Metal–Catalyzed Ethylene Hydrogenation: The Method of Interactive Search for Multiple Working Hypotheses

3 **AUTHORS**, INCLUDING:

Andrey V Zeigarnik

MAIK Nauka/Interperiodica

42 PUBLICATIONS   **445** CITATIONS

SEE PROFILE

Oleg Naumovich Temkin

Moscow State University of Fine Chemical Te…

143 PUBLICATIONS   **678** CITATIONS

SEE PROFILE

Metal-Catalyzed Ethylene Hydrogenation: The Method of Interactive Search for Multiple Working Hypotheses

Andrew V. Zeigarnik,*,[†] Raúl E. Valdés-Pérez,[‡] and Oleg N. Temkin[†]

Laboratory of Chemical Kinetics and Catalysis, Lomonosov Academy of Fine Chemical Technology, Moscow, 117571 Russia, and Computer Science Department, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

Recent research has led to the development of interactive computer programs that enable a comprehensive search for reaction mechanisms. These programs enable a new strategy of interactive mechanistic study which borrows heavily from the century-old method of multiple working hypotheses proposed by T. C. Chamberlin. We propose that mechanistic studies should follow the method of considering at the outset a complete set of plausible mechanisms, rather than just one or a small number, which has the drawbacks described well by Chamberlin. This general methodology has become much more practical with the development of interactive computer programs that search comprehensively while building on the experimenter's prior knowledge. This paper illustrates the methods in detail, using as a vehicle the hydrogenation of ethylene, which is among the most studied reactions in the history of heterogeneous catalysis.

Introduction

Until recently, techniques of mechanistic study were much less elaborate than they are today. Hence, mechanistic knowledge was relatively sparse, and even a single hypothesis about a reaction mechanism was considered a good result. Accordingly, the elucidation of a reaction mechanism usually followed this general pattern, which would take many years and involve investigators worldwide: exploratory studies ⇒ mechanistic hypothesis ⇒ disconfirmatory evidence ⇒ new hypothesis, and so on. For example, work on the mechanism of ethylene hydrogenation followed this pattern for more than 60 years.

The aim of this article is to propose a human/computer interactive methodology for mechanistic study which shortens the above pattern and thus may greatly accelerate the reliable elucidation of mechanisms. This interactive methodology builds on the capabilities of the computer and of recent computer programs[1−4] and makes newly relevant and practical a century-old scientific idea proposed by T. C. Chamberlin.[5]

We have used this methodology ourselves in recent work,[6] but the current article is motivated by the desire to illustrate our proposal on a long studied and widely known catalytic reaction. We have chosen ethylene hydrogenation as a vehicle for these arguments, but without claiming to offer new insights into its chemistry.

Mechanistic studies of ethylene hydrogenation first began in the 1930s, and various different mechanisms have since been advanced. We will illustrate how a chemist in collaboration with a computer program (MECHEM) might retrace the sequence of events, and thus show how such research could be done on a more systematic basis today, for example, by considering a fuller array of mechanisms and by designing experiments motivated by the outcome of chemist/computer interaction. We do not argue that programs are capable of generating novel hypothetical mechanisms, not because that would be false but because that is outside the scope of this article.

Method of Multiple Working Hypotheses

In a widely reprinted article originally published in *Science* in 1895, T. C. Chamberlin argued in favor of a new methodology of hypothesis formation which he called *The method of multiple working hypotheses*.[5] Chamberlin (1843−1928) was a geologist "noted for his contributions to glaciology and for his part in formulating the Chamberlin−Moulton (planetesimal) hypothesis of the origin of the earth." Among his other accomplishments, he founded the *Journal of Geology*, served as President of the AAAS and of the University of Wisconsin, and was Professor and Director of the Walker Museum at the University of Chicago.

Chamberlin pointed out that, in premodern science, new (or old) phenomena were explained by appealing to ruling theory, which need not have been established by systematic attention to evidence. The method of developing a working hypothesis from evidence was its successor, but it has its own drawbacks, concerning which we now quote at length from Chamberlin:[5]

"Conscientiously followed, the method of the working hypothesis is a marked improvement upon the method of the ruling theory; but it has its defects—defects which are perhaps best expressed by the ease with which the hypothesis becomes a controlling idea. To guard against this, the method of multiple working hypotheses is urged. It differs from the former method in the multiple character of its genetic conceptions and of its tentative interpretations. It is directed against the radical defect of the two other methods; namely, the partiality of intellectual parentage. The effort is to bring up into view every rational explanation of new phenomena, and to develop

---

* Corresponding author.
[†] Lomonosov Academy of Fine Chemical Technology.
[‡] Carnegie Mellon University.
(1) Valdés-Pérez, R. E.; Zeigarnik, A. V. *J. Mol. Catal., A: Chem.* **1997**, *119*, 405.
(2) Zeigarnik, A. V.; Valdés-Pérez, R. E.; Temkin, O. N.; Bruk, L. G.; Shalgunov, S. I. *Organometallics* **1997**, *16*, 3114.
(3) Valdés-Pérez, R. E. *Catal. Lett.* **1994**, *28*, 79.
(4) Zeigarnik, A. V.; Bruk, L. G.; Temkin, O. N.; Likholobov, V. A.; Maier, L. I. *Russ. Chem. Rev.* **1996**, *65*, 117.
(5) Chamberlin, T. C. *Science* **1890**, *15*, 92 (old series); reprinted in *Science* **1965**, *148*, 754.
(6) Bruk, L. G.; Gorodskii, S. N.; Zeigarnik, A. V.; Valdés-Pérez, R. E.; Temkin, O. N. *J. Mol. Catal, A: Chem.* **1998**, *130*, 29.

every tenable hypothesis respecting their cause and history. The investigator thus becomes the parent of a family of hypotheses; and, by his parental relation to all, he is forbidden to fasten his affections unduly upon any one."

