Computer-assisted generation of chemical reaction networks. Applications in mechanistic studies of organometallic catalysis

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The ChemNet computer program designed for mechanistic studies of organic reactions occurring in solutions of metal complexes and on the surface of heterogeneous catalysts is proposed. The use of the program is illustrated by applications to catalyzed homogeneous hydrocarboxylation and hydroformylation of ethylene and heterogeneous hydrogenolysis of ethane.

Key words: reaction mechanisms, application of computers, ChemNet program, ethane hydrogenolysis, ethylene hydrocarboxylation, ethylene hydroformylation, organometallic catalysis

Our recent studies on reaction mechanisms are based on the following three ideas: (1) any hypothetical mechanism cannot be proven but can only be rejected; (2) consideration of many hypothetical mechanisms for each particular reaction leads to more reliable reaction mechanisms and kinetic models based on them while lowering time and expenses for experimental studies; (3) hypothetical mechanisms can be proposed most efficiently using computer programs, which help the researcher (but do not replace him!). Computer programs permit the formulation and protocol of the initial data that are used to advance the hypotheses. A set of hypothetical mechanisms obtained using computer programs is complete within the specified set of constraints. Various aspects of this methodology[1–12] and related computer software[6,8–12] have been considered in our publications. Some philosophical problems faced by a researcher in studies of reaction mechanisms were noted in a popular monograph,[13] while some methodological aspects were described in a textbook.[14]

This paper is devoted to the computer program ChemNet, which we developed and used to study the mechanisms of catalytic reactions.[6,8] In a recent publication[15] we demonstrated that several programs can be used together to advance mechanistic hypotheses on reaction mechanisms. In particular, one program (ChemNet) was used to generate a reaction network (a set of elementary steps allowed by the given constraints), and another program (MECHEM) was employed to find the simplest mechanisms. The elementary steps found at the first stage served as input for MECHEM. In an experimental study of oxidative carbonylation of phenylacetylene catalyzed by Pd^{II} and Cu^{I} complexes[12,16,17]

$$\mathrm{PhC{\equiv}CH + CO + MeOH + 2\ NaOAc + 2\ CuCl_2} \rightarrow$$
$$\rightarrow \mathrm{PhC{\equiv}CCOOMe + 2\ AcOH + 2\ NaCl + 2\ CuCl},$$

we proposed, with the assistance of a computer, 41 hypothetical mechanisms. Using these mechanisms, we were able to design a target-directed experiment based on the measurement of the kinetic isotope effect. Of the 41 mechanisms, 32 were rejected based on this experiment[12,16]; we intended to verify the remaining mechanisms by other methods.

No publications devoted to the ChemNet program proper are available. The changes introduced recently into the program stimulated us to write this paper.

Description of the ChemNet program

The program uses initial data of three types, namely, starting compounds, transforms, and constraints. The program cannot run without any of these elements. The starting compounds are needed to launch the program. The transforms serve for converting compounds into other ones. The constraints are required to stop the program after arriving at a plausible solution.

The starting compounds are specified as structural formulas. Unlike many other programs, ChemNet allows one to specify not only traditional molecules in which one bond links two atoms but also η^n-bonds as well as radicals, carbenes, ions, and substances with any set of atoms.

Compounds appear on the monitor display as structural formulas; however, the internal representation of compounds is much more complex. It resembles the description of objects employed in databases and consists of several string and numerical variables. Each variable is decoded by the program when this information is required. This structure is convenient for the numerous checks performed by the program in order to find out whether or not a substance was found before

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and whether it contains a specified substructure. In particular, the program stores the following data:

1. The number of atoms in a molecule.
2. Description of each atom:
   — the unique name from the Periodic Table,
   — the charge,
   — the number of unpaired electrons (radical signs).
3. Additional characteristics for metal atoms:
   — the oxidation number,
   — the coordination number,
   — the number of valence electrons.
4. The description of bonds as triples (the first atom, the second atom, the bond multiplicity); multicentered bonds (*e.g.*, bonds in π-complexes) are described by several triples.

Each compound should be connected (*i.e.*, it cannot consist of separate parts). Transforms and the steps generated by the program are described in a similar way.

