KINETIC MODELS OF C_1–C_4 ALKANE OXIDATION AS APPLIED TO PROCESSING OF HYDROCARBON GASES: PRINCIPLES, APPROACHES AND DEVELOPMENTS

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Abstract

The topical problems existing in the modeling of oxidation processes in gas chemistry, particularly in oxidative transformations of light (C_1–C_4) alkanes, are outlined. It is demonstrated that the requirements to adequate description of process kinetics in this case differ significantly from those which are satisfactory in combustion kinetics and, on the other hand, in near-equilibrium petrochemical processes. The principles that could be utilized in developing consistent kinetic models are determined by the goal of modeling, which appears to be the most important factor controlling all the approaches and procedures. The models under discussion are aimed at (i) the rationalization of the reaction network responsible for the main features of the overall process, (ii) the description of light alkane oxidation, and (iii) optimization of the yield of some reactive intermediate product, such as olefins, saturated and non-saturated alcohols, aldehydes, acids, synthesis gas, etc. The latter defines the ranges of parameters (temperature, pressure, initial composition of reaction mixture) and the main ruling principles of modeling. It is concluded that comprehensive kinetic models should be based on the following principles: thermodynamic consistency, fullness, independence of kinetic parameters, openness of the description. The possibility of accurate description of phenomena under consideration is determined by a series of factors, including fullness of the model, adequate description of the reaction space (reactor itself and connecting tubing), correct accounting of heat- and mass-transfer processes, precision of kinetic parameters and even the form of their representation, etc. Another complicated problem is model verification. It is demonstrated that the comparison with experimental data is associated with serious difficulties and its applicability for the model verification is limited. Special attention is paid to the modeling of heterogeneous processes. Possible approaches to the description of elementary steps on oxide and metal surfaces and building of combined heterogeneous–homogeneous models are discussed. Some examples are given, mainly related to the joint description

of C_1–C_2 hydrocarbon oxidation, and the ways of its expansion on higher hydrocarbons are traced.

I. Introduction: Problem Statement

The increasing efficiency of chemical transformations is an ultimate goal of applied scientific research. Developments in hydrocarbon processing present numerous examples of the interplay between practical industrial needs and the advances in kinetic and mechanistic studies. For instance, the ''oil shocks'' of the mid- and late 1970s shifted interest from relatively high molecular weight hydrocarbons and light olefins to light alkanes as initial compounds for many industrial processes. Nowadays, this interest is increasing along with petroleum price. One of the most clearly revealed tendencies in both expert judgments and public opinion is a progressing understanding that oil is a finite resource and global peak in its production is imminent (see, for instance, web resources http://www.asponews.org, http://www.eia.doe.gov). According to some estimates, the decline in the world oil production and supply will become irreversible during the current decade.

Unlike oil, natural gas and its main components—light (C_1–C_4) alkanes—are much more abundant. The existing estimates of their assured resources in traditional gas fields are much more optimistic as compared to oil resources. Moreover, the Earth's mantle permanently releases additional amounts of methane, and its resources in the form of gas hydrates are estimated as more than a half of the organic carbon in the Earth's crust (Kvenvolden, 1988). The development of these giant resources becomes the strategic goal of the world economy and accordingly one of the priority directions in scientific research—both fundamental and applied (Melvin, 1988).

Nevertheless, the world economy remains oil-based and the production of almost the whole range of petrochemical and bulk organic chemical products (with a few exceptions, like methanol, urea, and cyanic acid) is still oriented toward the processing of liquid fossil hydrocarbons as the principal raw materials. Also, the same liquid hydrocarbons dominate in the production of motor fuels and lubricants. However, most if not all of the products traditionally produced from oil can be also obtained from gaseous hydrocarbons, including light alkanes. Unfortunately, up to now their utilization in the chemical industry is not satisfying.

One of the possible reasons for that is our insufficient understanding of light alkane chemistry and, consequently, our limited capability to develop efficient technologies. First of all, petrochemistry dominates not only in industry, but also in prevailing scientific and technical approaches. However, if we analyze the production of the same final products (for instance, liquid motor fuels) from light alkanes and higher hydrocarbons (oil), a distinct difference in the involved processes becomes clear. In the case of higher hydrocarbon processing we are dealing mainly with equilibrium reactions (cracking, isomerization, hydration, dehydration).

In contrast, in the case of low-molecular weight alkane processing, the main types of transformations relate to the cleavage of strong C–H bonds and building up the carbon skeleton. Such processes proceed most efficiently in the non-equilibrium oxidative (or redox) mode, which shifts the main emphasis to their kinetic aspects. As a result, if equilibrium petrochemical processes require first of all the use of active and durable catalysts, in light alkane processing (gas chemistry) the problem of selectivity with respect to reactive intermediate products is brought to the forefront.

Secondly, the problem of selectivity has been thoroughly scrutinized as applied to catalytic chemistry of olefins, aromatic hydrocarbons, oxygenates, etc. However, in the case of light alkanes we are facing a very different set of problems originating from relatively low reactivity of the starting molecules as compared to the molecules of the desired products. As a result, the applicability of existing approaches for the development of selective catalysts becomes doubtful and makes the role of kinetic factors crucial.

At last (not least!), oxidative transformations of light alkanes (both homogeneous and catalytic) as a rule proceed as high-temperature complex multi-step processes. In non-equilibrium conditions during alkane (e.g., methane) oxidation the complexity of the system is headily rising, as numerous intermediates participate in multiple elementary reactions. In such conditions the process is poorly accessible for direct mechanistic investigations. Even pathways of both formation and consecutive transformations of particular target products become difficult to trace. However, although processes taking place on the "elementary" level are undoubtedly responsible for the kinetically attainable yields of target product(s), the most successful and systematic descriptions of such limitations are still accessible in terms of comparative overall reactivity of products and initial hydrocarbon (Batiot and Hodnett, 1996; Isagulyants *et al.*, 2000).

In the conditions of insufficient understanding of chemistry and kinetics of light alkane transformations, the family of industrial processes based on methane conversion to synthesis gas (syngas—$CO + H_2$ mixture) is dominating. In its turn, syngas production is based on near-equilibrium reactions: steam and "dry" (with CO_2) reforming of methane, water-gas shift reaction and to some extent on oxidative reforming, which proceeds also under conditions close to equilibrium. Methane conversion to syngas is a high-temperature energy-consuming and capital-intensive process, but nevertheless it remains the basis of large-scale chemical processing of natural gas.

Although several other processes allowing bypass of the stage of syngas formation have been extensively investigated (see Arutyunov *et al.*, 1995a; Arutyunov and Krylov, 1998 and literature cited therein), now they are mostly considered as not proven and marginal technologies. There are just a few examples of their implementation on a small pilot-plant scale. The same can be said about oxidative processing of C_2–C_4 hydrocarbons with the exception of butane oxidation to maleic anhydride and (to some extent) propane oxidation to acrylic acid.

Obviously, some breakthrough in this field is required. All factors mentioned above make modeling the most promising (if not the only) approach to studying the details of kinetic behavior of such complex reaction systems and also the most valuable tool for process governing and optimization. Indeed, the number of publications in this area is rapidly increasing. However, it should be noted that up to now there is no unified and generally appreciated or accepted methodology for the modeling of complex processes. Moreover, in some cases the main purpose, basic statements and underlying principles of modeling are not clearly formulated, as well as the main procedures are not described. This makes the subject of study quite vague and the obtained results difficult to analyze.

In this work, the authors have attempted to outline the scope of topical problems existing in the modeling of oxidation processes in gas chemistry. We consider each section in this work as a formulation of the corresponding problem, but not as its solution, and, accordingly, the entire paper as an invitation to a broad discussion on the designated subject. Besides, we believe that the principles formulated below could be utilized in developing consistent kinetic models of the "open" type. The latter means that such models can be further built on as new reliable kinetic information becomes available.

Let us conclude the Introduction by a formulation of what cannot be found in the paper.

1. We tried to avoid any detailed or complete literature review concerning the subject under discussion; this would inevitably lead to vast and diffuse discussions and criticism. Instead, we attempted to point out the main problems and difficulties, to trace paths to possible solutions and to mention the achievements reached to date.
2. For the same reason we resisted the temptation to announce our own model, or even some core, which could be further built on. Moreover, all examples presented below are based on models already published by different authors, even if particular simulations are published here for the first time. We consider the substantiation and validation of basic principles as the ultimate goal of this paper. The core of the model based on such principles will be published separately.
3. The authors know from their own experience how attractive and fascinating, but at the same time meaningless can be "computer games" with equations, software, and model modifications. Based on this, we have almost completely refrained from consideration of any mathematical aspects and computational procedures, which are indeed very important in modeling and kinetic simulations. However, these topics require separate consideration, but only when

the main questions of physical, chemical, and kinetic matters are answered, or at least raised and discussed.

A. Modeling of Complex Reacting Systems: Purposes and Expectations

The modeling of any complex object is not trivial because there are no well-defined algorithms and recipes to perform it, so the procedures of model development in the general case cannot be formalized. The principal question in modeling that determines the entire sense of the work is its goal. There are several possible answers. First of all, as soon as a set of experiments is accomplished, the investigator may wish to build a continuous description of the process. In spite of the particular mathematical form of this description, it can very precisely fit the experimental data obtained in the given range of parameters. However, the width of a broader range to which the prediction of such a description can be extrapolated without a drastic decline in accuracy is always undefined.

The simplest mathematical description may be represented in the form of a table or as a set of curves demonstrating the process behavior (conversion, concentration of certain products, distribution of temperatures in the reacting system, etc.) at varying external parameters (initial composition and temperature, total pressure, flow rate, etc.). Such dependencies also can be expressed in the form of algebraic equations and used, for instance, for process optimization, almost exclusively by interpolation within the range of parameters where the initial set of experiments was carried out.

Compilation of a kinetic scheme containing a limited number of chemical equations and corresponding differential equations is another possible form of simple models. The chemical part of it cannot be considered as a detailed mechanism, but serves only as a phenomenological description of the process. As to the system of differential equations, on certain assumptions it can be solved and reduced to an algebraic form (for instance, in steady-state approximation). Models of this type are widely presented in the scientific literature.

When a detailed chemical description is not required, a limited set of a few stoichiometric equations can be included into the scheme just to describe the rate of heat evolution and change of total number of gas species in the system. Chemically oversimplified models of this kind are widely used, for instance, to describe heat-transfer and to optimize thermal regimes in reactors (see, e.g., Fukuhara and Igarashi, 2005; Kolios *et al.*, 2001). A similar approach is used to describe the fuel combustion and corresponding dynamic phenomena in engines of different types: simplified equations describing "kinetic" features are solved together with complex equations of heat- and mass-transfer and fluid dynamics (Frolov *et al.*, 1997; Williams, 1997).

More advanced kinetic models are developed for the interpretation and qualitative description of experimentally observed complex phenomena. The classical examples of such models are the first kinetic schemes proposed to describe oxidation of phosphorus, hydrogen, methane, and some other substances; they served as a basis for the creation and development of chain theory (Semenov, 1959). Of course, at that stage any detail in the mechanism for most of those processes was not and even could not be revealed. However, in spite of the "intuitive" character of those kinetic schemes, they laid a cornerstone for the theory, which in its turn has become the real basis of contemporary chemical kinetics of extraordinary descriptive and predictive power.

Let us finally dwell on one more type of model, which in principle does not require any preliminary experimental study of the process. Models of this kind themselves can be considered as tools for investigation of complex processes on a very intimate level. They constitute a hypothesis about the detailed chemical mechanism of the process (its micro-chemistry) that includes types of species present in the reacting system and chemical interactions between them. Being filled with kinetic parameters and treated in accordance with proper mathematical procedures, this type of model is supposed to reproduce the behavior (or evolution in time) of the system, which can be compared with some experiment in order to see if there are any matches or common features.

The obvious goal in this case could be an attempt to describe all phenomena ever observed in experiment within the framework of some broad, but uniform, mechanism. If this goal is reached, the model can be used to predict the system behavior even in the range of parameters far beyond those accessible in any realistic experiment. Such a range can be limited only by the physical and chemical sense of the kinetic scheme content and kinetic parameters. For instance, if we do not consider elementary reactions of excited species (e.g., carrying vibrational and/or electronic excitation), the scheme cannot be extrapolated to relatively high temperatures at which the effect of these factors becomes substantial.

In principle, there are no limitations for changing the chemical content of the model, as well as the values of kinetic parameters. Even some species and reactions, as well as the values of the kinetic parameters, which undoubtedly cannot exist in nature, can be included in order to answer the question such as: "What would happen if …".

Another very important feature of such models is their "openness": they can be built on and on to any direction from any given level. On the one hand, this in principle allows a very detailed elaboration of a given reaction. On the other hand, such "openness" is very helpful if more and more complicated systems must be analyzed. For instance, any action of additives (promoters, inhibitors, etc.) on hydrocarbon oxidation can be analyzed. On the other hand, a kinetic scheme describing the reaction of a certain compound can be spread on similar reactions of related compounds with gradually increasing complexity (e.g., from methane oxidation to analogous reactions of higher alkanes).

The main content of this paper will be devoted to the models mainly of this type. This is why here, in the very beginning, we would like to highlight some serious difficulties. First of all, we must stress the difference between so-called direct and inverse kinetic tasks. In the first case, the system evolution is simulated based on the kinetic scheme and accepted values of parameters. Such a task always has a solution; the only problem is to have a proper ‘‘calculator’’ (most frequently—specialized computer software).

As to an inverse kinetic task, it consists of the determination (or correction) of the kinetic scheme and kinetic parameters based on repeated solution of the direct task and comparison with experimental data. In order not to run ahead, we would just mention here that in general an inverse kinetic task has no definite solution. The uncertainty increases with increasing complexity of the system for a very simple reason: if the system under consideration is complex enough, there are always several combinations of parameters giving satisfactory agreement of the simulated behavior with that observed experimentally. Another fundamental limitation is an uncertainty (qualitative and quantitative), which is always present in the experimental data. Some other aspects of the comparison between simulated and experimental data will be discussed below. However, even at this initial level of consideration we can state that the development of a model to be used as a tool for studying the system of certain (high enough) complexity requires a formulation of some ruling principles. In their turn, these principles are determined by the goal of modeling, which appears to be the most important factor controlling all other approaches and procedures.

Another principal statement can be formulated as follows: the model of any complex process is a compromise between the precision and thoroughness of the description and its applicability and comprehensibility. Any extreme is irrational. The model can be so bulky that any attempt to analyze it would become useless, or it may be so incomplete that substantial intrinsic structure and connections would distort or even disappear from the description.

The number of computer codes and software packages for kinetic simulations and published kinetic models keeps increasing. This creates an illusion of ‘‘simplicity’’ (as compared to ‘‘complexity’’ of modern experimental techniques) of these exercises and makes ‘‘kinetic modeling’’ very popular. As the main positive result of such ‘‘modeling’’ the good agreement between model predictions and some experimental results, selected by authors, is usually considered. At the same time the attention paid both to the structure of the model and to the thorough analysis of its consequences is not sufficient. On the other hand, the preliminary analysis of experimental results chosen for the comparison with simulated data is also required. We have to be sure that these results are definite, comprehensive, and reliable enough and also that the conditions in the experimental reactor are adequately reproduced during the simulations.

There is one more aspect to which we have to pay special attention. The newly developed model can be a ‘‘mechanical’’ combination (a ‘‘sum’’ or ‘‘enclosure’’) of models previously used for other purposes. In that case we are facing a risk to put together some principally incompatible matters—to combine the elements or subsystems from different levels based on controversial principles. In Sections III.B–III.F we will demonstrate several examples of how it is important to analyze the applicability of existing models if we wish to use them for solving new problems.

Besides the precise definition of the ultimate goal and the main purposes, an adequate phenomenological description of the system under consideration is required. This should include its qualitative composition, phase (aggregative) state, ranges of parameters, first of all temperature, pressure, concentrations of components, type of reactor, heat- and mass-transfer conditions, flow regimes, etc. In other words, we need to have a clear conceptual vision of the reacting system and corresponding understanding of the main factors determining its behavior as far as the proclaimed goal of modeling is concerned.

Now let us turn to one of the key questions: what goals and purposes are worthwhile to pose for the modeling of light alkane oxidation? As we already mentioned, these reacting systems are so complex that the experimental study of their detailed mechanism is practically impossible. But modeling is capable of providing such a possibility. On the other hand, because of the great practical importance of these processes, we also need a tool for their optimization, as far as the efficiency of certain product formation is concerned. These two aspects—mechanistic studies and process optimization—can be considered as the main purposes for developing adequate kinetic models of light alkane oxidation.

Now let us look at the same problem at an angle of realistic expectations. We have to confess that at the current stage of understanding micro- and macrokinetic aspects of alkane oxidation it is practically impossible to anticipate a precise quantitative description and prediction of the system behavior, product yields, etc. This is not only due to our limited ability to build an adequate model, but also because of a limited accuracy and significant uncertainty in the parameters of any real experiment (see Sections IV.A and IV.B for a detailed analysis).

If we consider a better understanding as the main achievement of modeling, we should not fight for particular numbers or precise fit to certain experimental curve(s). The same model can describe very well one set of experimental data and be in a serious contradiction with the others. Also, models describing certain experimental curves well can be self-contradictory. Unfortunately, the examples of such "good" correlation between experiment and simulations are numerous.

A more realistic and useful result of modeling would be a qualitative description and interpretation of phenomena, which are of principal importance for the behavior of the system. Therefore, the predictive power of the model is the main criterion of its usefulness. In other words, the model should be considered as adequate if it provides a description and prediction of qualitative effects and phenomena that have been and/or can be experimentally observed. From this point of view, the development of the most efficient criteria for the comparison of simulated and experimental data is essential.

To summarize this section, we should state that a model cannot (and should not) be identical to the phenomenon or process (object) under consideration.

Even more so the object is not identical to its model. Consequently, we should not expect that the behavior of the real object is going to be necessarily equal to the model predictions and will be quantitatively described by the model. In many theoretically and practically important cases even a qualitative description and/or prediction of complex phenomena observed experimentally should be considered as a success of modeling and a serious breakthrough in understanding of the nature of the process under study.

Below we will focus mainly on the problems of compiling micro-chemical (micro-kinetic) schemes of alkane oxidation and populating it with kinetic parameters. Of course, we had to pay certain attention to some closely connected questions but it was impossible to analyze all of them in detail in the framework of one paper.

B. Circumscription of Subject and Area of Parameters

Oxidation of hydrocarbons is one of the oldest and traditional subjects for chemical kinetics. During several decades of widespread application of computers in chemistry, a vast number of publications concerning the modeling of these processes have appeared. As we noted above, the complexity of the chemical system designated as "hydrocarbon oxidation", even in the simplest case of light alkanes, practically excludes the possibility of the development of the sole and universal model suitable for all practically important applications. All models that have been extensively used have been developed for some particular processes over limited ranges of parameters, although by no means it is always clearly stated. Therefore, the first and the most important condition, which should be strongly executed when any kinetic model is announced, is the statement of the problem and the circumscription of the parameter space for which the model is to be developed.

Among the external parameters, temperature is the one that to the utmost determines the peculiar features of the oxidation process, to some extent even more than the number of carbon atoms in the alkane molecule. This is why all kinetic models for gas-phase alkane oxidation can be classified based on the temperature range in which the process is going to be described. In their turn, the temperature ranges could be delimited based on the main types of reactions taking place and typical products formed, as follows.

1. *Low-temperature oxidation.* It is characterized by very low rates, by the predominance of associative processes, and by the formation of complex peroxide compounds. Although chain oxidation can take place, the probability of branching is low. Characteristic times of homogeneous transformations in the low-temperature range are very long; they can exceed by far the times of diffusion to the walls of reactor from the flow core. On the other hand, even physically adsorbed species can form dense adsorbed layers on the surface.

This is why at such a temperature range the role of reactions taking place on the reactor walls is very important, even at elevated pressures. The surface can serve as the main "reaction zone" and, at the same time, as a "storage" for relatively reactive intermediates and heavy reaction products. The oxidation reactions of this type are very important for atmospheric chemistry (Gershenzon and Purmal, 1990). The upper temperature for them does not exceed 350–400 K. Nowadays, the interest to modeling low-temperature oxidation is increasing along with the environmental concerns (Gershenzon *et al.*, 1990; Larin and Ugarov, 2002).

2. *Elevated (moderate) temperatures* for alkane oxidation range up to 1,200–1,300 K. At such temperatures the probability of chain-branching increases; moreover in many cases it determines the main kinetic features of the process. Accordingly, peroxide compounds are becoming the branching intermediates, and the most abundant reaction products are represented by non-peroxide oxygenates and olefins. Surface(s) present in the reactor still play an important role, but different from that for lower temperatures. Heterogeneous reactions are considered as initiation, termination, and even as chain propagation and branching steps.
3. *High-temperature oxidation*, including combustion, is characterized by very fast elementary transformations. As a result, product distributions usually reflect the thermodynamic equilibrium state to which the system can arrive from the given composition of the initial gas mixture. Correspondingly, carbon oxides, water, hydrogen, and carbonaceous solids are among the main products. Besides them, the most thermodynamically stable hydrocarbons, such as acetylene, benzene, and cracking products (hydrocarbons with lower number of carbon atoms in the molecule compared to the initial alkane), can also form. As to the reaction intermediates, the species formed due to deep dehydrogenation of hydrocarbon molecules (CH_2, CH, C_2H, etc.) and soot precursors (poly-cycles and carbonaceous agglomerates) play a significant role in this temperature range.

Interestingly, the reactions of the high-temperature type also have the upper temperature limit. It is restricted, on the one hand, by the maximum (adiabatic) heating, which in its turn is determined by the heat of reaction and by the heat capacity of the products. On the other hand, the reaction temperature is limited by the increasing probability of the formation of excited species (in higher vibrational and electronic states). The latter favors the intense additional removal of energy from the reacting system due to irradiation. So, there is a physical limit for practically accessible temperatures in oxidation processes. On the other hand, as far as the process kinetics is concerned, it cannot be described in terms of reactions involving species in the ground state at temperatures substantially exceeding 1,300–1,500 K.

Of course, the "border lines" for each of the ranges denoted above cannot be defined unambiguously; also, inside them some sub-ranges can be distinguished.

Let us consider in more detail the range of elevated (or moderate) temperatures. It is the most interesting from the standpoint of oxidative light alkane processing. On the one hand, the rates of processes in this temperature range are high enough. On the other hand, it is still possible to restrain the process and to optimize the yield of desired non-equilibrium products. However, both lower and upper limits for the range of "elevated" temperatures are the least definite. Inside this range, an additional partition can be made based on some "practical" or kinetic reasoning. For instance, in methane oxidation, below a certain threshold (around 900 K) a predominant formation of oxygenates is taking place, whereas above it the products of methyl radical recombination (C_{2+} hydrocarbons) are efficiently formed (see Section III.E for more detail). Similarly, in propane oxidation, the border above which cracking processes are pronounced or even dominating is ~700 K.

The range of temperatures between 600 and 1,300 K is most "practical" for the efficient production of several compounds via oxidation of C_1–C_4 alkanes. Oxidation at these temperatures is very extensively studied using experimental methods. However, numerous short-lived intermediates crucially important for the process are at the same time very difficult for direct observations and investigation. Some of them, such as complex organic radicals formed via the abstraction of hydrogen atom(s) from relatively bulky molecules, are mysterious, needless to say about the products of O_2 molecule addition to them. Therefore, modeling in many cases is the only real way to gain an understanding of such puzzling reaction systems. Although the modeling of these processes attracts growing attention, this area is not sufficiently well developed as yet.

Higher temperature oxidation (including combustion) has been much more attractive for researchers during the last several decades. This is due to the reason that gas combustion is the basis for many important technologies, including those used for transportation and power generation. Numerous types of engines and burners utilize the heat and the tractive forces produced during alkane oxidation. This generates a great deal of interest in modeling. Fortunately, many ideas developed in this area (see Gardiner, 1984) are applicable also for the "moderate" temperature range. Also, review articles and databases dealing mainly with the data obtained in neighboring temperature regions (see, for instance, Cohen and Westberg, 1991; Tsang and Hampson, 1986; Warnatz, 1984) contain information very valuable for modeling at 600–1,300 K.

To conclude this section, let us define the area of parameters the most suitable for light alkane oxidative processing and, for this reason, being of interest for the development of corresponding kinetic models. As we already mentioned, the temperature range can be restricted to 600–1,300 K (300–1,000°C). Concerning the total pressure, transformations of light alkanes to the products of partial oxidation proceed efficiently at 1–100 bar (0.1–10 MPa). Also, as far as selective partial oxidation is concerned, it requires as a rule an oxygen-deficient (hydrocarbon-rich) composition of the initial reaction mixture. For instance, in the case of methane oxidation, selectivity to any partial oxidation products substantially decreases if the methane-to-oxygen ratio does not exceed two. From a practical standpoint this means that total conversion of the starting alkane as a rule cannot be achieved in one pass through the reactor at high selectivity with respect to partial oxidation products.

C. Accounting of Heterogeneous Processes

The adequate description of heterogeneous radical reactions is important both for gas phase kinetics (traditionally treated as “homogeneous”) and for a broad and rapidly developing area of heterogeneous catalytic oxidation of alkanes in which homogeneous chemistry can play a very significant role. Until recently, researchers working in these two areas had applied very different methodologies to solve the problem of heterogeneous–homogeneous coupling. This had not allowed even the comparison of results obtained in these two areas, not to mention their superposition. Fortunately, now we can conclude that things are slowly, but surely, changing. We consider this paper as our contribution to bridging the gap between the two areas. At least we attempt to define the cases when it is possible and to which extent and to highlight the remaining problems.

