. Experimental data (symbols) [12,13] versus model prediction (lines) using the mechanism MechB (dashed lines) and the final TU Wien dual fuel mechanism 2.0 (solid lines). The diagram in the upper left corner highlights the comparison between measured and calculated IDTs of methane–propane mixtures. The respective content of methane, propane, and *n*-heptane is given in mol% and corresponds to the values in Table 1.

By adapting the Arrhenius parameter of the reactions 235, 238, 244, 247, and 248, the TU Wien dual fuel mechanism 2.0 can reproduce the IDT-reducing effect of propane addition to a methane–air mixture well as shown in the diagram in the upper left corner of Figure 22. With the maximum investigated addition of 30 mol% propane, at which a significant deviation between the simulated and measured values was detected before the mechanism adaptation, the calculated values now lie within the uncertainty of the measured values. For the most part, an approximation of the calculated values to the experimental data can also be seen for the other investigated methane–propane mixtures. In the case of mixtures with an *n*-heptane content of less than 5 mol%, an almost continuous approximation to the experimental values can be observed. Since the *n*-heptane sub-mechanism changes transferred from [7] were adjusted and approximated to the original parameters of the San Diego mechanism, the simulated IDTs of the mixtures with the highest investigated *n*-heptane content of approximately 9 mol% show an increase in the temperature range from 850 to 1100 K, whereby the measured values at 950 K are therefore reproduced well, but between 1010 and 1080 K the IDT is overestimated.

3.2. Laminar Flame Speed Calculation with TU Wien Dual Fuel Mechanism 2.0

To adapt the laminar flame speed calculation, the Arrhenius parameters of the reactions 1, 25, and 56 were modified. The changes made had only a marginal effect on the calculated IDTs in the investigated parameter range, therefore the representation of the IDTs calculated with MechD is skipped. By the reaction parameter adjustment, the deviation between the measured and calculated laminar flame speed values could be reduced significantly. A comparison of the simulation results before and after the adjustment of the Arrhenius parameters of reaction 1, 25, and 56 is shown in Figure 23.



Figure 23. Measured laminar flame speeds of methane–air mixtures [112] as function of the fuel–air equivalence ratio ϕ in comparison with simulated values before (MechD; dashed lines) and after the Arrhenius parameter adaption of reactions 1, 25, and 56 (TU Wien dual fuel mechanism 2.0; solid lines).

3.3. Influence of Nitrogen Sub-Mechanism on IDT and Laminar Flame Speed Calculation

To determine the influence of the nitrogen sub-mechanism on the calculation of the IDT and the laminar flame speed, the nitrogen sub-mechanism was removed from the TU Wien dual fuel mechanism 2.0 for test purposes, followed by a re-run of the simulations. In Figures 24 and 25, the simulation results with the TU Wien dual fuel mechanism 2.0 are shown as lines, the simulation results with the nitrogen sub-mechanism are indicated with symbols.



Figure 24. IDT simulation with the TU Wien dual fuel mechanism 2.0 (lines) and the TU Wien dual fuel mechanism 2.0 without the nitrogen sub-mechanism (symbols). The respective content of methane, propane and *n*-heptane is given in mol% and corresponds to the values in Table 1.



Figure 25. Simulated laminar flame speed values as function of the fuel–air equivalence ratio ϕ using the TU Wien dual fuel mechanism 2.0 (lines) and the TU Wien dual fuel mechanism 2.0 without the nitrogen sub-mechanism (symbols).

The comparison shows that the nitrogen sub-mechanism has a negligible influence on the calculation of the IDT in the parameter range under consideration. The same applies to the calculation of the laminar flame speed, where no differences can be seen when the nitrogen sub-mechanism is taken into account or neglected.

It can be stated that by the modification of the TU Wien mechanism for dual fuel combustion presented in [7], the mechanism TU Wien dual fuel mechanism 2.0 was developed, which can reproduce the IDT of the investigated homogeneous methane, methane–propane, methane–*n*-heptane, and methane–propane–*n*-heptane mixtures in the pressure range 60 to 100 bar well and provides improved results in the calculation of the laminar flame speed of methane–air mixtures. The mechanism and associated transport and thermodynamic files are available online and can be downloaded from supplementary materials.

4. Conclusions

To describe the dual fuel combustion process and the ignition by injection of a diesel pilot into a natural gas–air mixture, the TU Wien mechanism for dual fuel combustion based on the Complete San Diego mechanism with heptane extension was developed and presented in a previous study. With this mechanism, it is possible to reproduce pressure curves measured with a rapid compression expansion machine operated in dual fuel mode using diesel and natural gas, satisfactorily. The mechanism was attuned to the rapid compression expansion machine measurements to achieve a high agreement between experiments and simulations, which results in a specific field of application for the mechanism. In order to simulate the ignition and combustion process within a manageable period of time, diesel and natural gas had to be replaced by substitutes due to the large number of species contained in the fuels. *n*-heptane was used as a one-component substitute of diesel, a mixture of methane and propane served as natural gas surrogate.

To obtain a mechanism applicable for a wider parameter range as well as to be able to calculate the formation of NO_x during combustion, the TU Wien dual fuel mechanism has been extended and further developed, leading to the TU Wien dual fuel mechanism 2.0 presented in this study. The focus in the optimization process was on the kinetically controlled ignition process. Therefore, the ignition properties of homogeneous mixtures with different proportions of methane, propane, and *n*-heptane were investigated as shown in Table 1, whereby, depending on the composition, the fuel–air equivalence ratio varied between 0.526 and 0.816, the pressure value between 60 and 100 bar, and the temperature ranged from 671 to 1284 K. The simulated values were compared with rapid compression machine and shock tube measurement results. As a first step, the Arrhenius parameter changes made in the previous study were revised to ensure that the reaction rate coefficient changes are supported by literature data taken from the National Institute of Standards and Technology chemical kinetics database. Since the ignition delay time-reducing effect of propane addition to a methane–air mixture was overestimated, by means of a sensitivity analysis using a mixture consisting of 70 mol% methane and 30 mol% propane, reactions with a significant impact on the ignition delay time were determined. By adapting the Arrhenius parameters of five reactions from the propane oxidation scheme, the overestimated ignition delay time-reducing effect of propane addition to methane–air mixtures was corrected.

After ignition by injecting a diesel pilot into the natural gas–air mixture in the dual fuel combustion process, the flame front spreads into the entire combustion chamber. In order to reproduce the flame propagation precisely, the mechanism must be able to correctly calculate the laminar flame speed. Since the background gas in the combustion chamber (mixture of natural gas and air) consists mainly of methane, the laminar flame speed of methane–air mixtures at pressures between 10 and about 20 bar, temperatures of 300 to 400 K and fuel–air equivalence ratios in the range of 0.7 to 1.4 was simulated and compared with experimental values from literature. The comparison revealed an underestimation of the laminar flame speed by the simulation at a fuel–air equivalence ratio higher than 0.9. By means of sensitivity analyses, those reactions were determined, which were suitable for adapting the mechanism in the corresponding fuel–air equivalence ratio range. A total of three reactions were used for the laminar flame speed adaptation process.

In both the ignition delay time calculation and the calculation of the laminar flame speed, a partly significant reduction of the difference between measurement and simulation results could be achieved by adapting the original mechanism. Especially, the improved consideration of the ignition delay time-reducing effect of propane addition to methane–air mixtures should be emphasized. Despite its compactness, the mechanism, which consists of 344 reactions and takes into account 75 species, is able to approximate the ignition delay time well over a large part of the investigated parameter range. With measured values between 0.06 ms and 92 ms, ignition delay times over about three orders of magnitude are covered.

In order not to restrict the possible field of applications of the mechanism by the optimization process, a careful adjustment of the Arrhenius parameters was performed to ensure that the resulting changes in the reaction rate coefficients could be justified by means of literature data. Therefore, more than 200 entries from the National Institute of Standards and Technology database were used to compare the adjusted reaction rate coefficients with data from the literature, where available. By specifying the temperature dependent courses of all modified reaction rate coefficients in this article in comparison to the available reference data, the user of the mechanism is able to determine and assess to what extent the mechanism is suitable for use under the envisaged condition.

Supplementary Materials: The following are available online at http://www.mdpi.com/1996-1073/13/4/778/s1, Adapted reaction mechanism and associated thermodynamic- and transport data (ZIP).

