Analysis of Heterogeneous-Homogeneous Model of Oxidative Coupling of Methane Using Kinetic Scheme Reduction Procedure

V. I. Lomonosov[a,] * and M. Yu. Sinev[a]

[a]Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, Moscow, 119991 Russia
*e-mail: vlomonosov@mail.ru

Abstract—The validity of using kinetic scheme reduction procedures to compare various kinetic models as well as the values of kinetic parameters of individual steps present in the literature is analyzed. The peculiarities of the development of the gas-phase reaction block as a part of the heterogeneous-homogeneous model of the oxidative coupling of methane (OCM) are considered and approaches to the selection of kinetic parameters of elementary steps are analyzed. It has been demonstrated that kinetic models developed in accordance with the principle of "independence of kinetic parameters" can exhibit low predictive power due to existing uncertainties in the values of the parameters presented in well-known review papers and databases. In addition, the effects of the accounting of the heterogeneous reaction block and variation of the OCM reaction conditions on the results of the reduction of the detailed kinetic scheme are addressed. It has been shown that the use of reduction procedures to analyze the mechanism of complex processes is limited due to the high degree of conjugation between their individual stages and the strong dependence of kinetic constants on the parameters of state.

Partial oxidation and oxidative dehydrogenation of light alkanes — the major components of natural and associated petroleum gases — are considered as promising alternative to the existing technologies for the production of basic intermediates of organic and petrochemical synthesis from petroleum feedstock [1]. A special place among them is occupied by oxidative coupling of methane (OCM) to higher hydrocarbons, including ethylene [2–6]. On the one hand, methane is abundant and relatively low-cost hydrocarbon feedstock. On the other hand, ethylene is one of the most demanded and scant intermediate products in petrochemistry.

A characteristic feature of the OCM reaction is that the activation of methane occurs over catalyst active sites and is accompanied by the release of free radicals to the gas phase [7–9]. Molecular products of OCM reaction are formed in a complex combination of secondary free-radical reactions both in the gas phase, and on active sites on the surface [10, 11]. For this reason, the kinetic features of the process are determined by the strong conjugation of heterogeneous and homogeneous factors. The experimentally observed values of the reaction rate are resulted from a complex combination of heterogeneous and homogeneous processes in which catalytic active sites play a dual role, participating both in the generation of primary radicals, and in the termination of homogeneous chains [10, 12]. Since OCM catalysts are also effective in high-temperature oxidative dehydrogenation and cracking of C_{2+} alkanes, which proceed via a similar mechanism [10, 13], the OCM reaction can be considered as a convenient model in studying a wide range of hydrocarbon oxidation processes. To analyze their kinetics, complex multistep schemes have to be utilized, which allow one to trace the development of the process in time, to determine the product formation pathways, and to predict the effect of various factors on the characteristics of the process. Such models are an efficient tool to investigate the detailed reaction mechanism and to analyze a complex kinetic phenomena accompanying the processes under consideration.

Soon after the discovery of the OCM, the first attempts were made to explain some of its regularities by the free radical nature of the process [14–16] and to describe them in the framework of heterogeneous–homogeneous kinetic schemes [17–19]. According to the most common approach, the kinetic scheme of a heterogeneous–homogeneous process is formed by two blocks, homogeneous and heterogeneous (see, e.g., [11, 12, 20]). The first block is a detailed descrip-

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Abbreviations and notation: OCM, oxidative coupling of methane; RT, relative tolerance; CAS, catalytically active sites.

tion of the processes taking place during hydrocarbon oxidation in a gas phase. All elementary steps involving molecular and radical species formed by the homogeneous oxidation also occur during the catalytic processes accompanied by the release of free radicals into the gas phase. The second block is required to describe the interaction of these species with surface active sites. The development of both blocks requires the compliance with a number of principles, including the completeness and openness of the description, its thermodynamic consistency, and also the independence of kinetic parameters [11].

In the present work, the peculiarities of the development of the gas-phase reaction block of the kinetic model were considered, and approaches to the selection of kinetic parameters of elementary steps are analyzed.

A large number of kinetic models of gas-phase oxidation of light hydrocarbons, which differ both in number of species and elementary steps, and in approaches to filling them with the kinetic parameters are currently available in open sources. In our opinion, the most comprehensive kinetic scheme of light alkane transformations is the model of the C_1-C_5 hydrocarbon oxidation developed by the Combustion Chemistry Center, National University of Ireland Galway (Galway, Ireland) [21]. This model is constructed hierarchically and includes blocks of oxidation of hydrogen, CO, C_1-C_5 hydrocarbons, and also various oxygen-containing compounds. The development of the model started in 2010 and is still in progress. Its most recent version, Aramco 3.0 (hereinafter referred to as AramcoMech), containing 3037 reactions of 581 species, was published in 2018 [22]. Numerous refinements and corrections were made both in the step scheme, and in the values of rate constants for individual elementary steps throughout the model development [23−30]. Moreover, in certain cases, the thermodynamic parameters of individual substances were also refined (see, e.g., [30]). In our opinion, an important advantage of AramcoMech model is that its authors avoided the fitting of the parameters of individual steps for increasing the accuracy of the description. The kinetic constants were selected based on the most recent and, according to the authors of the model, most reliable literature sources. The further optimization includes a detailed analysis of the entire scheme and its individual blocks (submechanisms), which is performed as follows. For example, methane oxidation was considered in reactors of various types (constant-pressure flow reactor, adiabatic reactor, jet-stirred reactor, shock tubes, etc.), and the sensitivity of individual elementary steps was analyzed [30]. Further, the kinetic parameters of the particular steps are verified by comparing the calculation results with experimental data obtained independently. Wherein only kinetic data published in open sources (both experimental data, and theoretical

estimates) are considered. In other words, maximum efforts were made to eliminate mechanistic (or, put it better, mathematical) fitting of the kinetic parameters and the simultaneous variation of the parameters of a significant number of elementary steps. The final model was verified on a large basis of independent experimental data obtained in a broad variety of reaction mixtures and reaction conditions. The calculation results were also compared with the results obtained using other kinetic schemes [31−36].

In many cases, the AramcoMech model most accurately described the available experimental data. The results of the comparative analysis are open access [21]. As noted above, this scheme can be considered the most comprehensive and consistent among the currently available in the literature. However, the approach accepted by the model developers for selection of the kinetic parameters of individual steps is indistinct. In particular, it was stated in [30] that filling the model with kinetic parameters should not be performed without referring to experimental data, i.e. comparison of simulation and experimental results is required. In other words, according to the authors, , a kinetic model with high predictive power and high computational accuracy cannot be developed if one strictly adheres to the principle of independence of kinetic parameters, i.e., uses the values of parameters presented in the most reliable reviews and databases. That is, it is necessary to assess how well different published values of kinetic parameters allow to describe the existing independent experimental data. In our opinion, it is of undoubted interest to independently evaluate the validity of this statement. For this purpose, in the present work, we performed a comparative analysis of simulation results obtained by models, the parameters of which were selected in accordance with to two different approaches: by strictly following the principle of using the kinetic parameters obtained from independent kinetic experiments [11] and by more flexible approach enabling the variation of parameter values over certain ranges determined by the scatter in the literature data [22].