The problem of interplay of heterogeneous and homogeneous processes during hydrocarbon oxidation has a long and complex history. On the one hand, the effect of heterogeneous factors upon homogeneous oxidation is commonly recognized as principally important. Suffice it to mention that heterogeneous termination is ranked as one of key factors in the theory of ignition (see, for instance, Semenov, 1959; Shtern, 1964). There is substantial experimental evidence for the participation of reactor walls in gas-phase oxidation. In some cases they control general kinetic features, degrees of conversion, and product distributions. It was repeatedly noted that initiation steps can proceed on the surfaces of reactors and/or “inert” fillings much faster than in the free gas phase. This may result in a substantial decrease of reaction temperatures and shortening (or even disappearance) of induction periods as compared to the predictions of “purely homogeneous” kinetic schemes.

There is substantial evidence (see, for instance, Garibyan, 1969, 1971) for the heterogeneous initiation in the homogeneous chain reaction of hydrogen and hydrocarbon oxidation in quartz reactors at relatively low temperatures. In particular, in the range between 723 and 988 K the initiation reaction

$$RH + O_2 \rightarrow R + HO_2$$

is characterized by two different values of apparent activation energy E_a. A lower value observed at lower temperatures ($E_a = 100\,\mathrm{kJ/mole}$) is attributed to a heterogeneous mechanism, whereas at higher temperatures ($E_a = 200$–$210\,\mathrm{kJ/mole}$) a homogeneous process is predominant.

The problem discussed in this section is caused to a considerable degree by the difference in approaches dominating two parts of chemical kinetics, namely gas-phase kinetics and in heterogeneous kinetics, including catalysis. Even the basic terminology and main principles of kinetic analyses formed in these two areas are different. This in turn causes serious difficulties in the description of borderline phenomena.

It is worth noticing here that during several decades so-called heterogeneous–homogeneous processes have been subject of debates. Interest in them had appeared in the bosom of "undivided" chemical kinetics when scientists studying gas reactions and heterogeneous processes in many cases were the same and at least spoke the same language (see Bogoyavlenskaya and Kovalskii, 1946; Polyakov, 1948). The main results obtained during this initial period were summarized in the monograph by Gorokhovatskii *et al.* (1972). In this book

- the processes including heterogeneous and homogeneous steps are classified;
- possible mechanisms of initial formation of free radicals are analyzed from a thermochemical point of view;
- experimental methods for the registration of active species in the gas phase and for the investigation of the overall heterogeneous–homogeneous processes are described;
- mechanistic and kinetic aspects of some particular processes are discussed.

Unfortunately, later the development of two areas—"homogeneous" kinetics and "heterogeneous" catalysis—occurred almost independently, which caused serious intrinsic discrepancies. For instance, the traditional chain theory implies the participation of surfaces also in chain termination, which determines the existence of the low-pressure ignition limit. In the framework of this approach, two regimes—diffusional and kinetic—are distinguished. In the latter case the parameter that describes the process is the probability of surface decay of chain carriers per one collision. It is worth noticing, however, that this assumes only a disappearance of active species from the gas phase, without any analysis of its mechanism and even stoichiometry. This is why the heterogeneous termination reactions are usually represented in kinetic models as a formal reaction:

$$C_XH_YO_Z \rightarrow \text{decay}$$

usually breaking even a material (atomic) balance. Their kinetic parameters, as a rule, are taken from macro-kinetic considerations (from the rate of radical diffusion through the gas to the reactor surface). They also are used as adjustable parameters during the modeling (Vedeneev *et al.*, 1988a, b, c, d) without paying any attention even to the fate of atoms constituting the decayed radical species. Especially in the latter case it is very difficult to assign any physical sense to the parameters, and even to the modeling procedure as a whole.

There is a series of studies by Azatyan and co-workers that stands apart from the main stream in gas-phase kinetics (see Azatyan, 1985, 2005 and literature cited therein). Based on the analysis of experimental data and kinetic schemes these authors claim that heterogeneous reactions participate in all main types of reactions taking place during the chain process (besides initiation and termination, also chain-branching and propagation). Therefore, they must be included in the kinetic scheme on equal terms with homogeneous steps. In our opinion such an approach is very logical from kinetic and even general chemical standpoints, since in its framework an artificial gap and difference in the description of elementary processes taking place simultaneously in one reaction system can be overcome.

One more reason why heterogeneous reactions are usually taken outside of regular analysis in gas kinetics is related to the possibility of experimental study of micro-kinetics. Whereas in the case of homogeneous reactions elementary reactions can be investigated and their kinetic parameters can be measured directly, at least in some important cases, this is practically impossible for heterogeneous reactions for several reasons. First of all, in most cases even the reaction stoichiometry is not definite. Even if only the surface of the reaction vessel is considered, it is influenced simultaneously by the totality of species present in the gas phase. Some of them can physically adsorb and reside on the surface for some time keeping their chemical nature and reactivity. Some of the others being very reactive towards the reactor material can rapidly interact with it causing serious local chemical changes in the surface layer and transforming themselves into different gas species with different reactivity. Species of the third type can be inert with respect to the wall material, but rapidly react with ad-species of different types, etc. The possibility to isolate the particular reaction, to determine its stoichiometry, and to measure its kinetics against a background of other reactions seems very doubtful.

Secondly, any solid surface present in the reactor (reactor walls and parts, various solid fillings inserted into it for different reasons) cannot be unambiguously characterized from the standpoint of its reactivity and adsorption power with respect to different gas species. This is due to the fact that the reaction medium strongly modifies (physically and chemically) any surface, up to almost total change of its nature. It is known, for instance, that during hydrocarbon oxidation any surface influenced by the reaction mixture is being covered by carbonaceous residues (see, for instance, Evlanov and Lavrov, 1977; Suleimanov *et al.*, 1986). The chemical nature and morphology of the latter are not strictly definite and unchanging (neither in time, nor moreover at varied surface and initial gas composition). As a result, surface reactions of species present in the gas phase become even less accessible for direct and distinct study.

At last, to study such interactions it is required to utilize certain experimental methods capable of monitoring the state of the surface and its evolution with time. As far as any spectral methods are concerned, their use requires a sufficient density of states subjected for observation in the zone of measurements. This can be achieved in some cases for heterogeneous catalysts with relatively high surface areas: even in their thin layers at short length of optical path the probing irradiation can collect enough information for further analysis. This is by far more complicated as far as reactor walls and other flat surfaces are concerned. In rare cases—mainly for metal surfaces—some spectral methods can provide valuable information about the composition of adsorbed layers and even about the rates of chemical transformations of certain ad-species (see for instance Firsov *et al.*, 1990; Shafranovsky, 1988). However, even in these rare cases we can speak only about model "*ex situ*" experiments, and the obtained information possesses a limited value for the analysis of real oxidation processes. In most cases, namely modeling provides the possibility to elucidate the nature of heterogeneous processes, which are thus far inaccessible to experimental investigation.

The revival of the interest in heterogeneous–homogeneous processes is associated with the discovery and extensive studies of oxidative coupling of methane (OCM) (Fang and Yeh, 1981; Keller and Bhasin, 1982). The direct observations of free radicals and preliminary kinetic analysis (Driscoll *et al.*, 1987; Lunsford, 1989; Sinev *et al.*, 1987, 1988) clearly demonstrated that the OCM process has a substantially heterogeneous–homogeneous nature. This implies that both heterogeneous and homogeneous steps are substantial for the main features of this process and—what is even more important—they cannot proceed and be analyzed separately. Particularly, activation of methane takes place at the catalyst surface and results in the formation of free methyl radicals. Further recombination of these radicals leads to the formation of the primary OCM product—ethane. As soon as such a scheme of the process became clear, it has become also obvious that its correct description requires a superposition of approaches accepted in heterogeneous catalysis with those developed in homogeneous kinetics of free radical reactions. Such an understanding has marked the new stage in modeling; this is why the OCM process remains a very important and valuable model reaction, without regard to the prospect of its practical implementation. The same can be said about oxidative dehydrogenation (ODH) of light alkanes over oxide catalysts, which in many aspects is very similar to OCM.

There is another important group of processes in which both heterogeneous and homogeneous processes play a substantial role, namely so-called stabilized combustion. Following Pfefferle and Pfefferle (1987), we assign this definition to the gas-phase combustion proceeding in the presence of the surface possessing a catalytic activity. This allows burning various fuels (hydrocarbons, hydrogen, CO) in their lean mixtures with air at substantially reduced temperatures and with almost negligible yield of pollutants (first of all, nitrogen oxides). Simultaneously the efficiency of the evolving heat is increasing (Pfefferle, 1974, 1975). Direct measurements of active species, such as OH radicals (Cattolica and Schefer, 1982; Pfefferle *et al.*, 1988, 1989) and O-atoms (Dyer *et al.*, 1990; Pfefferle *et al.*, 1989), demonstrated that depending on the conditions and properties of the surface, concentrations of such species in the gas can steadily decrease or pass through a maximum. If in the first case the process is likely localized on the surface or in near-surface gas layer, in the latter case we have a clear evidence for the chain process initiated by surface reaction.

Finally, one more very important group of processes in which a joint analysis of heterogeneous and homogeneous reactions is required proceeds in the presence of Pt-group metal catalysts at very short (millisecond) contact times (Davis *et al.*, 2000; Huff and Schmidt, 1993; Schmidt, 2001). It can be easily demonstrated that only some part of the gas molecules (in some cases as low as 20%) can access the active surface within the time of gas passing through the catalyst zone. If, nevertheless, complete conversion of the limiting reactant (as a rule, oxygen) is taking place, this strongly suggests that the reaction substantially proceeds in the gas phase. Another important indication for the conjugation between surface and gas reactions is product distributions. In some cases they are typical for gas-phase oxidation, whereas the reaction times are too short for the exclusively homogeneous reaction at a given temperature. However, in other cases product distributions vary substantially from catalyst to catalyst indicating that surface reactions strongly modify the process that occurs in the gas phase.

One can assume that most (if not all) high-temperature gas-phase catalytic reactions proceeding at temperatures above 800 K are substantially heterogeneous–homogeneous (in the meaning defined above). Consequently, their adequate kinetic description and modeling require a development of corresponding approaches and procedures.

D. Accuracy of Modeling and Influence of Macro-Kinetic Parameters

The possibility of more or less accurate description of a phenomenon based on hundreds of non-accurate parameters could be considered as really surprising. As follows from formal error analysis theory, the results of kinetic modeling should be regarded as completely inconsistent. Probably there exist some deep reasons, which lead to self-consistency of complex kinetic models and allow trusting the results of simulations.

It should be admitted that the question about kinetic parameters of elementary reactions that form complex process mechanisms is very complicated and even painful. Referring to the existing kinetic databases demonstrates that for some reactions the difference in kinetic rate constants reaches orders of magnitude. Each group of authors has particular arguments in support of "their" values. Obviously, among existing values only few (or even none!) are "correct". The reason why we put the word "correct" in quotation marks originates from the problem of representation of rate constants—it will be discussed in more detail in Section III.B. Here we just mention that for practical modeling the so-called "three-parametric" equation

$$k = A\left(\frac{T}{T_0}\right)^n \exp\left[\frac{-E}{RT}\right]$$

is generally accepted for representation of temperature dependence of rate constants.

Since the problem of severe discrepancy in kinetic parameters for one reaction does really exist, several very important questions arise, among which the following are crucial:

– Are there any rational criteria for selection of "true" parameters?
– What meaning should be assigned to the results of simulations if the uncertainty in the values of kinetic parameters of practically all elementary reactions cannot be eliminated?

The former question should probably be answered positively. Some approaches of such a kind are described in the literature and used for the compilation of "recommended" databases of kinetic parameters (Atkinson *et al.*, 1989; Baulch *et al.*, 1982, 1984, 1992, 1994; Cohen and Westberg, 1991; Kondratiev, 1970; Tsang and Hampson, 1986; and other). In brief, the rational approach should include at least the following essential criteria:

- The agreement of kinetic parameters with the physical sense of "three-parametric" equation. For example, if the value of a pre-exponential factor for a bi-molecular reaction in the gas phase is a few orders of magnitude higher than the possible frequency of collisions between certain species it should be considered as contradiction to the physical sense of the corresponding parameter. Another example of a similar kind is a negative activation energy, which most probably should be treated as evidence for the non-elementary character of the corresponding reaction.
- The agreement between the values of kinetic parameters and the thermodynamics of the process. On the one hand, the activation energy for an elementary endothermic reaction cannot be less than the heat of reaction. On the other hand, if the data about rate constants for both direct and reverse reactions are available, their ratio should be equal to the equilibrium constant calculated independently from thermodynamic data for species participating in the reaction.
- The conformity of given reaction parameters to those obtained from empirical correlations for reactions of the same type for one reactant with other partners and/or even with participation of other species. For instance, the Polanyi–Semenov equation is a good approximation for activation energy of hydrogen atom transfer between two species (radicals or molecules) (see, for instance, Kondratyev and Nikitin, 1974). If the parameters for some reaction seriously

contradict the values obtained from such estimations, this needs an explanation, or at least should be taken into account.

Let us come back to the problem of ‘‘accuracy’’ of kinetic simulations based on parameters, which in their turn have at least uncertain accuracy. On the one hand, all values of kinetic parameters contain both systematic and stochastic errors of measurement or calculation. On the other hand, it is known from modeling practice that variation of values for some parameters even within a narrow range allowed by criteria discussed above can lead to dramatic changes in the kinetics of the overall complex process. The simplest example of this type is the effect of chain-branching parameters. The commonly used approach to solve the problem is the ‘‘adjustment’’ of parameters for a number of stages, which allows fitting of the results of simulations to existing experimental data. Such an approach is acceptable, especially for interpolation-type models (Section I.A). Unlike that, the use of any adjustment or fitting procedures becomes doubtful, if the emphasis in modeling is placed on the mechanistic studies or on the analysis of the process over a wide range of parameters, especially beyond the range of basic experiments.

As a rational compromise, the comparison of modeling results with experiments may be considered as the way to select between alternative descriptions if other criteria cannot be applied. Otherwise it is hard to define the ambit beyond which an ‘‘optimization’’ of parameters for a limited set of important stages transforms into the total adjustment of the kinetic scheme to some particular experiment. This aspect will be further discussed in Section II.C.

In general, the problem of required accuracy of kinetic simulations strongly correlates with both the goal of modeling and the choice of criteria for comparison with experiments. We have to notice again that from the above formulated standpoint, the results of modeling can be considered successful if it allows one to describe some non-trivial effects observed in the processes under study, as well as qualitative trends in the yields of particular products upon some variation of external parameters. The latter means that the particular ranges of parameters (temperature, pressure, concentrations) where those effects are observed experimentally and found in modeling can significantly differ. One example of this kind is presented in Fig. 1: the experimentally observed negative temperature coefficient of reaction (NTC) in propane oxidation was reproduced in simulations (Vedeneev *et al.*, 1997a, b). Although there is no quantitative coincidence between experimental and simulated curves, the model makes such an effect comprehensible. This should be considered as a success, especially taking into account both the imperfections of the model and the inaccuracy of the parameters used, which in principal cannot be eliminated for objective reasons.

One prevalent source of deviations between experimental data and simulated kinetics is an inadequate accounting of macro-kinetic factors (heat- and mass-transfer), which can strongly affect the process. A more or less adequate description of transfer processes and fluid dynamics in chemical reactions requires

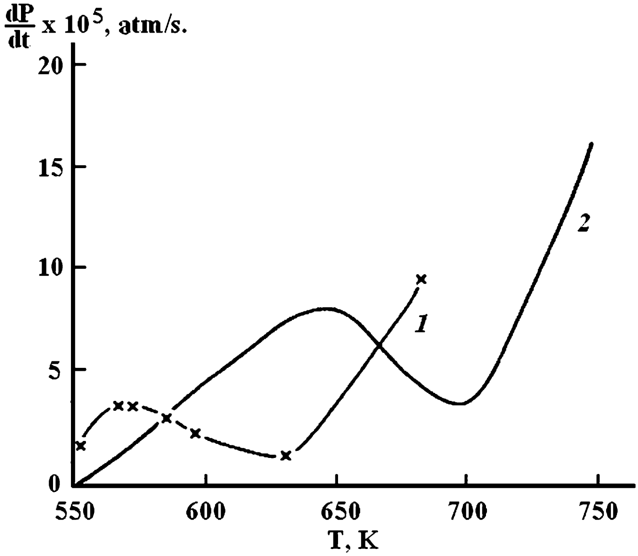


FIG. 1. Maximum pressure jump $d(\Delta p)/dt$ (reaction rate) during homogeneous propane oxidation vs. temperature (Vedeneev *et al.*, 1997a, b). (1) experimental; (2) calculated. Reaction conditions: initial pressure $P_0 = 200$ Torr; propane-to-oxygen ratio = 23.

the utilization of very complicated mathematical and computational procedures; as a result, micro-chemical filling of the model is usually sacrificed (see, for instance, Frolov *et al.*, 1997; Williams, 1997). On the other hand, an adequate description of macro-kinetic factors for each real experiment is hardly accessible. This makes their accounting in simulations even more complicated.

In any real reaction system, chemical processes generate temperature, pressure, and concentration gradients making the description more complex. In general, macro-kinetic factors play an important role in homogeneous partial oxidation, but probably in these processes they are not as important as in combustion. On the other hand, as far as heterogeneous catalytic reactions are concerned, transfer processes must be accounted for, at least in models aimed at practical application, since all these systems are spatially distributed. A vast literature is devoted to heat- and mass-transfer in both homogeneous kinetics and heterogeneous catalysis (see, for instance, Gardiner, 1984; Frank-Kamenetskii, 1969; Kiperman, 1979; Satterfield, 1970, 1980).

In the strict sense, the real reacting system could be mathematically described by chemical kinetic equations only taking into account the processes of diffusion and convection in self-generated non-uniform temperature fields. However, this problem, as we mentioned above, can be solved only at the expense of significant simplification of the chemical description. It is usually acceptable in studies of combustion and explosion processes where the chemical part may be reduced to a very schematic description, which defines the rate of heat release only. If we are particularly interested in routes of intermediate product formation and decay, a cardinal simplification of the chemical mechanism is impossible and we have to look for a trade-off between chemical and macro-kinetic precision.

One possible approach to estimate the potential significance of different macro-kinetic factors is a separate analysis of extreme cases. For example, isothermal and adiabatic regimes of chemical processes are two extreme cases characterized by extremely fast or extremely slow (in comparison with chemical transformation) heat-exchange between the reacting system and the external medium. All real heat-transfer regimes including both external heating of the reaction zone and auto-thermal reaction are intermediate cases between these two regimes. It is possible to compare the modeling of these two outermost cases in order to estimate how (qualitatively) and to what degree a heat-exchange regime can affect product yields. Figure 2 presents an example of such a comparison. Homogeneous methane oxidation was simulated using the kinetic model developed previously for methanol production at high pressures (Vedeneev *et al.*, 1995). In this case a comparison of certain product (methanol and formaldehyde) yields is plotted vs. conversion of the limiting reactant (oxygen). Without going into detail, let us conclude that the thermal regime of reaction has a strong effect on the behavior of the reacting system and heat-transfer should be optimized, as far as maximum yields of certain products are concerned. However, different products are subjected to this effect in somewhat different ways. The difference in the behavior of formaldehyde and methanol reflects particular differences in their formation and transformation pathways.

An accurate accounting of mass-transfer is especially important in heterogeneous systems, and, first of all, in catalytic oxidation. In this case the simultaneous presence of active surfaces and an "active" gas phase and occurrence of different processes involving different species in these two reaction zones makes the system puzzling. Some additional reasoning and examples illustrating the complexity of such systems and possible solutions will be discussed in Sections III.E and III.F. However, we must confess that a thorough elucidation of this extremely important and complicated problem is far beyond the scope of this paper.

II. Alternative Approaches to Modeling

As we stated in the Introduction, a complete review and thorough analysis of publications devoted to the subject overstep the bounds of this work. Below in this section we only present an overview illustrating some typical approaches to modeling of hydrocarbon oxidation. Among them, we distinguish two groups of models stipulatively defined as "additive" and "combinatorial". The former

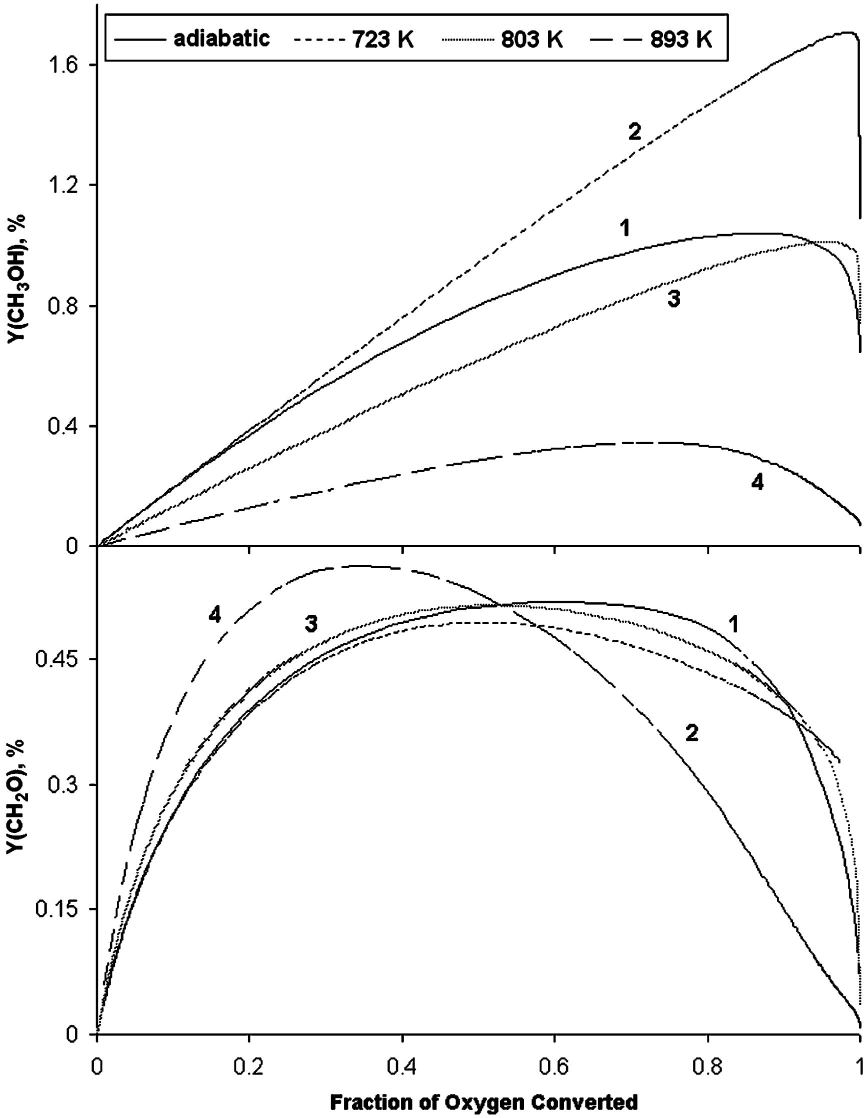


FIG. 2. Simulated yields of oxygenates (methanol and formaldehyde) vs. oxygen conversion in different heat-transfer regimes. (1) Adiabatic, $T_0 = 723$ K; (2) isothermal, $T = 723$ K; (3) isothermal, $T = 803$ K; (4) isothermal, $T = 893$ K.

group includes the models compiled by the addition of selected elementary steps, or groups of steps, to some initial core. The criteria for the selection of reactions to be included into the core, as well as for the further addition to it, are both defined by the investigator based on his (her) understanding of the process and simulation procedure. Alternatively, if the model of "combinatorial" type is developed, the investigator first defines the list of species taking part in the complex reaction network and then the kinetic scheme is formed as a combination of all chemically relevant elementary reactions of selected species.

A. "ADDITIVE" MODELS

The model aimed at the optimization of methanol production by methane partial oxidation at high pressures has been developed by Vedeneev and co-workers since 1988. Up to now it is one of the most successful examples of specialized models for moderate-temperature oxidative conversion of light alkanes. It is based on a deep understanding of the main ruling factors responsible for particular kinetic features of the process. Correspondingly, the blocks of elementary reactions for such features, and for the formation of methanol at high pressures in particular, were included into the kinetic scheme.

Next, it was declared that the comparison of calculations with selected experiments cannot be used as a universal criterion for model development and selection of rate constants, or should be restricted and at least performed very carefully. The values of the kinetic parameters were taken from independent measurements, theoretical calculations, or semi-empirical estimations. So, the invariability of rate constants for the description of any particular experiments was accepted as the one of the main principle.

Two possibilities were accepted for the further improvement of the model. The first one is a step-by-step addition of new elementary reactions in the case of the necessity for an adequate description or in the case if new reliable kinetic data are obtained. The second was a more accurate evaluation of kinetic parameters for elementary reactions already included into the model, but only on the basis of new direct experimental data or new calculations that are more advanced and precise. In one of the latter versions of this model (Vedeneev *et al.*, 1995), the thermodynamic consistency principle (see Section II.C for details) was realized.

As a result, a relatively compact model capable of predicting and capturing some features of the process over a given range of parameters (relatively low-temperature, high-pressure, low oxygen-to-methane ratios) was developed. As applied to the direct oxidation of methane-to-methanol (DOMM), it allowed the determination of several principally important qualitative features of the process. In particular, it was found that methane partial oxidation at high-pressure is a degenerative chain-branched process with very short chains and a long induction period. The chain-branching occurs via several parallel reactions, none of them which dominates.