Author Contributions: Conceptualization, S.S. and F.W.; methodology, S.S.; software, S.S.; validation, S.S.; formal analysis, S.S.; investigation, S.S.; resources, S.S.; data curation, S.S. and F.W.; writing—original draft preparation, S.S.; writing—review and editing, S.S. and F.W.; visualization, S.S.; supervision, F.W.; project administration, F.W.; funding acquisition, F.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Austrian Research Promotion Agency (FFG), grant number 850690.

Acknowledgments: We would like to show our gratitude to LOGE AB for providing the simulation software LOGEresearch. Open Access Funding by TU Wien.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Paris Agreement. Available online: https://ec.europa.eu/clima/policies/international/negotiations/paris_en (accessed on 20 November 2019).
- 2. Ge, J.C.; Kim, H.Y.; Yoon, S.K.; Choi, N.J. Reducing volatile organic compound emissions from diesel engines using canola oil biodiesel fuel and blends. *Fuel* **2018**, *218*, 266–274. [CrossRef]
- 3. Anto, S.; Mukherjee, S.S.; Muthappa, R.; Mathimani, T.; Deviram, G.; Kumar, S.S.; Verma, T.N.; Pugazhendhi, A. Algae as green energy reserve: Technological outlook on biofuel production. *Chemosphere* **2019**, 242, 125079. [CrossRef] [PubMed]
- 4. Schlick, H. Potentials and challenges of gas and dual-fuel engines for marine application. In Proceedings of the 5th CIMAC CASCADES, Busan, Korea, 23 October 2014.
- Yoshimoto, Y.; Kinoshita, E.; Luge, S.; Ohmura, T. Combustion Characteristics of a Dual Fuel Diesel Engine with Natural Gas (Lower limit of Cetane Number for Ignition of the Fuel). SAE Int. J. Fuels Lubr. 2012, 5, 1165–1173. [CrossRef]
- 6. Understanding Global Warming Potentials. Available online: https://www.epa.gov/ghgemissions/ understanding-global-warming-potentials (accessed on 9 December 2019).
- 7. Schuh, S.; Frühhaber, J.; Lauer, T.; Winter, F. A Novel Dual Fuel Reaction Mechanism for Ignition in Natural Gas–Diesel Combustion. *Energies* **2019**, *12*, 4396. [CrossRef]
- Eder, L.; Ban, M.; Pirker, G.; Vujanovic, M.; Priesching, P.; Wimmer, A. Development and Validation of 3D-CFD Injection and Combustion Models for Dual Fuel Combustion in Diesel Ignited Large Gas Engines. *Energies* 2018, 11, 643. [CrossRef]
- 9. Ritzke, J.; Andree, S.; Theile, M.; Henke, B.; Schleef, K.; Nocke, J.; Hassel, E. Simulation of a Dual-Fuel Large Marine Engines using combined 01-D and 3-D Approaches. In Proceedings of the CIMAC Congress, Helsinki, Finland, 6–10 June 2016.
- 10. Li, Y.; Li, H.; Guo, H.; Li, Y.; Yao, M. A numerical investigation on methane combustion and emissions from a natural gas-diesel dual fuel engine using CFD model. *Appl. Energy* **2017**, *205*, 153–162. [CrossRef]
- 11. Tschöke, H. Diesel- und Benzindirekteinspritzung V: Spraybildung, Simulation, Applikation, Messtechnik: Mit 29 Tabellen; Expert-Verlag: Renningen, Germany, 2009.
- 12. Schuh, S.; Ramalingam, A.K.; Minwegen, H.; Heufer, K.A.; Winter, F. Experimental Investigation and Benchmark Study of Oxidation of Methane–Propane–n-Heptane Mixtures at Pressures up to 100 bar. *Energies* **2019**, *12*, 3410. [CrossRef]
- Pachler, R.F.; Ramalingam, A.K.; Heufer, K.A.; Winter, F. Reduction and validation of a chemical kinetic mechanism including necessity analysis and investigation of CH₄/C₃H₈ oxidation at pressures up to 120 bar using a rapid compression machine. *Fuel* **2016**, *172*, 139–145. [CrossRef]
- 14. LOGEsoft. Available online: https://logesoft.com/ (accessed on 16 May 2019).
- 15. Sung, C.-J.; Curran, H.J. Using rapid compression machines for chemical kinetics studies. *Prog. Energy Combust. Sci.* **2014**, *44*, 1–18. [CrossRef]
- 16. Chemical-Kinetic Mechanisms for Combustion Applications, San Diego Mechanism Web Page, Mechanical and Aerospace Engineering (Combustion Research), University of California at San Diego. Available online: http://combustion.ucsd.edu (accessed on 4 October 2019).
- Manion, J.A.; Huie, R.E.; Levin, R.D.; Burgess, D.R., Jr.; Orkin, V.L.; Tsang, W.; McGivern, W.S.; Hudgens, J.W.; Knyazev, V.D.; Atkinson, D.B.; et al. *NIST Chemical Kinetics Database*, *NIST Standard Reference Database* 17; Version 7.0 (Web Version), Data Version 2015.09; National Institute of Standards and Technology: Gaithersburg, MD, USA, 2015.
- 18. Baker, R.R.; Baldwin, R.R.; Walker, R.W. The use of the H₂+O₂ reaction in determining the velocity constants of elementary reaction in hydrocarbon oxidation. *Symp. (Int.) Combust.* **1971**, *13*, 291–299. [CrossRef]
- Baulch, D.L.; Craven, R.J.B.; Din, M.; Drysdale, D.D.; Grant, S.; Richardson, D.J.; Walker, A.; Watling, G. Rates of hydroxy radical reactions with methane, ethane and propane over the temperature range 403–696 K. J. *Chem. Soc. Faraday Trans.* 1 *Phys. Chem. Condens. Phases* 1983, *79*, 689–698. [CrossRef]
- 20. Bonard, A.; Daële, V.; Delfau, J.-L.; Vovelle, C. Kinetics of OH Radical Reactions with Methane in the Temperature Range 295–660 K and with Dimethyl Ether and Methyl-tert-butyl Ether in the Temperature Range 295–618 K. *J. Phys. Chem. A* 2002, *106*, 4384–4389. [CrossRef]