In the current context, this paragraph speaks to the prevailing methodology in mechanistic chemistry whereby arriving at a single mechanistic hypothesis conforms to good practice. If plausible mechanisms were rare, like needles in a haystack, then the method of the single working hypothesis might be adequate, but evidence is accumulating that the density of mechanistic needles in this chemical haystack is surprisingly large. We return to Chamberlin on the advantages of his method:

"A special merit of the method is, that by its very nature it promotes thoroughness. The value of a working hypothesis lies largely in its suggestiveness of lines of inquiry that might otherwise be overlooked."

However, Chamberlin's method has its own disadvantages:

"We encounter an analogous difficulty in the use of the method with young students. It is far easier, and I think in general more interesting, for them to argue a theory or accept a simple interpretation than to recognize and evaluate the several factors which the true elucidation may require."

In brief, the method requires habits of reasoning that are taxing and which perhaps are not natural in a world where indecision and tentativeness are penalized.

Chamberlin summarizes the advantages of his method:

"There is a third result of great importance. The imperfections of our knowledge are more likely to be detected, for there will be less confidence in its completeness in proportion as there is a broad comprehension of the possibilities of varied action, under similar circumstances and with similar appearances."

The method of multiple working hypotheses, then, can be seen as an idealized method of scientific investigation which nevertheless has strong practical limitations. However, we assert that this old ideal acquires new vigor with the possibilities of a properly programmed computer carrying out a search for multiple working hypotheses, while constrained by the prior experimental and background knowledge articulated to it by the investigator. Thus, the drawbacks to Chamberlin's method can be largely remedied. We call this modern interpretation of Chamberlin the *Method of Interactive Search for Multiple Working Hypotheses*.

Overview of MECHEM

The computer program MECHEM is intended largely as an aid for the elucidation of reaction mechanisms. It is generally usable on any reaction, although so far its application has focused on catalysis (heterogeneous and homogeneous). Given the set of reaction starting materials, any observed products and intermediates, and user-defined constraints, the program searches comprehensively for all simplest reaction mechanisms, that is, containing the fewest number of conjectured species (i.e., any species that is not a declared starting material, intermediate, or product) and steps. Every declared intermediate and product is required to be present in any mechanism output by the program.

The user can override this default search behavior and search for next-simplest mechanisms, for example, by (i) asking the program to generate mechanisms containing new steps or new species, that is, that are absent from the mechanisms that were already found, and (ii) imposing

more constraints, with which previously generated (simplest) mechanisms are inconsistent. In either case, the program will necessarily explore more complex mechanisms that have either more conjectured species or more steps. Thus, we get a phenomenon which usually surprises first-time observers: adding more constraints often leads to the program finding a larger number of simplest mechanisms, whenever the current batch of simplest mechanisms is entirely ruled out by the new constraints. The reason for the increase is that allowing more conjectured species is analogous to allowing more free parameters in a theory, which usually enlarges the number of theories consistent with given evidence.

The prior knowledge about a reaction, whether empirical or theoretical, is expressed via a rich array of constraints that serve to discard implausible branches of the comprehensive search. Currently, MECHEM incorporates approximately 100 different types of constraints.

MECHEM's main goal is to find all simplest mechanisms that are consistent with constraints formulated by the user. There are a number of user conveniences, such as an ability to inspect what partially formed pathways the program is considering at the moment, as well as new auxiliary tools that can aid in the design of isotopic labeling experiments.

Scenario of Human/Computer Interaction

Further discussion will emphasize the mechanisms that have been proposed in the literature, but we will also speculate on other mechanisms without direct precedence but which contain steps that have been proposed for other metal-catalyzed reactions of hydrocarbons. For lack of space, we will disregard possible mechanisms beyond a certain level of complexity.

The first mechanisms of ethylene hydrogenation on metal catalysts were proposed in the 1930s by Horiuti and Polanyi[7,8] and by Twigg and Rideal,[9] and several more mechanisms have been proposed since.[9] Ethylene hydrogenation is still an active subject for research in catalysis today.[10–19]
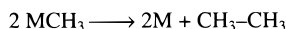
Our aim will be to generate multiple working hypotheses for ethylene hydrogenation in a way that emulates the long history of research on this reaction. We will show that a chemist/MECHEM interaction is able to generate the principal mechanisms that have been proposed. Along the way, we will see some mechanisms that remain unproposed in the literature. The advantage of selecting this case study is that one has available, from the literature, a stream of mechanisms proposed over time, together with the experimental evidence that motivated their introduction.

Our initial formulation of the problem for the program consists of the starting materials, the product, and some
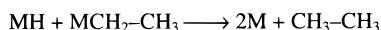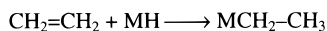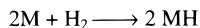
(7) Horiuti, J.; Polanyi, M. *Trans. Faraday Soc.* **1934**, *30*, 1164.

(8) Horiuti J.; Miyahara, K. *Natl. Bur. Stand. Ref. Data Ser.* **1968**, *13*, 3.

(9) Twigg, G. H.; Rideal, E. K. *Proc. R. Soc.* **1939**, *171*, 55.

(10) Glines, A. M.; Anton, B. A. *Surf. Sci.* **1993**, *286*, 122.

(11) Backman, A. L.; Masel, R. I. *J. Vac. Sci. Technol. A* **1991**, *9*, 1789.

(12) Merrill, P. B.; Madix, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 5062.

(13) Frünberger, B.; Chen, J. G. *J. Am. Chem. Soc.* **1996**, *118*, 11599.

(14) Rekoske, J. E.; Cortright, R. D.; Goddard, S. A.; Sharma, S. B.; Dumesic, J. A. *J. Chem. Phys.* **1992**, *96*, 1880.