It was shown that there are three main phases of the process (see Fig. 3). A very short initial phase is an auto-accelerating chain-branched reaction; the total concentration of chain carriers vs. time follows an S-shape curve, which is

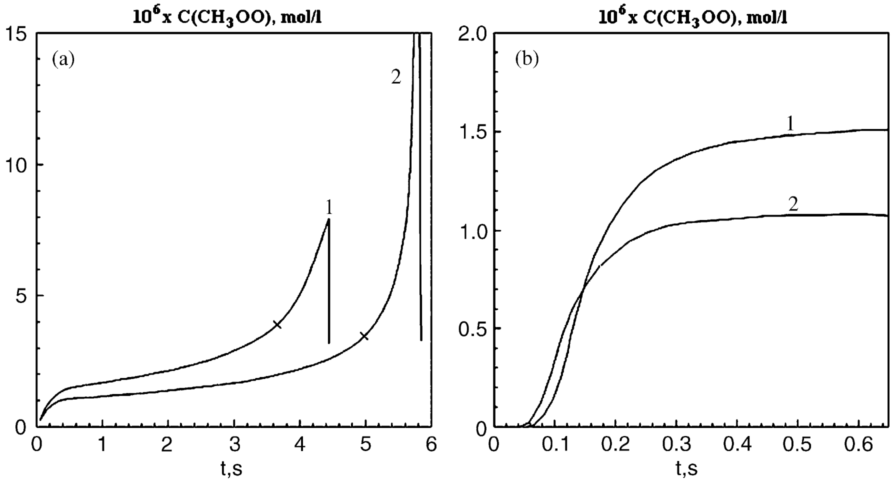


FIG. 3. Simulated concentration of CH_3OO radicals as a function of time during the DOMM reaction (Vedeneev *et al.*, 1988a, b, c, d; Arutyunov, 2004). $P_0(CH_4) = 80.9$ bar, $T = 680$ K. (1) $P(O_2) = 1.8$ bar, (2) $P(O_2) = 8.4$ bar; (a) for the first phase, (b) for the initial part of the second phase of the overall process.

very similar to hydrogen oxidation. This phase had not been observed experimentally before the modeling was performed.

The second phase is a quasi-stationary chain-branched process with a quadratic radical termination, which proceeds mainly via the recombination of methylperoxy radicals

$$CH_3O_2 + CH_3O_2 \rightarrow CH_2O + CH_3OH + O_2 \qquad (1)$$

at approximate equality of the rates of branching and radical recombination. During this phase, a slow accumulation of intermediate products and a slow increase of temperature are taking place. This leads to the fast self-acceleration of the reaction in the third phase, which is due to the chain-branching in the reactions involving intermediate products and self-heating. It was clearly demonstrated that the quasi-stationary behavior is the most striking feature of the process (Arutyunov, 2002, 2004; Arutyunov and Krylov, 1998).

The model also revealed the importance of non-linear interactions of chains, which determine the existence of two quasi-stationary oxidation modes. The difference in reaction rate between them is about four orders of magnitude. A critical transition between these modes is taking place due to small changes in reaction parameters, e.g., pressure. This critical transition leads to a very fast increase in the oxidation rate and an abrupt transition from the low-pressure slow oxidation to the fast high-pressure stationary chain-branching process. In the latter mode, radical generation is no more determined by a slow initiation reaction, but by very fast chain-branching reactions. It is the phenomenon that allows accomplishing this non-catalytic gas phase process at moderate temperatures.

The analysis of this model revealed some interesting qualitative effects, which were experimentally verified later. The competition of reactions (2) and (3) of active methoxy radicals CH_3O with methane and oxygen

$$CH_3O + CH_4 \rightarrow CH_3OH + CH_3 \quad (2)$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \quad (3)$$

leads in the first case to the formation of very active chain propagating CH_3 radicals and in the second case to much less active HO_2 radicals that mainly recombine to form hydrogen peroxide

$$HO_2 + HO_2 \rightarrow HOOH + O_2 \quad (4)$$

The latter reaction is equal to chain termination in this temperature range. This is the reason why in this reaction oxygen acts as an inhibitor if its initial concentration does not exceed 10 vol.% (see Fig. 4). Later this effect was experimentally proved (Arutyunov *et al.*, 1996). Thus, the model demonstrated its capability of finding new intimate information about the intrinsic reaction mechanism.

The approach called above as "additive" can also be identified as "pragmatic". Indeed, if we wish to describe some combination of kinetic features of the system, we include only a limited number of elementary reactions, which are responsible

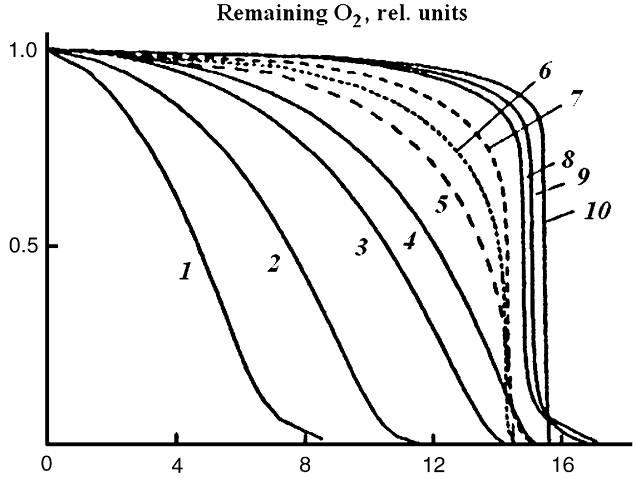


FIG. 4. Calculated kinetics of oxygen conversion (fraction of remaining oxygen in relative units) during methane oxidation at different initial oxygen concentrations in the mixture (in vol.%): 0.5 (1), 1 (2), 2 (3), 3 (4), 5 (5), 7 (6), 10 (7), 15 (8), 17 (9), 20 (10); $T_0 = 693$ K, $P = 10$ bar.

for the behavior of our interest. Any other reaction if it does not interfere with the phenomena to be described is not included into the scheme. It is clear, however, that such additional reactions can be very important for some other kinetic features, which for some reason remained out of consideration. Consequently, if one is intended to transfer such a "pragmatic" model to the description of related, but different processes, or to solve some very similar problem, but involving slightly different kinetic pecularities, this attempt may fail or give just misleading results.

In this sense, the attempt to extend the use of the above model for the description of the OCM process (Vedeneev *et al.*, 1997a, b) is very illustrative. A simple addition of a limited set of new reactions to the initial kinetic scheme is not successful: the process proceeds in different range of temperatures, pressures, and methane-to-oxygen ratios. As a result, in order to be adapted to the new application, the initial model has to be totally revised. The required changes must be deep to an extent that it is possible to speak about the compilation of a different model.

The applicability of an "additive" approach is very doubtful in many other cases too. For instance, a typical task for modeling is a description of the behavior of small additives to the reacting system. Such additives may serve as reaction rate modifiers (promoters or inhibitors). Another important area is a detoxification of pollutants in the conditions of hydrocarbon oxidation (combustion). In both cases the detailed mechanism of the process in the presence of additives (especially, if they contain heteroatoms, such as nitrogen, halogens, sulfur, or phosphorus) can undergo very serious changes, which can hardly be accounted for by the addition of a limited number of new elementary steps.

The above discussion can be illustrated by numerous attempts to describe oxidation of fuel-rich mixtures at 900–1,200 K in the framework of the kinetic scheme known as GRI-Mech (see Frenklach *et al.*, 1995). These attempts consisted of the replenishment of the initial scheme by new blocks containing the reactions of complex radicals that are characteristic for such temperatures. Then the whole scheme was subjected to the procedure routinely accepted for the optimization in the framework of GRI-Mech approach (see Section II.B below). However, no reliable proof of the effectiveness of such an "extended" description has been obtained.

Borisov *et al.* (2000) mentioned that some widely used kinetic models used even for combustion are self-contradictory. For instance, the scheme applicable for the developed high-temperature combustion process is also used to describe the values of self-ignition delays (SIDs). The latter usually take place at temperatures several hundred degrees lower than the combustion itself and may obey very different rules, at least if the combustion process is described in terms of the "pragmatic" approach. Authors of the cited work suggested the approach to modeling both ignition and combustion of C_1–C_3 hydrocarbons consisting of a combination of two blocks, one of which describes combustion, and the second—low-temperature oxidation. As a result, the authors arrived at a typical "additive" model and verified it by comparing measured and calculated values of SIDs.

B. "COMBINATORIAL" MODELS

At present, the most known and widely used kinetic model for light hydrocarbon oxidation and combustion is GRI-Mech (Smith *et al.*), which has been developed since the 1990s by the Gas Research Institute. The project was aimed at the development of the detailed micro-chemical mechanism that can be used for simulations of natural gas ignition and combustion. Now the model is optimized for two fuels, methane and natural gas. Recommended temperature and pressure ranges are 1,000–2,500 K and 1.3×10^{-3}–1 MPa, respectively; the fuel-to-oxidant equivalence ratio in premixed compositions is 0.1–5. Although the scheme includes some reactions of C_2–C_3 hydrocarbons and oxygenates participating in methane (natural gas) combustion, it is not recommended to use GRI-Mech for simulations of their oxidation (combustion) as the main initial fuels, since the model is not optimized for these purposes.

Initially the model was compiled using both experimentally measured and theoretically calculated kinetic parameters. Then, the results of simulations were compared with the data of multiple experiments and sensitivity analysis was employed to select the parameters, which should be corrected for the better agreement between experimentally observed and simulated kinetic behavior. The computation routine can perform the modification of each kinetic parameter within the range of its initial uncertainty. Such an approach gives a serious cause for criticism, since the discrepancies with experimental data are eliminated (or minimized) by changing the values of multiple parameters. First, this makes all of them correlated. Next, an independent correction of just one parameter in the model, or just a slight modification of the micro-chemical scheme leads to the readjustment of the whole system of kinetic parameters. This is in a certain sense equal to the solution of the inverse kinetic task, which, as we mentioned above, is an ill-conditioned problem.

Nevertheless, in spite of some difficulties, GRI-Mech signifies a new era in modeling of combustion and oxidation of light alkanes and other substances. The main principles of GRI-Mech serve as a basis for further widening the area of its application for related processes and substances (Curran, 2004).

It is appropriate mentioning here again the "accuracy" problem with respect to kinetic parameters and its relation with general modeling concepts. A distinct uncertainty in the selection of parameters and a wide "tolerance box" for their variation are among the main reasons for discrepancies between different models, which in turn stimulates the creation of new ones. This is the reason why the idea of using exclusively the kinetic parameters obtained by quantum chemical calculations instead of experimentally determined values seems attractive. Indeed, contemporary theoretical methods can give results, which in some simple cases are more reliable than mutually contradictory experimental data. One may even assume than in the case of serious discrepancies between experimental and theoretical data, the former should be called in question and revised first.

We cannot exclude that in the course of time this approach will become dominant and "consistent theoretical" models will help us to avoid the temptation to adjust the whole set of kinetic parameters as soon as some new experimental curve appears. However, the remaining problems are still tremendous and require serious effort; some of them will be discussed more thoroughly in Section III.B. Nevertheless, several publications reflect the results already obtained via this way (see, e.g., Green, 2001; Zabarnick, 2005).

The use of a computer not just for simulations as such, but also for the compilation of the model, is also stimulated by the sharply rising complexity with an increasing number of carbon atoms in the reacting hydrocarbon molecule. Some authors advance an opinion (Buda *et al.*, 2005; Green, 2001) that any comprehensive model for oxidation of alkanes higher than propane can be developed exclusively based on automated (computer) generation methods, which enable one to avoid serious errors in the course of its compilation and further processing. Green (2001) suggested such a combined computational procedure that includes quantum chemical and group-additivity methods to calculate most of the molecular properties and kinetic parameters. These authors claim that they for the first time succeeded to implement $k(T, P)$ calculations in a general way that is suitable for use in an automatic reaction generation algorithm.

A similar combinatorial approach can be also applied for complex catalytic reactions (Shalgunov *et al.*, 1999; Temkin, 2000; Temkin *et al.*, 1996; Zeigarnik and Valdes-Perez, 1998). It is based on the notion that the reaction network involves the formation of certain products (final or intermediate) from one precursor via different routes. Only a complete accounting of all junctions and connecting reactions in such a network treated together with the appropriate kinetic parameters can give a realistic representation of the overall process. Network compilation is a subject for a formal computerized procedure.

C. Ruling Principles for Comprehensive Modeling

Special analysis that was performed by request of Gas Technology Institute in 2001–2002 (private communication) had clearly demonstrated that all kinetic models developed to date for high-temperature oxidation of methane and its homologues can describe well some selected experiments but contradict others. The groups of experiments described well by different models cannot be clearly classified by their types, methods, or conditions. It was concluded that different models are initially connected with some groups of arbitrary selected experiments.

Nevertheless, we have to confess that any experimental data requires some "theoretical" comprehension and rationalization. This is an obvious driving force for the development of new models for "local use". If their authors need to describe a relatively narrow group of experiments, this creates certain problems for co-ordination with existing models describing the general behavior of a reacting system. On the one hand, the latter may be quite far from the particular needs of the given experimental study. But, on the other hand, such basic models are usually very bulky, and the temptation to skip "the excess details" in favor of those, which seem more important, can be very strong. Besides, expanded models may account for the reactions of very complex species (such as aromatic poly-cycles), but include them into the scheme in an arbitrary manner. Thus, although the description includes numerous elementary reactions, it bears the stamp of certain randomness. The latter is aggravated by the use of adjustment procedures often employed to compensate for the lack of reliable kinetic parameters. As a result, even if a good fit of experimental data is reached, such a model strongly suffers from the disturbance of inner ties.

We would not discount the utility of such models for certain practical needs. However, one should be very cautious while applying them for the analysis of intimate details of the reaction mechanism. Also, their capability to predict the system behavior outside of the given parameter range is at least suspect.

To proceed to the development of comprehensive models capable of working over a wide range of parameters and for diverse applications, we have to formulate first of all the basic requirements of such a model, which will be further called "ruling principles". A rigorous observance of them would impart to the model an intrinsic consistency and predictive power.

The starting-point and basic-level principles of models, which can be defined as comprehensive or inclusive, must be the following: the combinatorial approach for the compilation of a kinetic scheme and the use of independent values of kinetic parameters. The latter means the flat refusal to use any "parameter optimization" algorithms based on adjustment of the whole model or its blocks to some selected experimental data. These two basic principles are already discussed above in Sections II.A and II.B with reference to the GRI-Mech (combinatorial approach) and the methane-to-methanol oxidation model developed by Vedeneev and co-authors (use of independent kinetic parameters). However, we could not find any example of consistent employment of both principles in conjunction.

Let us mention again, however, that in the course of real modeling multiple compromises are inevitable. This first of all relates to the compromise between the thoroughness and rigorousness of the description and, on the other hand, the accessibility of primary information and "usefulness" of the model. This should be also addressed to both formulation of ruling principles and their execution. Accordingly, it is necessary to formulate them in order to realize their inherent limitations, i.e., the area of phenomena and ranges of parameters where the model can (and cannot) be applied.

The following principles have been formulated based on the stated goals and tasks of modeling and on the analysis of the existing approaches in this area.

Thermodynamic consistency. This is one of the most fundamental principles for the compiling of any model purporting to have a wide applicability. It can be considered as a particular manifestation of the more general kinetic principle of microscopic reversibility that insists the possibility for any elementary process to proceed in both the forward and backward directions. Accordingly, in a complex kinetic scheme any chemical step must be written together with a corresponding reverse reaction. Their rate constants are strongly correlated: their ratio must be equal to the equilibrium constant, which in its turn is determined by thermodynamic functions of substances being in equilibrium. No one elementary reaction consisting of a pair of reactants and products should be ignored in favor of another one, no matter what is the value of corresponding rate constant under given conditions. In other words, the model must assure the asymptotic approach to equilibrium for a given atomic composition at infinite reaction time.

Unfortunately this principle is very often disregarded, or is not taken into account in modeling. We have to stress, however, that only thermodynamically consistent kinetic schemes correctly vector the overall process simulation. Moreover, the faster the reaction in the "forward" direction, the sooner is the equilibration. That means that disregarding of reverse reactions can distort the whole reaction network.

It should be noted that the execution of this principle can meet formal difficulties related to the representation of the temperature dependence of rate and equilibrium constants. Because of the strong dependence of thermodynamic functions on temperature, it is difficult to describe rate constants for both forward and backward reactions in terms of Arrhenius or "three-parametric" equations (see Section III.B). It is possible that the form generally accepted for the representation of temperature dependence of rate constants requires modification. Anyway, it is evident that such formal difficulties should not put obstacles in the way of more adequate modeling of reaction kinetics.

Model fullness. Any kinetic model aimed at the solution of a wide range of tasks over a given range of parameters should be based on the full list of elementary steps. When we state such "fullness" as one of the main ruling principles, it is assumed that the scheme must reflect the whole totality of our knowledge about micro-chemical relationships in the reacting system under consideration. In other words, the kinetic scheme must be compiled in accordance with the combinatorial approach as thoroughly as possible. In addition, some new elementary reactions or even groups of reactions are to be added to the scheme, as new data pointing to such a necessity becomes available. And vice versa, some reactions can be removed from the scheme for the same reason.

Even though the model is supposed to be "full", it should be "rationally full". This means that species, which are believed to be not important for a given range of parameters, can be excluded from consideration. For instance, as far as alkane oxidation at moderate temperatures is concerned, reactions of excited molecules and radicals, which are important for high-temperature combustion, can be excluded. On the other hand, over the same temperature range one can also ignore the reactions of complex peroxides containing chains of more than two oxygen atoms, which are considered sometimes as important for low-temperature oxidation.

In Section V.A we will provide arguments for the joint kinetic description of oxidative transformations of methane and C_2 hydrocarbons. Regarding molecules containing more than two carbon atoms, their influence on the overall kinetics and on the formation of many important products is below the anticipated accuracy of simulations (Arutyunov *et al.*, 2005). This is why their formation and transformations can be not accounted for in methane and ethane oxidation models for many applications. At least it would not compensate the excessive complication of the model accounting for reactions of C_{3+} species.

Of course, in special cases when the modeling is aimed at the formation of higher hydrocarbons (Marinov *et al.*, 1996; Mims *et al.*, 1994), their reactions must be included. However, due to a relatively low concentration of these compounds, the requirements to the complete accounting of their reactions can be not very strict due to their relatively low importance. A typical example of such kind could be a chain-branching at the expense of hydroperoxides containing higher alkyl-groups.

The same can be related to oxidation of any other C_{2+} hydrocarbon. The kinetic scheme must include the reactions of lower hydrocarbons as its substantial part, but the reactions of species containing more C–C bonds than the initial hydrocarbon can be excluded for many applications without a substantial loss of accuracy.

In brief, the fullness is not a quantitative measure of the model, but more a qualitative one. The scheme containing fewer elementary steps may better meet this criterion than a much vaster one, if in the former case the reaction blocks related to species of a certain type (for instance, containing the same number of carbon atoms as the initial hydrocarbon and less) are more thoroughly taken into account.

Independence of kinetic parameters. Let us mention again that there are two alternative approaches to the relationships between the model and the kinetic parameters. In the first case, the data obtained in some experiment(s) are considered as the basis. The values of kinetic parameters for all (or some selected) elementary reactions included in the kinetic scheme are optimized in the framework of a certain fitting procedure, and the range of their variation can be determined in advance based on some considerations. As a result, the set of parameters assuring the best adjustment of the kinetic scheme to the basic experiment(s) is defined.

This approach provokes strong objections. First, the basic definition of "rate constant" becomes blurry. Indeed, none of the coefficients in the mass action law in the whole kinetic scheme can be considered as an independent physical value with a clear sense. If, however, selected parameters receive such privilege, this breaks the general principle and requires additional criteria.

Second, it is evident that the selection of different "basic" experiments should lead to different sets of "optimized" kinetic parameters. Since, as it was already mentioned, the inverse kinetic task is in general an ill-conditioned problem, such sets can differ significantly and it is difficult to define the criteria for the selection of the one (only one!) that should be used for modeling.

Lastly, practically in any kinetic experiment there are some uncertainties in its conditions and results. This concerns such factors as mixing of reactants, regimes of gas flow in different zones of the reaction system, wall effects, axial and radial temperature gradients, spatial distribution of reaction rates, concentrations, pressure, etc. A lot of effort must be applied even to measure the reactant conversion and the main product distributions at the exit of the reactor, needless to say anything about concentrations of active intermediates and concentration distributions inside the reactor. Moreover, up to now there is no clear understanding about which measured parameters are the most informative and should be preferred.

An alternative approach implies that all kinetic parameters used in the model are determined independently from the modeling itself. The probability of serious errors is still high in this case too, although for many parameters important for alkane oxidation and combustion such errors are evaluated (see, for instance, Tsang and Hampson, 1986; Warnatz, 1984). Despite that, it seems that in this case we are dealing with the lesser of two evils. Moreover,—and this is of principal importance—every value included into the scheme can be independently corrected as soon as newer and more reliable data appear. This does not require any modification of any other kinetic parameter in the model.

Therefore, we are inclined to use in modeling only the reliable recommended rate constants with the possibility of their correction only on the basis of independent experimental or theoretical results without any adjustment or fitting to experimental data.

The possibility to significantly improve the agreement between calculations and very reliable experimental data by variation of not more than one or two parameters may be considered as the maximum allowed adjustment procedure and as a cause for a more thorough analysis of accepted sources of kinetic parameters. Concerning the choice of the most reliable values of kinetic parameters, it is very difficult to make any general recommendation equally good for all possible cases. Every multi-step kinetic scheme consists of elementary reactions, which have been previously studied with very different thoroughness. Some reactions attract very rapt attention and are studied by various methods (direct and indirect). In this case such experimental data can be analyzed and some "weighted" values of parameters can be chosen. Another extreme can be represented by the reactions very poorly studied experimentally, or even hypothetical. In such case theoretical evaluation or even a semi-quantitative estimation using *ab initio*, semi-empirical, and/or empirical methods can be considered as the only way to obtain the primary information for modeling. But in any case it is possible to trace the sequence of sources with different levels of reliability. As far as the homogeneous elementary reactions in the gas phase are concerned, we no doubt believe that the review articles and databases, in which the analysis of the data is performed, can be considered as the most reliable ones. For instance, in the case of methane and ethane oxidation at moderate-temperature and pressures (600–1,300 K and 1–100 atm) the following sequence of sources (with decreasing universality and applicability) could be suggested.

- The recommended values presented in (Tsang and Hampson, 1986) and added to those recommended by Baulch *et al.* (1982, 1984, 1992, 1994) have a priority against any other.
- If the data are absent in these sources, the recommendations of (Warnatz, 1984) can be accepted.
- If none of the above reviews contains the recommendations about the reaction under consideration, but original experimental works containing the temperature dependence of rate constant(s) are available, the value for the closest temperature interval can be recommended.
- If no reliable data are available at all, the kinetic parameters can be evaluated by analogy with reactions for which the similar data are available. For instance, to evaluate rate constants for some bi-molecular reactions of C_2-radicals (C_2H_5O, $C_2H_5O_2$), the data for CH_3O and CH_3O_2 radicals can be used as a rough estimation.

Openness of the description. If we accept the independence of kinetic parameters as one of the main ruling principles and totally deny any adjustment of the kinetic scheme to particular experimental data, this gives the model an additional advantage making it fundamentally open. This means that the arrangement and tuning of the model can be done by the selection of more accurate values of kinetic parameters from independent sources and by the addition of elementary reactions required for the more detailed description of the reacting system. Moreover, once elaborated the core model can be further developed for a wider area of application by the addition of new elementary steps or their blocks. One example of such widening will be given in Section V.B.

To conclude this section, it is worth mentioning that any model, no matter how deeply it is developed, cannot be identical to the described phenomenon. This makes even more important the precise formulation of the goal of modeling and the right choice of corresponding instruments and tools. If we state that our goal is to develop the model, which in turn is going to be a tool for mechanistic investigations and to carry a certain predictive power, it must have no internal ties and connections with experimentation it should describe. We believe that such a goal can be reached in the framework of the united approach based on the principles formulated above.

D. Reduction of Models

The development of comprehensive quantitative models is the main goal and the "high road" in modeling. However, compact "illustrative" models for more clear understanding of the essential phenomena and their qualitative description will remain in demand. In the ideal case, such an "illustrative" model should result from the reduction of a more comprehensive one and keep the whole totality of features important for the behavior or for the phenomenon we wish to illustrate, as well as the relation to the overall process. Whereas the inverse procedure—the initial formulation of relatively "simple" schemes—can be acceptable only as a starting hypothesis that requires further development.

Several methods and mathematical tools have been suggested and elaborated to reduce complex kinetic models to be more concise. We believe that it would be important to mention briefly the main guiding principles and criteria for such reduction. First of all, again we must stress that the tools and ways are caused by the goal—in this case the goal of reduction.

The "importance" criterion implies the selection of reactions (which will remain in a "concise" scheme) based on sensitivity analysis. Note that this widely used approach may cause very serious faults even with very small changes of external parameters. Moreover, one may lose sight of the fact that reactions which do not substantially contribute in the oxidation processes in a given regime may become of crucial importance if the conditions are changed. Below we will give an example of such a type when the reactions, which do not participate over a certain temperature range, allow the process proceed into the particular direction (namely—the OCM products formation during methane oxidation, and the appearance of the "OCM Window"). Thus, even to describe qualitative effects, "rational" description may be based on the "reverse" importance criterion.

The partial equilibrium criterion goes back to the steady-state concentration method, which was widely used before the computer age. In the framework of this approach, only species participating in the slowest reaction are considered, while a steady-state equilibrium for all other components and fast reactions is assumed. If two or more species are connected by fast chemical reactions and the rate of their reciprocal conversion in these reactions is much higher than into other compounds, they form a steady-state subsystem. Their ratio in such a subsystem is determined by the rate constants of their reciprocal conversion. In the case of two fast reciprocally transforming compounds, their ratio is determined only by the equilibrium constant and current concentration. The particular values of the rate constants determine only the time of equilibration, and other reactions of these compounds only slightly disturb their ratio. In such a case the use of the partial equilibrium criterion can be fruitful.