Transforms in ChemNet are the prototypes of bimolecular and unimolecular reactions. Several reactions of the same type can be described as a single transform. For example, the addition of any complex containing an M—X fragment to a double bond of any molecule containing this type of bond can be represented as follows:

$$\text{M—X} + \text{C=C} \rightarrow \text{M—C—C—X}.$$

Unlike reaction, transform does not necessarily indicate atoms that are not involved in the transformation core and that are attached to C, M, and X, although the M and X atoms always need to be identified. For example, it can be specified that M = Pt or Pd, and X = H or Cl. If such a transformation is specified, the program will search for all the pairs of molecules (either introduced as starting compounds or generated by the program at an earlier stage) such that one molecule contains an M—X fragment (Pt—H, Pt—Cl, Pd—Cl, or Pd—H) and the other one has a C=C bond (ethylene, vinyl fragment, *etc.*). The transform affects each of these pairs by converting the molecules constituting the pair into other molecules. As a result, a reaction (elementary step) is formed. For example, if the above-mentioned transform has been specified and the program has found a pair consisting of $PdCl_2$ and C_2H_4 among the molecules, the transform makes the step

$$\text{Cl}\mathbf{Pd}\text{—}\mathbf{Cl} + \text{H}_2\mathbf{C}{=}\mathbf{C}\text{H}_2 \rightarrow \text{Cl}\mathbf{Pd}\text{—H}_2\mathbf{C}\text{—}\mathbf{C}\text{H}_2\text{—}\mathbf{Cl}.$$

If the resulting compound $ClPdCH_2CH_2Cl$ has not been obtained in previous steps, it supplements the list of compounds that are subjected to transforms.

Transforms describe the typical features of a change but the degree of detailing is determined by a user. The more detailed the transform, the smaller the number of compounds (or pairs of compounds) to which this transformation is applicable. For example, the two elementary processes

$$\text{M—C} + \text{C}{\equiv}\text{O} \rightarrow \text{M—C(O)—C}$$
$$\text{M—C}{\equiv}\text{C} + \text{C}{\equiv}\text{O} \rightarrow \text{M—C(O)—C}{\equiv}\text{C}$$

describe the same reaction but the latter transformation is more detailed. The difference is that in the former case, the program would "insert" CO into all compounds containing an M—C bond, whereas in the latter case, it would choose only molecules containing M—C≡C fragments.

The number of elementary steps generated by a single transform can differ substantially. On the one hand, the "generating capacity" of a transform depends on the constraints applied, which are discussed below. On the other hand, there are objective factors that allow one to judge what the consequences of using one or another transform are. For example, when a transform is defined without writing atoms in explicit form but using characters such as M, R, and X followed by introduction of various "substituents" (for example, M = Pt, Pd, Ru), it should be expected that the number of possible steps based on this transform can unwarrantedly increase.

The number of the corresponding steps in the reaction network correlates with the "degree of detailing" of a transform. Consideration of only those atoms between which the bond redistribution takes place and the bonds themselves corresponds to the least detailed transform and, hence, a larger number of implausible steps can appear; however, this ensures a larger degree of novelty. The other extreme position is inclusion of all the possible details in the transform. In the limiting case, the difference between a transform and a step, which is the goal in the generation of a reaction network, can be lost.

The degree of detailing of a transform can be characterized by a parameter, which we call the Y factor. This factor is defined as the ratio of the number of bonds that are cleaved or formed to the total number of bonds (that are either cleaved, or formed, or remain intact). For example, for the M—C + C≡O → M—C(=O)—C transform (insertion of CO), the total number of bonds is 6 (taking the multiplicity of the triple bond into account). Since four bonds change (the M—C bond is cleaved, the C≡O bond changes its order, and two bonds with the CO carbon atom are formed), the Y factor is 4/6 (*i.e.*, 2/3). In the case of the M—C≡C + C≡O → M—C(O)—C≡C transform, the total number of bonds is 9 (a triple bond has been added), while the number of bonds being changed has remained the same; thus, the Y factor is 4/9. The larger the Y factor, the less detailed the transform and the greater the number of steps it generates. In the limiting case, the Y factor is equal to unity (for example, M—C + C → M—C—C).