One of the most well-known kinetic schemes constructed according to the principle of independence of kinetic parameters is the Leeds methane oxidation mechanism developed in the early 2000s at the University of Leeds, Leeds, UK [34]. This model also contains blocks of oxidation of hydrogen, carbon monoxide, ethane, and ethylene. Its authors completely abandon the fitting of kinetic parameters for increasing the accuracy of the description, but unlike the AramcoMechv scheme [22], the Leeds model was filled with the kinetic parameters without referring to any experimental data. The values of the kinetic constants were obtained from open access databases [37, 38], and an algorithm was proposed in which the sources were arranged in the order of maximum reliability of presented data [39]. The rate constants for the reverse reactions were calculated using thermody-

namic data from the CHEMKIN software [40], which made the scheme thermodynamically consistent. It was shown that the obtained kinetic model describes well the experimental data on the velocity of the laminar flame propagation and ignition delays in the methane oxidation. As noted above, the model [22] was validated over a much wider array of independent experimental data and initial conditions. The comparative analysis performed by its authors showed that, in some cases, the difference between the results of the calculations according to the schemes [22] and [34] was significant. However, it is not clear if the observed disagreement in the results of simulation is related to the difference in the approaches to the selection of kinetic parameters. Strictly speaking, a direct comparison of the results of the calculations by schemes [22] and [34] is not correct because the considered models were initially developed for different applications and differ significantly in the sets of elementary steps. Filling the scheme [22] with the kinetic parameters in accordance with the "independent" approach [34] is time-consuming. For this reason, as an alternative approach to analyzing various descriptions and sets of parameters, we compared the kinetic schemes obtained by reduction of the initial "complete" models using standard approaches. This work describes the results of such comparative analysis, in which the model [22] was chosen as the base "complete" scheme. In addition, the effect of taking into account the block of heterogeneous reactions and variation of the initial reaction conditions on the results of the reduction of the detailed kinetic scheme with various sets of kinetic parameters are addressed.

The reduction of large kinetic models is of unique significance The increasing role of computational methods in investigating various processes and developing technologies and equipment (including chemical production) requires one to construct sufficiently compact kinetic models capable of being coupled with computation of hydrodynamics and heat and mass transfer. In this context, it is of interest to investigate in what extent the size of "complete" kinetic schemes (the number of components and reactions between them) can be reduced with retaining an initial accuracy of description. Bearing in mind the strong conjugacy of the kinetics of heterogeneous−homogeneous processes and the strong dependence of the rate constants of individual steps on the physical parameters (first of all, on temperature), we also considered the effect of taking into account the block of heterogeneous reactions and varying the OCM reaction conditions on the results of the reduction of the complete scheme.

COMPUTATION PROCEDURE

The kinetic simulations were performed using the Chemical WorkBench software (KintechLab, Russia) [41]. It allows one to analyze complex multistep processes in a wide range of initial conditions (operation modes, types of reactors). Methods of multistep kinetic scheme reduction and their main features were described in detail elsewhere [42]. The kinetic scheme [22] was reduced by successive application of three algorithms:

—DRG, method of analysis of direct relationship graph;

—CSP, graph of computational singular perturbations;

—DSA, method of direct sensitivity analysis.

All calculations were performed for a batch isothermal reactor of the calorimetric bomb type (at 900, 1000, 1100, and 1200 K) operating at constant pressure (1−10 atm) for the initial mixture containing 79 mol % CH_4, 20 mol % O_2, and 1 mol % N_2. A criterion of the proximity of the reduced mechanism to the initial ("complete") one was the requirement that the maximum relative tolerance (RT) of concentrations of the reactants (CH_4 and O_2) and the main products (CO_2, CO, C_2H_6, C_2H_4, and H_2) in the calculations according to the complete and reduced schemes at a given time should not exceed a certain threshold value. To estimate the effect of this parameter on the result of the reduction, two threshold values, 0.05 and 0.1, were considered. In the further calculations, RT was taken to be 0.1.

The determination of the kinetic parameters of the reduced model utilizing the "independent" approach was performed using the NIST Chemical Kinetics Database [37]. The priority sources were chosen to be the works [43−46]. If these works contained no data on some of the steps, then the kinetics parameters were not replaced; i.e., the parameters [22] were used.

A comparative analysis of the reduced schemes with different sets of kinetic parameters was performed by the direct sensitivity analysis method, which consists in the-determination of the change in the concentration of component i with varying rate constant for step j at a given time. One the one hand, this method enables allows one to determine the steps that make the essential contribution to the transformation of individual components of the reaction mixture, and on the other, to estimate the effect of the inaccuracy in the values of kinetic parameters of individual steps on the calculation results.

The heterogeneous−homogeneous reaction system was described using the previously developed approach [12], according to which a block of heterogeneous reactions was added to the complete AramcoMech scheme. The composition of this block and the corresponding rate constants were determined according to the procedure described previously (see [11, 47−49]). The reaction system was described in a quasi-homogeneous (or quasi-catalytic) approximation, i.e. catalytic active sites were added to the homogeneous gas mixture as free particles. Their concentra-

Table 1. Results of the reduction of the AramcoMech mechanism* at various relative tolerances (RT)

RT	Number of species	Number of reversible reactions
0.05	60	141
0.1	49	96

* Only reactions of species containing no more than three carbon atoms were taken in to account.

tion was varied from 0 to a value corresponding to the average concentration of surface sites in a unit volume of granules of a solid substance with a packed density of 1 g/cm^3 and a specific surface area of 10 m^2/g, i.e., ~2 × 10^{19} cm^{-3}. This value virtually overlaps the range of the average concentration of surface sites per unit volume of the reaction zone for the most efficient OCM catalysts.

RESULTS AND DISCUSSION

Effect of the Relative Tolerance on the Results of the Reduction

We started from the analysis of the effect of the relative tolerance value on the results of the AramcoMech kinetic scheme reduction. The calculation was performed for an isothermal reactor in the temperature range 900−1000 K and the pressure range 1−10 atm. To simplify the analysis, only reactions of species containing not more than three carbon atoms were taken into account. As a result, two descriptions were obtained, the main parameters of which are presented in Table 1. As it can be seen from the table, the rougher approximation results in the kinetic scheme reduced more significantly.