The minimization (even neglect) of chemical differences criterion admits the unified description of isomers (and even chemically related substances), if they can undergo the same types of chemical transformations. This criterion also should be applied with caution: even the comparison of two propyl radicals—of normal and *iso*-structure—demonstrates their serious difference, especially when relative importance of different reaction channels, including dehydrogenation and cracking (oxidative and non-oxidative), is analyzed. On the other hand, if the target products are olefins, any difference in the behavior of multiple oxygenates can be neglected, provided their further transformations do not lead to the target molecules and to chain-branching intermediates. In this case their formation with acceptable accuracy may be treated merely as the withdrawal of a sufficient amount of species from the main process.

The similarity criterion is analogous to the one just mentioned above. In this case, the same kinetic parameters are ascribed to different species participating in the reaction of particular type. Evidently, similar caution also should be taken. However, this approach becomes of principal importance for the modeling of higher hydrocarbon oxidation (e.g., transfer from C_1–C_2 to propane and butanes), or for processes in which some products with increasing complexity (like soot species) are formed.

The utility criterion supposes the selection (flow analysis) of the reaction set the most important for the particular behavior of the system, or for the particular product formation and transformations. This approach is very useful for the segregation of reactions, in which a particular substance (target product, leading radical, or key branching intermediate) forms or transforms. As a result, the analysis of the process under different conditions, or at different stages (when the ratio of various elementary reactions is changing) becomes available.

One should keep in mind that any reduction breaks the stringency of the description. The "reduced" description is only an illustration that should emphasize the chemical essence of the phenomenon under consideration, but cannot replace the "full-scale" modeling. Like in many other cases, we can consider reduced models as a compromise—on this occasion as a concession to clarity at the expense of thoroughness. Anyway, simulations using the comprehensive model should be employed to control the validity of thus obtained qualitative conclusions.

E. Modeling of Heterogeneous–Homogeneous Catalytic Reactions

Modeling of processes belonging to this group is discussed separately because of their significant specificity. As we already mentioned in Section I.C, systematic studies in this area started about 20 years ago, but they are still in the development stage.

Even from the very beginning it became clear that kinetic methods generally accepted in heterogeneous catalysis, which are based on the analysis of adsorption–desorption equilibria and surface reactions in the steady-state approximation, cannot be applied to the studies of heterogeneous–homogeneous processes. However, on the eve of 1980s no developed methodology applicable for joint analysis of catalytic and gas-phase reactions was at a researcher's disposal. For the description of the former group, models of the Langmuir–Hinshelwood, Eley–Rideal, and Mars–van Krevelen types were traditionally applied. Unlike them, the analysis of gas-phase reactions usually is based on kinetic schemes, which include multiple elementary steps and sets of corresponding kinetic parameters. The latter—in principle—can be determined (measured experimentally or theoretically calculated) independently.

The strategy previously applied for homogeneous reactions has been also accepted for modeling heterogeneous–homogeneous processes. It consists of

- Compiling a set of elementary steps (kinetic scheme) assumed to proceed in the reacting system with a corresponding kinetic description of each step (kinetic equation and parameters).
- Certain notions about heat- and mass-transfer in the reactor.
- Mathematical (computational) procedures enable the prediction of the development of the process in time (and space—in the case of spatially distributed systems).

Even if the influence of macro-kinetic factors (heat- and mass-transfer) is taken into account, the models of this type are usually called "micro-kinetic". This is due to the principal importance of the set of elementary reactions. In all cases these models are based on a guess (more or less experimentally and/or theoretically grounded) about the factors—chemical and physical—important for the behavior of the systems, as well as about the factors which can be ignored for certain purposes.

At least two circumstances stimulated a growing attention to modeling of heterogeneous–homogeneous processes. First is a great practical importance of natural gas processing reactions. For some catalytic processes belonging to this group (first of all OCM) their radical nature was proven; for others (methane partial oxidation to formaldehyde and synthesis gas, ODH of C_2–C_4 alkanes) the probability of such mechanisms was evaluated as being high. Scaling-up of such processes requires reliable kinetic models.

On the other hand, because of the serious complexity of the direct investigation of heterogeneous free radical reactions, as well as processes in adsorbed layers, modeling can serve as a powerful tool for mechanistic studies. However, poor knowledge about possible mechanisms and the lack of basic concepts still restrain progress in elaboration of kinetic schemes in which all kinetic parameters would be measured or evaluated independently. Moreover, as compared to elementary gas reactions, rate constants for heterogeneous processes, especially for reactions between adsorbed species, are hardly amenable to theoretical calculations. Even required thermochemical data are not accessible in most cases. Besides that, energetic characteristics and reactivity of surface sites and adsorbed species present a puzzling function of the state of surface and bulk of the solid and can be adequately accounted for only in rare cases.

Nevertheless, recently several approaches have been suggested and certain progress in theoretical methods applicable for heterogeneous kinetics has been achieved (see, for instance, Baranek *et al.*, 2000; Hansen and Neurock, 1999; Lichanot *et al.*, 1999; Neurock, 2003; Neurock *et al.*, 2004; Palmer *et al.*, 2002a, b; Shustorovich, 1990). Although the detailed analysis of this subject exceeds the bounds of our work, it is worth mentioning the most promising of them, namely Density Functional Theory (DFT) and the Unity Bond Index-Quadratic Exponential Potential (UBI-QEP) method. Whereas DFT is quantum-mechanics-based, UBI-QEP can be characterized as a phenomenological or semi-empirical approach. According to Shustorovich and Zeigarnik (2006), these two approaches are complimentary, and good agreement between their predictions testifies to a good understanding of the system under study. These are some examples of fruitful use of these two methods in the framework of one study (see, for instance, Hansen and Neurock, 1999; Mhadeshwar and Vlachos, 2005). The details of these two methods and examples of their application can be found in corresponding reviews (DFT: Bengaard *et al.*, 2002; Hammer and Nørskov, 2000; Van Santen and Neurock, 1995; UBI-QEP: Sellers and Shustorovich, 2002; Shustorovich and Sellers, 1998; Shustorovich and Zeigarnik, 2006; Zeigarnik and Shustorovich, in press).

Bypassing the detailed analysis of some achievements and remaining problems, let us just mention that there is a distinct difference between reactions catalyzed by oxides and metals. Here we provide preliminary characteristics of these two groups (see Table I). They will be further treated separately in Sections III.E and III.F.

III. "Elemental Base"

As was already mentioned, the core of each model is presented by the set of elementary reactions included. Their selection is based on the concept of the process under study and is determined by the goal of modeling. We assume that in the framework of the ultimate goal announced in this paper, maximum possible fullness is one of the main ruling principles for model compilation. A grounded selection of kinetic parameters is another crucial aspect of modeling. These two topics form a micro-kinetic basis of each model, which is the main subject of this paper. Below we present our vision of the sequence of stages needed to compile a working micro-kinetic scheme. Also, some difficulties existing along this path are highlighted.

A. Limitations of Species Taken into Account

As we mentioned in the beginning, the most important aspect of modeling is the stated objective. In the present case we attempt to compile a kinetic scheme,

TABLE I

Some Characteristics of Heterogeneous–Homogeneous Catalytic Reactions of Light Alkanes

Characteristics	Reactions over oxides	Reactions over metals
Examples	Oxidative coupling of methane (OCM), oxidative dehydrogenation of C_1–C_4 alkanes, partial oxidation of methane to synthesis gas[a], combined oxidative coupling of methane and toluene to styrene	Surface-stabilized combustion, partial oxidation of methane to synthesis gas[a], synthesis of cyanic acid from methane, ammonia, and oxygen[a]
Availability of direct experimental kinetic studies of elementary reactions	Limited; techniques—matrix isolation ESR (MIESR) Driscoll *et al.* (1987), Lunsford (1989), Garibyan and Margolis (1989–90), Tong and Lunsford (1991), Politenkova *et al.* (2001); ESR, optic spectroscopy Radzig (1993), Firsov *et al.* (1990)	Limited; techniques—molecular beams (including those with angular resolution) Smudde *et al.* (1993), Fairbrother *et al.* (1994), Hall *et al.* (1994), Kislyuk *et al.* (2000)
Availability of direct experimental studies of thermochemistry of surface centers/adsorbates	Limited; technique—*in situ* differential scanning calorimetry Sinev and Bychkov (1999)	(+/−)
Availability of theoretical (computation) methods for:		
a. Structure and energetics;	(+)[b]	(+)[a]
b. Kinetic parameters	(+)[b]	(+/−)[b]
Degree of surface (active sites) coverage by adsorbed species	Low[c]	Can be high
The main accepted method of kinetic scheme compilation	Addition of heterogeneous steps to existing homogeneous scheme	Compilation of assumed scheme of transformations is adsorbed layer and addition of homogeneous steps (or combination with homogeneous schemes); accounting of heat- and mass-transfer processes/fluid dynamics
Approaches to evaluation of kinetic parameters	1. By analogy with corresponding homogeneous reactions; 2. Use of thermochemical correlations	1. Evaluation using thermochemical data; 2. Quantum chemistry; 3. Optimization against experimental data

[a] Heterogeneous–homogeneous mechanism is assumed, but not proven for all cases;
[b] See text for comments;
[c] Hydroxylation of surface sites can be very high.

which would be applicable for the reactions of light alkane processing and satisfy the requirement of fullness. Stating this, we arrive at the necessity to identify first the range of species participating in the reactions to be further analyzed in the framework of the model.

This task is not trivial even in the case of the simplest hydrocarbons (C_1–C_4). Indeed, there are "obvious" participants in the process—initial reactants (hydrocarbon and oxidant), total oxidation products (water, CO_2), intermediates (target and side partial oxidation products). But already here we are facing a dilemma. The broader the list of species included (composition and structure of which do not contradict the chemical sense and which can be at least in principle present in the reaction mixture), the less definite is the available information about the kinetics of their transformation.

Further progress in building the model leads to increasing difficulties, since while deciding which species (and their reactions) should be included into the scheme, serious doubts about the reliability of even their thermochemical parameters appear.

Nevertheless, let us try to define which species should be included into the scheme, for instance, of methane transformations. They are supposed to be

1. Initial reactants (methane, oxygen).
2. Final products of total oxidation (water, carbon dioxide).
3. Incomplete oxidation products (methanol, formaldehyde, formic acid, CO, H_2).
4. Molecular products of radical transformations (first of all, C_2-hydrocarbons), molecular peroxides (H_2O_2, CH_3OOH).
5. Free radicals—products of sequential abstraction of H-atoms from the above molecules (CH_3, H, HO_2, OH, CH_3OO, CH_2OH, CH_3O, CHO, COOH, C_2H_5, C_2H_3).

In most cases in the range of conditions of interest to us (moderate temperatures and elevated—not less than ambient atmospheric—pressure), reactions of excited molecules can be excluded. The only exception will be discussed in detail in Section III.D—the group of total pressure-dependent reactions, which proceed via the formation and deactivation of excited molecules (compounds).

As we go further, some new questions arise about the necessity to account for additional species, for instance, products of deeper dehydrogenation of methane and ethane molecules (acetylene, CH_2, CH, C_2H radicals) and products of CH_3OO, CH_3O, and CH_2OH dehydration. Not all of these questions can be answered before the real analysis of the model begins. Some of those species should be kept in mind and added to the scheme (of course, together with complete blocks of their elementary reactions) as required based on the accepted logic of modeling.

B. Elementary Reactions

The elementary (or simple) reaction is one of the key concepts in the modeling of complex processes. An elementary reaction can be defined as a totality of all chemically identical elementary acts in which reordering of chemical substances and/or change of their state are taking place (see, for instance, Emanuel and Knorre, 1984). Since the following discussion deals with the development of kinetic schemes consisting of multiple reactions to which such "elementary" sense is attributed, a clear definition of this term is required. We will further call the reaction elementary if it passes through not more than one potential barrier in both directions (forward and reverse).

While modeling complex process kinetics, almost generally accepted is the rate equation for elementary reactions in the form of mass action law

$$W = k\Pi(C_i^m) \tag{3.1}$$

where k is the rate constant, C_i the concentration of reactant (i), m the reaction order with respect to reactant (i).

For many cases Eq. (3.1) serves as a good approximation. However, one must keep in mind that the more correct form of mass action equation must contain activity values, which in the general case differ from concentrations (or, in other words, activity coefficients are not equal to 1). Deviations of activities from concentrations are most pronounced at relatively low temperatures and high pressures, i.e., when properties of the reaction system display a pronounced difference from those of an ideal gas. Uncertainty of kinetic simulations can therefore increase if values of kinetic parameters obtained at low pressures are used to model high-pressure processes in the framework of Eq. (3.1). Among processes of interest announced in this work, at least one—oxidation of methane-to-methanol—severely needs high pressures, at which the non-ideality of the reaction system can in principle manifest itself.

The rate constant, k, in turn, as a rule, is presented in the form of the Arrhenius equation

$$k = Z \exp\left(\frac{-E_a}{RT}\right) \tag{3.2}$$

where Z and E_a are constants, to which somewhat different meanings are ascribed depending on the accepted interpretation of this exponential dependence. The activation energy E_a is usually treated as a barrier to be crossed by the reacting system to transform from reactant(s) into product(s). As to the pre-exponential factor Z, different theories interpret its physical sense differently and, correspondingly, give different mathematical expressions for it (see Alekseev, 1988; Emanuel and Knorre, 1984; Eyring *et al.*, 1980; Glasstone *et al.*, 1941). In particular, in the framework of active collision theory the pre-exponential factor for a bi-molecular reaction is considered as the frequency of collisions of a certain type. It is counted as

$$Z = \sigma \left(\frac{8RT}{\pi\mu} \right)^{1/2} \tag{3.3}$$

where σ is the collision cross-section, R gas constant, and μ the reduced molecular weight of colliding molecules.

On the other hand, following the activated complex theory, one can derive the value of the pre-exponential factor from the thermodynamic expression of the rate constant

$$k = \chi \frac{RT}{hN_\mathrm{A}} \exp\left[\frac{\Delta S^{\#}}{R}\right] \exp\left[-\left(\frac{\Delta H^{\#}}{RT}\right)\right] \tag{3.4}$$

where h is Planck's constant, N_A Avogadro number, χ the transmission coefficient, $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are standard entropy and enthalpy of formation of activated complex.

In spite of the difference in the underlying concepts and the forms of equations, Eqs. (3.3) and (3.4), both descriptions reflect the statistical sense of the rate constant. The latter statement is crucially important for better understanding of the problem existing in heterogeneous kinetics. Indeed, the above-mentioned theories are based on gas statistics and the given equations assume an equilibrium Maxwell–Boltzman distribution for gas species, which in the absence of reaction interact only via elastic collisions. If this can be considered as a satisfactory approximation for gas reactions at moderate temperatures and pressures discussed here (with some exceptions—see Section III.D), its applicability to the processes involving surface sites (i.e., elements of solid lattice) or adsorbed species is not so obvious.

Moreover, when rate constants are measured or derived somehow from experimental data, one can assume that the expression for the rate constant in the Arrhenius form can be used as an approximation, even if the meanings of Z and E_a are different from those followed from Eqs. (3.3) or (3.4). However, the situation is substantially different when we evaluate or calculate rate constants basing on some theoretical considerations. The discussion about applicability of such simple equations to reactions in condensed phase and/or interfaces has repeatedly ignited and extinguished during the last few decades. To our opinion, nowadays, when various theoretical methods are widely used for evaluation and calculation of rate constants, it is time to revert to the question.

A substantially macroscopic (in the thermodynamic sense) character of the parameter called the "rate constant" is its fundamental feature. Rigorously speaking, it is a statistical value (as well as temperature is) and can be applied only if the equilibrium distribution of Maxwell–Boltzman type is kept (see Knyazev and Tsang, 1999). Unfortunately, the requirement of using the more precise concept, namely reaction cross-section, in everyday practice would not be realistic even for homogeneous gas reactions. This is both because of the absence of corresponding data for a number of reactions, as well as due to the immense size of such a database if it would exist.

Taking a realistic stand, we nevertheless should keep in mind that not only any acceptable set of parameters, but also the shape of the mathematical expression, must be treated as approximations and may vary, for instance, with temperature. Evidently, we have to agree with the impossibility to derive an "absolutely-precise" expression of the rate constant, no matter how deep we go into the nature of elementary reactions.

One of the most striking examples of compromise between physical reality and a need for a "compact" and uniform mathematical description is the use of the so-called three-parameter form of the Arrhenius equation for the representation of the temperature dependence of rate constants

$$k = A\left(\frac{T}{T_0}\right)^n \exp\left(\frac{-E_a}{RT}\right) \tag{3.5}$$

Although non-Arrhenius behavior over a wide temperature range is more frequently a rule than an exception, the physical sense of the parameters A, n, and even E_a is not always clear. Moreover, parameters optimized for one temperature range may be poorly acceptable for extrapolation to another.

It is worth mentioning here that some other forms for representation of reaction rate and rate constants exist. Some of them are presented in Sandia National Laboratories document (Kee *et al.*, 1996). Nevertheless, the three-parameter form now is almost generally accepted in modeling practice, and the corresponding parameters (A, n, and E_a) can be found for the largest number of elementary reactions in original publications, databases, and review articles (see, for instance, http://www.nist.gov/srd/nist17.htm; Tsang and Hampson, 1986; Warnatz, 1984).

As we mentioned in Section II.C, one of the most important requirements, which is applicable to the overall structure of reaction schemes, is its *thermodynamic consistency*. In other words, the scheme, as written, must allow the process to proceed asymptotically to its equilibrium state at infinite time. This can be reached only if any elementary step is included into the overall scheme together with its reverse reaction. Let us consider the consequences for the description of the process kinetics. For the sake of simplicity, we assume that the reaction proceeds in the ideal gas mixture. The value of rate constants $k_{(+)}$ for forward and $k_{(-)}$ for reverse reactions must satisfy the connecting equation

$$\frac{k_{(+)}}{k_{(-)}} = K \tag{3.6}$$

where K is the equilibrium constant.

Equilibrium constants, in their turn, can be calculated from available thermodynamic parameters of reactants and products

$$K = \exp\left[\frac{-(\Delta H - T\Delta S)}{RT}\right] \tag{3.7}$$

where ΔH and ΔS are the differences between corresponding thermodynamic functions (enthalpy of formation and standard entropy) of products and reactants. These functions are tabulated nearly for all molecular compounds involved in the processes discussed here, as well as for many radical species. However, the form of their representation—especially fractional polynomial temperature dependence—may contradict the above equations for rate constants. What could be recommended for the calculation of rate constants for reverse reactions if $k_{(+)}$ and thermodynamic functions are available is to use the averaged values of ΔH and ΔS for the temperature range of interest. If this range is too wide, or better precision is required, one can calculate K and $k_{(-)}$ values for several temperatures using Eqs. (3.6 and 3.7), and then approximate them by the optimal set of parameters A, n, and E_a. In some software packages developed for kinetic simulations these or analogous procedures can be performed automatically.

The analysis of particular kinetic schemes and the results of simulations indicate that models which meet the requirement of thermodynamic consistency possess additional benefits, such as possibilities to describe multiple processes within one kinetic scheme:

- Oxidation of one hydrocarbon to different intermediate partial oxidation products;
- Catalytic reactions of different starting compounds.

Unfortunately, up to now we possess no generally accepted standards of selection, treatment, and representation of kinetic data obtained by one means or another. Although the attempts undertaken by the CHEMKIN package developers and other similar institutions and research groups must be appreciated, the analysis of publications and discussions taking place on several Internet forums demonstrates the absence of any consensus or even co-ordination in this crucial aspect. This makes the comparison of results obtained by different research groups almost impossible. The most complete and popular kinetic database nowadays is the one developed by the National Institute of Standards (see web resource http://www.nist.gov/srd/nist17.htm), but this is, in fact, a collection of all published experimental and calculated data, which require further critical evaluation before being utilized in simulation practice. On the other hand, widely known databases of recommended kinetic parameters (Baulch *et al.*, 1982, 1984, 1992, 1994; Kondratiev, 1970; Tsang and Hampson, 1986; Warnatz, 1984 and others) seriously suffer from incompleteness.

C. Selection of Rate Constants

The most consistent way to develop a theoretical kinetic model of a complex process can be described as follows. First, we determine the list of species participating in the process, and then compile a set of elementary reactions based on the fullness principle. The most logical step after this would consist of *ab initio* calculations of kinetic parameters for elementary reactions included into the model (kinetic scheme). If the parameters calculated in this way are in significant contradiction with values obtained from independent experiments, this should cause a re-consideration of the underlying principles of both the calculations and the experimental measurements. However, this must not influence the core of the model and values of other kinetic parameters.

The above statement reflects an ideal, or extreme, view. It is clear that such approach is not realistic. Moreover, taking into account our limited knowledge about dynamics of elementary processes (even homogeneous) and other limitations discussed here, we must conclude that strict adherence to such "rules" cannot lead to a satisfactory result. In other words, the experimentally measured values of kinetic parameters must be taken into account.

Unfortunately, even in this case we are facing several difficulties. First, different reactions included into a complex kinetic scheme cannot be preliminarily studied to the same extent using independent methods. So, if for some reactions numerous data are available in corresponding literature and databases, in other cases not a single reliable value could be found. This means that in the framework of one kinetic model we have to use parameters obtained using very different experimental methods (direct and indirect) and also by more or less well-grounded evaluations.

Second, if for some reactions multiple experimental data are available, kinetic parameters obtained by different authors using different methods as a rule are not in a close agreement, and in some cases are even contradictory. In this case we have to employ some reference argumentation in order to choose the one to be used. Some criteria for such selection are already discussed in Sections I.D and III.B. In any case, the final decision about each value is going to be taken by a particular investigator, no matter if he/she gives credence to the authors of preceding studies or makes his/her own evaluations.

D. Pressure-Dependent Reactions

Due to a broad width of temperature and pressure ranges to which the models of the processes under discussion should be applied, additional difficulties with the description of certain reactions arise. Such reactions proceed as multi-step processes with intermediate formation of excited species and their further deactivation via decay (dissociation) or via stabilization in collisions with other molecules ("third bodies"). Because of the latter, this group of processes is called sometimes “three-body reactions”. This group includes recombination of atoms and relatively small radicals, formation of RO_2 (and HO_2) radicals from light alkyl radicals (or H-atoms) and O_2 molecules. Also, the processes which formally proceed as a mono-molecular decay in fact require an excitation in molecular collisions to gain the excess energy for crossing the dissociation barrier. Reactions of these types (e.g., recombination and dissociation) can and must be treated simultaneously within the same approach. The latter requirement follows from the stated thermodynamic consistency principle.

These reactions play an extremely important role in hydrocarbon oxidation over the temperature range discussed here, and in some cases even small variations in their parameters can lead to serious deviations in the simulated kinetics.

For all reactions of this group, at a “low-pressure limit” the rate increases proportionally (as a rough approximation) to the total pressure, or to the sum of the concentration of all species present in the system, since any collision can lead to stabilization of excited species. Also, all gas species contribute to the excitation of stable molecules for further dissociation. As the total pressure increases, another limit can be reached, in which the reaction rate depends only on the concentration(s) of the reactant(s), but not on the total pressure, and the overall kinetic order decreases. Corresponding rate constants at the “low” and “high” pressure limits are usually denoted as k_0 and k_∞.

Several approaches can be realized in kinetic models to describe the rate of “three-body” reactions in the transition (fall-off) regions (at “moderate pressures”). One of them represents the rate of reaction in terms of the “high pressure limit”, but with a rate constant somewhat lower than k_∞. Corresponding decreasing coefficient asymptotically approaches 1 at increasing pressure and also decreases with temperature at a given total pressure. This approach requires knowledge about actual temperature and pressure dependencies; also additional correction of rate constants during the course of reaction must be performed. This substantially limits its adaptability and applicability.

Another approach proposed by Lindemann (1922) suggests the extended description of such reactions, which includes an explicit accounting of the formation of the excited species (marked with an asterisk) and two channels of its degradation

$$A + B \rightarrow AB^* \tag{L1}$$

$$AB^* + M \rightarrow AB + M \tag{L2}$$

$$AB^* \rightarrow A + B \tag{L3}$$

$$AB + M \rightarrow AB^* + M \tag{L4}$$

One can see that in the framework of this approach both directions (coupling and dissociation) are treated within one description. The main problem here consists of the absence of direct data about kinetic parameters of reactions (L1)–(L4). Their values should meet the following requirement: the overall description must approach the certain limits at high and low pressures and fit the data for fall-off region (if any available). Also, it is very desirable that these parameters are evaluated based on more or less grounded considerations.

The analysis of the scheme (L1)–(L4) shows that a steady-state concentration of excited species AB^* can be described as follows:

$$[\mathrm{AB}^*] = \frac{k_{\mathrm{L1}}[\mathrm{A}][\mathrm{B}] + k_{\mathrm{L4}}[\mathrm{AB}][\mathrm{M}]}{k_{\mathrm{L2}}[\mathrm{M}] + k_{\mathrm{L3}}} \tag{3.8}$$

If we ignore the contribution of reaction (L4), the rate of the product formation is equal to

$$W_{\mathrm{AB}} \approx \frac{k_{\mathrm{L1}}k_{\mathrm{L2}}[\mathrm{A}][\mathrm{B}][\mathrm{M}]}{k_{\mathrm{L2}}[\mathrm{M}] + k_{\mathrm{L3}}} \tag{3.9}$$

The latter equation can be used to describe two extreme cases. If decomposition by far prevails over deactivation a "low-pressure limit" approximation can be applied

$$k_{\mathrm{L2}}[\mathrm{M}] \ll k_{\mathrm{L3}} \quad \text{and} \quad k_0 = \frac{k_{\mathrm{L1}}k_{\mathrm{L2}}}{k_{\mathrm{L3}}} \tag{3.10}$$

In an opposite case with deactivation prevailing, the kinetics typical for the "high-pressure regime" are observed

$$k_{\mathrm{L2}}[\mathrm{M}] \gg k_{\mathrm{L3}} \quad \text{and} \quad k_\infty = k_{\mathrm{L1}} \tag{3.11}$$

Thus, in the scheme (L1)–(L4) one rate constant (k_{L1}) can be equated to the "high-pressure" constant k_∞. Constant k_{L4} can also be easily estimated: with high probability its activation energy can be equated to the enthalpy of step (L1), or to the energy of A–B bond dissociation. As to the pre-exponential factor, it can be derived from the active collision theory.