- 21. Bott, J.F.; Cohen, N. A shock tube study of the reaction of the hydroxyl radical with H₂, CH₄, c-C5H10, and i-C4H10. *Int. J. Chem. Kinet.* **1989**, *21*, 485–498. [CrossRef]
- 22. Bryukov, M.G.; Knyazev, V.D.; Lomnicki, S.M.; McFerrin, C.A.; Dellinger, B. Temperature-Dependent Kinetics of the Gas-Phase Reactions of OH with Cl₂, CH₄, and C₃H₈. *J. Phys. Chem. A* **2004**, *108*, 10464–10472. [CrossRef]
- 23. Calpini, B.; Jeanneret, F.; Bourqui, M.; Clappier, A.; Vajtai, R.; van den Bergh, H. Direct measurement of the total reaction rate of OH in the atmosphere. *Analusis* **1999**, *27*, 328–336. [CrossRef]
- 24. Cox, R.A.; Derwent, R.G.; Eggleton, A.E.J.; Lovelock, J.E. Photochemical oxidation of halocarbons in the troposphere. *Atmos. Environ.* (1967) **1976**, *10*, 305–308. [CrossRef]
- 25. Cox, R.A.; Derwent, R.G.; Holt, P.M. Relative rate constants for the reactions of OH radicals with H₂, CH₄, CO, NO and HONO at atmospheric pressure and 296 K. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **1976**, *72*, 2031–2043. [CrossRef]
- 26. Davis, D.D.; Fischer, S.; Schiff, R. Flash photolysis-resonance fluorescence kinetics study: Temperature dependence of the reactions $OH + CO \rightarrow CO_2 + H$ and $OH + CH_4 \rightarrow H_2O + CH_3$. *J. Chem. Phys.* **1974**, *61*, 2213–2219. [CrossRef]
- 27. Dixon-Lewis, G.; Williams, A. Some observations on the combustion of methane in premixed flames. *Symp.* (*Int.*) *Combust.* **1967**, *11*, 951–958. [CrossRef]
- 28. Dunlop, J.R.; Tully, F.P. A kinetic study of hydroxyl radical reactions with methane and perdeuterated methane. *J. Phys. Chem.* **1993**, *97*, 11148–11150. [CrossRef]
- Ernst, J.; Wagner, H.G.; Zellner, R. A Combined Flash Photolysis/Shock-Tube Study of the Absolute Rate Constants for Reactions of the Hydroxyl Radical with CH₄ and CF3H around 1300 K. *Ber. Bunsenges. Phys. Chem.* 1978, 82, 409–414. [CrossRef]
- 30. Fairchild, P.W.; Smith, G.P.; Crosley, D.R. A laser pyrolysis/laser fluorescence technique for combustion chemical kinetics. *Symp. (Int.) Combust.* **1982**, *19*, 107–115. [CrossRef]
- 31. Felder, W.; Madronich, S. High Temperature Photochemistry (HTP): Kinetics and Mechanism Studies of Elementary Combustion Reactions over 300-1700 K. *Combust. Sci. Technol.* **1986**, *50*, 135–150. [CrossRef]
- 32. Fenimore, C.P.; Jones, G.W. Rate of reaction of methane with H atoms and OH radicals in flames. *J. Phys. Chem.* **1961**, *65*, 2200–2203. [CrossRef]
- 33. Finlayson-Pitts, B.J.; Ezell, M.J.; Jayaweera, T.M.; Berko, H.N.; Lai, C.C. Kinetics of the reactions of OH with methyl chloroform and methane: Implications for global tropospheric OH and the methane budget. *Geophys. Res. Lett.* **1992**, *19*, 1371–1374. [CrossRef]
- 34. Fristrom, R.M. Radical concentrations and reactions in a methane-oxygen flame. *Symp. (Int.) Combust.* **1963**, *9*, 560–575. [CrossRef]
- 35. Gierczak, T.; Talukdar, R.K.; Herndon, S.C.; Vaghjiani, G.L.; Ravishankara, A.R. Rate Coefficients for the Reactions of Hydroxyl Radicals with Methane and Deuterated Methanes. *J. Phys. Chem. A* **1997**, *101*, 3125–3134. [CrossRef]
- Gordon, S.; Mulac, W.A. Reaction of the OH (X2π) Radical Produced by the Pulse Radiolysis of Water Vapor. Proc. Symp. Chem. Kinet. Data Upper Lower Atmos. 1975, 7, 289–299.
- 37. Greiner, N.R. Hydroxyl-Radical Kinetics by Kinetic Spectroscopy. I. Reactions with H₂, CO, and CH₄ at 300 °K. *J. Chem. Phys.* **1967**, *46*, 2795–2799. [CrossRef]
- Greiner, N.R. Hydroxyl Radical Kinetics by Kinetic Spectroscopy. IV. Some Deuterium Isotope Effects. J. Chem. Phys. 1968, 48, 1413. [CrossRef]
- 39. Greiner, N.R. Hydroxyl Radical Kinetics by Kinetic Spectroscopy. VI. Reactions with Alkanes in the Range 300–500 °K. *J. Chem. Phys.* **1970**, *53*, 1070–1076. [CrossRef]
- 40. Hong, Z.; Davidson, D.F.; Lam, K.-Y.; Hanson, R.K. A shock tube study of the rate constants of HO₂ and CH₃ reactions. *Combust. Flame* **2012**, *159*, 3007–3013. [CrossRef]
- 41. Horne, D.G.; Norrish, R.G.W. Rate of H-abstraction by OH from Hydrocarbons. *Nature* **1967**, *215*, 1373–1374. [CrossRef]
- 42. Howard, C.J.; Evenson, K.M. Rate constants for the reactions of OH with CH₄ and fluorine, chlorine, and bromine substituted methanes at 296 K. *J. Chem. Phys.* **1976**, *64*, 197–202. [CrossRef]
- Husain, D.; Plane, J.M.; Slater, N.K.H. Kinetic investigation of the reactions of OH (X²π) with the hydrogen halides, HCl, DCl, HBr and DBr by time-resolved resonance fluorescence (A²Σ^{+−}X²π). *J. Chem. Soc. Faraday Trans.* 2 1981, 77, 1949–1962. [CrossRef]

- Jeong, K.M.; Kaufman, F. Kinetics of the reaction of hydroxyl radical with methane and with nine chlorineand fluorine-substituted methanes. 1. Experimental results, comparisons, and applications. *J. Phys. Chem.* 1982, *86*, 1808–1815. [CrossRef]
- 45. Jonah, C.D.; Mulac, W.A.; Zeglinski, P. Rate Constants for the Reaction of OH + CO, OD + CO, and OH + Methane as a Function of Temperature. *J. Phys. Chem.* **1984**, *88*, 4100–4104. [CrossRef]
- 46. Lancar, I.T.; LeBras, G.; Poulet, G. Redetermination de la constante de vitesse de la reaction CH₄ + OH et son implication atmospherique. *C.R. Acad. Sc. Paris* **1992**, *315*, 1487–1492.
- 47. Madronich, S.; Felder, W. Direct measurements of the rate coefficient for the reaction OH+CH₄ → CH₃+H₂O over 300-1500 K. *Symp. (Int.) Combust.* **1985**, *20*, 703–713. [CrossRef]
- 48. Margitan, J.J.; Kaufman, F.; Anderson, J.G. The reaction of OH with CH₄. *Geophys. Res. Lett.* **1974**, *1*, 80–81. [CrossRef]
- Mellouki, A.; Teton, S.; Laverdet, G.; Quilgars, A.; Le Bras, G. Kinetic studies of OH reactions with H₂O, C₃H₈ and CH₄ using the pulsed laser photolysis—laser induced fluorescence method. *J. Chim. Phys.* **1994**, *91*, 473–487. [CrossRef]
- 50. Overend, R.P.; Paraskevopoulos, G.; Cvetanović, R.J. Rates of OH Radical Reactions. I. Reactions with H₂, CH₄, C₂H₆, and C₃H₈ at 295 K. *Can. J. Chem.* **1975**, *53*, 3374–3382. [CrossRef]
- 51. Peeters, J.; Mahnen, G. Reaction mechanisms and rate constants of elementary steps in methane-oxygen flames. *Symp. (Int.) Combust.* **1973**, *14*, 133–146. [CrossRef]
- 52. Sharkey, P.; Smith, I.W.M. Kinetics of elementary reactions at low temperatures: Rate constants for the reactions of OH with HCl ($298 \ge T/K \ge 138$), CH₄($298 \ge T/K \ge 178$) and C₂H₆($298 \ge T/K \ge 138$). *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 631–637. [CrossRef]
- 53. Smith, G.P.; Fairchild, P.W.; Jeffries, J.B.; Crosley, D.R. Laser pyrolysis/laser fluorescence studies of high-temperature reaction rates: Description of the method and results for OH + CH₄, C₃H₈, and C₃H₆. *J. Phys. Chem.* **1985**, *89*, 1269–1278. [CrossRef]
- 54. Srinivasan, N.K.; Su, M.C.; Sutherland, J.W.; Michael, J.V. Reflected Shock Tube Studies of High-Temperature Rate Constants for OH + CH₄ → CH₃ + H₂O and CH₃ + NO₂ → CH₃O + NO. *J. Phys. Chem. A* **2005**, *109*, 1857–1863. [CrossRef] [PubMed]
- 55. Steinert, W.; Zellner, R. Rates of Reaction of OH with CO and CH₄ over an Extended Temperature Range. *Deuxiene Symp. Eur. Combust.* **1975**, *2*, 31.
- 56. Sworski, T.J.; Hochanadel, C.J.; Ogren, P.J. Flash photolysis of water vapor in methane. Hydrogen and hydroxyl yields and rate constants for methyl reactions with hydrogen and hydroxyl. *J. Phys. Chem.* **1980**, *84*, 129–134. [CrossRef]
- 57. Tully, F.P.; Ravishankara, A.R. Flash photolysis-resonance fluorescence kinetic study of the reactions hydroxyl + molecular hydrogen → water + atomic hydrogen and hydroxyl + methane → water + methyl from 298 to 1020 K. *J. Phys. Chem.* **1980**, *84*, 3126–3130. [CrossRef]
- 58. Vaghjiani, G.L.; Ravishankara, A.R. New measurement of the rate coefficient for the reaction of OH with methane. *Nature* **1991**, *350*, 406–409. [CrossRef]
- 59. Wilson, W.E.; Westenberg, A.A. Study of the reaction of hydroxyl radical with methane by quantitative ESR. *Symp. (Int.) Combust.* **1967**, *11*, 1143–1150. [CrossRef]
- 60. Yetter, R.A.; Dryer, F.L. Inhibition of moist carbon monoxide oxidation by trace amounts of hydrocarbons. *Symp. (Int.) Combust.* **1992**, *24*, 757–767. [CrossRef]
- 61. Zellner, R. Rate Measurements of Some Bimolecular Reactions of the Hydroxyl Radical over an Extended Temperature Range. *Mol. Rate Process. Pap. Symp.* **1975**, *7*, 1.
- 62. Zellner, R.; Steinert, W. A flash photolysis study of the rate of the reaction $OH + CH_4 \rightarrow CH_3 + H_2O$ over an extended temperature range. *Int. J. Chem. Kinet.* **1976**, *8*, 397–409. [CrossRef]
- 63. Atkinson, R. Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions. *Chem. Rev.* **1986**, *86*, 69–201. [CrossRef]
- 64. Atkinson, R.; Baulch, D.L.; Cox, R.A.; Hampson, R.F.; Kerr, J.A.; Rossi, M.J.; Troe, J. Evaluated Kinetic, Photochemical and Heterogeneous Data for Atmospheric Chemistry: Supplement V. IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. *J. Phys. Chem. Ref. Data* **1997**, *26*, 521–1011. [CrossRef]