Another result was less expected. It was demonstrated that the significantly more compact scheme, which was obtained at RT = 0.1, contained several reactions that were not present in the reduced scheme at RT = 0.05. Apparently, the exclusion of reactions that do not largely affect the total conversion/formation of certain components of the reaction mixture leads to significant rearrangement of the contributions of various reaction pathways. This indicates that the described reduction procedure is strictly formal and can be applied for the process optimization, but is unsuitable to analyze the mechanism of a complex process.

Results of the Reduction of the AramcoMech Scheme with Different Sets of Kinetic Parameters

An essential drawback of the direct sensitivity analysis procedure is that the calculated "sensitivity"—the derivative $dC_i/d(\ln k_j)$—depends on the initial selection of kinetic parameters included in the model. The same can be applied to the other reduction methods used in this work.

Comparison of reduced kinetic schemes cannot reveal the effect of the values of parameter on the result of the reduction procedure because of structural difference between the initial descriptions. To evaluate this effect directly, the following approach was proposed. The initial AramcoMech model was reduced at 1000 K and atmospheric pressure. Next, the kinetic parameters of the elementary steps included in the reduced scheme were replaced in the initial model by those presented in the literature [31−34], and then such a modified kinetic model was reduced. For simplicity, the scheme produced by the reduction with the kinetic parameters accepted in the work [22] is further referred to as "initially reduced"; and the one reduced with the kinetic parameters from the database [37] is further referred to as "modified." The reduced scheme, two sets of kinetic parameters, and the rate constants calculated for a temperature of 1000 K are presented in Table 2.

As can be seen from the Table 3, the model obtained by the reduction of the modified scheme does not include a number of important steps involving the methyl radical. One of them is the formation and decomposition of the CH$_3$O$_2$ radical. This process determines the position of the left boundary of the "OCM window" and the abrupt decrease in the selectivity to C$_2$ hydrocarbons at low conversions in the temperature range <900−950 K [11, 16]. The obtained result is likely to be due to the fact that if the kinetic parameters [43−46] are used, this significantly increases the rates of steps (18), (30), and (39) (see Table 2). This results in the decrease in the contributions of the other reactions involving the methyl radical to the overall process. The increase in the rate of step (39) in the modified scheme also leads to the fact that Scheme 2 contains more steps involving the C$_2$H$_3$ radical than Scheme 1. Thus, this example very clearly demonstrates the effect of uncertainties in the values of the kinetic parameters of individual steps on the composition of the reduced kinetic Schemes.

The data in Table 2 show that, for some elementary steps, the difference in the values of the rate constants exceeds one order of magnitude. Such a difference in the parameters predictably affects the calculation results. In particular, if the concentration of oxygen (the limiting reactant in the standard settings of the OCM process) at a given time is used as a criterion to estimate the overall process rate, then the reaction in the modified scheme proceeds slightly faster (Fig. 1). The difference between the two schemes is even more significant if the distributions of the methane oxidation products are compared (Figs. 2a−2d). The sensitivity analysis demonstrated that, in the modified kinetic scheme, the current oxygen concentration is most sensitive to steps (13), (17), (18), and (30). According to the analysis results, the first three reactions favorably affect the oxygen conversion rate (i.e.,

Table 2. Step scheme obtained by reducing the AramcoMech 3.0 model (1000 K, 1 atm)*

№	Reaction	AramcoMech 3.0 [22]				NIST database [37]***					k (NIST)/k (Aramco)
		A**	N	E_a, kcal/mol	k (1000 K)	A**	N	E_a, kcal/mol	k (1000 K)	reference	
1.	$O_2 + H \rightleftarrows O + OH$	1.73×10^{-10}	0	15.29	7.88×10^{-14}	1.62×10^{-10}	0	14.84	9.25×10^{-14}	[46]	1.17
2.	$H_2O_2 + M \rightleftarrows OH + OH + M$	Troe approximation			8.99×10^{-18}	2.01×10^{-7}	0	45.51	2.27×10^{-17}	[46]	2.53
3.	$HO_2 + HO_2 \rightleftarrows H_2O_2 + O_2$	1.66×10^{-10}	0	11.04	6.41×10^{-13}	7.01×10^{-10}	0	11.98	1.69×10^{-12}	[46]	2.63
4.	$HO_2 + HO_2 \rightleftarrows H_2O_2 + O_2$	3.16×10^{-13}	0	−1.41	6.41×10^{-13}	No data					–
5.	$H + O_2 + M \rightleftarrows HO_2 + M$	Troe approximation			9.23×10^{-33}	3.89×10^{-30}	−0.80	0.00	1.55×10^{-32}	[46]	1.68
6.	$CO + OH \rightleftarrows CO_2 + H$	1.16×10^{-19}	2.05	−0.36	2.01×10^{-13}	1.05×10^{-17}	1.50	−2.08	9.46×10^{-13}	[45]	4.71
7.	$CO + OH \rightleftarrows CO_2 + H$	9.56×10^{-12}	−0.66	0.33	8.24×10^{-14}	No data					–
8.	$CO + HO_2 \rightleftarrows CO_2 + OH$	2.61×10^{-19}	2.18	17.94	1.08×10^{-16}	2.51×10^{-10}	0	23.65	1.70×10^{-15}	[43]	15.69
9.	$CH_3 + H + M \rightleftarrows CH_4 + M$	Troe approximation			5.07×10^{-30}	1.71×10^{-24}	−1.80	0.00	6.80×10^{-30}	[45]	1.34
10.	$CH_4 + H \rightleftarrows CH_3 + H_2$	1.02×10^{-18}	2.50	9.59	2.59×10^{-13}	2.20×10^{-20}	3.00	8.03	3.87×10^{-13}	[45]	1.50
11.	$CH_4 + O \rightleftarrows CH_3 + OH$	1.69×10^{-15}	1.50	8.60	7.07×10^{-13}	1.15×10^{-15}	1.56	8.49	7.67×10^{-13}	[45]	1.09
12.	$CH_4 + OH \rightleftarrows CH_3 + H_2O$	9.68×10^{-20}	2.60	2.19	2.03×10^{-12}	2.60×10^{-17}	1.83	2.78	1.98×10^{-13}	[45]	0.98
13.	$CH_4 + HO_2 \rightleftarrows CH_3 + H_2O_2$	1.88×10^{-23}	3.74	21.01	7.97×10^{-17}	1.50×10^{-11}	0	24.64	6.17×10^{-17}	[45]	0.78
14.	$CH_4 + CH_3O_2 \rightleftarrows CH_3 + CH_3O_2H$	1.59×10^{-24}	3.77	17.81	4.17×10^{-17}	3.01×10^{-13}	0	18.48	2.75×10^{-17}	[43]	0.66
15.	$CH_3 + HO_2 \rightleftarrows CH_4 + O_2$	1.93×10^{-19}	2.23	−3.02	4.32×10^{-12}	5.99×10^{-12}	0	0.00	5.99×10^{-12}	[43]	1.39
16.	$CH_3 + O_2 + M \rightleftarrows CH_3O_2 + M$	Troe approximation			1.11×10^{-32}	1.59×10^{-22}	−3.30	0.00	2.01×10^{-32}	[45]	1.80
17.	$CH_3 + HO_2 \rightleftarrows CH_3O + OH$	1.66×10^{-12}	0.27	−0.69	1.50×10^{-11}	3.01×10^{-11}	0	0.00	3.01×10^{-11}	[45]	2.00
18.	$CH_3 + O_2 \rightleftarrows CH_2O + OH$	4.39×10^{-24}	3.28	8.11	5.24×10^{-16}	5.50×10^{-13}	0	8.94	6.11×10^{-15}	[45]	11.66
19.	$CH_3O_2 + CH_3 \rightleftarrows CH_3O + CH_3O$	8.44×10^{-12}	0	−1.41	1.72×10^{-11}	4.00×10^{-11}	0	0.00	4.00×10^{-11}	[43]	2.33
20.	$CH_3O_2H \rightleftarrows CH_3O + OH$	6.31×10^{14}	0	42.30	3.59×10^5	6.00×10^{14}	0	42.33	3.36×10^5	[46]	0.94
21.	$CH_3O + O_2 \rightleftarrows CH_2O + HO_2$	7.27×10^{-43}	9.50	−5.50	3.66×10^{-13}	3.60×10^{-14}	0	1.75	1.49×10^{-14}	[46]	0.04
22.	$CH_2O + O_2 \rightleftarrows HCO + HO_2$	1.34×10^{-8}	0	53.42	2.83×10^{-20}	1.00×10^{-10}	0	40.74	1.25×10^{-19}	[45]	4.41
23.	$CH_2O + H \rightleftarrows HCO + H_2$	9.53×10^{-17}	1.90	2.74	1.20×10^{-11}	2.10×10^{-16}	1.62	2.17	5.10×10^{-12}	[46]	0.42
24.	$CH_2O + HO_2 \rightleftarrows HCO + H_2O_2$	3.12×10^{-20}	2.70	11.52	1.19×10^{-14}	5.00×10^{-12}	0	13.08	6.92×10^{-15}	[45]	0.58
25.	$CH_2O + CH_3 \rightleftarrows HCO + CH_4$	6.36×10^{-23}	3.36	4.31	8.73×10^{-14}	1.29×10^{-31}	6.10	1.97	9.57×10^{-14}	[46]	1.10
26.	$CH_2O + CH_3O_2 \rightleftarrows HCO + CH_3O_2H$	3.30×10^{-12}	0	11.66	9.35×10^{-15}	3.30×10^{-12}	0	11.66	9.33×10^{-15}	[43]	1.00
27.	$HCO + M \rightleftarrows H + CO + M$	9.47×10^{-13}	0.66	14.87	5.08×10^{-14}	No data					–
28.	$HCO + O_2 \rightleftarrows CO + HO_2$	1.26×10^{-11}	0	0.41	1.02×10^{-11}	8.50×10^{-11}	0	1.69	3.63×10^{-11}	[43]	3.55