One has to resort to additional assumptions to evaluate the constants k_{L2} and k_{L3} (such as lifetimes of excited species, deactivation probability in reaction (L2)) and the connecting relation subsequent upon the Eqs. (L1–L4)

$$\frac{k_{\mathrm{L3}}}{k_{\mathrm{L2}}} = \frac{k_\infty}{k_0} \tag{3.12}$$

In some cases an adjustment of both constants (k_{L2} and k_{L3}) must be performed in Eq. (3.12) in order to impart a physical sense upon them. A substantial simplification of this procedure is taking place if direct data about deactivation and/or about the pressure dependence of the apparent "high limit" constant are available.

As we already mentioned, similar considerations can be suggested and analogous expressions can be obtained for reverse processes, i.e., for reactions, which are usually considered as dissociation under the conditions of hydrocarbon oxidation. Typical examples are hydrogen peroxide and alkyl hydroperoxide decomposition. Despite existing difficulties, the Lindemann approach can be recommended as it allows:

- To use a uniform representation of all rate constants included into the kinetic scheme;
- To describe direct and reverse processes within one scheme;
- To account for new data about the kinetics of excited species (e.g., about efficiency of different "colliders" in reactions (L2) and (L4)) without changing the structure of the overall scheme.

There are also some other methods that provide a more accurate description of the fall-off region than does the simple Lindemann form. The details can be found in corresponding publications (see, for example, Allison, 2005; Gilbert *et al.*, 1983; Stewart *et al.*, 1989; Wagner and Wardlaw, 1988). Some kinetic simulation packages (e.g., CHEMKIN) optionally realize these approaches for representation of "three-body reaction" rates (Kee *et al.*, 1996).

Finally, we mention that there are certain reactions, which to our opinion must be with no doubt described as "three-body processes". Among them, first of all, are

- Recombination of methyl radicals and H-atoms;
- Formation and dissociation of hydro-, methyl- and ethyl-peroxy radicals;
- Dissociation of hydrogen peroxide and alkylhydroperoxides.

E. HETEROGENEOUS–HOMOGENEOUS CATALYTIC REACTIONS ON OXIDE CATALYSTS

Evidently, OCM was the first process the heterogeneous–homogeneous nature of which has been studied in detail. In this example many substantial features of this class of processes were rationalized. This includes the elaboration of the principles of modeling starting from the micro-chemical level. It is worth noticing that OCM is a striking example of the impossibility to adequately describe the behavior of complex systems if some "insignificant" elementary reactions are not included into the kinetic scheme. In this process the key step leading to the formation of higher hydrocarbons—the recombination of methyl radicals—can take place only if gas reactions between CH_3 and O_2 are not taking place. This is exactly what happens in the temperature range of 873–1,223 K at atmospheric pressure and oxygen concentrations below 20 vol.%. In these conditions the equilibrium constant of reaction

$$CH_3 + O_2 \rightleftharpoons CH_3O_2 \tag{5}$$

is already small enough, but the rate constants of methyl radical oxidation

$$CH_3 + O_2 \rightarrow CH_3O + O \tag{6}$$

$$CH_3 + O_2 \rightarrow CH_2O + OH \tag{7}$$

are not yet high enough to compete with recombination, despite the fact that the oxygen concentration in the reaction mixture is much higher than that of CH_3 radicals (see Fig. 5). As a result, the "OCM window" appears. It is important that in the same temperature range reactions with $E_a \approx 200$ kJ/mole (roughly one-half of the C–H bond strength in methane) can proceed with a relatively high rate. This is an additional, but not the main, factor providing for the possibility of the formation of higher hydrocarbons during methane oxidation. Although any standard procedure can demonstrate "insignificance" of reactions (5)–(7) under typical OCM conditions, their removal from the kinetic scheme of the reaction leads to the impossibility to describe the existence of the "OCM window". This would also lead to the loss of predictive power of the model, as far as variation of parameters (total pressure, concentration of oxygen) is concerned.

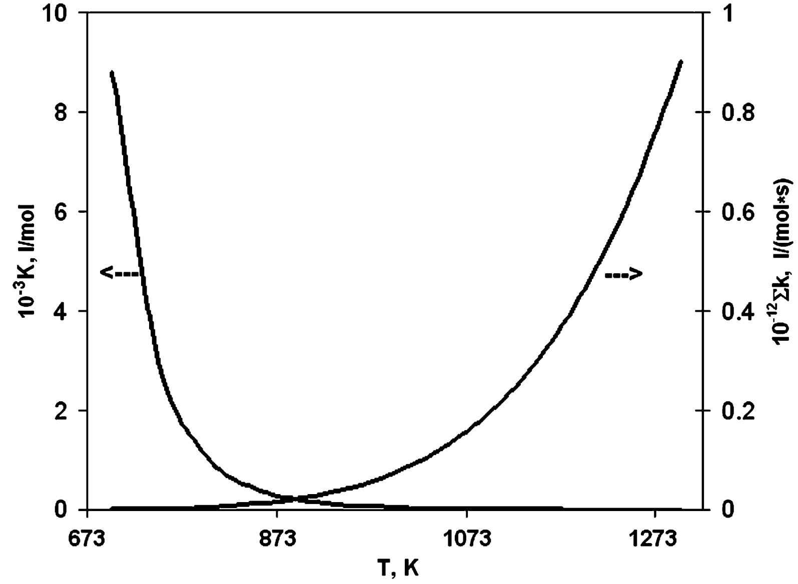


FIG. 5. The origin of the "OCM window": effect of temperature upon equilibrium constant of CH_3O_2 formation (*K*) and CH_3 oxidation rate constant (Σk).

At the initial stage of studying the mechanism of OCM, the analysis of the reciprocal influence of heterogeneous and homogeneous factors was confined to explanations of some important, but selected, peculiarities of the process using a limited number of CH_3 reactions in the gas phase. In particular, Lunsford and co-workers (Ito and Lunsford, 1985; Lin *et al.*, 1986) first pointed out that the increase of C_2-selectivity at rising temperatures can be explained by the competition of recombination with other reactions of CH_3 radicals: interaction with active surface sites and with oxygen in the gas phase. Soon after that, a "short" kinetic scheme consisting of five elementary reactions was suggested (Sinev *et al.*, 1987) that reflected some substantial channels of CH_3 transformation

$$CH_3 + O_2 \rightleftharpoons CH_3O_2 \tag{5}$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \tag{8}$$

$$CH_3O_2 + CH_3O_2 \rightarrow 2\,CH_3O + O_2 \tag{9}$$

$$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + CH_2O + O_2 \tag{10}$$

$$CH_3 + CH_3O_2 \rightarrow 2\,CH_3O \tag{11}$$

If one assumes that

- reaction (5) is in equilibrium,
- only reaction (8) leads to the formation of OCM products,
- reactions (9)–(11) lead to O-containing products and to the removal of methyl radicals from the main OCM path,

the following expression for ethane selectivity at low conversions was derived:

$$S_{\mathrm{Lim}} = \left\{1 + K_5 C_{O_2}\left[\frac{K_5 C_{O_2}(k_9 + k_{10})}{k_8}\right] + \frac{k_{11}}{k_8}\right\}^{-1} \tag{3.13}$$

The S_{LIM} value was named "limiting" as in real system in addition to reactions (5), (8)–(11) many processes (homogeneous and heterogeneous, parallel and sequential) leading to the formation of products other than C_2-hydrocarbons can proceed. Figure 6 shows "S_{LIM} vs. temperature" curves simulated assuming temperature independence of rate constants for reactions (8)–(11). Experimental data obtained by different authors prove that at low conversions it is impossible to obtain an OCM selectivity higher than that predicted by Eq. (3.13). At the early stage of investigations in this area, such a kinetic argument was strong evidence for the exclusive formation of ethane via CH_3 recombination in the gas phase. Later on, clear experimental evidence for this conclusion has been obtained using TAP (Temporal Analysis of Products)

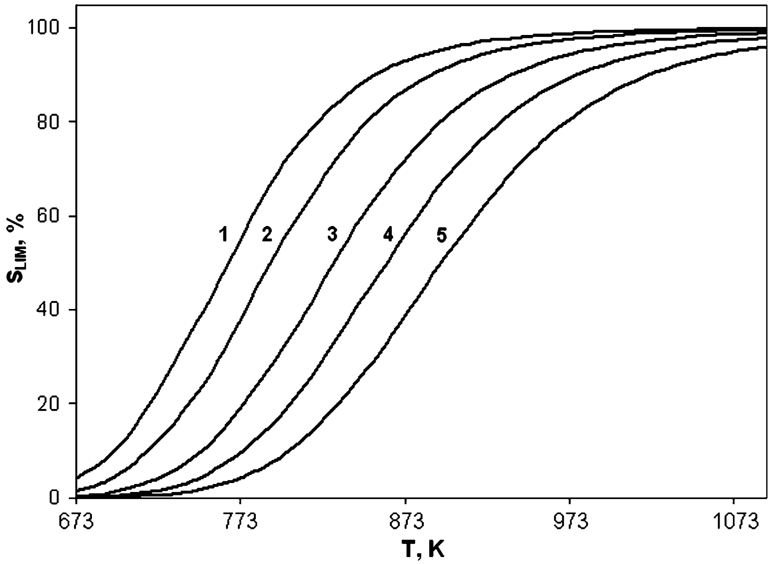


FIG. 6. Limiting selectivity (S_{LIM}) as a function of temperature at different oxygen partial pressures: (1) 0.01 bar; (2) 0.02 bar; (3) 0.05 bar; (4) 0.1 bar; (5) 0.2 bar.

(Buyevskaya *et al.*, 1994; Mallens *et al.*, 1994) and SSITKA (Steady-State Isotopic Transient Kinetic Analysis) (Nibbelke *et al.*, 1995) techniques. It was demonstrated that ethane—the primary OCM product—is leaving the reactor with the same characteristic time as an inert tracer. This surely indicates that no intermediates noticeably residing on the surface participate in its formation.

Further development of kinetic models for the OCM process followed the path of addition of a limited number of heterogeneous steps (first of all—initiation or generation of primary methyl radicals) to homogeneous schemes of methane oxidation (Aparicio *et al.*, 1991; Hatano *et al.*, 1990; McCarty *et al.*, 1990; Shi *et al.*, 1992; Vedeneev *et al.*, 1995; Zanthoff and Baerns, 1990). There was certain logic in such an approach: since the most efficient OCM catalysts are almost exclusively oxides with no transition metal ions (some Mn-containing oxide systems are the only exception), any reactions in adsorbed layers at such temperatures can be neglected. In the framework of such models some substantial features of the process could be described. For instance, they predicted the limit in the C_2-hydrocarbon yield close to that reliably observed experimentally over the most efficient catalysts (20–25%).

Such relatively simple kinetic models also allowed one to analyze simultaneously the development of radical processes and mass-transfer on different levels (inside catalyst pores, in inter-particle space, in reactor bulk—see for instance Bristolfi *et al.*, 1992; Couwenberg, 1994; Hoebink *et al.*, 1994; Reyes *et al.*, 1993). This can be considered as another important achievement.

However, the more careful analysis indicates that all the schemes discussed above suffer from one intrinsic contradiction. Indeed, if the main process of activation of the initial hydrocarbon (e.g., methane) is a homolytic C–H bond cleavage on an oxidative surface center

$$[O]_S + CH_4 \rightarrow [OH]_S + CH_3 \tag{12}$$

it is logical to assume that any other species from the gas phase must undergo reactions of the same type (H-atom transfer). Moreover, for most of them corresponding rate constants should be higher than that for methane (due to weaker H-atom bonding).

The same can be said about re-oxidation of reduced surface sites (e.g., oxygen vacancies $[..]_S$): if the addition of an oxygen molecule to vacancies

$$2[\ ]_S + O_2 \rightarrow 2[O]_S \tag{13}$$

is considered as the main re-oxidation path, any other O-containing species, such as radicals (peroxy, alkoxy, hydroxy) and even more oxygen atoms, should actively interact with the same vacancies, for instance via reactions

$$[\ ]_S + CH_3O_2 \rightarrow [O]_S + CH_3O \tag{14}$$

$$[\ ]_S + CH_3O \rightarrow [OCH_3]_S \tag{15}$$

Moreover, since most oxides known as efficient OCM and ODH catalysts are characterized by high values of the oxygen binding energy, dehydroxylation, which is usually considered as an evident step in catalytic cycle, is strongly reversible. This means that in the presence of high concentrations of water in the reaction mixture one should anticipate high degrees of surface coverage by OH-groups. Consequently, it is logical also to include into the consideration their interactions with gaseous species having high H-atom affinity—practically with all atoms and radicals present in the gas phase during hydrocarbon oxidation, as well as with molecular oxygen

$$[OH]_S + X \rightarrow [O]_S + XH \tag{16}$$

It is also important to notice that reactions similar to (12)–(16) must be taken into account from another point of view. Even in the presence of low-surface area catalysts, the total number of species in the gas phase inside the catalyst bed can be less than the number of surface sites. For instance, at 1 bar and 1,000 K the total number of species in 1 cm^3 of gas is 8×10^{18}. It is less than the total number of sites on an MgO surface at 1 m^2/g specific surface area and 1 g/cm^3 bulk density ($\sim 2 \times 10^{19}$ sites/cm^3). This means that even statistically gas species have a higher probability to collide with surface sites than with any other gas particle.

Such extension of a kinetic scheme can very seriously influence the results of simulations qualitatively changing our notions about pathways of processes under consideration. Indeed, rapid interaction of the most active gas species with surface sites and an increasing number of transformation channels would inevitably cause corresponding changes in the state of the working catalyst surface, as well as in the gas composition predicted by the model. As a result, the interpretation of experimental data of the overall rate and product distributions will change correspondingly. However, if this approach is valid, the reliability of the description and the predictive power of the model should increase significantly.

There is a serious obstacle on a path leading to building such advanced models, namely the absence of a generally accepted concept of how free radicals react with surfaces of different nature. Does this interaction always proceed as a direct collision or in some cases it is proceeded by more or less stable adsorbed precursor? What properties of the solid surface—local or collective—are responsible for directions and rates of such reactions to a greater extent? Which approaches are more fruitful for evaluation of kinetic parameters in this case? What experimental information could be relevant and helpful for building more adequate models and for a more precise evaluation of kinetic parameters? What type of experimental data should be employed to examine the efficiency of such models?

Before we expound upon possible alternative to answer the above set of questions, it should be noted once again that no model of complex phenomena can be identical to the object under study. Proceeding to the modeling we should say to ourselves: "Let us imagine that some totality of properties of the system can be described in such-and-such terms in such-and-such way (chemically, physically, mathematically). Let us look how the model based on these principles behaves in the range of parameters of our interest. Let us check if this behavior has any common features with the behavior of the real system under study. If so, there is a chance that we have succeeded in reflecting some substantial properties of the system in the model. Then let us check if there is any difference in the behavior of the model and the real system—this would suggest the direction of the further development of the concept and help to estimate whether or not any further improvement can be achieved at the current level of knowledge".

Such target setting allowed one of us to suggest the following approach to the analysis of heterogeneous–homogeneous OCM over oxide catalysts (Sinev, 1992, 1994, 1995; Sinev *et al.*, 1995), which later has been extended over some other processes of lower alkane oxidation (Sinev *et al.*, 1997a, b; Sinev, 2003, 2006).

1. Substantial features of processes under consideration can be described in the framework of a multi-step scheme, analogous to those used in homogeneous gas-phase kinetics.

2. All heterogeneous reactions of gas species are considered as their stoichiometric elementary reactions with surface sites of distinct chemical nature.
3. Active surface sites participating in the main catalytic route are strongly-bonded oxygen species (surface lattice oxygen). They can exist in two main forms—oxidized and reduced (in the form of surface OH-groups) further denoted as $[O]_S$ and $[OH]_S$, respectively. Subsequent elimination of surface OH-groups (dehydroxylation) can lead to the formation of surface oxygen vacancies.
4. Reactions of gas species with surface sites in oxidized and reduced forms, as well as with oxygen vacancies, proceed in the same way as their bi-molecular homogeneous reactions, i.e., as direct collisions without any preliminary equilibrium adsorption. The same groups of reactions as in the gas phase are considered:
   - H-atom transfer;
   - O-atom transfer;
   - Capture of particle by a surface site (analogous to recombination in the gas).
5. All paired interactions leading to any reaction of above type should be considered, if possible.
6. Since a direct measurement of rate constants for the heterogeneous reactions included into the scheme is practically impossible, all of them must be evaluated basing on uniform principles following the same procedure.
7. No adjustment of kinetic parameters for "improvement" or "fitting" to any experimental data is allowed.
8. The main regularities of heterogeneous reactions are analogous to those for elementary gas processes of the same type.

Let us consider the last statement in more detail. Keeping in mind serious doubts stated in Section III.B, we nevertheless assume that pre-exponential factors for rate constants of collision-type reactions between gas species and surface sites can be evaluated as a gas-surface collision frequency (ν). The dimension (or cross-section) of the surface sites (σ) and their concentration per unit surface area (ϑ), as well as a steric factor (ξ) should also be taken into account. The latter value shows the probability of reciprocal orientation of two reactants optimal for the reaction to proceed during the collision. As a result, the pre-exponential factor can be calculated as follows:

$$Z = \sigma\vartheta\xi\left[\frac{RT}{2\pi\mu_g}\right]^{1/2} \tag{3.14}$$

where μ_g is the molecular weight of gas particle.

Data on ionic radii can be utilized for the evaluation of σ. For instance, for lattice oxygen ions $\sigma \approx 6 \times 10^{-20}\,m^2$ can be accepted. Concentrations of surface sites ϑ can be obtained, for instance, from gas titration experiments (Sinev *et al.*, 1990), if bulk diffusion of oxygen does not play a significant role. As to the steric factors ξ, their values can be taken the same as for analogous homogeneous reactions of the same particle with spatially non-constrained partners (e.g., O- or H-atoms).

Thus, what we still need for description of heterogeneous rate constants is a method for evaluation of activation energies. One important observation helped to solve this problem. While studying kinetics and thermochemistry of redox processes over typical OCM catalysts, it was found (Bychkov *et al.*, 1989; Sinev *et al.*, 1990) that the activation energy of methane interaction with $[O]_S$ sites can be sufficiently well described in terms of the well-known Polanyi–Semenov correlation (see Fig. 7)

$$E_a = a + b|\Delta H| \tag{3.15}$$

where ΔH is enthalpy change in the process, a and b are constants.

Simultaneously the same conclusion was derived from methane interactions with active centers on activated silica surface (Bobyshev and Radzig, 1988, 1990).

The analysis of existing data for numerous gas processes shows that the values of a and b vary for reactions of different types. For H-transfer reactions we can set $a = 0$, if the transfer proceeds between two electronegative atoms (e.g., O and F, or O and O), and $a \approx 30$ kJ/mole in all other cases. As to the b value, it depends on the sign of ΔH: in the case of endothermic reactions it can be taken with acceptable precision as 1; for exothermic H-transfer processes

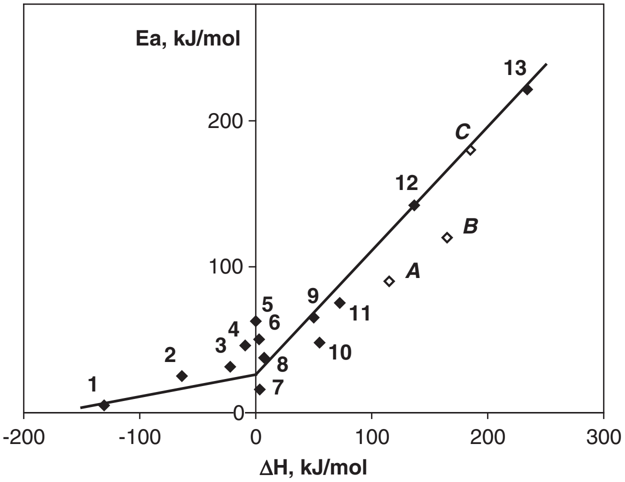


FIG. 7. Polanyi–Semenov-type "E_a vs. ΔH" correlation for $CH_4 + X \rightarrow CH_3 + XH$ reactions. X = F (1), OH (2), C_6H_5 (3), CF_3 (4), CH_3 (5), H (6), Cl (7), O (8), SH (9), CH_3O (10), Br (11), I (12), O_2 (13), Li/MgO (A), K/Al_2O_3 (B), Pb/Al_2O_3 (C).

$b \approx 0.25$–0.3. In the case of O-transfer reactions, $a \approx 0$ and $b \approx 1$. For capture processes, $E_a = 0$ was accepted.

Thus, thermochemistry of catalyst surface sites is a key factor determining their reactivity and, consequently, kinetic parameters of elementary heterogeneous reactions. For all of them the values of ΔH can be evaluated based on two thermochemical values—H-atom affinity of surface active sites (or O–H bond dissociation energy in surface OH-groups, $E_{[O-H]}$) and oxygen binding energy, $E_{[O]s}$. These values were measured experimentally for three different OCM catalysts—Li/MgO, Pb/Al_2O_3, and K/Al_2O_3 (Bychkov *et al.*, 1989; Sinev *et al.*, 1990); they are presented in Table II.

The above thermochemical values were used to fill the "heterogeneous module" of the kinetic scheme for the OCM reaction over a model Li/MgO catalyst with corresponding kinetic parameters (see Table III). In combination with a scheme of homogeneous methane oxidation, this set of reactions forms the desired micro-kinetic description. It allowed us to re-consider specific features of the OCM process and to obtain some unexpected results.

Let us first discuss the simulated data obtained with increasing concentration of catalytic active sites $[O]_S$ in a reacting methane–oxygen mixture. The results presented in Fig. 8 show corresponding changes of the development of the process in time. Whereas the kinetic curve for the "purely homogeneous" process is typical for radical chain scenario with a pronounced induction period and almost exponential growth of the reaction rate, at gradually increasing concentration of active sites the initial reaction rate linearly increases. Simultaneously the acceleration of the process caused by development of chains becomes less and less significant. Finally, at $[O]_S$ concentrations comparable with those present in real catalytic systems, the process becomes practically "linear", i.e., it starts with a maximum rate which gradually decreases along with the current concentrations of initial reactants. This indicates that catalytic sites play a combined role: they actively generate primary radicals, but at the same time they terminate development of chains. As a result, the catalyst totally changes the character of the process: remaining free radical, it becomes non-chain due to a very rapid quadratic termination via recombination of heterogeneously-generated CH_3 radicals and to a high probability of secondary reactions of any radical existing in the gas mixture.