- 65. Atkinson, R.; Baulch, D.L.; Cox, R.A.; Hampson, R.F.; Kerr, J.A.; Troe, J. Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement III. IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. J. Phys. Chem. Ref. Data 1989, 18, 881–1097. [CrossRef]
- 66. Atkinson, R.; Baulch, D.L.; Cox, R.A.; Hampson, R.F.; Kerr, J.A.; Troe, J. Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement IV. IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. J. Phys. Chem. Ref. Data 1992, 21, 1125–1568. [CrossRef]
- 67. Baulch, D.L.; Bowers, M.; Malcolm, D.G.; Tuckerman, R.T. Evaluated Kinetic Data for High-Temperature Reactions. Volume 5. Part 1. Homogeneous Gas Phase Reactions of the Hydroxyl Radical with Alkanes. *J. Phys. Chem. Ref. Data* **1986**, *15*, 465–592. [CrossRef]
- 68. Baulch, D.L.; Cobos, C.J.; Cox, R.A.; Esser, C.; Frank, P.; Just, T.; Kerr, J.A.; Pilling, M.J.; Troe, J.; Walker, R.W.; et al. Evaluated Kinetic Data for Combustion Modelling. *J. Phys. Chem. Ref. Data* **1992**, *21*, 411–734. [CrossRef]
- 69. Cohen, N.; Westberg, K.R. Chemical Kinetic Data Sheets for High-Temperature Chemical Reactions. *J. Phys. Chem. Ref. Data* **1983**, *12*, 531–590. [CrossRef]
- 70. DeMore, W.B.; Sander, S.P.; Golden, D.M.; Hampson, R.F.; Kurylo, M.J.; Howard, C.J.; Ravishankara, A.R.; Kolb, C.E.; Molina, M.J. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling: Evaluation Number* 11; Jet Propulsion Lab., California Inst. of Tech.: Pasadena, CA, USA, 1994; p. 18.
- DeMore, W.B.; Sander, S.P.; Golden, D.M.; Hampson, R.F.; Kurylo, M.J.; Howard, C.J.; Ravishankara, A.R.; Kolb, C.E.; Molina, M.J. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling. Evaluation No.* 12; Jet Propulsion Lab., California Inst. of Tech.: Pasadena, CA, USA, 1997; p. 20.
- 72. Tsang, W.; Hampson, R.F. Chemical Kinetic Data Base for Combustion Chemistry. Part I. Methane and Related Compounds. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1087–1279. [CrossRef]
- 73. Warnatz, J. Rate Coefficients in the C/H/O System. In *Combustion Chemistry*; Gardiner, W.C., Ed.; Springer: New York, NY, USA, 1984; pp. 197–360. [CrossRef]
- 74. Westenberg, A.A.; Fristrom, R.M. Methane-oxygen flame structure. iv. chemical kinetic considerations. *J. Phys. Chem.* **1961**, *65*, 591–601. [CrossRef]
- 75. Wilson, W.E. A Critical Review of the Gas-Phase Reaction Kinetics of the Hydroxyl Radical. *J. Phys. Chem. Ref. Data* **1972**, *1*, 535–573. [CrossRef]
- 76. Zellner, R. Non-Arrhenius behavior in bimolecular reactions of the hydroxyl radical. *J. Phys. Chem.* **1979**, *83*, 18–23. [CrossRef]
- 77. Bravo-Pérez, G.; Alvarez-Idaboy, J.R.; Jiménez, A.G.; Cruz-Torres, A. Quantum chemical and conventional TST calculations of rate constants for the OH+alkane reaction. *Chem. Phys.* **2005**, *310*, 213–223. [CrossRef]
- 78. Cohen, N. The use of transition-state theory to extrapolate rate coefficients for reactions of oh with alkanes. *Int. J. Chem. Kinet.* **1982**, *14*, 1339–1362. [CrossRef]
- 79. Cohen, N. Are reaction rate coefficients additive? Revised transition state theory calculations for OH + alkane reactions. *Int. J. Chem. Kinet.* **1991**, *23*, 397–417. [CrossRef]
- 80. Cohen, N.; Benson, S.W. Transition-state-theory calculations for reactions of hydroxyl radicals with haloalkanes. J. Phys. Chem. 1987, 91, 162–170. [CrossRef]
- 81. Dobbs, K.D.; Dixon, D.A.; Komornicki, A. Ab initio prediction of the barrier height for abstraction of H from CH₄ by OH. *J. Chem. Phys.* **1993**, *98*, 8852–8858. [CrossRef]
- 82. Gaillard-Cusin, F.; James, H.; Rouan, J.-P. No. 105.—Le phenomene d'inhibition-promotion par le methane de la combustion de hautes pressions de l'oxyde de carbone. *J. Chim. Phys.* **1969**, *66*, 751–756. [CrossRef]
- 83. Gonzalez, C.; McDouall, J.J.W.; Schlegel, H.B. Ab initio study of the reactions between methane and hydroxyl, hydrogen atom, and triplet oxygen atom. *J. Phys. Chem.* **1990**, *94*, 7467–7471. [CrossRef]
- 84. Leroy, G.; Sana, M.; Tinant, A. Etude theorique des reactions d'abstraction d'hydrogene RH + X = R + HX, avec R, X≡H, CH₃, NH₂, OH et F. *Can. J. Chem.* **1985**, *63*, 1447–1456. [CrossRef]
- 85. Masgrau, L.; González-Lafont, À.; Lluch, J.M. The reactions CHnD4−n+OH→P and CH₄+OD→CH₃+HOD as a test of current direct dynamics multicoefficient methods to determine variational transition state rate constants. II. *J. Chem. Phys.* **2001**, *115*, 4515–4526. [CrossRef]
- 86. Masgrau, L.; González-Lafont, À.; Lluch, J.M. The reactions CHnD4−n+OH→P and CH₄+OD→CH₃+HOD as a test of current direct dynamics computational methods to determine variational transition-state rate constants. I. *J. Chem. Phys.* **2001**, *114*, 2154–2165. [CrossRef]