Table 2. (Contd.)

№	Reaction	AramcoMech 3.0 [22]				NIST database [37]***					k (NIST)/ k (Aramco)
		A^{**}	N	E_a, kcal/mol	k (1000 K)	A^{**}	N	E_a, kcal/mol	k (1000 K)	reference	
29.	$CH_3O + M \rightleftarrows CH_2O + H + M$	Troe approximation			1.20×10^{-13}	No data					–
30.	$CH_3 + CH_3 + M \rightleftarrows C_2H_6 + M$	Troe approximation			2.57×10^{-30}	3.51×10^{-7}	-7.00	2.76	8.74×10^{-29}	[46]	34.00
31.	$C_2H_6 + H \rightleftarrows C_2H_5 + H_2$	1.91×10^{-16}	1.90	7.53	2.16×10^{-12}	2.39×10^{-15}	1.50	7.41	1.82×10^{-12}	[45]	0.84
32.	$C_2H_6 + OH \rightleftarrows C_2H_5 + H_2O$	2.46×10^{-17}	1.90	0.95	7.64×10^{-12}	1.19×10^{-17}	2.00	0.86	7.74×10^{-12}	[45]	1.01
33.	$C_2H_6 + CH_3 \rightleftarrows C_2H_5 + CH_4$	9.22×10^{-28}	4.72	3.23	2.62×10^{-14}	2.48×10^{-31}	6.00	6.04	1.19×10^{-14}	[45]	0.45
34.	$C_2H_4 + H + M \rightleftarrows C_2H_5 + M$	Troe approximation			3.65×10^{-31}	7.69×10^{-30}	0	0.76	5.25×10^{-30}	[45]	14.38
35.	$C_2H_5 + HO_2 \rightleftarrows C_2H_5O + OH$	1.83×10^{-11}	0	0.00	1.83×10^{-11}	No data					–
36.	$C_2H_5 + O_2 \rightleftarrows C_2H_4 + HO_2$	Logarithmic interpolation			1.08×10^{-13}	1.69×10^{-13}	0	-2.19	5.09×10^{-13}	[45]	4.71
37.	$C_2H_4O(1-2) \rightleftarrows CH_3 + HCO$	3.63×10^{13}	0	57.20	11. 4	7.00×10^{15}	0	81.67	9.88×10^{-3}	[45]	8.65×10^{-4}
38.	$C_2H_4 + OH \rightleftarrows C_2H_3 + H_2O$	3.70×10^{-20}	2.75	2.22	2.09×10^{-12}	3.40×10^{-11}	0	5.94	1.71×10^{-12}	[45]	0.82
39.	$C_2H_4 + CH_3 \rightleftarrows C_2H_3 + CH_4$	1.62×10^{-21}	2.95	15.15	5.49×10^{-16}	6.91×10^{-12}	0	11.13	2.55×10^{-14}	[45]	46.45
40.	$C_2H_4 + HO_2 \rightleftarrows C_2H_4O(1-2) + OH$	5.55×10^{-12}	0	17.19	9.72×10^{-16}	1.00×10^{-14}	0	7.95	1.83×10^{-16}	[43]	0.19
41.	$C_2H_3 + O_2 \rightleftarrows CH_2O + H + CO$	Logarithmic interpolation				No data					–
42.	$CH_3 + CH_2O \rightleftarrows C_2H_5O$	4.98×10^{-13}	0	6.34	2.05×10^{-14}	No data					–
43.	$C_3H_8 + M \rightleftarrows CH_3 + C_2H_5 + M$	Troe approximation			2.12×10^{-21}	1.30×10^{-5}	0	64.98	8.15×10^{-20}	[46]	38.46
44.	$C_3H_6 + O_2 \rightleftarrows CH_2CHCH_2 + HO_2$	9.90×10^{-5}	-1.67	46.19	7.75×10^{-20}	3.20×10^{-12}	0	39.15	8.88×10^{-21}	[46]	0.11
45.	$C_3H_6 + CH_3 \rightleftarrows CH_2CHCH_2 + CH_4$	3.67×10^{-24}	3.50	5.68	6.67×10^{-15}	3.68×10^{-24}	3.50	5.68	6.67×10^{-15}	[43]	1.00
46.	$C_3H_6 + H \rightleftarrows C_2H_4 + CH_3$	Logarithmic interpolation				No data					–