Yet another factor (which we call the X factor) is related to the degree of unsaturation of atoms involved in the transform. The program conventionally specifies the "normal" valence for each sort of atoms (for example, the normal valence of carbon is 4, that for oxygen is 2, *etc.*). The X factor is equal to the sum of the valences of the atoms involved in the transform divided by the sum of their normal valences. Thus, this factor shows the average number of neighbors of an atom that have been omitted. The greater the X factor, the more detailed the transform.

Having calculated the X and Y factors, the program suggests to the user that a transform should better be more detailed or, conversely, less detailed. However, there is no need to strictly follow this advice. If necessary, it can be completely ignored.

Constraints. The third type of initial data includes constraints (or selection rules). The constraints fulfill two functions: they rule out the formation of false branches of the reaction tree and create conditions for program termination. The program allows the following constraints:

— The maximum number of atoms in a generated molecule and the maximum number of atoms of any sort (C, H, O, ...). If no constraint of this type is imposed, the program may require manual termination. In fact, if a transform of the M—C + C≡O → M—C(O)—C type is considered but no maximum number of atoms or maximum number of carbon (or oxygen) atoms is specified, the program would infinitely "polymerize" CO to give $M-[C(O)]_n-C$.

— The user specifies the maximum number of valence electrons, the maximum coordination number, and the range of possible oxidation states for each metal atom. If necessary, the user can use the values recommended based on published data. However, one should be aware of the fact that, in this case, constraints might be too weak.

— The molecularity of transforms and elementary reactions should not exceed two. This constraint is unchangeable. In essence, it reflects a compromise between chemical and combinatorial realities. If the user attempts to enter a transform with three reacting or forming fragments, the command will not be executed.

— If the user foresees that the specified transforms would cause the program to generate undesirable molecules, some specific fragment (substructure) can be forbidden. Before adding a new substance into a file, the program makes sure that the compound does not contain the forbidden substructure. If the whole molecule rather than a fragment is undesirable, it also can be forbidden. As the program runs, it shows every new compound on the display. The user is able to stop the program at any time and forbid a compound or a fragment.

— Some constraints are related to the number and size of charged atoms in a molecule (for example, the number of charged atoms in one molecule should not exceed some specified value). Similar constraints will be introduced for radical reactions.

In addition, the program checks automatically the balance for each type of atoms, charges, and unpaired electrons (in the case of radical reactions) for each transform.

The idea of algorithm. The program starts its operation by attempting to use the first transform; for this purpose, it selects pairs of compounds containing the fragments described in the transform from the set of compounds specified by the user. If the program succeeds in finding such compounds, it then records the corresponding elementary step and new compounds that are formed. Then the program looks through the augmented list of compounds and attempts again to apply the transform. At a certain point, it turns out that new compounds no longer appear with the given constraints. Then the program passes to the second transform and continues the whole procedure; then it passes to the third, the fourth transform, *etc.* After that, the program returns to the first transform, and the search starts once again (based on the augmented list of compounds). If the program has run through all of the transforms but has failed to form new elementary steps, it stops. Every new compound generated by the program is tested against the constraints and rejected if necessary. In the latter case, the corresponding elementary step is not included in the list either.

Naturally, not any transform is applicable to an arbitrary pair of compounds. Thus transform T can be applied to a pair of S1 and S2 if

— S1 and S2 contain all the fragments specified in T as "starting compounds."

— The products formed comply with the constraints.

— The products differ from S1 and S2; *i.e.*, degenerate reactions are excluded, but one of the products may be the same as either S1 or S2.

Analogous conditions should be met if a transform describes a unimolecular reaction.

Processing of the results. The results obtained can be examined and edited. For example, if some undesirable intermediates or products were still produced during the generation of the reaction network, the user can remove them. The reaction network should be analyzed for connectivity. The branches of the reaction network that originate from the removed compound should also be eliminated.