- 87. Melissas, V.S.; Truhlar, D.G. Interpolated variational transition state theory and tunneling calculations of the rate constant of the reaction OH+CH₄ at 223–2400 K. *J. Chem. Phys.* **1993**, *99*, 1013–1027. [CrossRef]
- Schwartz, M.; Marshall, P.; Berry, R.J.; Ehlers, C.J.; Petersson, G.A. Computational Study of the Kinetics of Hydrogen Abstraction from Fluoromethanes by the Hydroxyl Radical. *J. Phys. Chem. A* 1998, 102, 10074–10081. [CrossRef]
- 89. Shaw, R. Semi-empirical extrapolation and estimation of rate constants for abstraction of H from methane by H, O, HO, and O₂. *J. Phys. Chem. Ref. Data* **1978**, *7*, 1179–1190. [CrossRef]
- 90. Truong, T.N.; Truhlar, D.G. Ab initio transition state theory calculations of the reaction rate for OH+CH₄→H₂O+CH₃. *Ber. Bunsenges. Phys. Chem.* **1990**, *93*, 1761–1769. [CrossRef]
- 91. Mayer, S.W.; Schieler, L. Activation energies and rate constants computed for reactions of oxygen with hydrocarbons. *J. Phys. Chem.* **1968**, *72*, 2628–2631. [CrossRef]
- 92. Skinner, G.B.; Lifshitz, A.; Scheller, K.; Burcat, A. Kinetics of Methane Oxidation. J. Chem. Phys. 1972, 56, 3853–3861. [CrossRef]
- 93. Yamaguchi, Y.; Teng, Y.; Shimomura, S.; Tabata, K.; Suzuki, E. Ab Initio Study for Selective Oxidation of Methane with NOx (x = 1, 2). *J. Phys. Chem. A* **1999**, *103*, 8272–8278. [CrossRef]
- 94. Baldwin, R.R.; Jones, P.N.; Walker, R.W. Determination of the rate constant for $HO_2 + CH_4 \rightarrow H_2O_2 \rightarrow H_2O_2 + CH_3$ at 443 °C. *J. Chem. Soc. Faraday Trans.* 2 **1988**, *84*, 199–207. [CrossRef]
- 95. OriginLab Corporation. OriginPro; Version 2017; OriginLab Corporation: Northampton, MA, USA, 2017.
- 96. Soyhan, H.S.; Mauss, F.; Sorusbay, C. Chemical kinetic modeling of combustion in internal combustion engines using reduced chemistry. *Combust. Sci. Technol.* **2002**, 174, 73–91. [CrossRef]
- Løvås, T.; Amnéus, P.; Mauss, F.; Mastorakos, E. Comparison of automatic reduction procedures for ignition chemistry. *Proc. Combust. Inst.* 2002, 29, 1387–1393. [CrossRef]
- Ji, W.; Ren, Z.; Law, C.K. Evolution of sensitivity directions during autoignition. *Proc. Combust. Inst.* 2019, 37, 807–815. [CrossRef]
- 99. Darnall, K.R.; Atkinson, R.; Pitts, J.N. Rate constants for the reaction of the hydroxyl radical with selected alkanes at 300 K. J. Phys. Chem. 1978, 82, 1581–1584. [CrossRef]
- 100. Atkinson, R.; Aschmann, S.M.; Carter, W.P.L.; Winer, A.M.; Pitts, J.N., Jr. Kinetics of the reactions of OH radicals with n-alkanes at 299 ± 2 K. *Int. J. Chem. Kinet.* **1982**, *14*, 781–788. [CrossRef]
- Atkinson, R. Estimations of OH radical rate constants from H-atom abstraction from C–H and O–H bonds over the temperature range 250–1000 K. *Int. J. Chem. Kinet.* 1986, 18, 555–568. [CrossRef]
- Hu, W.-P.; Rossi, I.; Corchado, J.C.; Truhlar, D.G. Molecular Modeling of Combustion Kinetics. The Abstraction of Primary and Secondary Hydrogens by Hydroxyl Radical. J. Phys. Chem. A 1997, 101, 6911–6921. [CrossRef]
- Tsang, W. Chemical Kinetic Data Base for Combustion Chemistry. Part 3: Propane. J. Phys. Chem. Ref. Data 1988, 17, 887–951. [CrossRef]
- 104. Baldwin, R.R.; Fuller, A.R.; Longthorn, D.; Walker, R.W. *Combustion Institute European Symposium*; Academic Press: London, UK, 1973.
- 105. Zhou, C.-W.; Li, Y.; Burke, U.; Banyon, C.; Somers, K.P.; Ding, S.; Khan, S.; Hargis, J.W.; Sikes, T.; Mathieu, O.; et al. An experimental and chemical kinetic modeling study of 1,3-butadiene combustion: Ignition delay time and laminar flame speed measurements. *Combust. Flame* 2018, 197, 423–438. [CrossRef]
- 106. Baker, R.R.; Baldwin, R.R.; Walker, R.W. Velocity constants for the reactions of alkyl radicals with oxygen. J. Chem. Soc. D Chem. Commun. 1969, 1382–1383. [CrossRef]
- 107. Baker, R.R.; Baldwin, R.R.; Walker, R.W. Addition of C₃H₈ to slowly reacting mixtures of hydrogen and oxygen at 480 °C. *Trans. Faraday Soc.* **1970**, *66*, 3016–3031. [CrossRef]
- Baldwin, R.R.; Langford, D.H.; Matchan, M.J.; Walker, R.W.; Yorke, D.A. The high-temperature oxidation of aldehydes. *Symp. (Int.) Combust.* 1971, 13, 251–259. [CrossRef]
- Baldwin, R.R.; Walker, R.W.; Yorke, D.A. Reaction of n-propyl radicals with oxygen, hydrogen and deuterium. J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases 1973, 69, 826–832. [CrossRef]
- Slagle, I.R.; Park, J.-Y.; Gutman, D. Experimental investigation of the kinetics and mechanism of the reaction of n-propyl radicals with molecular oxygen from 297 to 635 K. *Symp. (Int.) Combust.* **1985**, *20*, 733–741. [CrossRef]
- 111. DeSain, J.D.; Klippenstein, S.J.; Miller, J.A.; Taatjes, C.A. Measurements, Theory, and Modeling of OH Formation in Ethyl + O₂ and Propyl + O₂ Reactions. *J. Phys. Chem. A* **2003**, *107*, 4415–4427. [CrossRef]

- 112. Ranzi, E.; Frassoldati, A.; Grana, R.; Cuoci, A.; Faravelli, T.; Kelley, A.P.; Law, C.K. Hierarchical and comparative kinetic modeling of laminar flame speeds of hydrocarbon and oxygenated fuels. *Prog. Energy Combust. Sci.* **2012**, *38*, 468–501. [CrossRef]
- 113. Baldwin, R.R.; Melvin, A. 348. The reaction of hydrogen atoms with oxygen and with ethane. *J. Chem. Soc.* (*Resumed*) **1964**, 1785–1791. [CrossRef]
- 114. Baulch, D.L.; Cobos, C.J.; Cox, R.A.; Frank, P.; Hayman, G.; Just, T.; Kerr, J.A.; Murrells, T.; Pilling, M.J.; Troe, J.; et al. Evaluated Kinetic Data for Combustion Modeling. Supplement I. J. Phys. Chem. Ref. Data 1994, 23, 847–848. [CrossRef]
- Baulch, D.L.; Drysdale, D.D.; Horne, D.G. An assessment of rate data for high-temperaturesystems. *Symp.* (*Int.*) Combust. 1973, 14, 107–118. [CrossRef]
- Dixon-Lewis, G. Spherically Symmetric Flame Propagation in Hydrogen-Air Mixtures. *Combust. Sci. Technol.* 1983, 34, 1–29. [CrossRef]
- 117. Du, H.; Hessler, J.P. Rate coefficient for the reaction H+O₂→OH+O: Results at high temperatures, 2000 to 5300 K. *J. Chem. Phys.* **1992**, *96*, 1077–1092. [CrossRef]
- 118. Kaufman, F.; Del Greco, F.P. Fast reactions of OH radicals. Symp. (Int.) Combust. 1963, 9, 659–668. [CrossRef]
- 119. Masten, D.A.; Hanson, R.K.; Bowman, C.T. Shock tube study of the reaction hydrogen atom + oxygen → hydroxyl + oxygen atom using hydroxyl laser absorption. *J. Phys. Chem.* **1990**, *94*, 7119–7128. [CrossRef]
- 120. Miller, J.A.; Pilling, M.J.; Troe, J. Unravelling combustion mechanisms through a quantitative understanding of elementary reactions. *Proc. Combust. Inst.* **2005**, *30*, 43–88. [CrossRef]
- 121. Pirraglia, A.N.; Michael, J.V.; Sutherland, J.W.; Klemm, R.B. A flash photolysis-shock tube kinetic study of the hydrogen atom reaction with oxygen: $H + O_2 \rightleftharpoons OH + O$ (962 K $\leq T \leq 1705$ K) and $H + O_2 + Ar \rightarrow HO_2 + Ar$ (746 K $\leq T \leq$ 987 K). *J. Phys. Chem.* **1989**, 93, 282–291. [CrossRef]
- 122. Semenov, N. On the Constants of the Reactions $H+O_2==OH+O$ and $H_2+O_2=2OH$. Acta Physicochim. URSS 1945, 20, 292.
- 123. Turányi, T.; Nagy, T.; Zsély, I.G.; Cserháti, M.; Varga, T.; Szabó, B.T.; Sedyó, I.; Kiss, P.T.; Zempléni, A.; Curran, H.J. Determination of rate parameters based on both direct and indirect measurements. *Int. J. Chem. Kinet.* **2012**, *44*, 284–302. [CrossRef]
- 124. Yang, H.; Gardiner, W.C.; Shin, K.S.; Fujii, N. Shock tube study of the rate coefficient of H + O₂ → OH + O. *Chem. Phys. Lett.* **1994**, 231, 449–453. [CrossRef]
- 125. Yu, C.L.; Frenklach, M.; Masten, D.A.; Hanson, R.K.; Bowman, C.T. Reexamination of Shock-Tube Measurements of the Rate Coefficient of H + O₂.fwdarw. OH + O. J. Phys. Chem. **1994**, 98, 4770–4771. [CrossRef]
- 126. Aganesyan, K.T.; Nalbandyan, A.B. The determination of the rate constants for the reactions between hydrogen and oxygen atoms and ammonia molecules. *Dokl. Phys. Chem. (Engl. Transl.)* **1965**, *160*, 18.
- 127. Aleksandrov, E.N.; Arutyunov, V.S.; Dubrovina, I.V.; Kozlov, S.N. Kinetics of hydrogen oxidation near the lower explosion limit. *Int. J. Chem. Kinet.* **1984**, *16*, 817–834. [CrossRef]
- 128. Azatyan, V.V. Combustion limitation method in the heterogeneous termination of chains in diffusion range. *Arm. Khim. Z.* **1967**, *20*, 577–584.
- 129. Azatyan, V.V.; Nalbandyan, A.B.; Ts'ui, M.-Y. Determination of the rate constant of the reaction between atomic oxygen and ethane. *Dokl. Akad. Nauk SSR* **1962**, *147*, 361–364.
- 130. Azatyan, V.V.; Voevodskii, V.V.; Nalbandyan, A.B. Determination of the rate constant of the reaction of atomic oxygen with molecular hydrogen. *Kinet. Katal.* **1961**, *2*, 340–349.
- 131. Balakhnin, V.P.; Gershenzon, Y.M. A quantitative study of the mechanism of hydrogen combustion close to the lower explosion limit. *Dokl. Phys. Chem. (Engl. Transl.)* **1967**, *170*, 659–662.
- 132. Baldwin, R.R. The first limit of the hydrogen + oxygen reaction in potassium chloride-coated vessels. *Trans. Faraday Soc.* **1956**, *52*, 1344–1354. [CrossRef]
- 133. Belles, F.E.; Brabbs, T.A. Experimental verification of effects of turbulent Boundary layers on chemical-kinetic measurements in a shock tube. *Symp. (Int.) Combust.* **1971**, *13*, 165–175. [CrossRef]
- 134. Biordi, J.C.; Lazzara, C.P.; Papp, J.F. Molecular beam mass spectrometry applied to determining the kinetics of reactions in flames II. A critique of rate coefficient determinations. *Combust. Flame* **1976**, *26*, 57–76. [CrossRef]
- Bowman, C.T. Non-equilibrium radical concentrations in shock-initiated methane oxidation. *Symp. (Int.) Combust.* 1975, 15, 869–882. [CrossRef]