(15) Goddard, S. A.; Cortright, R. D.; Dumesic, J. A. *J. Catal.* **1992**, *137*, 186.

(16) Cortright, R. D.; Goddard, S. A.; Rekoske, J. E.; Dumesic, J. A. *J. Catal.* **1991**, *127*, 342.

(17) Zaera, F.; Janssens, T. V. W.; Öfner, H. *Surf. Sci.* **1996**, *368*, 371.

(18) Öfner, H.; Zaera, F. *J. Phys. Chem. B* **1997**, *101*, 9069.
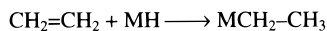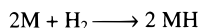
(19) Zaera, F. *Langmuir* **1996**, *12*, 88.

Scheme 1

Mechanism 1

$$2M + CH_2{=}CH_2 \longrightarrow MCH_2{-}CH_2M$$

$$H_2 + MCH_2{-}CH_2M \longrightarrow 2\,MCH_3$$

$$2\,MCH_3 \longrightarrow 2M + CH_3{-}CH_3$$

Mechanism 2

$$2M + H_2 \longrightarrow 2\,MH$$

$$CH_2{=}CH_2 + MH \longrightarrow MCH_2{-}CH_3$$

$$MH + MCH_2{-}CH_3 \longrightarrow 2M + CH_3{-}CH_3$$

Mechanism 3

$$2M + H_2 \longrightarrow 2\,MH$$

$$CH_2{=}CH_2 + MH \longrightarrow MCH_2{-}CH_3$$

$$H_2 + MCH_2{-}CH_3 \longrightarrow CH_3{-}CH_3 + MH$$

constraints that reflect consensus knowledge of the reaction, which is articulated in the form of constraints.

(i) Starting materials: H_2, $CH_2{=}CH_2$, and M.

(ii) Products: $CH_3{-}CH_3$.

(iii) Constraints: (1) Free H cannot be present; (2) every conjectured species has at most two carbon atoms; (3) every conjectured species has at most three metal sites; (4) all elements must be at full valence (the default valence for the metal site is 1); (5) the metal site must participate in all steps; and (6) reactants involve jointly at most two carbon atoms.

Note that we did not require the program to generate only mechanisms that give the overall stoichiometry of the reaction $H_2 + C_2H_4 \rightarrow C_2H_6$. This constraint can be used if we want the program to explain the steady-state kinetic data or just focus on the main route and avoid generating byproducts or unreactive intermediates. Therefore, some of the mechanisms discussed below contain conjectured species that do not react further.

On this problem formulation, MECHEM reported the three (simplest) mechanisms shown in Scheme 1, which have two conjectured species and three steps (the reversibility of steps is neglected).

As can be seen from Scheme 1, MECHEM reported σ-diadsorbed ethylene. However, one should understand that, within the framework of the above problem statement, the program cannot distinguish between σ-diadsorbed and π-coordinated ethylene. Although π-coordinated ethylene can be modeled by metallacyclopropane (where M has the valence of 2), we decided not to increase the valence of M because of chemical and combinatorial reasons. From the standpoint of combinatorics, an increase in the maximum valence of M will lead to generating many mechanisms that will be just false drops and will not carry new ideas about mechanisms. For instance, all mechanisms with σ-diadsorbed ethylene will be supplemented with similar mechanisms in which σ-diadsorbed ethylene is replaced with π-bonded ethylene. From the chemical standpoint, the reasons for not suggesting two reactive species for adsorbed ethylene are these: (1) Ethylene geometrically occupies two metal sites on the surface regardless of the nature of bonding. (2) According to Rekoske et al.,[14] bond breaking/forming calculations suggest a small energetic difference between the two forms of adsorbed ethylene. (3) Recent kinetic molecular beam studies suggest that π-bonded ethylene

is essential for ethylene hydrogenation to ethane, whereas σ-diadsorbed ethylene may be neglected.[13] Therefore, in all mechanisms reported by MECHEM, $MCH_2{-}CH_2M$ should regarded as π-ethylene.

All of the three mechanisms in Scheme 1 seem to be wrong. Let us first consider step 2 of mechanism 1:

$$H_2 + MCH_2{-}CH_2M \rightarrow 2MCH_3$$

The available experimental evidence suggests that $C{-}C$ bond scission does not occur. The current paradigm is that a $C{-}C$ bond becomes weaker as a C_2 is dehydrogenated. Slavin et al.[20] studied thermal fragmentations of ethylene on Rh(100) between 200 and 800 K by HREELS, LEED, and TDS and found that ethylidyne, which is always present in ethylene hydrogenation systems, is thermally stable up to 380 K, above which temperature $C{-}C$ bond scission does take place. The $M_3C{-}CM_2H$ species remains intact up to about 450 K. Similar data exist for thermal $C{-}C$ bond scission over Fe(111), Ni-(111), Ni(100), Ni[(5(111)$\times$(110)], Pt(111), Rh(111), Pd-(111), Pd(100), Ru(001), and Rh(100).[20] Considering that in ethylidyne and C_2H species the $C{-}C$ bond must be weaker than that in adsorbed ethylene irrespectively of the form of adsorption, step 2 in the mechanism does not seem plausible.

The hypothesis of $C{-}C$ bond scission was tested by Beebe and Yates.[21] They showed that, over Pd/Al_2O_3 at 300 K under conditions of maximum coverage of the Pd surface with $^{13}C^{13}C$-ethylidyne, the hydrogenation of $^{12}C^{12}C$-ethylene yields $^{13}C^{13}C$-ethylidyne, $^{12}C^{12}C$-ethylidyne, $^{12}C^{12}C$-ethane, and $^{13}C^{13}C$-ethane. No scrambled $^{13}C^{12}C$-products were observed in the adsorption spectra. These data, however, do not disprove the step if we consider other (platinum or nickel) surfaces.