This substantially extended model allows one to simulate more subtle effects, which are, however, extremely important for a better understanding of both

TABLE II
MEASURED THERMOCHEMICAL CHARACTERISTICS (PARAMETERS) OF THREE OCM CATALYSTS

Parameter	Li/MgO	Pb/Al_2O_3	K/Al_2O_3
$E_{[O-H]}$, kJ/mole	320	250	270
$E_{[O]s}$, kJ/mole	535	407	450

TABLE III
Accounted Heterogeneous Reactions and their Estimated Kinetic Parameters (Li/MgO)

No.	Reaction	K[a]	N	E_a (kJ/mole)
1	$LO + CH_4 = LOH + CH_3$	1.225×10^8	0.50	90
2	$LOH + O_2 = LO + HO_2$	8.7×10^7	0.50	115
3	$LOH + LOH = LO + L + H_2O$	5.6×10^{13}	−0.50	250
4	$LO + L + H_2O = LOH + LOH$	1.16×10^5	0.50	0
5	$L + L + O_2 = LO + LO$	8.7×10^4	0.50	0
6	$LOH + H = LO + H_2$	4.9×10^8	0.50	15
7	$LO + H = LOH$	4.9×10^8	0.50	0
8	$LOH + HO_2 = LO + H_2O_2$	8.4×10^5	0.50	0
9	$L + HO_2 = LO + OH$	8.4×10^5	0.50	10
10	$LOH + OH = LO + H_2O$	1.20×10^8	0.50	0
11	$LO + H_2O_2 = LOH + HO_2$	8.4×10^7	0.50	44.5
12	$L + OH = LOH$	1.20×10^8	0.50	0
13	$LO + HO_2 = LOH + O_2$	8.4×10^6	0.50	0
14	$L + O = LO$	1.20×10^8	0.50	0
15	$LOH + O = LO + OH$	1.20×10^8	0.50	0
16	$LO + CH_3 = LOCH_3$	1.26×10^6	0.50	0
17	$L + OCH_3 = LOCH_3$	1.0×10^7	0.50	0
18	$LOCH_3 + O_2 = LOCH_2 + HO_2$	6.0×10^7	0.50	188
19	$LOCH_3 + HO_2 = LOCH_2 + H_2O_2$	4.0×10^5	0.50	52.5
20	$LOCH_3 + OH = LOCH_2 + H_2O$	1.8×10^8	0.50	19
21	$LOCH_3 + CH_3 = LOCH_2 + CH_4$	1.5×10^5	0.50	50
22	$LOCH_3 + CH_3O = LOCH_2 + CH_3OH$	1.20×10^6	0.50	16.5
23	$LOCH_3 + CH_3O_2 = LOCH_2 + CH_3OOH$	7.0×10^4	0.50	56.5
24	$LOCH_3 + CH_2 = LOCH_2 + CH_3$	1.5×10^7	0.50	48
25	$LOCH_3 + C_2H_5 = LOCH_2 + C_2H_6$	1.5×10^7	0.50	56.5
26	$LOCH_3 + C_2H_3 = LOCH_2 + C_2H_4$	1.5×10^7	0.50	48
27	$LOCH_3 + C_2H = LOCH_2 + C_2H_2$	2.5×10^7	0.50	0
28	$LOCH_3 + O = LOCH_2 + OH$	8.0×10^7	0.50	21
29	$LOCH_3 + H = LOCH_2 + H_2$	1.00×10^8	0.50	27
30	$LOCH_3 + LO = LOCH_2 + LOH$	1.5×10^{14}	−0.50	42
31	$LOCH_2 + O_2 = LOCHO + OH$	1.4×10^6	0.50	21
32	$LOCHO + O_2 = LO + CO_2 + OH$	1.0×10^6	0.50	0
33	$LOH + CH_3 = LO + CH_4$	1.26×10^6	0.50	15
34	$LOH + CH_3O_2 = LO + CH_3OOH$	7.0×10^5	0.50	0
35	$L + CH_3O_2 = LO + CH_3O$	7.0×10^7	0.50	10
36	$LOH + CH_3O = LO + CH_3OH$	3.0×10^7	0.50	0
37	$L + CH_3O = LO + CH_3$	1.0×10^7	0.50	10
38	$L + CH_3O = LOCH_3$	1.0×10^7	0.50	0
39	$LO + CH_3O = LOH + CH_2O$	6.0×10^7	0.50	0
40	$LOH + CH_2OH = LO + CH_3OH$	6.0×10^7	0.50	21
41	$LO + CHO = LOH + CO$	6.0×10^7	0.50	0
42	$LO + CH_2O = LOH + CHO$	6.0×10^7	0.50	12.5
43	$LO + CH_3OH = LOH + CH_2OH$	6.0×10^7	0.50	41.5
44	$LO + CH_3OH = LOH + CH_3O$	3.0×10^7	0.50	83.5
45	$L + CH_2O = LOCH_2$	1.0×10^7	0.50	0
46	$LOCH_2 + CH_3 = LOH + C_2H_4$	1.26×10^6	0.50	0

Table III (*continued*)

No.	Reaction	K^a	N	E_a (kJ/mole)
47	$LO + C_2H_5 = LOH + C_2H_4$	6.0×10^7	0.50	0
48	$LO + C_2H_6 = LOH + C_2H_5$	9.0×10^7	0.50	75.5
49	$LO + C_2H_4 = LOH + C_2H_3$	9.5×10^7	0.50	103.5
50	$LO + H_2 = LOH + H$	3.5×10^8	0.50	95

[a] *k*—in mole/l, s.

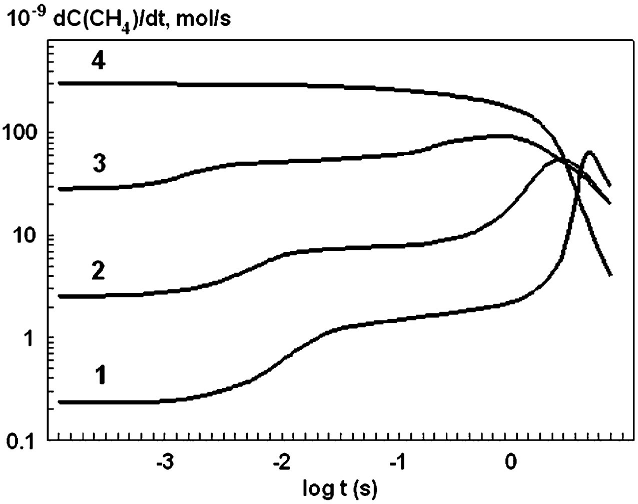


FIG. 8. Methane conversion rate vs. time curves at different concentrations of catalytic active sites; quasi-homogeneous simulation; 1,000 K, 1 bar, CH_4:O_2 = 10:1. C(LX), mol/l = 0 (1); 5×10^{14} (2); 5×10^{15} (3); 5×10^{16} (4).

surface and free radical chemistries. Let us consider as an example in more detail the regularities of catalyst re-oxidation. The following experimental results were obtained (Sinev *et al.*, 1990) during Li/MgO catalyst sequential reduction by hydrogen or methane and re-oxidation with molecular oxygen and N_2O:

- Reduction by methane pulses results in the formation of ethane, but not water;
- Reduction with hydrogen leads to its consumption without water evolution;
- If N_2O pulses are supplied onto the sample pre-reduced in methane or H_2, only some insignificant amounts of nitrogen and oxygen are formed; only purging in dry helium for 1 h at 700°C leads to some additional N_2 evolution and oxygen consumption in the few first few pulses of nitrous oxide indicating the appearance of some oxygen vacancies;

- Re-oxidation of the catalyst by O_2 pulses leads to the immediate formation of water, i.e., the characteristic time of this process is less than the time during which the oxygen pulse resides in the layer of catalyst (<1 s);
- Apparent activation energies of reduction and re-oxidation evaluated from initial rates of consumption of methane over pre-oxidized and oxygen over pre-reduced catalyst are equal to 63 and 105 kJ/mole, respectively, whereas under steady-state conditions the apparent activation energy of the process at low conversions exceeds 210 kJ/mole.

These facts are indicative of a complex mechanism of the dehydroxylation process, which is not surprising if we keep in mind a high oxygen binding energy for this catalyst (see Table II). Also, they are suggestive of the possibility of re-oxidation without intermediate formation of oxygen vacancies.

Simulations based on the kinetic scheme described above (Sinev and Bychkov, 1993) indeed show the possibility of an alternative re-oxidation path via the sequence of steps:

$$[\mathrm{OH}]_\mathrm{S} + \mathrm{O_2} \rightarrow [\mathrm{O}]_\mathrm{S} + \mathrm{HO_2} \tag{17}$$

$$[\mathrm{OH}]_\mathrm{S} + \mathrm{HO_2} \rightarrow [\mathrm{O}]_\mathrm{S} + \mathrm{H_2O_2} \tag{18}$$

$$\mathrm{H_2O_2} \rightarrow 2\mathrm{OH} \tag{19}$$

$$[\mathrm{OH}]_\mathrm{S} + \mathrm{OH} \rightarrow [\mathrm{O}]_\mathrm{S} + \mathrm{H_2O} \tag{20}$$

Among them, steps (18) and (20) are exothermic and their activation energies should be insignificant. Step (17) must have a relatively low E_a close to the value obtained from the re-oxidation experiments (with oxygen as on oxidant). As to step (19), its activation energy is high (about 190 kJ/mole), which determines the apparent value obtained from experimental data. Thus, the following conclusions were formulated:

- Re-oxidation of the oxide catalyst can proceed via a heterogeneous–homogeneous free radical path;
- The rate of steady-state catalytic reaction is determined not by activation of methane and formation of ethane, but by the most activated step in the sequence that leads to the formation of the second main product, namely water; the latter is required for closing the catalytic cycle.

It is also important to notice that the nature of the prevailing re-oxidation mechanism—via dehydroxylation or via the reaction set (17)–(20)—may differ from one catalyst to another depending on the values of the thermochemical parameters of surface oxygen species (Sinev and Bychkov, 1993). In this case an elegant experimental way to validate the model predictions can be suggested. If the catalyst was pre-treated by oxygen of normal isotopic composition, and methane (or any other hydrogen-containing reactant) is oxidized in the presence of $^{18}O_2$, the isotopic composition of forming water (correctly taking into account independently measured rates of oxygen hetero-exchange) should unambiguously indicate the proportion of two routes.

It is necessary to acknowledge that some existing experimental data indicates that oxygen can be removed from Li/MgO directly during the reduction in hydrogen at temperatures as low as 873 K (see, for instance, Leveles, 2002). Such discrepancies with the data described above might be due to some difference in catalyst preparation/pretreatment procedures, which leads to the formation of active sites with somewhat different thermochemical characteristics. What is important is to attribute the evaluated kinetic parameters to the catalysts of particular thermochemistry.

In the framework of this description an attempt to model an effect of spatial non-uniformity of real catalytic systems was made (Bychkov *et al.*, 1997). It was assumed that reaction proceeds in a heterogeneous system represented by two active infinite plane surfaces and in the gas gap between them. Surface chemistry was treated as for the Li/MgO catalyst (see Table III). Because of substantial complexity of the kinetic scheme consisting of several hundred elementary steps, the mass-transfer was described in this case as follows. The whole gas gap was divided into several (up to 10) layers of the same thickness, and each of them was treated as a well-stirred reactor. The rate of particle exchange between two layers was described in terms of the first-order chemical reaction with a rate constant:

$$k_{Di} = \frac{D_i}{(d)^2} \tag{3.16}$$

where k_{Di} is the "diffusional" rate constant for *i*th particle, D_i the coefficient of gas-phase molecular diffusion for *i*th particle (which for simplicity was estimated as diffusion coefficient in air), and d the characteristic dimension (thickness) of one layer.

Two edge layers included surface species chemically and kinetically described as discussed above and considered together with all other species within one quasi-homogeneous mixture. In other words, in edge layers the catalytic active sites were equally accessible to all gas species. Surface sites were not allowed to react with each other and to migrate from the edge layers.

Evidently, such an approach represents a significant simplification. In particular, the use of molecular diffusion coefficients at small distances from reaction surfaces contradicts its physical sense. Nevertheless, even this estimation reveals some essential features of a spatially distributed reaction system. First, as shown in Fig. 9, at low gas gap thickness the total rate of conversion is entirely determined by the generation of primary CH_3 radicals in catalytic cycles on the surface. Second, even when the thickness of gas gaps reaches macroscopic values, heterogeneous reactions have a strong effect on the process that

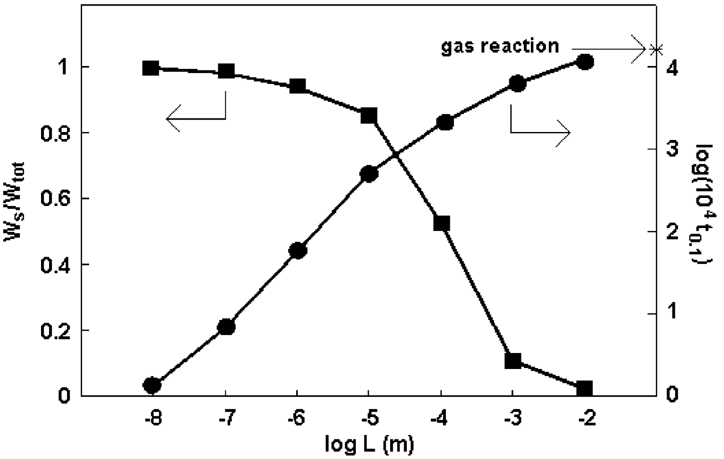


FIG. 9. Methane oxidation in spatially distributed system: effect of gas gap thickness on $t_{0.1}$ (time of reaching 10%-conversion) and relative efficiency of heterogeneous and homogeneous methane activation (W_{hom}/W_{tot}) (Sinev *et al.*, 1997a, b).

proceeds predominantly in the gas phase. This conclusion is also important for evaluation of the significance of surface (“wall”) reactions in gas-phase oxidation usually considered as “homogeneous”.

At last, when the gas gap thickness is within some “critical” area ($\sim$0,1 ÷ 1 mm), a sharp change in the probability of chain propagation in the gas phase is predicted. It is worth noticing that the variation of catalyst particle size within the same range leads to sharp changes in the contribution of homogenous reactions to total conversion also during the ODH of C_3–C_4 alkanes in the presence of V-containing oxide catalysts (Vislovskiy *et al.*, 2000). This is very likely due to a sharp increase of chain length in homogenous reactions in gaps between catalyst species.

Of course, such accounting for mass-transfer is an oversimplification of real processes taking place during alkane oxidation over real catalysts. Additional studies are required to estimate the possibility to integrate a detailed micro-chemical (and micro-kinetic) description with methods capable of advanced accounting of mass-transfer on the inter- and intra-particle level and in the bulk of reactor (see, for instance, Couwenberg, 1994; Hoebink *et al.*, 1994).

To conclude this section, we should mention again that the phenomena taking place during alkane oxidation over oxide catalysts are much more complex than any description which can be expressed in the form of micro-kinetic schemes of the type given in Table III. For instance, such schemes cannot reflect deep changes in the catalyst, which can occur under the influence of gas mixtures containing water and CO_2 as reaction products. Such changes can lead to a very substantial modification of catalyst chemistry ranging from poisoning (reversible and irreversible) of active sites with carbon oxides

$$[O]_S + CO_2 \rightleftharpoons [OCO_2]_S \tag{21}$$

$$[O]_S + CO \rightarrow [OCO]_S \tag{22}$$

to total changes in catalyst chemical and phase compositions, morphology, surface area, and density of active sites. Of course, reactions similar to (21) can be included into the overall scheme in order to describe the modification of catalyst activity by carbon oxides, especially if the data on adsorbed CO_X lifetimes under different conditions are accessible (Leveles, 2002). Their influence can also be accounted for in analytical form, as it is done by Xu *et al.* (1992). However, at the moment we do not see any rational way of accounting for and including into models of the discussed type the whole totality of factors, which can be called ''effect of reaction mixture upon catalyst chemistry and morphology''. Consequently, any quantitative coincidence of simulated and experimental data should not be expected. And vice versa, this is an additional reason to resist the adjustment of kinetic parameters or their ''optimization'' against experimental data.

F. Heterogeneous–Homogeneous Catalytic Reactions on Metal Catalysts

Another very important group of light alkane oxidation processes is represented by reactions catalyzed by metals, and by Pt-group metals in particular. Pioneering publications by Schmidt and co-workers (Hickman and Schmidt, 1992, 1993; Huff and Schmidt, 1993) had opened the area of catalysis at short (millisecond) contact times. After that, several groups have contributed to methane (Bui *et al.*, 1997; Deutschmann and Schmidt, 1998; Deutschmann *et al.*, 1994; Heitnes *et al.*, 1994; Mallens *et al.*, 1995) and higher alkane (Beretta and Forzatti, 2001; Beretta *et al.*, 1999; Reyes *et al.*, 2001; Zerkle *et al.*, 2000) oxidation over noble metal catalysts (monoliths, foils, gauzes, in annular reactors). Both experimental attempts and modeling have been employed in order to elucidate the main features of reaction mechanisms and also to find the conditions for optimal yields of particular products (oxygenates, olefins, synthesis gas).

In such systems modeling meets very serious difficulties, since the problem of formulation of a kinetic description of reactions in the adsorbed layer on the active metal is added and interferes with other problems stated above. One of the first attempts to suggest such a description was done by Hickman and Schmidt (1992, 1993). Analyzing a nearly 10-year period of development in the area, Schmidt (2001) concluded that ''… these apparently simple processes are in fact far more complicated than the usual packed bed catalytic reactor assumptions used for typical modeling. First, the temperatures are sufficiently high that some homogeneous reaction may be expected to occur, even at very short reaction times. Second, the gradients in all properties are so large that all conventional assumptions may be inaccurate".

Indeed, a great discrepancy between different authors exists concerning the role and contribution of surface and gas-phase reactions in these very complex processes. Evaluations range from the recognition that the metal surface plays a dominant (or even sole) role in the formation of products (de Smet *et al.*, 2000; Deutschmann *et al.*, 2001; Mhadeshwar and Vlachos, 2005) to the conclusion about almost complete formation of target products in the gas phase ignited by the oxidation reaction on the metal surface (Beretta and Forzatti, 2001; Beretta *et al.*, 1999; Reyes *et al.*, 2001). Even for practically the same reactions there are very different opinions. Liebmann and Schmidt (1999) claim on the purely heterogeneous reaction systems for C_1–C_3 partial oxidation, heterogeneously assisted homogeneous reactions of C_{5+} reaction systems, and a mixed mechanism for C_4. However, other authors (e.g., Beretta and Forzatti, 2001; Beretta *et al.*, 1999; Reyes *et al.*, 2001; Silberova *et al.*, 2003; Tulenin *et al.*, 2001) provide arguments for the formation of olefins from light alkanes via catalyst-assisted gas-phase process.

By contrast, there is no doubt or any contradictions in literature concerning the importance of macro-kinetic factors (heat- and mass-transfer processes) in the reactions discussed in this section. It is generally realized that these processes proceed in spatially distributed systems and generate sharp gradients of parameters (temperature, pressure, density, concentrations, etc). It could be noted here a distinct similarity of alkane oxidation over Pt-group metals at short contact times and well studied and practically implemented ammonia oxidation and cyanic acid synthesis reactions, in which transfer processes play a dominant role (see Satterfield, 1970).

Let us, however, focus on the chemical and micro-kinetic sense of modeling. As we mentioned several times, the success in kinetic simulations that is sparking further progress in gas processing is associated with the development of models meeting certain requirements. Among the latter, the requirement of "fullness" is crucial.

Unfortunately, our knowledge about reactions in the adsorbed layer is far from complete. In such conditions, it is very difficult to meet the requirement of "fullness" of the reaction scheme. As a result, we fall into an exclusive circle. On the one hand, the necessary information about certain reaction intermediates and elementary steps, which has to be accounted for in the model, is missing. But, on the other hand, if some intermediates are not accounted for, reaction pathways related to them become omitted in simulations. For instance, if the escape of active species (atoms, radicals, excited molecules) from the metal surface to the gas phase and their capture by surface active sites are not accounted for, no coupling between gas-phase and surface chemistries can be derived from the modeling.

Another important aspect is a detailed accounting of reverse elementary reactions, i.e., the thermodynamic consistency of the reaction scheme. If this requirement is not executed, even the possibility of achieving correct final state in equilibrium reactions (or in limited quasi-equilibrium blocks inside a complex reaction network) is doubtful. We have to mention here that it is very difficult to say *a priori* which reverse reactions can be neglected in particular conditions. Unfortunately, in the case of reactions in adsorbed layers any reliable information about thermodynamic properties of surface intermediates, especially in mixed ad-layers, is scarce. Although recent developments in quantum chemistry and complimentary semi-empirical and phenomenological methods are encouraging (as applied to methane oxidation—see, for instance, Mhadeshwar and Vlachos, 2005, and literature cited therein), there is still a lack of information required for modeling of alkane oxidation kinetics over metal catalysts.

We would like also to mention some specific problems as far as the modeling of reactions on active metals is concerned.

1. Rate constants of heterogeneous reactions are usually represented in the "three-parameter" form discussed above. However, this form has a clear physical sense only for reactions in ideal gases at a strictly kept equilibrium Maxwell–Boltzman distribution. Despite several attempts to adopt transition-state theory to heterogeneous reactions, and to those proceeding in adsorbed layers in particular (e.g., Krylov *et al.*, 1972; Zhdanov *et al.*, 1988), its applicability in these cases is doubtful.
2. The most efficient metal catalysts consist of relatively small clusters with tens or hundreds of atoms exposed to the gas phase and accessible as adsorption sites. On the other hand, a detailed description of reaction in the adsorbed layer, even in the case of methane, can include a comparable number of *types* of surface intermediates: for instance, Mhadeshwar and Vlachos (2005) take into consideration 18 different surface species. In the latter case the authors modeled the reaction on a "macroscopic" surface, but anyway, certain caution is required when we apply "normal" kinetic equations to a reacting system where the conditions for statistical behavior are not assured.
3. Reactions on metals, including many oxidation processes, are known to proceed in a way very different from stochastic collision types, which can be described by mass action (or "acting surfaces"). The number of systems in which collective effects or topochemical type processes (via nucleation and growth of nuclei) are proved to determine the kinetic behavior is increasing. Despite the extensive literature on reactions in oscillatory regimes and spatially-structured reactions on surfaces (Gorodetskii *et al.*, 2005; Latkin *et al.*, 2003; Peskov *et al.*, 2003), such facts have not yet found an adequate reflection in the area under consideration.
4. In some practically important cases, e.g., partial oxidation of methane over Pd, Ni, and Co catalysts (Deng and Nevell, 1996; Hu and Ruckenstein, 1998; König *et al.*, 1994; Ozkan *et al.*, 1977; Tulenin *et al.*, 1996; Zhang *et al.*, 2003) complex kinetic behavior is caused by oxygen storage in the catalyst, which leads to the formation of bulk or sub-surface oxides. This process is

accompanied (or alternated) by the periodic formation of oxide layer(s) and carbonaceous deposits (see, for instance, Tulenin *et al.*, 1999, 2004; Zhang *et al.*, 2005). The latter form in thermodynamically non-equilibrium state and their thermochemistry and reactivity are changing with time (Bychkov *et al.*, 2002a, b, 2003). Although these factors make the process extremely complicated, they also must be accounted for inadequate kinetic models.

In spite of the above listed complications, there is distinct progress in the kinetic description of alkane (first of all—methane) partial oxidation over metal catalysts in some particular cases. One bright example of this kind is represented by a recent publication by Mhadeshwar and Vlachos (2005) summarizing their achievements in the modeling of methane transformations and related reactions of oxygenates (methanol and formaldehyde) over a Rh surface. Among them:

1. Compiling a kinetic scheme that meets the requirement of thermodynamic consistency;
2. Accounting of homogeneous reactions and analysis of heterogeneous–homogeneous coupling;
3. Utilization of kinetic parameters independently measured or calculated using UBI-QEP and DFT;
4. Accounting of adsorbate–adsorbate self- and cross-interactions for a more accurate evaluation of kinetic parameters in the adsorbed layer.

Even though the authors could not avoid some adjustment of selected kinetic parameters, what is explicable taking into account the extraordinary complexity of the system. As a result, they succeeded in reproducing in their simulations some important features of the real system and validated their micro-kinetic model against high-pressure spatially resolved experimental data for catalytic partial oxidation of methane.

To conclude this section, we state that the area is very actively developing. The main achievements by now are reached in experimental techniques, in developing computational codes and software, and in accounting for the role of heat- and mass-transfer. These results and developments are worth to be used in related areas, first of all in catalytic oxidation of alkanes over oxides. Corresponding information can be found (and in some cases even discussed) on personal web sites of scientists involved into such investigations (see for instance the site of Prof. Olaf Deutshchmann: http://www.detchem.com) and companies and research groups developing commercial or semi-free software for kinetic simulations (e.g., www.kintecus.org, CHEMKINusergroup@reactiondesign.com).

A brief survey demonstrates that kinetic models taking into account both heterogeneous and homogeneous elementary steps potentially can serve as powerful tools for analysis of experimental data, development of catalytic systems, and selection of optimal reaction conditions. Despite a lack of information about kinetic parameters of numerous elementary reactions, more detailed kinetic schemes, even filled with preliminary (estimated) kinetic parameters, can offer very important mechanistic information. At the same time, shorter (trimmed) schemes can give misleading simulation results due to the ambiguity of routes to certain products in a complex reaction network. In other words, ‘‘fullness’’ of the scheme should always dominate over the use of ‘‘correct’’ values of kinetic parameters if both requirements cannot be executed simultaneously.

IV. Modeling and Experimentation

A. Comparison with Experiment

Experiment is the beginning and the end, the starting-point and final objective of any modeling. Despite the fact that the model is fundamentally not identical to the object of modeling, only experiment suggests the initial guess and provides primary data concerning the structure of the reaction scheme and the values of the kinetic parameters. In their turn, model verification and validation can be done only by comparison with experimental data.

Vedeneev *et al.* (1988a, b, c, d) regarded the model as acceptable if it describes the main peculiarities of the process and possesses some predictive power. Such target setting assumes the gradual upgrading of the model aimed at improving its quantitative agreement with various and regularly replenished experimental data.

In many cases modeling gives more definite and clearly interpretable results than experiment. It can also provide an understanding of the reasons for the discrepancy between different experiments. In modeling we have a possibility to set well-determined conditions (temperature, pressure, reactant flows, heat- and mass-transfer, including very complex regimes) and to vary them broadly. Also, a mapping of complex values, such as reaction (overall and elementary) rates, concentrations of reactive intermediates, pressure, flows, and even temperature, which is hardly accessible in experiment, can be obtained by adequate modeling. Such information is crucially important for optimization of various processes and their selected parameters. On the other hand, the design of complex experiments becomes much better grounded if it is based on preliminary modeling.

In the case of the processes of heterogeneous–homogeneous type, their intrinsic micro-chemical mechanisms can be revealed almost exclusively by modeling (see Sections I.C, II.D, III.E, and III.F).

Despite such deep interdependence, in practice the relationships between modeling and experimentation are not so cloudless for several reasons. One the one hand, any experiment carries various errors, uncertainties and effects of numerous non-accountable factors, and kinetic simulations in their turn are always non-ideal because of an inevitable incompleteness of the model and inaccuracy of kinetic parameters. This is why any deviations between compared experimental and simulated data would not be surprising. On the other hand, very often "good fits" to experimental results are reported for models, which by no means seem to be adequate for particular applications.

One of the most intriguing and paradoxical example of this kind was already mentioned in Section II.A, namely simulation of the SID. This gross parameter, which is very important for combustion kinetics, is very often used to prove the validity of kinetic models because of the ease and lack of ambiguity of its experimental determination. Since combustion itself is a high-temperature process, the SID values are also often simulated in the framework of kinetic schemes developed for the high-temperature regime of oxidation. As a rule, it is not a big problem to reach agreement between calculated SID values with experimental data, which would evoke wonder and disappointment rather than satisfaction. Why, the ignition takes place at low or moderate temperatures, whereas high-temperature models as a rule do not account for the reactions crucially important for these temperature ranges, but indeed unessential at temperatures of combustion, where they were developed. The existence of such examples suggests a high probability of reciprocal annihilation of errors in the course of simulations in the framework of complex kinetic schemes. This may cause very serious failures and lead to false conclusions.