- 136. Brabbs, T.A.; Belles, F.E. Experimental Study of Effects of Laminar Boundary Layers on Chemical-Kinetic Measurements in a Shock Tube. *Proc. Int. Symp. Shock Tubes Waves* **1971**, *67*, 24.
- 137. Brabbs, T.A.; Belles, F.E.; Brokaw, R.S. Shock-tube measurements of specific reaction rates in the branched-chain H₂-CO-O₂ system. *Symp. (Int.) Combust.* **1971**, *13*, 129–136. [CrossRef]
- 138. Buneva, V.N.; Kabasheva, G.N.; Panfilov, V.N. Determination of the reaction rate constant of hydrogen splitting in a rarefied flame by means of isotope exchange. *Kinet. Catal.* **1969**, *10*, 1007.
- Chiang, C.-C.; Skinner, G.B. Resonance Absorption Measure- ments of Atom Concentrations in Reacting Gas Mixtures. 4. Measurements of H and D Atoms in Oxidationof H₂, D₂ and CD₄. *Proc. Int. Symp. Shock Tubes Waves* 1980, 12, 629.
- Dean, A.M.; Kistiakowsky, G.B. Oxidation of Carbon Monoxide/Methane Mixtures in Shock Waves. J. Chem. Phys. 1971, 54, 1718–1725. [CrossRef]
- 141. Dixon-Lewis, G.; Sutton, M.M.; Williams, A. Some reactions of hydrogen atoms and simple radicals at high temperatures. *Symp. (Int.) Combust.* **1965**, *10*, 495–502. [CrossRef]
- 142. Eberius, K.H.; Hoyermann, K.; Wagner, H.G. Experimental and mathematical study of a hydrogen-oxygen flame. *Symp. (Int.) Combust.* **1971**, *13*, 713–721. [CrossRef]
- 143. Fenimore, C.P.; Jones, G.W. Rate of Reaction in Hydrogen, Nitrous Oxide and in Some Other Flames. J. Phys. Chem. 1959, 63, 1154–1158. [CrossRef]
- 144. Frank, P.; Just, T. High Temperature Reaction Rate for $H + O_2 = OH + O$ and $OH + H_2 = H_2O + H$. Ber. Bunsenges. Phys. Chem. **1985**, 89, 181–187. [CrossRef]
- 145. Fujii, N.; Shin, K.S. Rate constant for H+O₂→O+OH by laser absorption spectroscopy of OH in shock-heated H₂-O₂-Ar mixtures. *Chem. Phys. Lett.* **1988**, 151, 461–465. [CrossRef]
- 146. Gutman, D.; Hardwidge, E.A.; Dougherty, F.A.; Lutz, R.W. Shock-Tube Study of the Recombination Rate of Hydrogen Atoms with Oxygen Molecules. *J. Chem. Phys.* **1967**, *47*, 4400–4407. [CrossRef]
- 147. Gutman, D.; Schott, G.L. Shock-Tube Study of Chain Branching during the Induction Period of the Hydrogen—Oxygen Reaction. *J. Chem. Phys.* **1967**, *46*, 4576–4584. [CrossRef]
- 148. Jachimowski, C.J.; Houghton, W.M. Shock-tube study of the induction-period kinetics of the hydrogen-oxygen reaction. *Combust. Flame* **1970**, *15*, 125–132. [CrossRef]
- 149. Karmilova, L.V.; Nalbandyan, A.B.; Semenov, N.N. Hydrogen combustion kinetics with oxygen below the lower autoignition temperature. *Z. Fiz. Khim.* **1958**, *32*, 1193–1204.
- 150. Kochubei, V.F.; Moin, F.B. Kinetics of the Reaction of Atomic Hydrogen with Oxygen. *Sov. Prog. Chem. (Engl. Transl.)* **1973**, *39*, 88.
- 151. Kurzius, S.C.; Boudart, M. Kinetics of the branching step in the hydrogen-oxygen reaction. *Combust. Flame* **1968**, 12, 477–491. [CrossRef]
- 152. Lovachev, L.A. The rate constant of reaction $H+O_2 \rightarrow OH+O$. Combust. Flame 1963, 7, 388–389. [CrossRef]
- 153. Miller, J.A. Nonstatistical effects and detailed balance in quasiclassical trajectory calculations of the thermal rate coefficient for O+OH→O₂+H. *J. Chem. Phys.* **1986**, *84*, 6170–6177. [CrossRef]
- 154. Myerson, A.L.; Watt, W.S. Atom-Formation Rates behind Shock Waves in Hydrogen and the Effect of Added Oxygen. *J. Chem. Phys.* **1968**, *49*, 425–433. [CrossRef]
- 155. Namoradze, M.A.; Troshin, A.F.; Azatyan, V.V.; Dzotsenidze, Z.G.; Museridze, M.D. Effect of Initial Conditions on the Intensity of Chemiluminescence during Carbon Monoxide Oxidation. *Soobshch. Akad. Nauk Gruz. SSR* **1974**, *73*, 377.
- 156. Pamidimukkala, K.M.; Skinner, G.B. Resonance Absorption Measurements of Atom Concentrations in Reacting Gas Mixtures. 9. Measurements of O atoms in Oxidation of H/sub 2/ and D/sub 2; Wright State Univ., Dept. of Chemistry: Dayton, OH, USA, 1981.
- 157. Ripley, D.L.; Gardiner, W.C. Shock-Tube Study of the Hydrogen—Oxygen Reaction. II. Role of Exchange Initiation. *J. Chem. Phys.* **1966**, *44*, 2285–2296. [CrossRef]
- 158. Schott, G.L. Further studies of exponential branching rates in reflected-shock heated, nonstoichiometric H₂COO₂ systems. *Combust. Flame* **1973**, *21*, 357–370. [CrossRef]
- 159. Schott, G.L.; Kinsey, J.L. Kinetic Studies of Hydroxyl Radicals in Shock Waves. II. Induction Times in the Hydrogen-Oxygen Reaction. *J. Chem. Phys.* **1958**, *29*, 1177–1182. [CrossRef]
- 160. Shin, K.S.; Michael, J.V. Rate constants for the reactions H+O₂→OH+O and D+O₂→OD+O over the temperature range 1085–2278 K by the laser photolysis–shock tube technique. *J. Chem. Phys.* **1991**, *95*, 262–273. [CrossRef]