Isotopic labeling experiments of this sort are often very informative, but sometimes it is arduous to interpret their results. The current version of the MECHEM program allows the user to formulate constraints that capture the results of isotopic labeling experiments. For example, if someone carries out the ethylene hydrogenation reaction with a mixture of $^{12}C^{12}C$-ethylene and $^{13}C^{13}C$-ethylene and does not observe $^{12}C^{13}C$-ethane in the products, there is a way to express that to the program and MECHEM will not generate mechanisms that contradict this observation.

There are also indirect theoretical arguments (e.g. ref 22) that the activation barrier for the above elementary step must be high. Therefore, we rejected this step.

In the other two mechanisms, ethylene from the gas phase reacts with the surface hydride. In the catalysis literature, this step is not discussed for several reasons: (1) Several species that are direct products of ethylene adsorption were proven capable of hydrogenating to ethane. For example, to make transmission IR spectroscopic observations of intermediates in ethylene hydrogenation, Moshin et al. had to remove ethylene from the gas phase after prior precovering of the Pt/Al_2O_3 catalyst surface. After that, the products of ethylene adsorption still yielded ethane.[23] (2) The reaction order was found to be zero or even negative in ethylene and to vary between half order and first order in hydrogen, which seem to conflict with the direct insertion of ethylene into the

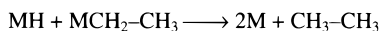(20) Slavin, A. J.; Bent, B. E.; Kao, C.-T.; Somorjai, G. A. *Surf. Sci.* **1988**, *206*, 124.

(21) Beebe, T. P., Jr.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 663.

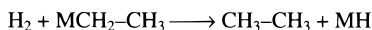(22) Shustorovich, E.; Bell, A. T. *Surf. Sci.* **1988**, *205*, 492.

(23) Moshin, S. B.; Trenary, M.; Robota, H. J. *J. Phys. Chem.* **1988**, *92*, 5229.
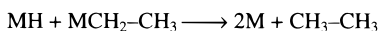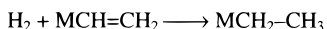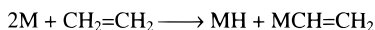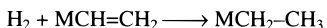
Scheme 2

Mechanism 4

$$2M + CH_2{=}CH_2 \longrightarrow MCH_2{-}CH_2M$$

$$H_2 + MCH_2{-}CH_2M \longrightarrow MH + MCH_2{-}CH_3$$

$$MH + MCH_2{-}CH_3 \longrightarrow 2M + CH_3{-}CH_3$$

Mechanism 5

$$2M + CH_2{=}CH_2 \longrightarrow MCH_2{-}CH_2M$$

$$H_2 + MCH_2{-}CH_2M \longrightarrow MH + MCH_2{-}CH_3$$

$$H_2 + MCH_2{-}CH_3 \longrightarrow CH_3{-}CH_3 + MH$$

Mechanism 6

$$2M + CH_2{=}CH_2 \longrightarrow MH + MCH{=}CH_2$$

$$H_2 + MCH{=}CH_2 \longrightarrow MCH_2{-}CH_3$$

$$MH + MCH_2{-}CH_3 \longrightarrow 2M + CH_3{-}CH_3$$

Mechanism 7

$$2M + CH_2{=}CH_2 \longrightarrow MH + MCH{=}CH_2$$

$$H_2 + MCH{=}CH_2 \longrightarrow MCH_2{-}CH_3$$

$$H_2 + MCH_2{-}CH_3 \longrightarrow CH_3{-}CH_3 + MH$$
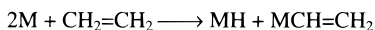
metal−hydrogen bond. Also, it was found that hydrogen must compete for metal sites on the platinum catalyst surface.[14] (3) Ethylene adsorption on the surfaces of virtually all transition metals occurs more readily than hydrogen adsorption. Thus, the yield of ethane is usually higher if the surface is first exposed to hydrogen and then to ethylene. If instead the surface is exposed first to ethylene, the yield is smaller.[24]

Therefore, we prohibited also the step

$$CH_2{=}CH_2 + MH \rightarrow MCH_2{-}CH_3$$

Because of these new constraints, mechanisms of greater complexity needed to be considered, and the result was four mechanisms containing one more (for a total of three) conjectured species. These mechanisms are shown in Scheme 2.

Mechanism 4 was first proposed by Twigg and Rideal[9] for catalysis by nickel. They suggested that H_2 is not adsorbed dissociatively on the nickel surface but rather that the adsorption is physical. Apel'baum and Temkin adopted the Twigg−Rideal mechanism for ethylene hydrogenation over a palladium membrane.[25]

Mechanism 5 is very similar, differing only in the third step. Again, nonchemisorbed hydrogen rather than metal hydride acts as a hydrogenation agent. In fact, it is surprising why Twig and Rideal suggested mechanism 4 instead of mechanism 5. They explained their reasoning thus:

"The state of adsorption of the hydrogen is not evident. It is clear, however, that it cannot be chemisorbed on neighbouring nickel atoms since chemisorbed atoms are not present in large quantity. We must infer that it is held in the molecular state in the Van der Waals layer above and between the chemisorbed molecules of ethylene."

(24) Beeck, O. *Discuss. Faraday. Soc.* **1950**, *8*, 118.
(25) Apel'baum, L. O.; Temkin, M. I. *Russ. J. Phys. Chem.* **1961**, *35*, 1012.

If so, it is not clear enough why this reasoning bears on one step of the mechanism and not on the other step.