* The kinetic parameters are represented for the three-parameter for the Arrhenius equation: $k = A(T)^N e^{(-Ea/RT)}$.
** A are measured in cm^3 $molecule^{-1}$ s^{-1}.
*** References to works given in the database [37] (see text).

with increasing rate constant, the process rate increases), whereas reaction (30) affects adversely.

Figure 1 presents the results of the calculations, which show that the alternating replacement of the kinetic parameters of steps (13), (17), (18), and (30) from the works [45, 46] by the data from [22] affects oxygen conversion. In the case of steps (13) and (17), the observed effect is less significant, which is likely to be due to a relatively small difference between the rate constants for these reactions (see Table 1). For reactions (18) and (30), the rate constants at 1000 K as calculated from the data [45, 46] are by factors of 12 and 34, respectively, higher than those calculated from the data [22]. The rates of the steps of the chain branching (18) and termination (30) decrease in the transition from the data [45, 46] to [22]. Correspondingly, in the former case, the process rate abruptly decreases, and in the latter, it increases (Fig. 1, curves *3* and *4*). It is interesting to note, that the effects of the replacements of the kinetic parameters of the considered steps compensate each other: after the simultaneous replacement of the parameters for steps (13), (17), (18), and (30), the change in the oxygen conversion over reaction time becomes insignificant (Fig. 1, curve *5*). However, in this case, the distribution of the reaction products changes significantly: the fraction of C_2 hydrocarbons decreases, and the fraction of carbon oxides simultaneously increases (Figs. 2a−2d). Such a redistribution of the products toward deep oxidation is expectable because the value of the rate constant for the recombination of methyl radicals accepted in the AramcoMech model is much lower. The further analysis revealed that the amount of the formed ethylene also noticeably depends on the rate of step (39) − of the ethylene molecule interaction with the methyl radical, for which the rate constant calculated from the data [45] is by a factor of 46 higher than that accepted in the model [22]. Correspondingly, with varying rate constant for this step, the amount of ethylene in the reaction products changes substantially (Fig. 2b). As for carbon oxides, the analysis of the kinetic scheme showed that their concentrations are most sensitive to a change in the parameters of step (15). The rate constant for this reaction calculated from the data [43] is by a factor of 16 higher as compared to that calculated from the data of [22]. Predictably, the replacement of the parameters of this step leads to a substantial change in the ratio between the concentrations of carbon oxides (Figs. 2c, 2d). Noteworthily, the rate constant for reaction (15) affects weakly the amount of the formed C_2 hydrocarbons (Figs. 2a, 2b).

The following analysis demonstrated that the concentrations of the products and the reactants have much lower sensitivity to the parameters of all the other individual steps, and the differences observed in Figs. 1 and 2 between the corresponding curves are caused by the accumulation of differences in the values of the kinetic parameters (Table 1).

Table 3. Differences between the step schemes obtained by reducing the AramcoMech 3.0 model (1000 K, 1 atm) at various initial values of the kinetic parameters*

No. of step	Reaction
Present in Scheme 1, absent in Scheme 2	
1	$H + O_2 + M \rightleftarrows HO_2 + M$
2	$CH_3 + H + M \rightleftarrows CH_4 + M$
3	$CH_4 + CH_3O_2 \rightleftarrows CH_3 + CH_3O_2H$
4	$CH_3 + O_2 + M \rightleftarrows CH_3O_2 + M$
5	$CH_3O_2 + CH_3 \rightleftarrows CH_3O + CH_3O$
6	$CH_3O_2H \rightleftarrows CH_3O + OH$
7	$CH_3O + O_2 \rightleftarrows CH_2O + HO_2$
8	$CH_2O + CH_3O_2 \rightleftarrows HCO + CH_3O_2H$
9	$HCO + M \rightleftarrows H + CO + M$
10	$C_2H_4 + H + M \rightleftarrows C_2H_5 + M$
11	$C_2H_5 + HO_2 \rightleftarrows C_2H_5O + OH$
12	$C_2H_4O(1-2) \rightleftarrows CH_3 + HCO$
13	$C_2H_4 + HO_2 \rightleftarrows C_2H_4O(1-2) + OH$
Present in Scheme 2, absent in Scheme 1	
14	$CH_2O + OH \rightleftarrows HCO + H_2O$
15	$C_2H_3 + O_2 \rightleftarrows CH_2CHO + O$
16	$C_2H_3 + O_2 \rightleftarrows CHOCHO + H$
17	$C_2H_3 + O_2 \rightleftarrows CH_2O + HCO$
18	$C_2H_4 + O \rightleftarrows CH_2CHO + H$
19	$C_2H_6 + HO_2 \rightleftarrows C_2H_5 + H_2O_2$
20	$CH_2CHO + M \rightleftarrows CH_3 + CO + M$
21	$CH_2CHO + O_2 \rightleftarrows CH_2O + CO + OH$

* Scheme 1 was obtained by reducing the initial AramcoMech 3.0 model; Scheme 2, by reducing the AramcoMech 3.0 model with modified kinetic parameters.

Thus, the performed analysis shows that the most significant contribution to the observed difference in calculation results based on the data of [22] and [45] is due to the effect of the kinetic parameters of steps (15), (18), (30), and (39), which differ by more than an order of magnitude. Below, we consider each of these reactions in more detail.

Oxidation of CO by the hydroperoxide radical. The reaction

$$CO + HO_2 \rightleftarrows CO_2 + OH \qquad (15)$$
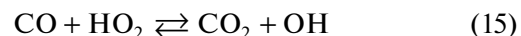
is one of the most important in the conversion of CO to CO_2. Moreover, this reaction transforms the HO_2 radical, which is relatively low active in hydrogen atom abstraction reactions, into the highly active OH radical.