- 161. Shub, F.S.; Apel'baum, L.P.; Temkin, M.I. The accelerating effect of oxygen in a homogeneous reaction of water gas. *Kinet. Catal.* **1971**, *11*, 931.
- 162. Yuan, T.; Wang, C.; Yu, C.; Frenklach, M.; Rabinowitz, M. Determination of the rate coefficient for the reaction $H + O_2 \rightarrow OH + O$ by a shock tube/laser absorption/detailed modeling study. *J. Phys. Chem.* **1991**, *95*, 1258–1265. [CrossRef]
- 163. Baldwin, R.R.; Cowe, D.W. The inhibition of the hydrogen + oxygen reaction by formaldehyde. *Trans. Faraday Soc.* **1962**, *58*, 1768–1781. [CrossRef]
- Browne, W.G.; Porter, R.P.; Verlin, J.D.; Clark, A.H. A study of acetylene-oxygen flames. *Symp. (Int.) Combust.* 1969, 12, 1035–1047. [CrossRef]
- 165. Dixon-Lewis, G.; Linnett, J.W. Flame structure and flame reaction kinetics—V. Investigation of reaction mechanism in a rich hydrogen+nitrogen+oxygen flame by solution of conservation equations. *Proc. R. Soc. Lond. A. Math. Phys. Sci.* 1970, 317, 235–263. [CrossRef]
- 166. Germann, T.C.; Miller, W.H. Quantum Mechanical Pressure-Dependent Reaction and Recombination Rates for O + OH → H + O₂, HO₂. J. Phys. Chem. A **1997**, 101, 6358–6367. [CrossRef]
- 167. Miller, J.A. Collision dynamics and the thermal rate coefficient for the reaction H+O₂→OH+O. *J. Chem. Phys.* 1981, 74, 5120–5132. [CrossRef]
- 168. Miller, J.A.; Garrett, B.C. Quantifying the non-RRKM effect in the H + $O_2 \rightleftharpoons OH + O$ reaction. *Int. J. Chem. Kinet.* **1997**, *29*, 275–287. [CrossRef]
- Westenberg, A.A.; Fristrom, R.M. H and O atom profiles measured by ESR in C₂ hydrocarbon-O₂ flames. Symp. (Int.) Combust. 1965, 10, 473–487. [CrossRef]
- 170. Dixon-Lewis, G.; Wilson, W.E.; Westenberg, A.A. Studies of Hydroxyl Radical Kinetics by Quantitative ESR. *J. Chem. Phys.* **1966**, 44, 2877–2884. [CrossRef]
- 171. Dixon-Lewis, G.; Linnett, J.W. Flame structure and flame reaction kinetics. VII. Reactions of traces of heavy water, deuterium and carbon dioxide added to rich hydrogen + nitrogen + oxygen flames. *Proc. R. Soc. of Lond. A. Math. Phys. Sci.* **1972**, 330, 219–245. [CrossRef]
- 172. Dixon-Lewis, G.; Sutton, M.M.; Williams, A. Reactions contributing to the establishment of the water gas equilibrium when carbon dioxide is added to a hydrogen-oxygen flame. *Trans. Faraday Soc.* **1965**, *61*, 255–262. [CrossRef]
- 173. Jost, W.; Schecker, H.G.; Wagner, H.G. Messungen der Geschwindigkeit der Einstellung des Wassergas-Gleichgewichtes. Z. Phys. Chem. 1965, 45, 47–57. [CrossRef]
- 174. Herron, J.T. Mass-Spectrometric Study of the Rate of the Reaction CO + OH. J. Chem. Phys. 1966, 45, 1854–1855. [CrossRef]
- 175. Heath, G.A.; Pearson, G.S. Perchloric acid flames: Part III. Chemical structure of methane flames. *Symp.* (*Int.*) *Combust.* **1967**, *11*, 967–977. [CrossRef]
- 176. Porter, R.P.; Clark, A.H.; Kaskan, W.E.; Browne, W.E. A study of hydrocarbon flames. *Symp. (Int.) Combust.* **1967**, *11*, 907–917. [CrossRef]
- 177. Wilson, W.E.; O'Donovan, J.T. Mass-Spectrometric Study of the Reaction Rate of OH with Itself and with CO. *J. Chem. Phys.* **1967**, *47*, 5455–5457. [CrossRef]
- 178. Greiner, N.R. Hydroxyl Radical Kinetics by Kinetic Spectroscopy. V. Reactions with H₂ and CO in the Range 300–500 °K. *J. Chem. Phys.* **1969**, *51*, 5049–5051. [CrossRef]
- 179. Kochubei, V.F.; Moin, F.B. Kinetics of the reaction of CO₂ with hydrogen. *Kinet. Catal.* 1969, 10, 992.
- Baldwin, R.R.; Walker, R.W.; Webster, S.J. The carbon monoxide-sensitized decomposition of hydrogen peroxide. *Combust. Flame* 1970, 15, 167–172. [CrossRef]
- Dean, A.M.; Kistiakowsky, G.B. Oxidation of Carbon Monoxide by Oxygen in Shock Waves. J. Chem. Phys. 1970, 53, 830–838. [CrossRef]
- Shub, F.S.; Apel'baum, L.O.; Temkin, M.I. The kinetics of the homogeneous water gas reaction. *Kinet. Catal.* 1970, 11, 462.
- 183. Izod, T.P.J.; Kistiakowsky, G.B.; Matsuda, S. Oxidation of Carbon Monoxide Mixtures with Added Ethane or Azomethane Studied in Incident Shock Waves. J. Chem. Phys. **1971**, 55, 4425–4432. [CrossRef]
- 184. Stuhl, F.; Niki, H. Pulsed Vacuum-uv Photochemical Study of Reactions of OH with H₂, D2, and CO Using a Resonance-Fluorescent Detection Method. *J. Chem. Phys.* **1972**, *57*, 3671–3677. [CrossRef]
- Eberius, K.H.; Hoyermann, K.; Wagner, H.C. Structure of lean acetylene-oxygen flames. *Symp. (Int.) Combust.* 1973, 14, 147–156. [CrossRef]