More recently it was found that ethylene hydrogenation may occur even at 73 K over ZrO_2. Krylov and Matyshak suggest that, at this temperature, heterolytic dissociation of H_2 is impossible and Zr−H bonds are not formed.[26] Therefore, reactions in which hydrogen reacts from the gas phase or is physisorbed on the surface are not improbable. However, at this stage we rejected the step

$$H_2 + CH_2M{-}CH_2M \rightarrow HM + CH_3{-}CH_2M$$
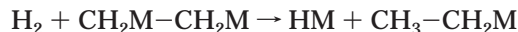
The other mechanisms (6 and 7) suggest the formation of the surface vinyl species by the oxidative addition of an ethylene H−C bond to the metal. The possibility of this step was considered by Rideal[27] and may explain H/D exchange in ethylene on the metal surface. Although ethylene adsorption on the surface is a more likely step, the oxidative addition of this sort cannot be a priori excluded. According to van Broekhoven and Ponec,[28] C−H bonds in olefins are rather reactive, but the oxidative addition should not occur because competitive ethylene adsorption occurs more readily and only after adsorption does C−H bond scission take place. Therefore, we prohibited the step

$$C_2H_4 + 2M \rightarrow MH + MCH{=}CH_2$$

in further runs and began to explore more complex mechanisms. At the next stage, the program reported the four mechanisms shown in Scheme 3.

Mechanisms 8 and 9 contain a step that is similar to step 2 in mechanism 2 but which is allowed by symmetry rules. The other criticisms of this step remain in force, and thus we will consider it implausible:

$$CH_2{=}CH_2 + MH \rightarrow H_2 + MCH{=}CH_2$$
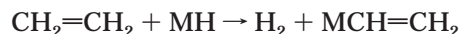
We note, however, that Basset et al. recently proposed similar steps for metathesis[29] and room-temperature hydrogenolysis[30] of simple alkanes. Also, C−H bonds in olefins are more reactive than those in alkanes. However, in the case of olefins the formation of a π-complex is preferable. Although mechanisms 8 and 9 can be excluded from consideration here, in the general case this route of ethylene activation should be tested experimentally.

Mechanism 10 is the Horiuti−Polanyi mechanism.[7] Mechanism 11 is a strange hybrid of the Horiuti−Polanyi and Twigg−Rideal mechanisms, which does not seem very plausible.

There is a trend in heterogeneous catalysis to disregard Eley−Rideal mechanisms, although it is not always possible to rule them out. MECHEM offers the user the option of explicitly rejecting Eley−Rideal mechanisms from the start or at any stage of the interaction. Here, if the user prohibited such mechanisms, the program would reject all mechanisms shown in Schemes 1−3 except the Horiuti−Polanyi mechanism 10. That is, the Horiuti−Polanyi mechanism is the unique simplest non-Eley−Rideal mechanism. This is probably a psychological explanation of the consensus among heterogeneous chem-

(26) Krylov, O. V.; Matyshak, V. A. *Intermediates in Heterogeneous Catalysis*; Nauka: Moscow, 1996; in Russian.
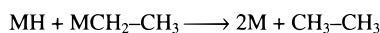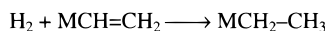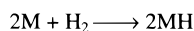(27) Rideal, E. K. *Concepts in Catalysis*; Academic Press: New York, 1968.
(28) van Broekhoven, E. H.; Ponec, V. *Prog. Surf. Sci.* **1985**, *19*, 351.
(29) Corker, J.; Lefebvre, F.; Lecuyer, C.; Dufaud, V.; Quignard, F.; Choplin, A.; Evans, J.; Basset, J.-M. *Science* **1996**, *271*, 966.
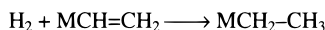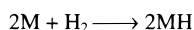(30) Vidal, V.; Theolier, A.; Thivolle-Cazat, J.; Basset, J.-M. *Science* **1997**, *276*, 99.
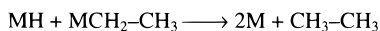
Scheme 3

Mechanism 8

$$2M + H_2 \longrightarrow 2MH$$
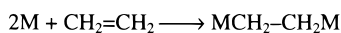
$$CH_2{=}CH_2 + MH \longrightarrow H_2 + MCH{=}CH_2$$

$$H_2 + MCH{=}CH_2 \longrightarrow MCH_2{-}CH_3$$

$$MH + MCH_2{-}CH_3 \longrightarrow 2M + CH_3{-}CH_3$$

Mechanism 9

$$2M + H_2 \longrightarrow 2MH$$

$$CH_2{=}CH_2 + MH \longrightarrow H_2 + MCH{=}CH_2$$

$$H_2 + MCH{=}CH_2 \longrightarrow MCH_2{-}CH_3$$

$$H_2 + MCH_2{-}CH_3 \longrightarrow CH_3{-}CH_3 + MH$$

Mechanism 10

$$2M + CH_2{=}CH_2 \longrightarrow MCH_2{-}CH_2M$$

$$2M + H_2 \longrightarrow 2MH$$

$$MCH_2{-}CH_2M + MH \longrightarrow 2M + MCH_2{-}CH_3$$

$$MH + MCH_2{-}CH_3 \longrightarrow 2M + CH_3{-}CH_3$$

Mechanism 11

$$2M + CH_2{=}CH_2 \longrightarrow MCH_2{-}CH_2M$$

$$2M + H_2 \longrightarrow 2MH$$

$$MCH_2{-}CH_2M + MH \longrightarrow 2M + MCH_2{-}CH_3$$

$$H_2 + MCH_2{-}CH_3 \longrightarrow CH_3{-}CH_3 + MH$$
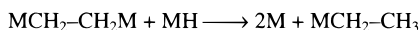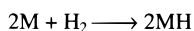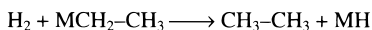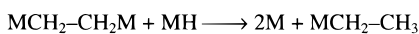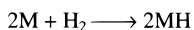
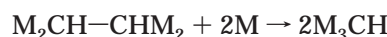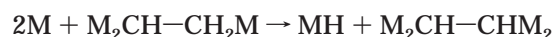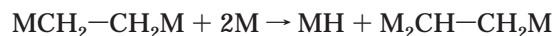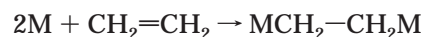ists that the Horiuti−Polanyi mechanism (or its variants) is the most plausible.