Factors retarding the program. The quality of the results obtained depends on the user's skill and knowledge because the user is the main source of knowledge employed in the program. In addition, the user should have an idea of the "combinatorial consequences" of each action. In particular, one should realize that the following factors (most of which are obvious) retard the program operation and make the resulting reaction network difficult to analyze:

(1) the absence of rather strict constraints on the maximum number of atoms in the resulting molecules;

(2) the use of too general transforms;

(3) the use of "substituents" in the formulation of transforms; the increase in the resulting number of steps is often out of proportion to the number of substituents;

(4) the use of complex forbidden substructures or a large number of substructures (in this case, the program would spend too much time verifying the presence of these substructures in each new compound);

(5) the use of many transforms.

It is most important to understand that the enormous number of operations executed by the program is due to counting and searching for variants; therefore, the time it takes increases out of proportion to the dimension of the problem.

In most cases, when working with the program, one has to compromise the desire to embrace as many steps as possible (this improves the chance for finding new mechanisms) and the desire to obtain these steps over a reasonably short time. On the other hand, the use of a too detailed transform would barely provide any new interesting result. The contradiction between "novelty" and "combinatories" is natural; anyway, the capacity of any method is limited. A user can perform computer experiments by varying the degree of detailing in the specification of transforms. By analyzing the resulting reaction network, one can attain the optimum degree of detailing in the formulation of transforms with the constraints chosen.

The library of transforms. The transforms and constraints employed by a user reflect the cumulative knowledge on the reaction under study, which can be translated into the language of structural transforms employed by ChemNet. This knowledge could be obtained by preliminary experiments, derived from theoretical statements, or taken from the literature. A user can rely on intuition, which is often the case both with and without computers. Indeed, the descriptions of mechanisms presented in scientific papers are often more detailed than the reliable data available on these mechanisms.

A reference library of transforms based on analysis of published data (mainly monographs and reviews on metal complex catalysis and organometallic chemistry) is the latest addition to ChemNet. The reference library of ChemNet is provided with minimum search capabilities needed to select necessary transforms. This is attained using filters, which restrict the set of records from the library proposed for selection. The features to be sought for, such as cleavage and/or formation of the desired bonds, can be specified in the filters; steps involving a metal center, radicals, or ions can be chosen. The selected transforms may (and even need to) be edited.

Since the species adsorbed on the surface of a solid catalyst actually participates in the same chemical transformations as fragments of metal complexes, it can be assumed that the transform library developed for homogeneous metal-complex catalysis is also applicable to heterogeneous catalysis.

Examples of application of the program

Hydrocarboxylation and hydroformylation of ethylene (homogeneous catalysis). Among other examples, the program was tested using the set of reactions for ethylene carbonylation. Here, we did not mean to obtain the full reaction network. The transforms formulated for this problem are presented below.

1. $\mathrm{Co^{I}{-}H + C{=}C \rightarrow Co^{I}{-}C{-}C{-}H}$
2. $\mathrm{Co^{0}{-}Co^{0} + H{-}H \rightarrow Co^{I}{-}H + Co^{I}{-}H}$
3. $\mathrm{R^{1}{-}CH{-}Co^{I}{=}C{=}O \rightarrow Co^{I}{-}C({=}O){-}CH{-}R^{1}}$
   $\mathrm{R^{1} = C, H, O}$
4. $\mathrm{Co^{0} + C{\equiv}O \rightarrow Co^{0}{=}C{=}O}$
5. $\mathrm{Co^{0} + Co^{0} \rightarrow Co^{0}{-}Co^{0}}$
6. $\mathrm{Co^{I}{-}C{=}O + C{=}C \rightarrow Co^{I}{-}C{-}C{-}C{=}O}$
7. $\mathrm{Co^{I}{-}C{=}O + H{-}O{-}H \rightarrow O{=}C{-}OH + Co^{I}{-}H}$
8. $\mathrm{Co^{0}{-}Co^{0} + C{=}C \rightarrow Co^{I}{-}C{-}C{-}Co^{I}}$
9. $\mathrm{Co^{I} + C{\equiv}O \rightarrow Co^{I}{=}C{=}O}$
10. $\mathrm{O{-}Co^{I}{=}C{=}O \rightarrow Co^{I}{-}C({=}O){-}O}$
11. $\mathrm{Co^{0}{-}Co^{0} + H{-}O{-}H \rightarrow Co^{I}{-}O{-}H + Co^{I}{-}H}$
12. $\mathrm{Co^{I}{-}C + H{-}H \rightarrow Co^{I}{-}H + C{-}H}$
13. $\mathrm{Co^{I}{-}H + Co^{I}{-}H \rightarrow Co^{0}{-}Co^{0} + H{-}H}$
14. $\mathrm{Co^{I}{-}O{-}H + Co^{I}{-}H \rightarrow Co^{0}{-}Co^{0} + H{-}O{-}H}$
15. $\mathrm{Co^{I}{-}C + Co^{I}{-}H \rightarrow Co^{0}{-}Co^{0} + H{-}C}$