- 186. Gardiner, W.C.; Mallard, W.G.; McFarland, M.; Morinaga, K.; Owen, J.H.; Rawlins, W.T.; Takeyama, T.; Walker, B.F. Elementary reaction rates from post-induction-period profiles in shock-initiated combustion. *Symp. (Int.) Combust.* **1973**, *14*, 61–75. [CrossRef]
- 187. Smith, I.W.M.; Zellner, R. Rate measurements of reactions of OH by resonance absorption. Part 2.—Reactions of OH with CO, C₂H₄ and C₂H₂. *J. Chem. Soc. Faraday Trans. 2 Mol. Chem. Phys.* **1973**, 69, 1617–1627. [CrossRef]
- 188. Westenberg, A.A.; de Haas, N. Rates of CO + OH and H₂ + OH over an extended temperature range. *J. Chem. Phys.* **1973**, *58*, 4061–4065. [CrossRef]
- Howard, C.J.; Evenson, K.M. Laser magnetic resonance study of the gas phase reactions of OH with CO, NO, and NO₂. J. Chem. Phys. 1974, 61, 1943–1952. [CrossRef]
- 190. Trainor, D.W.; Vonrosenberg, C.W. Energy partitioning in the reaction $OH + CO \rightarrow CO_2 + H$. *Chem. Phys. Lett.* **1974**, *29*, 35–38. [CrossRef]
- 191. Biordi, J.C.; Lazzara, C.P.; Papp, J.F. Flame structure studies of CF3Br-Inhibited methane flames: II. Kinetics and mechanisms. *Symp. (Int.) Combust.* **1975**, *15*, 917–932. [CrossRef]
- 192. Trainor, D.W.; von Rosenberg, C.W. Energy partitioning in the products of elementary reactions involving OH-radicals. *Symp. (Int.) Combust.* **1975**, *15*, 755–764. [CrossRef]
- 193. Vandooren, J.; Peeters, J.; Tiggelen, P.J.V. Rate constant of the elementary reaction of carbon monoxide with hydroxyl radical. *Symp.* (*Int.*) *Combust.* **1975**, *15*, 745–753. [CrossRef]
- 194. Atkinson, R.; Perry, R.A.; Pitts, J.N. Kinetics of the reactions of OH radicals with CO and N2O. *Chem. Phys. Lett.* **1976**, 44, 204–208. [CrossRef]
- 195. Atri, G.M.; Baldwin, R.R.; Jackson, D.; Walker, R.W. The reaction of OH radicals and HO₂ radicals with carbon monoxide. *Combust. Flame* **1977**, *30*, 1–12. [CrossRef]
- 196. Chan, W.H.; Uselman, W.M.; Calvert, J.G.; Shaw, J.H. The pressure dependence of the rate constant for the reaction: $HO + CO \rightarrow H + CO_2$. *Chem. Phys. Lett.* **1977**, *45*, 240–244. [CrossRef]
- 197. Overend, R.; Paraskevopoulos, G. The question of a pressure effect in the reaction OH + CO at room temperature. *Chem. Phys. Lett.* **1977**, *49*, 109–111. [CrossRef]
- 198. Biermann, H.W.; Zetzsch, C.; Stuhl, F. On the Pressure Dependence of the Reaction of HO with CO. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 633–639. [CrossRef]
- Butler, R.; Solomon, I.J.; Snelson, A. Pressure dependence of the CO + OH rate constant in O₂ + N2 mixtures. *Chem. Phys. Lett.* **1978**, *54*, 19–24. [CrossRef]
- 200. Clyne, M.A.A.; Holt, P.M. Reaction Kinetics Involving Ground $X^2\pi$ and Excited $A^2\Sigma^+$ Hydroxyl Radicals. Part 1.—Quenching Kinetics of OH $A^2\Sigma^+$ and Rate Constants for Reactions of OH $X^2\pi$ with CH₃CCl₃ and CO. *J. Chem. Soc. Faraday Trans.* 2 **1979**, *75*, 569. [CrossRef]
- 201. Ravishankara, A.R.; Thompson, R.L. Kinetic study of the reaction of OH with CO from 250 to 1040 K. *Chem. Phys. Lett.* **1983**, *99*, 377–381. [CrossRef]
- 202. Demore, W.B. Rate constant for the OH + CO reaction: Pressure dependence and the effect of oxygen. *Int. J. Chem. Kinet.* **1984**, *16*, 1187–1200. [CrossRef]
- 203. Hofzumahaus, A.; Stuhl, F. Rate Constant of the Reaction HO + CO in the Presence of N2 and O₂. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 557–561. [CrossRef]
- 204. Niki, H.; Maker, P.D.; Savage, C.M.; Breitenbach, L.P. Fourier transform infrared spectroscopic study of the kinetics for the hydroxyl radical reaction of 13C16O-carbon monoxide and 12C18O-carbon monoxide. *J. Phys. Chem.* **1984**, *88*, 2116–2119. [CrossRef]
- 205. Smith, I.W.M.; Williams, M.D. Kinetics of OH(v = 0 and 1) and OD(v = 0 and 1) studied by time-resolved laser-induced fluorescence. *Ber. Bunsenges. Phys. Chem.* **1985**, *89*, 319. [CrossRef]
- 206. Larson, C.W.; Stewart, P.H.; Golden, D.M. Pressure and temperature dependence of reactions proceeding via a bound complex. An approach for combustion and atmospheric chemistry modelers. Application to HO + CO → [HOCO] → H + CO₂. Int. J. Chem. Kinet. **1988**, 20, 27–40. [CrossRef]
- 207. Frost, M.J.; Sharkey, P.; Smith, I.W.M. Energy and structure of the transition states in the reaction OH + CO → H + CO₂. *Faraday Discuss. Chem. Soc.* **1991**, *91*, 305–317. [CrossRef]
- 208. Frost, M.J.; Sharkey, P.; Smith, I.W.M. Reaction between hydroxyl (deuteroxyl) radicals and carbon monoxide at temperatures down to 80 K: Experiment and theory. *J. Phys. Chem.* **1993**, *97*, 12254–12259. [CrossRef]
- 209. Wooldridge, M.S.; Hanson, R.K.; Bowman, C.T. A shock tube study of the CO+OH→CO₂+H reaction. *Symp.* (*Int.*) *Combust.* **1994**, 25, 741–748. [CrossRef]

- Forster, R.; Frost, M.; Fulle, D.; Hamann, H.F.; Hippler, H.; Schlepegrell, A.; Troe, J. High pressure range of the addition of HO to HO, NO, NO₂, and CO. I. Saturated laser induced fluorescence measurements at 298 K. J. Chem. Phys. **1995**, 103, 2949–2958. [CrossRef]
- 211. Lissianski, V.; Yang, H.; Qin, Z.; Mueller, M.R.; Shin, K.S.; Gardiner, W.C. High-temperature measurements of the rate coefficient of the H + CO₂ → CO + OH reaction. *Chem. Phys. Lett.* **1995**, 240, 57–62. [CrossRef]
- 212. Wooldridge, M.S.; Hanson, R.K.; Bowman, C.T. A shock tube study of CO + OH → CO₂ + H and HNCO + OH → products via simultaneous laser absorption measurements of OH and CO₂. *Int. J. Chem. Kinet.* 1996, 28, 361–372. [CrossRef]
- 213. Bohn, B.; Zetzsch, C. Formation of HO₂ from OH and C₂H₂ in the presence of O₂. *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 1203–1210. [CrossRef]
- 214. Chen, W.-C.; Marcus, R.A. On the theory of the reaction rate of vibrationally excited CO molecules with OH radicals. *J. Chem. Phys.* 2006, 124, 024306. [CrossRef]
- 215. Li, J.; Zhao, Z.; Kazakov, A.; Chaos, M.; Dryer, F.L.; Scire, J.J., Jr. A comprehensive kinetic mechanism for CO, CH₂O, and CH₃OH combustion. *Int. J. Chem. Kinet.* **2007**, *39*, 109–136. [CrossRef]
- Browne, W.G.; White, D.R.; Smookler, G.R. A study of the chemical kinetics of shock heated H₂/CO/O₂ mixtures. *Symp. (Int.) Combust.* 1969, 12, 557–567. [CrossRef]
- 217. Day, M.J.; Thompson, K.; Dixon-Lewis, G. Some reactions of hydroperoxyl and hydroxylradicals at high temperatures. *Symp.* (*Int.*) *Combust.* **1973**, *14*, 47–59. [CrossRef]
- 218. Mozurkewich, M.; Lamb, J.J.; Benson, S.W. Negative activation energies and curved Arrhenius plots. 2. Hydroxyl + carbon monoxide. *J. Phys. Chem.* **1984**, *88*, 6435–6441. [CrossRef]
- Dzegilenko, F.N.; Bowman, J.M. Recovering a full dimensional quantum rate constant from a reduced dimensionality calculation: Application to the OH+CO→H+CO₂ reaction. *J. Chem. Phys.* **1996**, 105, 2280–2286. [CrossRef]
- 220. Zsély, I.G.; Nagy, T.; Simmie, J.M.; Curran, H.J. Reduction of a detailed kinetic model for the ignition of methane/propane mixtures at gas turbine conditions using simulation error minimization methods. *Combust. Flame* 2011, 158, 1469–1479. [CrossRef]
- 221. Varga, T.; Olm, C.; Nagy, T.; Zsely, I.G.; Valko, E.; Palvolgyi, R.; Curran, H.J.; Turanyi, T. Development of a Joint Hydrogen and Syngas Combustion Mechanism Based on an Optimization Approach. *Int. J. Chem. Kinet.* **2016**, *48*, 407–422. [CrossRef]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).