Step by step, the user of MECHEM is able to articulate more and more constraints and to arrive at increasingly complex mechanisms which tend to become more numerous. We are unable to discuss all mechanisms found by the interactive search because of the lack of space and because there too many of them sometimes differing only slightly. So we consider here only the more interesting among them.

Above we prohibited step 2 of mechanism 1, but we have to mention that in general C−C bond scission is not impossible. The scission of a C−C bond occupies an essential role in ethane hydrogenolysis[31−33] and may take place in ethylene hydrogenation if the temperature and catalyst are appropriate. According to Goddard et al.,[32] the extent to which ethane is dehydrogenated before the C−C dissociates is unclear. According to bond-order-conservation calculations,[22] the activation energy of C−C bond scission steps is a complex function of the extent of C_2 hydrogenation and the symmetry of the molecule. The higher the symmetry of a C_2 species and the lower the degree of dehydrogenation, the weaker is a C−C bond. Experimental results provide scant insight into this pattern. Therefore, it is quite possible that, under appropriate conditions, some surfaces will form ethyl, which will dissociate with C−C bond rupture, as reported

by Gudkov et al.[33] Other interesting results of C−C bond scission over various surfaces are discussed in the review article by Zaera.[34]

At first sight, C−C bond cleavage followed by its restoration looks unreasonable, but mechanistic chemistry contains many precedents, in which the "one-step-back−two-steps-forward" principle works better than just one step forward. Also, C−C bond cleavage may be a side route of the ethylene hydrogenation reaction.

An example of a hypothetical mechanism with C−C bond cleavage is as follows:

$$2M + CH_2{=}CH_2 \rightarrow MCH_2{-}CH_2M$$

$$2M + H_2 \rightarrow 2MH$$

$$MCH_2{-}CH_2M + 2M \rightarrow MH + M_2CH{-}CH_2M$$

$$2M + M_2CH{-}CH_2M \rightarrow MH + M_2CH{-}CHM_2$$

$$M_2CH{-}CHM_2 + 2M \rightarrow 2M_3CH$$

$$MH + M_3CH \rightarrow 2M + M_2CH_2$$

$$MH + M_2CH_2 \rightarrow 2M + MCH_3$$

$$2MCH_3 \rightarrow 2M + CH_3{-}CH_3$$
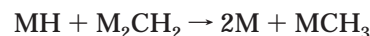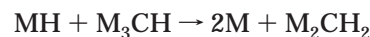
The formation of the doubly diadsorbed species $M_2CH{-}CHM_2$ and its participation in ethylene hydrogenation was proposed by Beeck,[24] who studied the effect of ethylene self-hydrogenation. On the surface of Cu, Pt, Ni, or W, adsorption of ethylene is accompanied by the formation of small amounts of ethane at the expense of $M_2CH{-}CHM_2$ formation:

$$2C_2H_4 + \langle Surface \rangle \rightarrow C_2H_6 + C_2H_2 {\cdot} \langle Surface \rangle$$
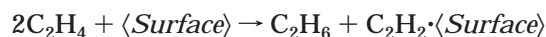
Kesmodel et al.[35] documented the formation of the strongly adsorbed species ethylidyne and ethylidene observed in LEED studies. More recently, Zaera and Somorjai[36] proposed a mechanism in which ethylidyne species on Pt(111) play the role of the hydrogen-transfer agent/catalyst on the surface covered with ethylidyne and ethylidene complexes. Evidence in favor of this mechanism is the fact that ethylene hydrogenation occurs readily on Pt(111) surfaces both when covered and not covered with an ethylidyne overlayer. [14]C radiotracer methods showed that the same ethylidyne species are present on the single-crystal surface before and after the reaction. Ethylidyne is readily formed upon ethylene adsorption. However, Davis et al.[37] showed that the hydrogenation of ethylidyne on Pt(111) is several orders of magnitude slower than the hydrogenation of ethylene to ethane. Despite this finding, Zaera and Somorjai argued that conditions in laboratory reactors and real reactors are different. In mechanistic studies, single-crystal surfaces are clean and the reaction is often carried out in ultrahigh vacuum. In real reactors, the surface is covered with a carbonaceous overlayer and reactant pressures are several atmospheres.

Beebe and Yates employed in situ IR spectroscopy to monitor the behavior of surface species on Pd/Al$_2$O$_3$ and found that the role of ethylidyne in hydrogenation is not
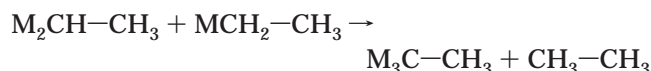
(31) Sinfelt, J. H. *Adv. Catal.* **1973**, *23*, 91.

(32) Goddard, S. A.; Amiridis, M. D.; Rekovske, J. E.; Cardona-Martinez, N.; Dumesic, J. A. *J. Catal.* **1989**, *117*, 155.

(33) Gudkov, B. S.; Guczi, L.; Tétényi, P. *J. Catal.* **1982**, *74*, 207.

(34) Zaera, F. *Chem. Rev.* **1995**, *95*, 2651.

(35) Kesmodel, L. L.; Dubois, L. H.; Somorjai, G. A. *Chem. Phys. Lett.* **1978**, *56*, 267.