In the model [22] uses the data from the recent work [50], in which the kinetic parameters of step (15) were estimated based on quantum-chemical calcula-
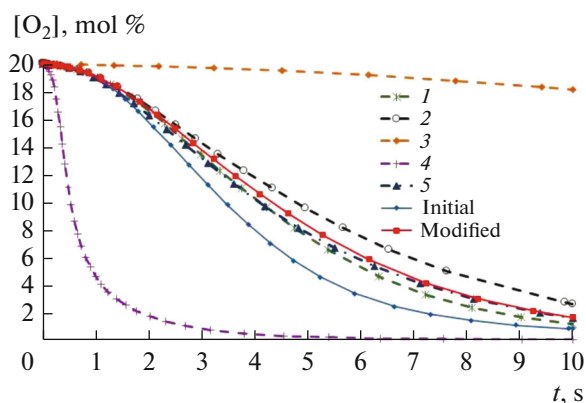
[O$_2$], mol %

Fig. 1. Dependence of the current oxygen concentration on the reaction time. Curves *1–5* were obtained by the replacement of the kinetic parameters of individual steps of the modified scheme by the parameters of the AramcoMech scheme: the replacement of the parameters of (*1*) step (13); (*2*) step (17); (*3*) step (18); (*4*) step (30); and (*5*) steps (13), (17), (18), and (30).

tions. Since the works [45, 46] contain no data on the kinetic parameters of step (15), let us consider the parameters proposed in the works [43, 44]. As is seen from Table 4, the rate constants calculated from the data of the works [43] and [44] are virtually the same, whereas their difference based on the data from the work [50] is more than an order of magnitude. The kinetic parameters from the works [43] and [44] were used in the models [31] and [33], respectively. The values of parameters accepted in the schemes [35, 36] give intermediate values of the rate constant for step (15). Thus, the performed analysis showed that the kinetic parameters of step (15), which were used by the developers of the model [22], also may require refinement.

Oxidation of methyl radicals. The analysis of the data on the kinetic parameters of the reactions of the methyl radical interaction with oxygen:

$$CH_3 + O_2 \rightleftarrows CH_2O + OH. \qquad (18)$$
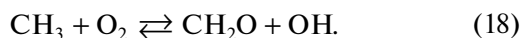
is even more complicated. This reaction is the key step responsible for the sharp decrease in the selectivity in the OCM process at temperatures above 1100−1200 K (thus determining the upper boundary of the OCM window [11]) and for the formation of syngas in the homogeneous partial oxidation of methane.

The authors of the model [22] indicated "Klippenstein S.J. Personal communication, 2009" as the primary source of information about the parameters for this step. One can assume that the authors of the model used the parameters presented by S. J. Klippenstein in a private communication. It is unknown whether or not these data are published. The database [37] contains few sources of data for reaction (18); most of the data were obtained in the high-temperature range (>1500 K). Along with the data of the work [45], Table 5 also presents the rate constants calculated from the data of the recent experimental works [51, 52]. With regard to the other kinetic schemes, the parameters close to those from the work [52] are accepted in the model [31], whereas the parameters from the work [45] are utilized in the schemes [33] and [35]. The reaction (18) is not included in the model [36].

Thus, a significant difference between the kinetic parameters for step (18) presented in the work [45] and used by the authors of the kinetic schemes [22, 32, 33, 35, 36] is revealed.

Recombination of methyl radicals. The reaction

$$CH_3 + CH_3 + M \rightleftarrows C_2H_6 + M \qquad (30)$$

determines the very possibility of the formation of C$_{2+}$ hydrocarbons during the methane oxidation, and the efficiency of this reaction (in comparison with the other reactions of methyl radical) governs the primary selectivity of the process.

Table 6 illustrates the temperature dependence of the rate constants for reaction (30) at 800−1300 K that were calculated from the data [22] and [46]. The data in the model [22] are based on the results of the experimental work [53]. As is seen from the presented data, the rate constants calculated from the data of the works [22] and [46] differ by more than an order of

Table 4. Temperature dependence of the rate constants for the reaction $CO + HO_2 \rightleftarrows CO_2 + OH$ according to various sources

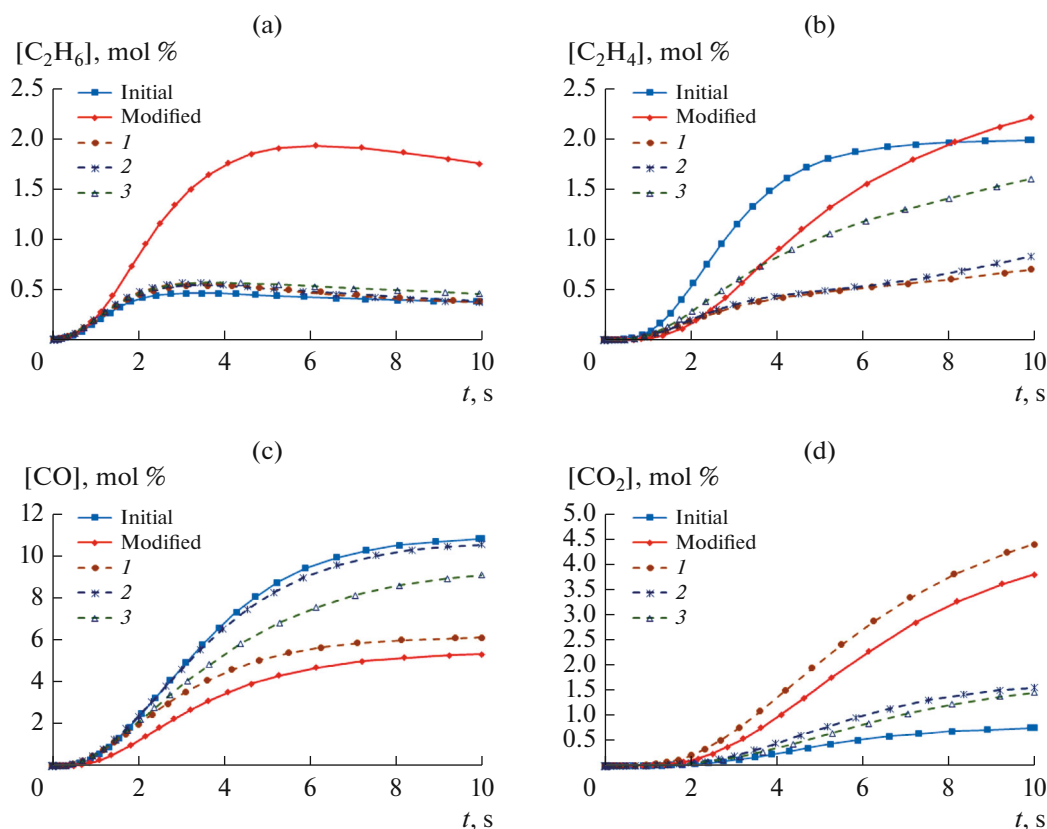| Reaction	T, K	$k \cdot 10^{17}$, cm^3 molecule^{-1} s^{-1}				
		Aramco 3.0 [22]	Tsang et al. [43], Konnov [33]	Warnatz [44], Gri-mech 3.0 [31]	San Diego [35]	Milan [36]
$CO + HO_2 \rightleftarrows CO_2 + OH$	800	0.7	8.7	8.9	1.8	2.6
	900	3.2	45.3	46.2	9.1	12.9
	1000	10.8	170.0	173.0	32.8	46.8
	1100	30.3	501.7	509.4	93.6	134.1
	1200	72.6	1236.1	1252.7	224.0	322.2
	1300	154.3	2651.1	2682.2	468.9	676.7