Thus, the investigator is urged to treat more carefully the qualitative adequacy of the model for the particular experimentation.

The problem of adequacy is very serious also from the side of experimentation. Here we revert to the question about the goal, in this case the goal of comparison of experimental and simulated data, which determines

- The optimal parameters and criteria for comparison of calculated and experimental data;
- The main requirements of the experiment, which could be compared with results of modeling.

We have to confess that very often such questions are not taken into account and by no means does every experiment meet the minimal requirements for comparison with simulated data. Vast experience gained in the area of heat- and mass-transfer in combustion (Frank-Kamenetskii, 1969) indicates that the most appropriate for comparison with model calculations are relative parameters and criteria, which are less influenced by the particular experimental "hardware" and the scale of process.

As applied to the oxidative processing of light alkanes, and the formation of certain valuable products in particular, the switch to relative values would mean, for instance, the use of product distributions and yields instead of absolute concentrations and degrees of conversion instead of reaction time. This can be illustrated by the example given in Fig. 2. In this case—in methane-rich conditions—the level of conversion is controlled by oxygen. The use of oxygen conversion as an "independent" parameter is much more fruitful and convenient if characteristic times of processes in different conditions can differ very significantly. But what is even more important, such relative characteristics are much less sensitive to the particular values of kinetic parameters and, consequently, are more suitable for the analysis of the structure of the kinetic scheme.

Similar ideas will be further developed in the next section, along with some other criteria and requirements. In our opinion, a strict adherence to them would improve the efficiency of the interaction between experimentation and modeling. To conclude this section, let us formulate in brief the main tasks addressed concerning the comparison of modeling with experimental data as far as the optimization of the model targeted toward the studies of the reaction mechanism and process optimization over a wide range of parameters are concerned. In our opinion, such comparison must reveal the factors that have been underestimated and overestimated in the kinetic scheme. As to the values of kinetic parameters, they definitely can be "optimized", but this optimization should be based on exact physical and chemical (experimental and theoretical) arguments, but not on formal mathematical procedures.

B. Requirements of Experiment

It is clear now that the comparison of measured and simulated data suggests strict requirements not only for kinetic models, but also for the experiment. A common shortcoming of many experimental studies consists of incompleteness of the data. On the one hand, incompleteness in the description of reaction conditions does not allow for an adequate comparison with simulation, since the effect of some very important factors can be lost or at least distorted. On the other hand, irregular measurements of some parameters in the course of reaction, or even the absence of some important data, nullify the value of such studies for the comparison with modeling.

Any experiment suffers to some extent from the influence of various uncontrolled factors, such as mass- and heat-transfer regimes in different parts of the reaction system, irregularity of temperature fields and flow profiles, dead spaces, poor mixing, and independent flow of reactants, "wall chemistry" and its variation with time, etc. Another problem is a correlation between signals received from different sensors and real values of measured physical parameters. There is a voluminous literature on this subject; here we just mention the pitfalls related to the measurements of surface and gas temperatures in the course of reaction involving very active radical species.

In many cases in the reactor (and even in connecting tubing) reactions proceed at the conditions different from those recorded in the experimental protocol. Despite numerous attempts to avoid such effects of uncontrolled factors, the problem of an adequate description of reaction conditions is far from the exhaustive solution. Moreover, trying to solve some local problems we can modify the system to an extent that it may lose its identity. For example, Mantashyan and co-workers suggested (see Mantashyan, 1998 and literature cited therein) a so-called ‘‘wall-less’’ reactor as an approach to exclude the effect of surface processes. In this case, the reaction in the gas is initiated by a laser pulse at a distance from the reactor walls, and during some time the process can develop via a true homogeneous regime. However, we in fact dealing with the process affected by strong local heating in the zone where the laser beam interacts with the reacting gas and by sharp gradients of all the main physical parameters. In other words, trying to avoid some ‘‘disturbing’’ factor (reactor walls in particular) we introduce another one (laser beam) and substantially change the sequence of processes taking place in the reacting system.

Undoubtedly, such ‘‘differentiating’’ methodologies can be successfully used to highlight and isolate selected parts or features of the complex system and provide extremely valuable kinetic information. However, along with them the experimentation of ‘‘integrating’’ type is very important for verification and validation of kinetic models. Accordingly, the arrangement of such experiments should meet well-defined requirements. First of all, we have to define the parameters to be used for the most unambiguous comparison of experimental and simulated data.

For instance, a considerable number of studies in the area of partial oxidation are devoted to the optimization of target product(s) yield or selectivity at total oxygen conversion in hydrocarbon-rich conditions. However, one can insist that the results of such experiments are the most indefinite, since ‘‘total conversion’’ reflects only the sensitivity of the analytical method used (oxygen detection threshold). It does not characterize the stage of reaction from which a given yield is obtained. But the latter is crucial for the comparison with results of modeling, since some reactions of target and side products can substantially modify their distributions in ‘‘anaerobic’’ conditions. The solution of the problem can be found in the way of sampling from different sections of the reactor (e.g., along the axis in a flow system). Since in many cases such sampling is difficult, wide variations of gas flow (residence time) could be an alternative way to collect the data for the comparison with simulated results.

The use of conversion instead of time as an independent variable can be very distinctive and informative for model verification. Also, as can be seen from Fig. 2, the ‘‘yield (or selectivity) vs. conversion’’ relationship can serve as a characteristic function describing the behavior of the system under various conditions.

The optimal product distribution in many cases is an ultimate goal of applied and even basic research. From the standpoint of the subject under discussion, product distributions are among the most important criteria for the comparison of modeling with experiment. However, it is worth noticing that many experimental details can strongly affect the values used for comparison. For instance, the whole spectrum of components of reaction mixtures formed during alkane oxidation includes permanent gases (O_2, N_2, CH_4, CO, H_2), carbon dioxide, alkanes and unsaturated hydrocarbons C_2–C_4, condensable oxygenates, and water. If they are analyzed using gas chromatography, a wide range of analysis sensitivity towards different compounds is the least egregious problem. It is more important that they practically cannot be analyzed in one probe. Often gaseous compounds are analyzed on-line, whereas condensable products are first collected in cooled traps. During the collection (which may last relatively long) the condition in the reactor or reaction rate may change for several reasons, even if the process is studied in a stationary state. Moreover, condensation is never complete, and additional chemical processes (condensation, oligomerization) can proceed to some extent even in the trap, despite the low temperature and addition of inhibitors. All these factors hamper the correct determination of the mixture composition and assigning it to certain experimental conditions.

In our opinion, more definite correspondence between experiment and modeling can be established based on relative concentrations of selected (kinetically relevant) products and different conversions. Such products should be formed in comparable amounts and, if possible, analyzed in one probe (gaseous or liquid). Kinetic relevance means that there should be definite notions concerning the relationships between certain components in the proposed kinetic scheme: they should form from the same intermediate, or one from another, or have different relations at different stages of reaction. For example, in the case of methane oxidation, this could be the ratios of methanol and formaldehyde concentrations in a trapped liquid phase or $(CO+CO_2)/(C_2H_6+C_2H_4)$ in the gas. As to the CO_2-to-CO ratio, its variation with conversion can be very indicative of the contribution of reactor walls in gas-phase oxidation: carbon dioxide can form in homogeneous steps only via CO interaction with O-containing radicals (peroxy, hydroxy, alkoxy) or at relatively high temperatures with molecular oxygen. However, it can form directly from organic intermediates via a sequence of surface reactions (alkoxides → carboxylates → formiates → carbonates). Accordingly, if the fraction of CO_2 in the sum of CO_X does not tend to zero at low conversions, this is evidence for its heterogeneous formation and a reason for the corresponding modification of the kinetic scheme.

The completeness of the reaction mixture analysis is a very painful problem. In some cases the researcher even cannot guess which products can form and, correspondingly, what is the most adequate analytical methodology. More often the qualitative composition of the reaction mixture (excluding the most unstable intermediates) is known for the most part, but the complete quantitative analysis cannot be performed for technical reasons. In the latter case the chosen analysis always reflects some pre-assumptions about the kinetic (or mechanistic) relevance of different products. Unfortunately, a wrong initial guess in this case cannot be compensated for at later stages of investigation because the required information is irretrievably lost.

A typical example of this kind is a measurement of some "side" products during alkane oxidation. For instance, traditionally in experimental studies, in which gas chromatography is used as the main analytical method, water and hydrogen concentrations are not measured for different reasons. Quantitative measurement of water in the reaction mixture is difficult due to its high adsorbability. As to hydrogen, it is often believed that it does not form in oxidative processes. Moreover, the sensitivity of the most frequently used detectors—TCD (thermal conductivity detectors)—with respect to H_2 is very low (when helium is used as a carrier gas). As a result, whereas carbon balance is considered as one of the main criteria of the quality of the experimental procedure and setup, hydrogen balance is usually omitted. However, the concentration of molecular hydrogen and/or the H_2/H_2O (H_2/CO, H_2/olefins) ratio can serve as one of the main criteria indicating the routes of reaction and the nature of intermediates involved in the formation of various C-containing products (see, for instance, Sinev *et al.*, 2003).

It can be asserted that a special experimental methodology should be developed for a proper verification and validation of modeling. Definite reaction conditions and complete analysis of the reaction mixture are the principal requirements for such experiments. Let us consider in more detail this requirement with reference to the reaction temperature. As it was mentioned in Section I.B, this is the most important parameter determining not only reaction rates and equilibrium states, but also the general type of oxidation process. Since oxidation is a substantially exothermic process, it proceeds to a considerable extent in a self-generated temperature regime, which can vary from isothermal to adiabatic, depending on the intensity of heat removal from the reaction zone. Correspondingly, very different temperature profiles (axial and radial) can exist in the reactor strongly affecting the reaction. In order to model the process correctly, one must have information about these profiles. Alternatively, they can be obtained as one of results of modeling, but in the latter case anyway the mapping of the temperature distribution is required in order to compare it with a calculated one. Such profiles can be obtained by placing multiple thermocouples into the reactor, or by measuring the temperature by one or a few thermocouples moving along the reactor in the axial and radial directions. However, one must take into account that the material of the thermocouple or of a cover can be active at the conditions of the oxidative process and affect (and modify) both the reaction itself and the results of temperature measurements.

Another possible solution of the problem is to perform the reaction at a very low initial oxygen concentration. Although in the case of alkane partial oxidation this is not favorable for obtaining high yields of target products (oxygenates, olefins, synthesis gas), an almost uniform temperature field can be achieved.

Coming back to the problem of surface reactions in homogeneous oxidation, let us mention briefly that their role can be revealed by varying the total pressure, reactor dimensions, wall material, and pre-treatment (see, for instance, Arutyunov *et al.*, 2002; Burch *et al.*, 1989).

Thus, one can conclude that reliable verification and validation of kinetic models require a special arrangement of experiments. In the ideal it includes a thorough description of reaction conditions, complete analysis of the reaction mixture, and use of adequate criteria for the comparison of experimental and calculated data. We must confess, however, that a consistent execution of these requirements is very time and resource consuming. This is why a pragmatic (trade-off) approach can be elaborated for the design of experiments. The following elements of this approach can be also employed for the selection of already published experimental data for verification of kinetic models:

- Low initial concentrations of oxygen for diminishing self-generated temperature gradients;
- Availability of the data for different conversions varied over a maximum possible range to construct characteristic curves "yield (or selectivity) vs. conversion";
- Availability of concentrations of products measured in one probe to diminish the distorting effect of sampling;
- Wide variation of experimental conditions (temperature, total pressure, initial concentrations, heterogeneous factors) to display possible qualitative effects revealing intimate peculiarities of kinetic scheme.

The above consideration does not purport to be full. We did not even mention here very powerful methods providing extremely valuable kinetic information, such as various spectroscopies (especially performed in *"in situ"* mode) and isotope tracing and labeling. Although these methods substantially improve the efficiency of model validation and elucidation of reaction pathways (see, for instance Mims *et al.*, 1994), they have not yet become very common in "kinetic experimentation for kinetic modeling". Instead, we focused on some problems typical for everyday practice and just traced possible solutions.

V. Some Examples and Comments

The examples given below illustrate and supplement the principles and general reasoning stated in the previous sections.

A. C_1–C_2 JOINT DESCRIPTION

As we emphasized above, although the oxidation of methane is accompanied by the formation of a variety of compounds, C_2-hydrocarbons play among them a special role. First of all, recombination of methyl radicals, which are primary and in some cases the most abundant radicals in the system, leads to a quadratic termination of the chain process and to a large extent controls the overall reaction rate. As a result, ethane forms as one of the main and "early" products (in terms of the number of reaction steps leading to its formation). As its reactivity is somewhat higher than that of methane (due to a pronounced difference in C–H bond strength), it becomes involved in the process all along. This means that practically all elementary steps of the transformation of ethane (and consequently, ethylene and acetylene) with no doubt must be included into the kinetic scheme of methane oxidation. Some of these reactions play a very important role in the overall process (see, for instance, Section V.C). Thus, any model developed for methane oxidation that does not take into account the formation and subsequent reactions of C_2 hydrocarbons (e.g., Vedeneev *et al.*, 1988a, b, c, d) does not meet the requirement of "fullness" and for most of applications cannot be considered as a good approximation.

On the other hand, if we start from ethane or any other C_2 hydrocarbon as an initial reactant, active intermediate species typical of the methane oxidation scheme appear in the reaction mixture at relatively early stages of the process. Among them are methyl radicals, which almost immediately produce methane by abstracting H-atom from the parent ethane molecule. In other words, the qualitative composition of the reaction mixture during C_2 hydrocarbon oxidation does not differ significantly from the one forming when methane as a starting reactant is oxidized.

In addition to the above reasoning, there is ample experimental evidence for the expediency of the joint analysis of C_1–C_2 hydrocarbon oxidation within a uniform kinetic scheme. One recent example of this kind was obtained recently during the oxidation of methane–ethane mixtures (Arutyunov *et al.*, 2005). It was demonstrated that the α value characterizing the relative "burning out" of two hydrocarbons and expressed as

$$\alpha = \frac{([CH_4]_f/[C_2H_6]_f)}{([CH_4]_0/[C_2H_6]_0)} \tag{5.1}$$

where "0" and "f" subscripts designate initial and final concentrations, remains very close to 1 and just slightly varies over a wide range of initial methane-to-ethane ratios (Fig. 10), despite a significant difference in their reactivities. Such behavior can be adequately simulated in the framework of the joint kinetic scheme of C_1–C_2 hydrocarbon oxidation. On the contrary, in the course of oxidation of the methane mixtures with propane and butane, the latter compounds are burnt out first, which is indicated by the fast increase of methane concentration in the mixture (Fig. 11). It means that oxidation pathways of C_{3+} hydrocarbons are less conjugate with those of methane. As the first approximation, they can be neglected in a kinetic model of methane and ethane oxidation, unless the formation of higher hydrocarbons is among the main subjects of investigation (like in Marinov *et al.*, 1996; Mims *et al.*, 1994). Unlike that, oxidation of methane and ethane cannot be modeled separately.

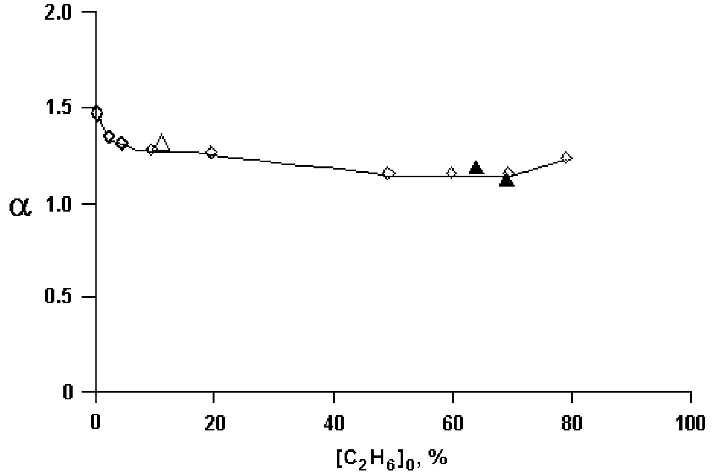


FIG. 10. Relative "burn out" of C_1–C_2 alkanes α as a function of initial ethane concentration. (-◇-)—Simulations ($T = 673$ K, $P = 70$ bar, $[O_2]_0 = 5\%$); (▲)—experiment ($T = 720$ K, $P = 25$ bar, $[O_2]_0 = 4$–6%); (△)—experiment ($T = 720$ K, $T = 35$ bar, $[O_2]_0 = 3\%$).

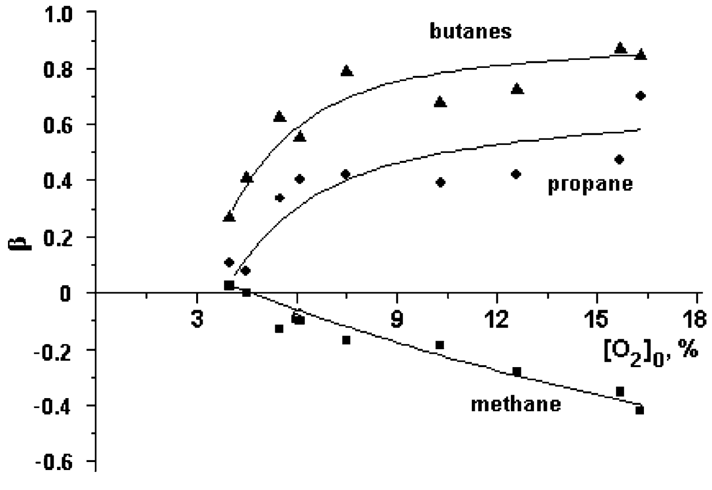


FIG. 11. Relative reactivities of methane and C_3–C_4 alkanes at different initial oxygen concentrations; $\beta = (C_{i,0} - C_{i,f})/C_{i,0}$. ($T = 800$ K, $P = 30$ bar). (■)—methane, (●)—propane, (▲)—butanes.

B. EXPANSION ON HIGHER HYDROCARBONS

If we accept the prohibition of varying or adjustment of rate constants as a ruling principle of model development, this opens the prospect for using the joint C_1–C_2 description as a basis for an expansion on some different areas. One possible direction is a description of catalytic processes, over oxide catalysts in particular, which was discussed in Section III.E. Another possibility is a step-by-step development of kinetic models of higher hydrocarbon oxidation. Of course, the expansion on C_3–C_4 alkane oxidation is the first aim. There are some factors making such expansion possible, including the deep analogy between corresponding reactions of C_1–C_2 and C_3–C_4 hydrocarbons and the similarity of intermediate species and main reaction routes of their oxidation.

However, there are also very important limitations. As we mentioned above, even in oxidation of methane and ethane many elementary reactions are not accessible for direct and detailed investigation. When we shift from ethane to propane, not only the number of carbon atoms in the molecule increases, but also the complexity of the reaction network. In particular, one may assume that even in propane oxidation the formation of complex oxygenate intermediates, including bi-radicals and complex peroxides, may take place. Although such compounds can play a principal role in kinetically relevant steps (such as chain-branching), up to now our knowledge about such compounds is negligible.

Another important difference between oxidation of C_1–C_2 and C_{3+} hydrocarbons is the appearance in the latter case of "degeneration" of the primary alkyl radicals. Already in the case of propane, the existence of two isomeric forms of propyl species (not always taken into account) can lead to substantial kinetic consequences because of the distinct difference in their thermochemistry and reactivity. Even certain reaction channels may vary depending on the isomeric form of propyl radicals. This factor may cause a substantial uncertainty especially in the case of modeling of catalytic oxidation due to a poor knowledge about thermochemistry and reactivity of surface active sites and chemisorbed species.

Nevertheless, there is a possibility to solve restricted tasks using approaches described above. In particular, the utility principle (see Section II.C) can be fruitfully utilized. For instance, such an approach was utilized by Vedeneev *et al.* (1997a, b) to describe the NTC behavior in propane oxidation. Generally speaking, if we are interested in the optimization of some particular product yield, we can select a block of reactions in which it is formed and further transformed and analyze it taking into account qualitative or even semi-quantitative notions about the reaction environment.

An important example of this kind is a contribution of cracking processes to partial oxidation of propane and higher hydrocarbons. In particular, in the case of catalytic propane ODH, the formation of lower hydrocarbons—first of all ethylene and methane—can substantially reduce propylene selectivity. The analysis of possible homogeneous and heterogeneous pathways of C–C bond breaking can provide valuable guidelines for further improvement of catalyst formulation and/or overall process design.

Figure 12 shows the lifetimes of *n*- and *iso*-propyl radicals in gas-phase reactions of H-atom and CH_3-radical elimination leading to the formation

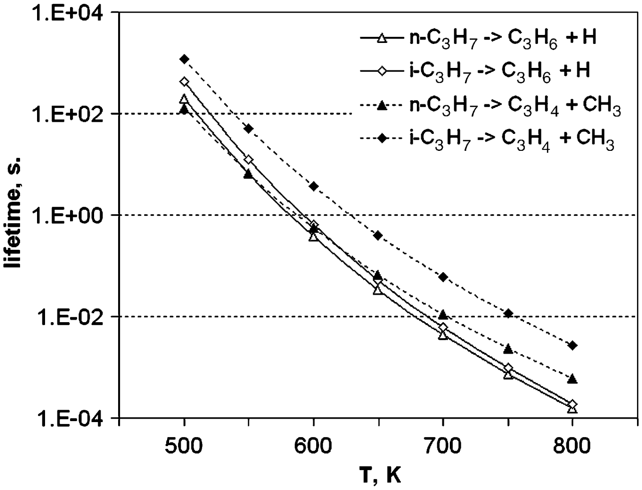


FIG. 12. Lifetimes of propyl radicals (*n*- and *iso*-) in the gas phase in reactions of H-atom and CH_3-radical elimination.

of propylene ($C_{3=}$) and ethylene ($C_{2=}$), respectively

$$C_3H_7 \rightarrow C_3H_6 + H \tag{23}$$

$$C_3H_7 \rightarrow C_2H_4 + CH_3 \tag{24}$$

If propyl radicals are generated into the gas phase by an active catalyst, the comparison of residence time with lifetimes given Fig. 12 can say whether or not such reactions can proceed while the gas mixture resides in the reactor. Also, if only these reactions are controlling the olefin distribution, the ($C_{3=}$)-to-($C_{2=}$) ratio would be as shown in Fig. 13. The relative amount of propylene formed from both isomeric radicals is increasing with temperature. In fact, some additional amounts of propylene that can form in homogeneous reactions should be even higher due to several additional processes

$$C_3H_7 + X \rightarrow C_3H_6 + XH \tag{25}$$

where X is C_3H_7 and other radicals (and also maybe O_2—see Section V.C).

The same reaction can proceed via a participation of an oxidized surface active site

$$C_3H_7 + [O]_S \rightarrow C_3H_6 + [OH]_S \tag{26}$$

Propyl decomposition and the above two processes (reaction (25) and (26)) should increase the ($C_{3=}$)-to-($C_{2=}$) ratio at rising temperature. However, experimental data indicate (see, e.g., Leveles, 2002) that, as a rule, the ethylene fraction in sum of $C_{3=}$ and $C_{2=}$ olefins increases.

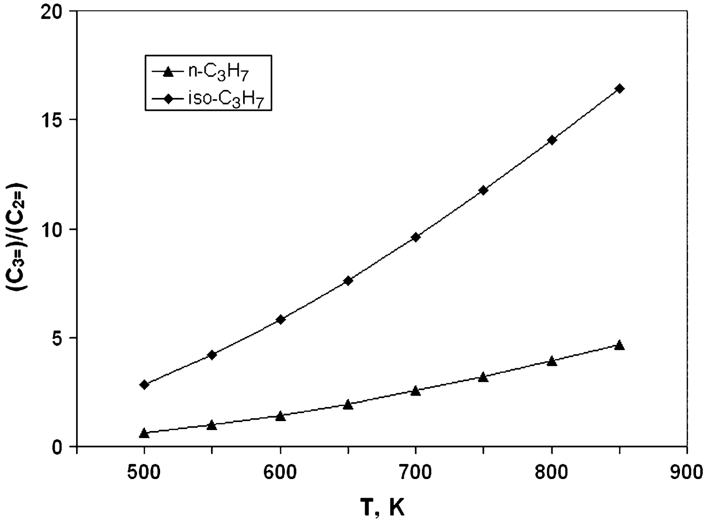
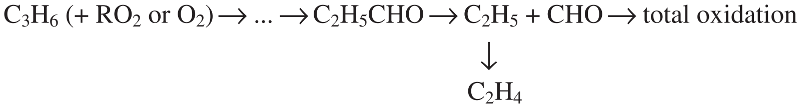


FIG. 13. Relative amounts of propylene and ethylene formed in homogeneous reactions of propyl radicals at different temperatures.