(36) Zaera, F.; Somorjai, G. A. *J. Am. Chem. Soc.* **1984**, *106*, 2288.

(37) Davis, S. M.; Zaera, F.; Gordon, B. E.; Somorjai, G. A. *J. Catal.* **1985**, *92*, 240.
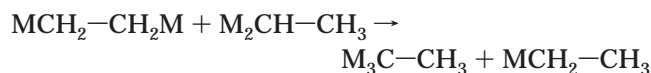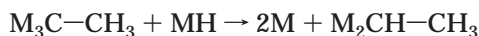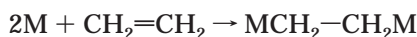
essential in the case of catalysis by supported palladium.[21] Under high hydrogen pressures, ethylidyne has not been formed. The kinetic study with ^{13}C labels on ethylidyne by the same authors showed that ethylidyne formation and hydrogenation are two to three orders of magnitude slower than the rate of ethylene formation on the metal surface, suggesting that ethylidyne is a spectator species. However, more recent transmission IR spectroscopic studies of Beebe and Yates on different alumina-supported metals showed that, at 300 K, Pt and Rh exhibit IR band intensities 2−3 times greater than those of Pd and Ru.[38] In our opinion, these findings suggest that the roles of ethylidyne in hydrogenation over Pt and Pd may be different.

MECHEM generated the mechanism proposed by Zaera and Somorjai[36] when the maximum number of carbon atoms per step was increased to four:

$$2M + CH_2{=}CH_2 \rightarrow MCH_2{-}CH_2M$$

$$H_2 + 2M \rightarrow 2MH$$

$$M_3C{-}CH_3 + MH \rightarrow 2M + M_2CH{-}CH_3$$

$$MCH_2{-}CH_2M + M_2CH{-}CH_3 \rightarrow$$
$$M_3C{-}CH_3 + MCH_2{-}CH_3$$

$$M_2CH{-}CH_3 + MCH_2{-}CH_3 \rightarrow$$
$$M_3C{-}CH_3 + CH_3{-}CH_3$$

The idea of hydrogen-transfer catalysis by $M_3C{-}CH_3$ on Pt(111) was recently tested by Cremer et al.[39] using infrared−visible sum frequency generation correlated with reaction kinetics. The main findings of the study were as follows: Ethylidyne and di-σ-adsorbed ethylene compete for the surface sites, but their concentrations do not correlate with the hydrogenation rates. These two species were concluded to be spectators. By contrast, π-bonded ethylene does not compete for sites and is always present regardless of the ethylidyne concentration. The concentration of π-bonded ethylene may be only 4% of the monolayer, which suggests an activity much higher than that of other species. The relative hydrogenation rates of the adsorbed species can be arranged in the following series:

π-bonded ethylene $\gg$ di-σ-adsorbed ethylene $\gg$
ethylidyne

Zaera et al. also revisited the problem of π-bonded ethylene reactivity in ethylene hydrogenation and a number of other reactions occurring in the same system and under the same conditions.[17,18] The main outcome from their studies relevant to our discussion here is that ethylidyne is formed via ethylidene, the main role of which consists of blocking the surface sites, while the main route to ethane involves weak adsorption of ethylene (π-bonding of ethylene) and further stepwise hydrogenation to ethyl and then to ethane. That is, recent findings by Somorjai and Zaera and their co-workers[17,18,39] suggest that ethane is produced by the Horiuti−Polanyi mechanism complicated by several steps of blocking the surface with ethylidyne species.

In the Zaera−Somorjai mechanism,[36] the key step is the transfer of carbon-bonded hydrogen from one surface species to another:
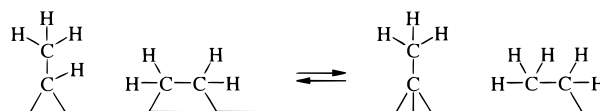
Hydrogen-transfer steps such as this one were first proposed by Thompson and Webb.[40] Although hydrogen-transfer steps are poorly studied, our experience with interactive searches reveals their possibly critical importance in the heterogeneous catalysis of hydrocarbon conversions. The reason is that the number of prima facie plausible hypothetical mechanisms becomes much higher, because of combinatorics, when such steps are allowed than when they are excluded from consideration. We have observed this phenomenon repeatedly on reactions of these types: olefin hydrogenation, alkane hydrogenolysis, dehydrogenation, metathesis, and Fischer−Tropsch synthesis.[41] A similar problem arises in the case of alkyl-transfer steps. Therefore, experiments or quantum-chemical calculations to explicitly test the likelihood of hydrogen-transfer steps would be very useful, because if such steps could be excluded, it would greatly reduce the density of plausible mechanistic hypotheses.

It is noteworthy that even though ethylene hydrogenation has been studied intensively by generations of surface scientists and kineticists, Zaera[19] regards its mechanism as "far from settled". We suggest that our proposed method can enhance the goal of its elucidation, as well as that of the vast majority of less well-studied reactions, although some important questions remain outside the scope of the current approach (e.g., "intimate" details of reactant adsorption on the surface, mutual effects of adsorbed species on their reactivities and the energetic nonuniformity of the reactive surface, reversibility of steps, the presence of fast equilibria, etc.).

Summary of the Interactive Method of Mechanistic Study

The above historically oriented emulation shows that the interactive use of MECHEM leads to comprehensively generating all mechanisms of ethylene hydrogenation ever proposed by researchers. Perhaps more interestingly, other mechanisms without direct precedents in the literature were found, and these contain elementary steps that are analogous to steps from the mechanisms of other reactions (e.g., ethane hydrogenolysis, alkane metathesis, etc.).