Fig. 2. Dependence of the current concentration of (a) ethane, (b) ethylene, (c) CO, and (d) CO_2 on the reaction time. Curves $1-5$ were obtained by the replacement of the kinetic parameters of individual steps of the modified scheme by the parameters of the AramcoMech scheme: the replacement of the parameters of (1) steps (13), (17), (18), and (30); (2) steps (13), (15), (17), (18), and (30); and (3) steps (13), (15), (17), (18), (30), and (39).

magnitude. As it was demonstrated above, such a difference has a critical effect on the simulation results. For the further analysis the kinetic parameters of the reaction (30) accepted in the well-known kinetic models of the oxidation of light alkanes [31, 33, 35, 36] were chosen. The values of the rate constant calculated from these data are the same order, and the data [53] almost completely coincide with the data [33]. Thus, the observed difference between the results of the simulations using the well-known and well-proven models and those based on the data of the review [46] raises doubts about the validity of the parameters presented in it.

Reaction of ethylene with the methyl radical. The description of the interaction of ethylene with the methyl radical is probably the most ambiguous. The step
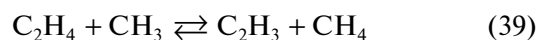
$$C_2H_4 + CH_3 \rightleftarrows C_2H_3 + CH_4 \qquad (39)$$

Table 5. Temperature dependence of the rate constants for the reaction $CH_3 + O_2 \rightleftarrows CH_2O + OH$ according to various sources

Reaction	T, K	$k \times 10^{17}$, cm³ molecule⁻¹ s⁻¹					
		Aramco 3.0 [22]	Baulch et al. [45]	Gri-mech 3.0 [31]	Konnov [33], San Diego [35]	Srinivasan et al. [51]	Yu et al. [52]
$CH_3 + O_2 \rightleftarrows CH_2O + OH$	800	9.1	198.5	1.1	198.5	21.6	0.9
	900	23.6	370.9	4.5	370.9	55.5	3.7
	1000	52.4	611.5	13.9	611.5	118.2	11.4
	1100	103.9	920.5	35.2	920.5	219.2	28.8
	1200	188.2	1294.3	76.3	1294.3	366.9	62.4
	1300	318.0	1727.0	147.1	1727.0	567.4	120.0

Table 6. Temperature dependence of the rate constants for the reaction $CH_3 + CH_3 + M \rightleftarrows C_2H_6 + M$ according to various sources

Reaction	T, K	$k \times 10^{30}$, cm^6 molecule^{-2} s^{-1}					
		Aramco 3.0 [22]	Baulch et al. [46]	Gri-mech 3.0 [31]	Konnov [33]	San Diego [35]	Milan [36]
$CH_3 + CH_3 + M \rightleftarrows C_2H_6 + M$	800	2.9	294.5	2.5	3.3	2.4	2.6
	900	2.8	156.6	2.3	3.0	2.3	2.3
	1000	2.6	87.4	2.0	2.7	2.1	1.9
	1100	2.3	50.9	1.7	2.4	1.7	1.5
	1200	2.1	30.8	1.4	2.0	1.4	1.2
	1300	1.8	19.2	1.2	1.7	1.1	0.9

Table 7. Temperature dependence of the rate constants for the reaction $C_2H_4 + CH_3 \rightleftarrows C_2H_3 + CH_4$ according to various sources

Reaction	T, K	$k \times 10^{15}$, cm^3 molecule^{-1} s^{-1}					
		Aramco 3.0 [22]	Baulch et al. [46], Konnov [33]	Tsang et al. [43]	Warnatz [44]	Gri-mech 3.0 [31]	Milan [36]
$C_2H_4 + CH_3 \rightleftarrows C_2H_3 + CH_4$	800	0.04	6.3	1.5	0.6	0.7	0.3
	900	0.2	13.7	4.6	1.4	1.8	0.7
	1000	0.5	25.5	11.6	2.6	3.7	1.7
	1100	1.5	42.5	25.5	4.3	6.8	3.4
	1200	3.3	64.9	50.6	6.6	11.5	6.3
	1300	6.9	92.9	92.4	9.4	18.1	10.6

is quite important because it determines the rate of homogeneous activation and consecutive transformations of ethylene, which results in the decrease of OCM selectivity at relatively high conversions: of all the radical species, methyl radicals have the maximum concentration in the reaction mixture.

The description of the model [22] contains no data on the source of the kinetic parameters for this step. The rate constant calculated from the parameters used in the model [22] differs from that obtained based on the data [46] by a factor of more than 40 (see Table 7). Note that the values calculated from the data of the other works, including well-known reviews [43, 44], and the kinetic models [31, 36], also differ from each other and are intermediate between the data [22] and [46]. The kinetic parameters from work [46] is accepted in the scheme [33], while the model [35] does not include the reaction (39).

Effect of Taking into Account the Heterogeneous Reactions on the Results of the Reduction

As already noted, the OCM process is free-radical and at the same time heterogeneous catalytic; i.e., its total rate and the product composition are determined by a set of a large number of steps occurring both in the gas phase and with the participation of the catalyst surface sites. It was shown above that the values of the kinetic parameters of homogeneous steps significantly affects both the simulation results and the results of reduction procedure. It can be expected that the addition of heterogeneous reaction block can significantly affect not only the calculation results (what have already been reported earlier [12]), but also the results of the reduction procedure of the homogeneous part of the combined model.

It was previously shown [11, 12, 49] that the addition of the block of heterogeneous reactions to the detailed kinetic scheme of gas-phase methane oxidation leads to several main changes. For example at increasing concentration of catalytically active sites (CAS), the part of the kinetic curve corresponding to an increasing reaction rate gradually disappears and at the highest CAS concentrations the process becomes linear, i.e., starts with the maximum reaction rate, which gradually decreases as the reactants are consumed. Although the maximum reaction rate can be reached in the pure homogeneous process (due to the development and branching of chains, the time of attaining a certain conversion decreases with increasing CAS concentration. The selectivity to the desired products of the OCM reaction (C_2 hydrocarbons) passes through a maximum with increasing CAS concentration: the selectivity increases at low concentra-

tions because of the high rate of generation of methyl radicals and the increasing efficiency of their recombination and then drops due to the-contribution of the heterogeneous deep oxidation.