The starting compounds introduced in the program were $\mathrm{Co^{0}}$, $\mathrm{C_2H_4}$, $\mathrm{H_2}$, $\mathrm{H_2O}$, and CO. The constraints were as follows: the maximum number of atoms in generated molecules was 18, the maximum number of carbon atoms was 6, the maximum number of oxygens was 4, that for cobalt atoms was 2, and the maximum coordination number of cobalt was 2. The number of valence electrons was not controlled and the oxidation numbers were controlled only through transforms. The generation yielded 187 reactions (five of them were later removed, see below) and 49 new compounds.*

The generation of the reaction network yielded virtually all of the products identified for hydroformylation and hydrocarboxylation of ethylene, namely, ethane, propionaldehyde, propionic acid, diethyl ketone, and succinic acid. Each product could form *via* several routes

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* The complete reaction networks for the processes considered here are available from the authors.

that are present in the reaction network. For example, the program found the following mechanisms for the formation of ethane, which is a typical side product in this type of process.[18]

Mechanism I

1. $Co_2(CO)_n + C_2H_4 \rightarrow$
$\rightarrow (CO)_{n-m}CoCH_2CH_2Co(CO)_m$

2. $(CO)_{n-m}CoCH_2CH_2Co(CO)_m + H_2 \rightarrow$
$\rightarrow (CO)_{n-m}CoCH_2Me + HCo(CO)_m$

3. $(CO)_{n-m}CoCH_2Me + H_2 \rightarrow$
$\rightarrow HCo(CO)_{n-m} + C_2H_6$

Mechanism II

1. $Co_2(CO)_n + C_2H_4 \rightarrow$
$\rightarrow (CO)_{n-m}CoCH_2CH_2Co(CO)_m$

2. $(CO)_{n-m}CoCH_2CH_2Co(CO)_m + H_2 \rightarrow$
$\rightarrow (CO)_{n-m}CoCH_2Me + HCo(CO)_m$

3. $(CO)_{n-m}CoCH_2Me + HCo(CO)_m \rightarrow$
$\rightarrow Co_2(CO)_n + C_2H_6$

Mechanism III

1. $Co_2(CO)_n + H_2 \rightarrow$
$\rightarrow HCo(CO)_{n-m} + HCo(CO)_m$

2. $HCo(CO)_x + C_2H_4 \rightarrow$
$\rightarrow (CO)_xCoCH_2Me$ $(x = n - m, m)$

3. $(CO)_xCoCH_2Me + H_2 \rightarrow$
$\rightarrow HCo(CO)_x + C_2H_6$

Mechanism IV

1. $Co_2(CO)_n + H_2 \rightarrow$
$\rightarrow HCo(CO)_{n-m} + HCo(CO)_m$

2. $HCo(CO)_x + C_2H_4 \rightarrow$
$\rightarrow (CO)_xCoCH_2Me$ $(x = n - m, m)$

3. $(CO)_xCoCH_2Me + HCo(CO)_x \rightarrow$
$\rightarrow (CO)_xCo_2(CO)_x + C_2H_6$