The mechanistic model-building strategy that we propose, and which we ourselves are carrying out in ongoing work elsewhere, is depicted schematically in Scheme 4. We can summarize how this general scheme has been applied in this article (with a historical emphasis) to the case study of ethylene hydrogenation:

(i) Express constraints to the program based on articulating preliminary knowledge and other general considerations. Arrive at mechanisms 1−3.
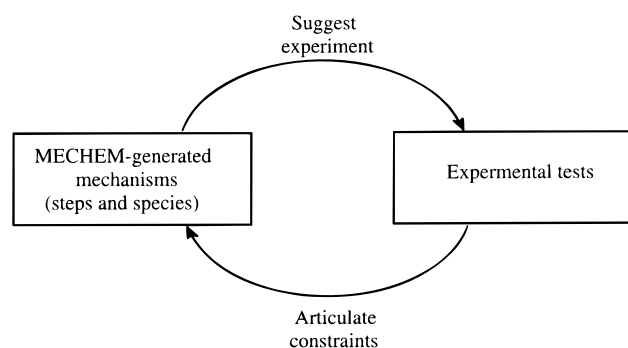
(ii) Examine the steps appearing in these mechanisms. Test the possibility of steps $H_2 + MCH_2{-}CH_2M \rightarrow 2MCH_3$ and $CH_2{=}CH_2 + MH \rightarrow MCH_2{-}CH_3$ (e.g., by designing experiments to check whether ethylene can react from the gas phase). If ethylene is always adsorbed on the surface before being hydrogenated, formulate new constraints (e.g., *ethylene cannot react unless it forms a complex with the metal; a C−C bond cannot be cleaved in the reaction with H_2*).

(38) Beebe, T. P., Jr.; Yates, J. T., Jr. *J. Phys. Chem.* **1987**, *91*, 257.
(39) Cremer, P. S.; Su, X.; Shen, Y. R.; Somorjai, G. A. *J. Phys. Chem.* **1996**, *100*, 16302.

(40) Thompson, S. J.; Webb, G. *J. Chem. Soc., Chem. Commun.* **1976**, 526.
(41) Valdés-Pérez, R. E.; Zeigarnik, A. V. Unpublished.

Scheme 4

Suggest
experiment

```
┌─────────────────────┐                    ┌──────────────────────┐
│  MECHEM-generated   │                    │                      │
│     mechanisms      │                    │  Experimental tests  │
│  (steps and species)│                    │                      │
└─────────────────────┘                    └──────────────────────┘
```

Articulate
constraints

(iii) Generate new mechanisms 4−7. Design experiments to monitor H_2 behavior at the initial stages. Suppose the hypothesis of gas-phase hydrogen participation is rejected. Then, test the possibility of the step $C_2H_4 + 2M \rightarrow MH + MCH{=}CH_2$. Suppose this step can be ruled out. Then, articulate new constraints that prohibit this specific step or, if possible, a more general class of steps of which the former step is a member.

(iv) Generate new mechanisms 8−11. Design experiments to test the possibility of the step $CH_2{=}CH_2 + MH \rightarrow H_2 + MCH{=}CH_2$. Suppose this step can be excluded. Then, express new constraints to prohibit this step or a more general class.

(v) Generate new mechanisms. Design experiments to test the likelihood of hydrogen-transfer steps or the role of ethylidene and ethylidyne species.

(vi) Generate new mechanisms. Design experiments to test the possibility of C−C bond scission.

The proposed method of interactive search for multiple working hypotheses has been illustrated here by reference to a well-known catalytic reaction and with a historical flavor. However, other work outside the scope of this article has employed this exact method in homogeneous catalysis, specifically the palladium-catalyzed synthesis of methyl phenylpropiolate:[6]

$$PhC{\equiv}CH + CO + MeOH + 2NaOAc + 2CuCl_2 \rightarrow$$
$$PhC{\equiv}CCOOMe + 2AcOH + 2NaCl + 2CuCl$$
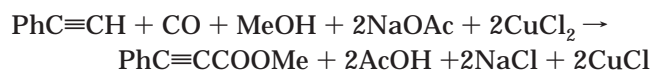
We formulated 41 mechanistic hypotheses with the assistance of MECHEM and a separate computer program, ChemNet.[4,6] In this case, ChemNet's role was to initially generate a large reaction network of possible steps that reflected our best estimation of the *types* of elementary step that could occur; any step that MECHEM generated that was absent from this large reaction network was then prohibited. To discriminate among these 41 multiple working hypotheses, we chose a very informative experiment based on kinetic isotope effects. This experiment led to rejecting 32 out of 41 mechanisms. Several others were rejected by different experiments. All of the remaining mechanisms can be considered working hypotheses, in (parental) relation to which, we, following Chamberlin's prescription, regard with equal affection.

Conclusion

We have shown that a chemist/program interaction, which builds on experimental evidence in the form of constraints, can systematically generate all mechanisms of ethylene hydrogenation that have ever been proposed in the literature. (MECHEM also generates mechanisms that lack direct precedent but which borrow elementary steps from the published mechanisms of other reactions such as ethane hydrogenolysis, alkane metathesis, and the like.) This result, which uses ethylene hydrogenation as a vehicle, supports our main aim: to affirm that the method of interactive search for multiple working hypotheses is an effective new methodology but with century-old roots in an idea which modern computers have made newly practical.

Besides the general advantages already claimed by Chamberlin, the proposed methodology has these advantages over current practice: (1) plausible mechanistic ideas are unlikely to be overlooked, or at least they will need to be explicitly rejected; (2) the reasoning that leads to working hypotheses becomes explicit and replicable; (3) the bias of received views, or of uncertain analogies with similar reactions, can be minimized, or at least controlled; and (4) experiments can be designed to be highly discriminating among a larger set of hypotheses, which are assembled at an early stage of a study.