The results of the reduction depend on the introduction of CAS to the system. However, this dependence is nonmonotonic. At a relatively low CAS concentration ($\sim 7 \times 10^{17}$ cm^{-3}), the total number of steps in the homogeneous part of the reduced system increases. Due to the sharp increase in the rate of generation of-methyl radicals and concentration of C_2 and C_3 hydrocarbons, an increase in the contribution of reactions of these substances is observed. Meanwhile, the reduced scheme does not include 11 reactions of species containing ≤2 carbon atoms, which were present in the scheme before adding CAS.

With a further increase in the CAS concentration, the number of homogeneous reactions in the reduced scheme progressively decreases. At a CAS concentration of $\sim 1 \times 10^{19}$ cm^{-3}, only 25 reversible reactions remain in the scheme. Variation of the CAS concentration causes no change in the composition of the heterogeneous block in the reduced scheme.

Thus, the results of both simulations and reduction of the heterogeneous–homogeneous scheme of the oxidation of methane indicate a significant effect of the heterogeneous factors on the overall process due to the strong kinetic coupling between homogeneous and heterogeneous processes. In particular, the addition of the heterogeneous block to a detailed kinetic scheme of methane oxidation leads to a significant changes of the observed kinetic features and affects the relative contributions of individual steps. In practical terms, the presence of surface active sites significantly alters the selectivity to the desired products.

Effect of Temperature on the Results of Reduction

The high sensitivity of the result of the reduction to the values of the kinetic parameters should inevitably lead to the fact that the set of steps comprising the reduced kinetic scheme changes with varying reaction conditions and initial values of physical parameters. Indeed, e.g., due to the strong temperature dependence of the rate constants, the ratios between the contributions of different steps to the overall kinetics also vary widely with varying temperature. Hence, the relative "weight" of different steps changes with varying temperature in the isothermal process and much more in the non-isothermal (e.g., adiabatic or autothermal) process.

In this work, the effect of temperature (900–1200 K at an interval of 100 K) on the results of reduction was studied for the initial kinetic scheme consisting of the homogeneous and heterogeneous blocks (CAS concentration 7×10^{18} cm^{-3}). As in the variation of the CAS concentration, the composition of the heterogeneous block in the reduced scheme changes slightly

with varying temperature. However, the homogeneous part of the scheme is strongly affected by temperature. An increase in temperature leads to a decrease in the contribution of reactions of alcohols and aldehydes (substances that form mainly through CH_3O_2 radicals) and an increase in the contribution of reactions of C_1–C_2 species in high oxidation states, which are intermediates in the formation of carbon oxides (first of all, CO) through steps of type of (18) (see above). As a result, the number of reversible homogeneous reactions in the reduced scheme increases from 25 at 1000 K to 45 at 1200 K.

Importantly, because of the high exothermicity of the reactions of the formation of carbon oxides, using "short" schemes, which were obtained by reduction at relatively low temperatures (e.g., 1000 K) and neglected high-temperature steps, can lead to significant errors in calculating the adiabatic or autothermal (with a partial loss of the released heat) process. Similarly, at relatively low temperatures, for more accurate reproduction of selectivity data, the scheme should be supplemented with steps that are absent in reduced schemes obtained for high temperatures.

We considered two approaches to obtaining reduced schemes, which are valid over a wide temperature range. One of them is to perform the reduction during the calculation of the adiabatic process. The second is to combine the schemes obtained in different temperature ranges by adding substances and reactions from high-temperature schemes to low-temperature ones (or vice versa). Although the size of the descriptions obtained using the second approach is higher, the accuracy of the calculations using these descriptions is generally much higher (the results are closer to those obtained using the complete schemes) than in the case of using the first approach.

SUMMARY

Compliance with the principle of independence of kinetic parameters; i.e., the complete abandonment of the fitting of the values of kinetic parameters for reaching an agreement between the calculation results and experimental data, is one of the main requirements in creating a consistent and unambiguous description of a process [11]. Otherwise, the parameters within a complex scheme become strongly coupled with each other and with the results of the "base" experiments. Such fitting also imposes restrictions on the further development of the model and ambiguates the results of calculations in the parameter ranges outside those of the base experiments. Ideally, the determination of the parameters of the kinetic model should be carried out using open databases without tying or fitting to experimental data. However, the analysis performed in this work showed that the models obtained using this approach may have low predictive power because of the existing uncertainties in the

values of parameter presented in the well-known review papers and databases [43−46].

As an alternative compromise, the approach proposed by the authors of the model [22] can be considered. This approach also requires the abandonment of the fitting of the values of the kinetic parameters. The main criterion for the parameters selection is the maximum proximity of the description to the experimentally observed features over a wide range of reaction mixtures and reaction conditions. The authors of the model [22] assert that the kinetic parameters presented in independent sources (e.g., in [43−46]) do not take into account the reciprocal influence of all the elementary reactions and species, which emerges in their introduction to the total kinetic description. Therefore, the simple determination of such parameters of the kinetic scheme does not give sufficiently accurate description of the process. This statement contradicts one of the main concepts of chemical kinetics, namely, the principle of independence of rates of elementary steps. For this reason, the opinion of the authors of the AramcoMech model [30] can probably be understood only in the sense that some published values of the kinetic parameters were obtained not in a direct experiment, but by analyzing the regularities of complex processes and using some kinetic models. Because of this, certain values of parameters are model-dependent. In other words, if their determination from the existing data on the characteristics of the overall process used other models with other sets of steps and/or parameters, the numerical values might be different. In such an interpretation, the approach proposed by the authors of the model [22] is a reasonable trade-off between the strict adherence to the principle of independence of kinetic parameters together with a priori preference of some literature data over others and arbitrary fitting of values of kinetic parameters for maximizing the accuracy of the description of the model experiments.

In the present work we demonstrated that the reduction of large kinetic schemes is a convenient and reliable tool to compare different kinetic descriptions and sets of parameters available in the literature. However, using the obtained reduced descriptions (both for analyzing the mechanism of processes, and for modeling real processes and reactors) requires great care. In the former care, the results of comparing the calculated and experimental data may be interpreted incorrectly because complex reactions may have several routes with strong conjugation between them. In the latter case, significant calculation errors may emerge because of the strong parametric dependences (on temperature, pressure, and reactant concentrations) of the kinetic constants and the rates of the entire process. The real combinations of the parameters may differ significantly from those at which the reduction was performed. Finally, the reactions and even components of the reaction mixture that are not included in the kinetic description may become quite significant in some stages of the process under the particular conditions.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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