Mechanism V

1. $Co_2(CO)_n + C_2H_4 \rightarrow$
$\rightarrow (CO)_{n-m}CoCH_2CH_2Co(CO)_m$

2. $Co_2(CO)_n + H_2 \rightarrow$
$\rightarrow HCo(CO)_{n-k} + HCo(CO)_k$

3. $(CO)_{n-m}CoCH_2CH_2Co(CO)_m + HCo(CO)_x \rightarrow$
$\rightarrow (CO)_{n-m}CoCH_2Me + Co_2(CO)_{x+m}$
$(x = k, n - k)$

4. $(CO)_{n-m}CoCH_2Me + H_2 \rightarrow$
$\rightarrow HCo(CO)_{n-m} + C_2H_6$

Mechanism VI

1. $Co_2(CO)_n + C_2H_4 \rightarrow$
$\rightarrow (CO)_{n-m}CoCH_2CH_2Co(CO)_m$

2. $Co_2(CO)_n + H_2 \rightarrow$
$\rightarrow HCo(CO)_{n-k} + HCo(CO)_k$

3. $(CO)_{n-m}CoCH_2CH_2Co(CO)_m + HCo(CO)_x \rightarrow$
$\rightarrow (CO)_{n-m}CoCH_2Me + Co_2(CO)_{x+m}$
$(x = k, n - k)$

4. $(CO)_{n-m}CoCH_2Me + HCo(CO)_x \rightarrow$
$\rightarrow Co_2(CO)_{n-m+x} + C_2H_6$

To the best of our knowledge, only mechanisms I and II have been discussed previously in the literature, whereas the others have not been considered.

The pathways to propionaldehyde differ in the mechanisms of formation of the σ-organocobalt alkyl derivative and decomposition of the acylcobalt derivative. The ethane formation mechanisms imply two pathways to the alkyl intermediate. The acyl complex is formed upon the migratory insertion of coordinated carbon monoxide. The reaction network contains two pathways to the acyl derivative

$(CO)_xCoCH_2Me + CO \rightarrow (CO)_xCoCOCH_2Me,$

$(CO)_{n-m}CoCH_2CH_2Co(CO)_m + CO \rightarrow$
$\rightarrow (CO)_{n-m}CoCOCH_2CH_2Co(CO)_m.$

The acyl derivatives are converted *via* reactions of two types

$(CO)_xCoCOCH_2Me + H_2 \rightarrow HCo(CO)_x + MeCH_2CHO,$

$(CO)_xCoCOCH_2Me + HCo(CO)_n \rightarrow$
$\rightarrow Co_2(CO)_{x+n} + MeCH_2CHO.$

Thus, the reaction network comprises at least 8 different mechanisms of the formation of propionaldehyde. Within each scheme, more detailed mechanisms for the formation of each product can be presented.

The set of sequences of steps leading to the main reaction products includes all the reactions previously considered in the literature[18–23] and several new steps. In addition, analysis of the reaction network allows one to predict the formation of some amounts of formic and carbonic acids, the dialdehyde $OHCCH_2CH_2CHO$, the aldehydo acid $OHCCH_2CH_2COOH$, and the keto aldehyde $EtC(O)CH_2CH_2CHO$. Molecules containing more atoms (*e.g.*, $EtC(O)CH_2CH_2COOH$) were not generated due to the constraints imposed. Neither cyclization reactions nor hydrogenation of the carbonyl group (the formation of anhydrides, lactones, quinones, or hydroquinones) were covered by the transforms used.

The resulting reaction network can be used in two fundamentally different ways. On the one hand, it can be considered as the maximum mechanism in which individual steps are to be verified; on the other hand, it can be separated into partial mechanisms describing the formation of individual products and then these reaction pathways should be verified separately; this is exactly what we had done in the study of the oxidative carbonylation of phenylacetylene catalyzed by Pd^{II} and Cu^{I} complexes.[12,16]

Hydrogenolysis of ethane (heterogeneous catalysis). We applied the ChemNet program to hydrogenolysis of ethane. After analysis of relevant publications,[24—29] we formulated five transforms, which could serve as a good model for the chemistry of ethane hydrogenolysis. In addition, the use of these transforms allowed us to avoid the difficulties associated with combinatorics, which usually arise during working with ChemNet and similar programs. This model implies, however, that the carbene and carbyne carbon atoms bind to *different* centers on the catalyst surface; fragments of the $M{\equiv}C{-}$ type are described as $M_3{\equiv}C{-}$, and $M{=}C{<}$ fragments are represented as $M_2{=}C{<}$. Steric, energetic, or kinetic factors were not taken into account. Only five transforms were used but they were rather general and contained substituents:

1. $M{-}M + R^1{-}H \rightarrow M{-}H + M{-}R^1$, R^1 = C or H

2. $M{-}H + M{-}R^1 \rightarrow M{-}M + R^1{-}H$, R^1 = C or H

3. $M{-}R^2 + C{-}H \rightarrow M{-}C + H{-}R^2$, R^2 = C, H, or M

4. $M{-}C + H{-}R^2 \rightarrow M{-}R^2 + C{-}H$, R^2 = C, H, or M

5. $M{-}CR^3R^4{-}CR^5R^6R^7 + M{-}R^8 \rightarrow$
$\rightarrow M{-}CR^3R^4{-}M + CR^5R^6R^7R^8$. R^i = H or M
(i = 3, ..., 8)

The program generated a reaction network consisting of 150 reversible (the mutually inverse reactions were combined to make reversible steps) and 24 irreversible elementary steps and 16 substances. The following constraints were used: the maximum number of atoms in a molecule was 11, the maximum number of carbon atoms was 2, the maximum number of the metal atoms was 6, and the maximum number of hydrogen atoms was 6. Each metal atom M was regarded as a surface active site with a coordination number equal to unity. The reaction network contained all the mechanisms that we had found in the literature. For example, hydrogenolysis of ethane on iridium films has been studied[26] over a broad range of partial pressures of each reagent at 80—205 °C, and a mechanism consisting of the following steps was proposed:

$M{-}M + Me{-}Me \leftrightarrow Me{-}CH_2M + MH$,

$M{-}M + H_2 \leftrightarrow 2\ MH$,

$Me{-}CH_2M + M{-}M \leftrightarrow MH + Me{-}CHM_2$,

$MCH_2{-}Me + M{-}H \rightarrow 2\ M{-}Me$,

$M{-}Me + MH \leftrightarrow M{-}M + CH_4$.

It was assumed that the C—C bond in the ethyl complex is cleaved under the action of the hydride MH and the resulting methyl complexes with the surface are hydrogenated to methane. In another work,[27] this reaction was carried out in the presence of the Pt/SiO_2 and $PtFe/SiO_2$ catalysts and two alternative hypotheses on the reaction mechanism were proposed. In the opinion of the researchers cited, these mechanisms are valid for different reaction conditions. One mechanism includes the following steps:

$M{-}M + Me{-}Me \leftrightarrow Me{-}CH_2M + MH$,

$M{-}M + H_2 \leftrightarrow 2\ MH$,

$MCH_2{-}Me + M{-}M \rightarrow M_2CH_2 + M{-}Me$,

$M_2CH_2 + MH \leftrightarrow M{-}M + M{-}Me$,

$M{-}Me + MH \leftrightarrow M{-}M + CH_4$.

In this case, the C—C bond is also cleaved in the ethyl complex but upon interaction with the catalyst surface. The second mechanism includes the following steps:

$M{-}M + Me{-}Me \leftrightarrow Me{-}CH_2M + MH$,

$M{-}M + H_2 \leftrightarrow 2\ MH$,

$Me{-}CH_2M + M{-}M \leftrightarrow MH + MCH_2{-}CH_2M$,

$MCH_2{-}CHM_2 + M{-}M \leftrightarrow MH + M_2CH{-}CHM_2$,

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

$M_3CH + MH \leftrightarrow M{-}M + M_2CH_2$,

$M_2CH_2 + MH \leftrightarrow M{-}M + MMe$,

$MMe + MH \leftrightarrow M{-}M + CH_4$.