Methyl radicals formed simultaneously with ethylene can rapidly capture a hydrogen atom from any organic molecule in the gas (first of all, from propane) and transform it into methane. The latter is almost inert under the conditions of propane ODH. This means that methane-to-ethylene ratios close to 1 or above serve as evidence for predominantly homogeneous "anaerobic" degradation of the C–C–C skeleton. On the other hand, such degradation can also proceed via oxidative paths with the participation of molecular oxygen and/or oxidized (oxidative) intermediates. One of the most probable is an "aldehyde route"



$$C_3H_6\,(+\,RO_2 \text{ or } O_2) \longrightarrow \ldots \longrightarrow C_2H_5CHO \longrightarrow \underset{\displaystyle \overset{\downarrow}{C_2H_4}}{C_2H_5} + CHO \longrightarrow \text{total oxidation} \qquad (27)$$

Thus, a preliminary analysis of olefin production pathways can be performed based on the methane-to-ethylene ratio and on temperature dependence of the $(C_{3=})$-to-$(C_{2=})$ ratio. A more detailed elaboration can be reached from experiments with varied oxygen concentration and from the detailed analysis of the product distribution (including hydrogen formation). However, ethylene formation itself is strong evidence for the contribution of the radical route in product formation. The analysis of experimental data about product distribution during propane oxidation (Kondratenko *et al.*, 2005) demonstrates that over rare-earth oxide catalysts radical route is prevailing in olefin formation. On the other hand, over supported V-containing catalysts, propylene forms predominantly via heterogeneous dehydrogenation of propane (or propyl radical intermediate), since over this catalyst only traces of ethylene are formed.

An examination of the nearest consequences of propyl radical transformation in the gas phase indicates that a substantial part of propane reaction proceeds within the above-discussed C_1–C_2 kinetic scheme. This fact opens up the prospect for the development of a propane oxidation scheme by the stepwise build-up of a C_1–C_2 joint description. In the course of this procedure special attention should be paid to the execution of the "fullness" principle. Although, as we mentioned above, in the case of C_{3+} hydrocarbon oxidation the contribution of several "mysterious" types of intermediates may substantially increase, the blocks accounting for the elementary reaction of "normal" species must be described as thoroughly as possible.

C. Reactions between Alkyl Radicals and Oxygen and Transformations of Alkylperoxy Radicals

The last statement of the previous section needs a more precise definition in some important cases, one of which will be discussed here. The central role of reactions between alkyl radicals and molecular oxygen and further transformations of alkylpreoxy species for combustion chemistry has been extensively discussed elsewhere (see, for instance, Miller and Klippenstein, 2001; Slagle *et al.*, 1986, and literature cited therein). Let us mention just some aspects of alkylperoxy chemistry and kinetics, which are of crucial importance for partial oxidation processes.

1. Alkylperoxy radicals are direct precursors of hydroperoxides—the key intermediates causing a degenerate chain-branching; thus, transformations of alkylperoxy species determine the overall kinetic features of the process.
2. Alkyl radicals are primary (and in many cases the most abundant) radical species during alkane oxidation, both homogeneous and catalytic heterogeneous–homogeneous (at least over oxides). Since the concentration of molecular oxygen in the system is much higher than that of any reactive radical up to very high conversions, namely reactions between alkyls and O_2 determine prevailing reaction pathways and control product distributions.
3. During methane oxidation, the equilibrium between formation and dissociation of methylperoxy (CH_3O_2) radicals determines the overall direction of the process. If CH_3O_2 formation dominates, oxygenates (methanol, formaldehyde) can form. On the contrary, in the condition of predominate dissociation (higher temperatures, lower oxygen partial pressures) the probability of CH_3 recombination and higher hydrocarbon formation (ODH selectivity) are increasing (see Section III.E).

In oxidative processing of higher alkanes, reactions under discussion also to a considerable degree determine the product distribution. Let us consider reactions of ethyl species as a representative example. First of all, as all reactions of C-centered radicals with oxygen, reaction between ethyl and O_2 can proceed as a reversible formation of ethylperoxy radical

$$C_2H_5 + O_2 \rightleftharpoons C_2H_5O_2 \tag{28}$$

The relative importance of different channels of further transformations of peroxy radicals determines the overall rate of reaction and selectivities to certain products. Reactions with any H-containing substance (first of all—with parent alkane) finally lead to degenerate chain-branching and exponential growth of the reaction rate

$$C_2H_5O_2 + RH \rightarrow C_2H_5OOH \rightarrow C_2H_5O + OH \tag{29}$$

Ethoxy species C_2H_5O are precursors for the formation of C_2-oxygenates. On the other hand, there is another (different from C–O bond dissociation) channel of decomposition

$$C_2H_5O_2 \rightarrow C_2H_4 + HO_2 \tag{30}$$

This reaction gives the product of another type—ethylene—and thus can play a key role in ethane ODH (including catalytic).

Additional problems arise due to the possibility of one more reaction, namely isomerization

$$C_2H_5O_2 \rightarrow CH_2CH_2OOH \tag{31}$$

Hydroperoxyethyl radicals formed can transform into ethylene oxide

$$CH_2CH_2OOH \rightarrow C_2H_4O + OH \tag{32}$$

or even react with one more oxygen molecule

$$CH_2CH_2OOH + O_2 \rightarrow OOCH_2CH_2OOH \tag{33}$$

Although this reaction is not among usually discussed in the literature, there are no serious arguments for its absence in nature. However, if we consider it and, consequently, further transformations of complex hydroperoxo–peroxocompounds, this may result in a serious change of the reaction rate (e.g., additional fast branching).

At last (not least!), ethyl radicals can react with oxygen giving ethylene and HO_2 radical directly ("direct H-abstraction")

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2 \tag{34}$$

Reaction (33) is moderately exothermic (about −70 kJ/mole), so its activation energy should not exceed 15–20 kJ/mole. This means that it should be highly

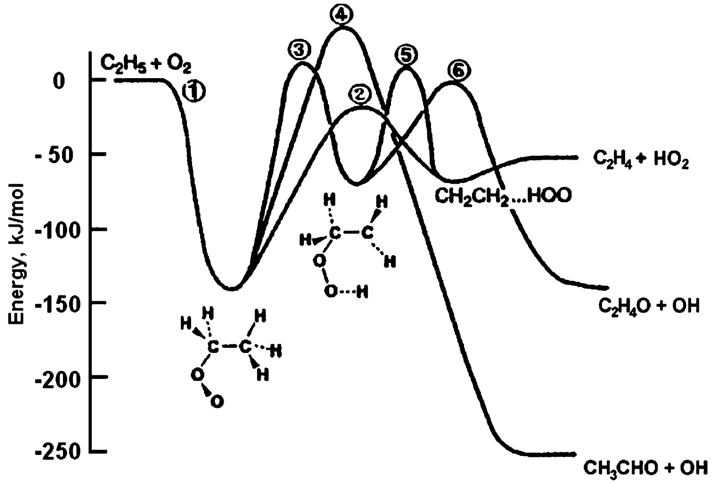


FIG. 14. Energetic diagram of possible channels of $C_2H_5 + O_2$ reaction and corresponding barriers.

competitive, even taking into account exothermicity and the non-activated character of alkylperoxy formation.

Despite extensive studies in this area, even for the reaction of ethyl radicals with oxygen a certain discrepancy remains between different authors. Separate kinetic experiments are better explained in the framework of different descriptions (see, for instance, Miller and Klippenstein, 2001; Naik *et al.*, 2004). The main problem consists of a very small difference in thermal effects and barriers of reactions (see Fig. 14). As shown by Naik *et al.* (2004), very small variations in parameters obtained by theoretical calculations can seriously improve the coincidence with experimental data. It is worth noticing that as a rule such a tiny difference in kinetic parameters is hardly distinguishable in kinetic experiments.

Simulations demonstrate, however, that variations in kinetic parameters of reactions under consideration lead to substantial consequences. Figure 15 shows how relatively small variations in the rate constant for reaction (30) influence the SID in methane–ethane mixtures. In such a reaction system (which models real compositions of natural gas) competition of different channels of ethyl-oxygen reaction overlaps (and very probably interferes) with methyl-oxygen chemistry. The latter is even somewhat qualitatively different: there are no variations in mono-molecular reactions of methylperoxy radicals at temperatures below 900 K (only dissociation to methyl and O_2) and all their bi-molecular reactions lead to branching as a nearest consequence. As to the ethyl-oxygen chemistry, it is much more “rich” and much less definite at the same time. So in this particular case, small variations in kinetic parameters lead to very substantial consequences.

One may expect the increase of complexity as soon as we move further and try to analyze reactions of C_3 radicals. We abstain from speculations concerning

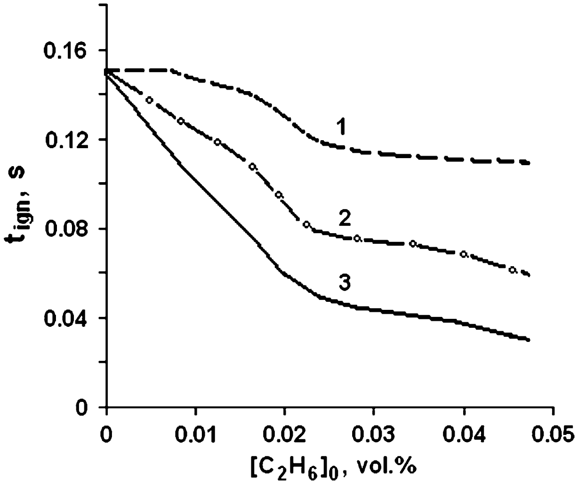


FIG. 15. Effect of initial ethane concentration on the self-ignition delay values (t_{ign}) in oxidation of methane–ethane mixtures; modeling at different values of reaction (28) rate constant ($T = 773$ K, $P = 70$ bar, $[O_2]_0 = 15.4\%$). (1) $k_{28} = 3 \times 10^5\,s^{-1}$, (2) $k_{28} = 6 \times 10^5\,s^{-1}$, (3) $k_{28} = 1.2 \times 10^6\,s^{-1}$.

elementary reaction of C_3-peroxo radicals; this topic is still waiting for a detailed development.

D. CAPABILITIES OF PROCESS INFLUENCING, GOVERNING AND DESIGN

A very intriguing aspect of the reciprocal influence of homogeneous and heterogeneous processes is a possibility of intensification, or tuning gas-phase processes by precise (or directed) action of solid surfaces. At first glance, governing high-temperature oxidation processes in order to improve the formation of certain valuable products cannot be very prospective. Indeed, a catalyst containing very active surface sites can substantially accelerate the formation of initial free radicals (chain carriers), but the same effect can be also achieved using various physical methods. What is more important, even if the initiation rate could be substantially increased, the possibility of channeling the reaction of free radicals towards certain desired products is usually considered as doubtful.

One widely known example of such ineffective attempts is the direct oxidation of methane-to-methanol (DOMM) (see Arutyunov and Krylov, 1998 and literature cited therein). Whereas at atmospheric or somewhat higher pressures the introduction of catalysts (or homogeneous promoters) accelerates the process and increases product (mainly formaldehyde) yield to some extent, at increasing pressures their efficiency sharply drops. As a result, the methanol yield cannot be increased by any means above the level attainable in high-pressure homogeneous oxidation.

The kinetic simulations (Arutyunov, 2004; Arutyunov *et al.*, 1999) based on the relatively simple homogeneous methane oxidation model (Vedeneev *et al.*, 1988a, b, c, d) allowed resolving the origin of such behavior. It turned out that in the pressure range of several atmospheres the critical transition from slow radical chain mode to a fast quasi-stationary chain-branched mode occurs. In this high-pressure mode, the rate of radical generation in the endothermic homogeneous initiation reaction is a factor of ~10^4 slower than in chain-branching steps (Arutyunov, 2004). The rate of reaction is quasi-steady-state and does not turn into the chain explosion only because of radical decay via second-order termination steps. In order to be efficient under the conditions where this chain-branched mode is dominating, the rate of additional catalytic initiation must be comparable with that of fast branching reactions. Figure 16 shows the calculated methanol yield and reaction time vs. relative rate of additional methyl radical generation w_{eff} (normalized to "normal" homogeneous thermal initiation w_{therm}) imitating catalyst action. The calculations show that some increase in methanol yield can be expected, but at very intense additional injection of primary radicals. Besides that, this simulation does not account for the rise of heterogeneous decay of radicals and subsequent reactions of methanol, which could be also accelerated in the presence of catalyst capable of such strong initiation. The latter is the most probable explanation of the failure of any attempts to improve the DOMM process by heterogeneous catalysis.

Nevertheless, a more thorough analysis of kinetic schemes of oxidative transformations shows that there are additional possibilities, which have not been rationalized so far. Owing to the fundamentally non-linear nature of these

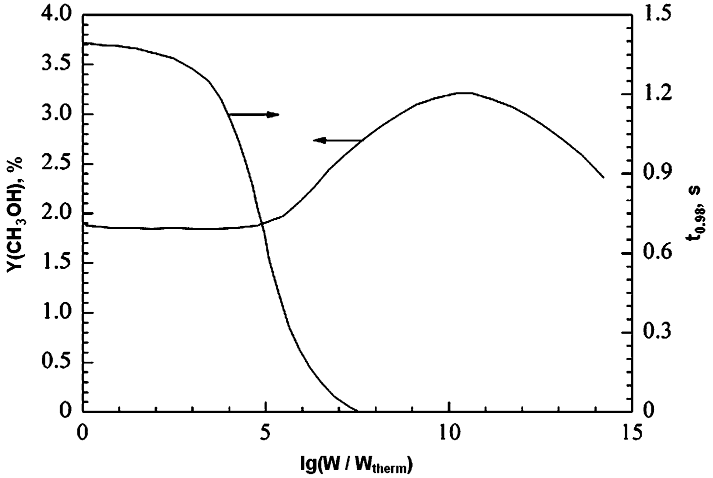


FIG. 16. Simulated methanol yield and time of 98% oxygen conversion ($t_{0.98}$) as functions of relative initiation rate (Arutyunov, 2004; Arutyunov *et al.*, 1999). $T = 683$ K; $P = 100$ bar, CH_4:O_2 = 19:1

reactions beginning very far from equilibrium and including multiple intermediates cross-linked by complex mutual transformations, there appears a principal possibility of affecting the overall process by relatively "tiny" influences. As a result, the system can attain substantially different steady states characterized by significantly different overall rates and product distributions.

The existence of multiple evolution paths is a fundamental feature of complex non-linear systems. Moreover, whereas far from the point of critical transition between two (or more) stationary states (bifurcation point) a limited impact can affect the behavior only quantitatively, near the bifurcation point even very small correction of one parameter is able to drastically change the direction of further evolution. It is worth noticing that light alkane oxidation belongs to that type of process in which various non-linear phenomena (such as cool flames, multiple and oscillating flashes, negative temperature reaction rate coefficients, hysteresises of different type) are taking place (Arutyunov *et al.*, 1995b; Lewis and Elbe, 1987; Shtern, 1964; Sokolov *et al.*, 1995; Vedeneev *et al.*, 2000). Bearing this in mind, we can consider the modeling as a tool for searching the conditions for the reaction parameters and stages the most suitable for efficient forwarding the system evolution to a desired direction.

One example of such a type is described below. Figure 17 demonstrates simulated data of concentrations of different products at the early stages of methane oxidation. It is very clearly seen that characteristic times of coming into action for different species significantly differ. A selective "turning off" of particular intermediates may have dramatic consequences at later stages of reaction. In a more practical case—in a plug-flow reactor—such temporal development can be turned into a spatial evolution along the length of the reactor. The process can be influenced by placing catalytic material(s) into different cross-sections of the reactor and/or by varying the flow rate (in the latter case the location of catalyst can be unchanged). Schmidt (2001) presented indirect evidence for such a possibility: varying contact times in the millisecond range in methane oxidation over Pt leads to a substantial change of temperature and concentration profiles and to the shift in product distributions between preferential formation of synthesis gas ($CO + H_2$), oxygenates (formaldehyde), and C_2 hydrocarbons.

Hargreaves *et al.* (1990) also observed the shift from CO to C_2 hydrocarbons during methane oxidation over MgO catalyst at varying flow rate. However, in this case authors explained this effect in terms of the difference in kinetic orders of two reactions—OCM and oxidation to CO—with respect to CH_3 radical concentration, which in turn is changing at varied flow rate.

Similar effects can be achieved by changing the feed composition. Sinev *et al.* (1993) demonstrated that over the same phosphate catalysts it is possible to direct methane oxidation to different products by varying the initial oxygen concentration. Whereas at low oxygen content almost exclusive formation of ethane is observed, a gradual increase of oxygen concentration leads to a proportional increase of formaldehyde selectivity. It is important that the sum of

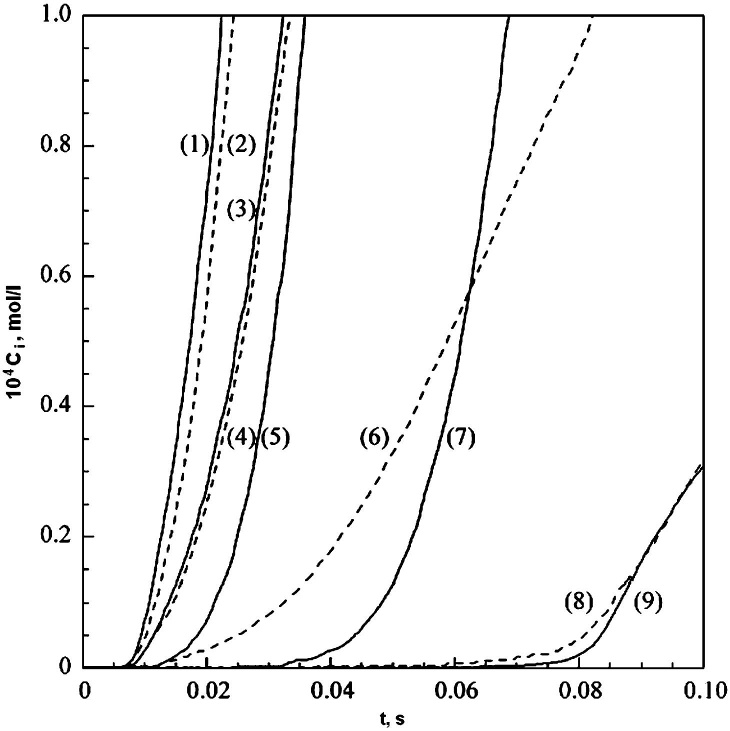


FIG. 17. Simulated concentration profiles of selected products on the initial stage of methane oxidation (Arutyunov, 2004) ($T = 733\,\text{K}$, $P = 84\,\text{bar}$, $CH_4{:}O_2 = 21{:}1$). (1) CH_2O, (2) H_2O, (3) H_2O_2, (4) CH_3OH, (5) CO, (6) H_2, (7) CO_2, (8) C_2H_6, (9) C_2H_5OH.

ethane and formaldehyde selectivities remains constant. This effect can be explained by shifting the equilibrium in reaction (5). However, there is an additional contribution to it from the catalyst side: at given oxygen concentration the ethane-to-formaldehyde ratio changes from one phosphate catalyst to another.

Although the above examples illustrate the possibility of influencing the formation of different products, all these experimental results were obtained independently of modeling and analysis of kinetic schemes. Indeed, the examples of modeling-driven directed process governing and design are scarce so far. This reflects the current state of the area and our understanding of the alkane oxidation mechanism and free radical chemistry in particular. However, one example of more advanced tuning of the reaction is given below.

While modeling the OCM process over oxide catalysts, it was demonstrated that a substantial fraction of methyl radicals (up to 95%) generated via reaction (12) are transformed back into methane in the reverse process

$$[OH]_S + CH_3 \rightarrow [O]_S + CH_4 \qquad (35)$$

It was assumed that the yield of OCM products could be enhanced by increasing the efficiency of CH_3 recombination, which competes with reaction (35). Since the recombination of methyl radicals is a three-body process (see Section III.D), its efficiency can be increased by increasing total pressure, or by introducing an additional "inert" surface, which can play a role of third body. Indeed, it was demonstrated that the increase of inert gas (He or Ar) pressure at constant pressures of methane and oxygen leads to a substantial increase of OCM selectivity and yield (Sinev *et al.*, 1996). Moreover, the addition of a 10-fold amount of various solid materials possessing a very low activity under the same conditions (quartz, fused MgO, Mg phosphate) to a relatively efficient OCM catalyst (Nd/MgO) led to a drastic increase (up to twofold) in the yield of OCM products (Sinev *et al.*, 1997a, b).

Indeed, the area outlined in this section is in its infant state. Further development of kinetic models can play a significant role both in obtaining new information about the intrinsic mechanisms of processes under discussion and in its utilization for practical applications.

VI. Concluding Remarks

The main conclusion that could be derived from the above analysis is the ascertaining of the extraordinary complexity of the system we attempt to model. Even staying at the level of "micro-chemical" modeling we must accept as a fact the fundamental difference between the phenomenon and its model and, as a result, the impossibility to develop the description that reflects the reality in all its manifestations. A possible solution of the modeling problem, as applied to light alkane oxidative processing, can be found on the way of stepwise and successive execution of the basic principles stated below.

1. Precise formulation of the objective.
2. Elucidation of principal chemical and physical features of the system and relationships between its parts.
3. Compilation of kinetic scheme which meets the requirement of fullness. The latter assumes the accounting of all species and elementary reactions potentially relevant for the formation and transformations of certain product(s). We must emphasize here that the requirement of fullness includes the thermodynamic consistency as the essential constituent.
4. Determination of general kinetic features of each accounted elementary reaction (or groups of analogous reactions, e.g., "simple" homogeneous, pressure-dependent, heterogeneous, reactions in adsorbed layers, etc.). This includes, first of all, types of applicable kinetic description (e.g., mass action law, topochemical equations, probability of interaction on phase boundaries, etc.) and adequate form of representation of kinetic parameters.

5. Selection of the most reliable values of kinetic parameters available in literature, databases, etc. In the case of absence, parameters of certain reactions can be calculated or evaluated using various procedures. However, what should be avoided is fitting (or adjustment) of parameters to the experimental data in the framework of the same reaction scheme, which is going to be utilized for modeling also. The latter would mean the solution of the inverse kinetic problem, which in general (and in the most of particular cases of complex reactions consisting of hundreds of elementary steps) is a mathematically ill-conditioned (or even illegal) procedure.

Now let us raise the question—what the result of such modeling would mean? The answer is as follows: if the system under consideration is arranged as described by the model, its behavior would be as predicted by simulations. Taking into account all mentioned difficulties (first of all, imperfection of micro-chemical information and uncertainty of kinetic parameters), we have to confess that it is not realistic to expect good and moreover quantitative coincidence of simulated kinetics with some particular experimental data. Since any experimental result also cannot be considered as "absolute reality", the best way is to compare the results of modeling with experimental observations on a phenomenological level. In other words, at the current stage of understanding the comparison of observations and predictions is more fruitful in terms of phenomena and qualitative effects, rather than in numbers, approximation equations, or any other quantitative characteristics.

In spite of apparent "micro-chemical extremism", we greatly appreciate the efforts made by scientists and groups working in neighboring areas, such as measuring, calculation and evaluation of kinetic parameters, modeling of heat- and mass-transfer, development of simulation codes and software, etc. The problem lies in the plane of adequate use of achievements reached in one area for further development of the adjacent one and in solving the modeling problem as a whole.

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LIST OF SYMBOLS

A	pre-exponential factor in "three-parametric" form of Arrhenius equation (in mol, l, s.)

[A]	concentration of reactant (A), vol.%
a	constant (coefficient) in Polanyi–Semenov equation, kJ/mol
b	constant (coefficient) in Polanyi–Semenov equation (dimensionless)
C_i or $C(i)$	concentration of *i*th reactant, mol/l
D_i	coefficient of gas-phase molecular diffusion for *i*th particle, m^2/s
d	characteristic dimension (thickness) of one layer, *m*
E_a	activation energy, kJ/mol
h	Plank constant (6.6256×10^{-34} J s.)
K_j	equilibrium constant of *j*th reaction (in mol, l)
k_j	rate constant of *j*th reaction (in mol, l, s.)
k_0	rate constant of pressure-dependent reaction in low pressure limit (in mol, l, s.)
k_∞	rate constant of pressure-dependent reaction in high pressure limit (in mol, l, s.)
$k_{(+)}$	rate constant for forward reaction (in mol, l, s.)
$k_{(-)}$	reverse reactions must satisfy the connecting equation (in mol, l, s.)
k_{Di}	"diffusional" rate constant for *i*th particle, s^{-1}
L	gas gap thickness in spatially distributed system, *m*
m	reaction order with respect to *i*th reactant (dimensionless)
N_A	Avogadro number ($6.0225 \times 10^{23}\,mol^{-1}$)
P	total pressure, bar
R	gas constant (8.314 J/(mol K), or 0.082061 atm/(mol K))
T	temperature, K
T_0	comparative temperature (as a rule, 273 or 298 K), K
t	time, s
$t_{0.1}$	time of reaching 10%-conversion, s
t_{ign}	self-ignition delay, s
W	rate of reaction, mol/(l s)
W_{tot}	total rate of methane activation, mol/(l s)
W_{hom}	rate of homogeneous activation of methane, mol/(l s)
$Y(P)$	yield of product *P*, %
Z	pre-exponential factor (for bi-molecular reactions—collision factor) in Arrhenius equation (in mol, l, s.)
ΔH	enthalpy change in the process (differences between enthalpy of formation of products and reactants), kJ/mol
$\Delta H^{\neq}$	enthalpy of formation of activated complex, kJ/mol
S_{LIM}	limiting selectivity to C_2-hydrocarbon formation
ΔS	change in the process (differences between standard entropy of products and reactants), J/(mol K)
$\Delta S^{\neq}$	entropy of formation of activated complex, J/(mol K)
α	relative "burning out" of two hydrocarbons in their mixture (dimensionless)
β	relative change of concentration of individual alkanes during the oxidation of their complex mixture (dimensionless)

χ	transmission coefficient (dimensionless)
μ	reduced molecular weight of colliding molecules, kg/mol
μ_g	molecular weight of gas particle, kg/mol
ν	gas-to-surface collision frequency, s^{-1}
ϑ	concentration of surface sites per unit surface area, m^{-2}
σ	collision cross-section, m^2
σ_S	cross-section of the surface site, m^2
ξ	steric factor (dimensionless)

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