According to the second mechanism, the C—C bond is cleaved in a symmetrical surface complex, $CHM_2{-}CHM_2$. The mechanisms of ethane hydrogenolysis on Pt, Pd, Ir, and Co catalysts supported on silica have also been studied.[28] This resulted in a general mechanism consisting of the following steps:

1. $M{-}M + Me{-}Me \leftrightarrow Me{-}CH_2M + MH$

2. $M{-}M + H_2 \leftrightarrow 2\ MH$

3. $Me{-}CH_2M + M{-}M \leftrightarrow MH + MCH_2{-}CH_2M$

4. $MCH_2{-}CHM_2 + M{-}M \leftrightarrow MH + M_2CH{-}CHM_2$

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

6. $MCH_2{-}CH_2M + M{-}M \rightarrow 2\ M_2CH_2$

7. $M_2CH{-}CH_2M + M{-}M \rightarrow M_3CH + M_2CH_2$

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

9. $M_3CH + MH \leftrightarrow M{-}M + M_2CH_2$

10. $M_2CH_2 + MH \leftrightarrow M{-}M + MMe$

11. $MMe + MH \leftrightarrow M{-}M + CH_4$

Three pathways were considered, namely, *A* (steps 1—3, 6, 10, and 11), *B* (steps 1—3, 4, 7, and 9—11), and *C* (steps 1—3, 4, 5, 8, and 9—11). It was found that pathway *C* involving the formation of $CHM_2—CHM_2$ is not operative before the C—C bond cleavage, which conflicts with other data.[27] Pathways *A* and *B* may predominate depending on the catalyst and reaction conditions. It was suggested[29] that hydrogenolysis of ethane on the Pt(111) surface occurs *via* the formation of ethylidyne fragments. The proposed mechanism includes the following steps:

$$M—M + Me—Me \leftrightarrow Me—CH_2M + MH,$$

$$Me—CH_2M + M—M \leftrightarrow MH + Me—CHM_2,$$

$$Me—CHM_2 + M—M \leftrightarrow MH + Me—Me,$$

$$M_3CH + MH \leftrightarrow M—M + M_2CH_2,$$

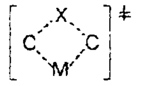
$$M_2CH_2 + MH \leftrightarrow M—M + MMe,$$

$$MMe + MH \leftrightarrow M—M + CH_4,$$

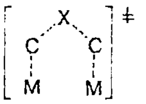
$$Me—Me + 4\ M \rightarrow 2\ CHM_3 + MH$$

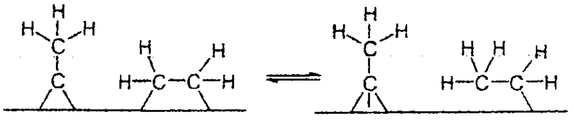
The last reaction can hardly be regarded as a single kinetic step; our reaction network did not include this step but it can be expanded into several elementary steps.

Apart from the steps that had been considered in one or another way for hydrogenolysis of hydrocarbons on various catalysts and for other reactions of hydrocarbons on heterogeneous catalysts, the reaction network contained a large number of steps that had not been considered by the majority of researchers but could, in principle, occur. They are characterized by similar transition states:



Steps with these transition states can participate in the mechanism; if they are included, the number of hypothetical mechanisms becomes too large. Some generalization leads to the assumption that similar transformations involving two metallic centers on the surface are also possible, for example, in the reaction





The modern methods of quantum chemistry might help in elucidating the role of these reactions in the conversions of hydrocarbons on a metal surface.

* * *

Thus, our ChemNet program performs the following task. The program employs specified starting compounds, components of the catalytic system, transforms, which serve as templates for elementary steps, and constraints to generate the full set of elementary steps. This set of steps is often referred to as the *maximum mechanism*. The maximum mechanism can be analyzed by various procedures. For example, individual steps can be verified and rejected in cases where they do not pass the necessary tests. One can also distinguish individual pathways in a reaction network and study them. Experimental and theoretical analysis of the steps is beyond the scope of this work.

A user normally works interactively with the program; as a rule, it is impossible to obtain a reaction network that would not contain a large number of undesirable steps over a short period of time. In addition, while analyzing the reaction network, a user often realizes the necessity of changing the initial data (constraints or transforms). Some changes can be made after suspending the generation process.

The program is designed for personal computers and runs in DOS but can also be run in Windows of any version. The program has a convenient graphical interface.

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