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A graph-theoretic method to identify candidate mechanisms for deriving the rate law of a catalytic reaction

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Abstract

Stoichiometrically, exact candidate pathways or mechanisms for deriving the rate law of a catalytic or complex reaction can be determined through the synthesis of networks of plausible elementary reactions constituting such pathways. A rigorous algorithmic method is proposed for executing this synthesis, which is exceedingly convoluted due to its combinatorial complexity. Such a method for synthesizing networks of reaction pathways follows the general framework of a highly exacting combinatorial method established by us for process-network synthesis. It is based on the unique graph-representation in terms of P-graphs, a set of axioms, and a group of combinatorial algorithms. In the method, the inclusion or exclusion of a step of each elementary reaction in the mechanism of concern hinges on the general combinatorial properties of feasible reaction networks. The decisions are facilitated by solving linear programming problems comprising a set of mass-balance constraints to determine the existence or absence of any feasible solution. The search is accelerated further by exploiting the inferences of preceding decisions, thereby eliminating redundancy. As a result, all feasible independent reaction networks, i.e. pathways, are generated only once; the pathways violating any first principle of either stoichiometry or thermodynamics are eliminated. The method is also capable of generating those combinations of independent pathways directly, which are not microscopically reversible. The efficiency and efficacy of the method are demonstrated with the identification of the feasible mechanisms of ammonia synthesis involving as many as 14 known elementary reactions.

Keywords: Reaction pathways; Identification; Synthesis; Algorithm; P-graph

1. Introduction

Reaction-pathway determination plays a key role in the study of the kinetics of chemical or biochemical reactions. A reaction pathway, comprising the steps of elementary reactions, routes the precursors (starting reactants) of the reaction to the targets (final products) and vice versa in the opposite direction; in other words, a reaction pathway signifies the mechanism of the reaction. The reaction pathway per se yields no information on the rate, reversibility, equilibrium, and extent of the reaction although knowledge of them facilitates, or is even essential for, the ultimate identification of the definitive mechanism.

The determination of a reaction pathway or mechanism apparently involves two phases for any given overall reaction or set of reactions. The first phase entails the identification of all feasible candidate mechanisms, and the second phase requires the selection of the ultimate pathway or mechanism from those iden-

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tified in the first phase. The dichotomy between these two phases of reaction-pathway determination has seldom been explicitly stated. More often than not, those engaged in the reaction-pathway determination have dabbled variously in both phases. Nevertheless, the development of a formal or systematic procedure to execute the two phases successively and iteratively might facilitate the determinations in the light of the fact that the two phases involve vastly different tasks and that each phase poses a unique set of complexities.

Every reaction pathway is in the form of a network of the steps of elementary reactions containing a loop or loops. In constituting a pathway or network directed from the starting reactants (precursors) towards the final products (targets) or vice versa, each elementary reaction in the list of plausible elementary reactions contributes the forward, reverse or no step to the network. As such, the possible combinations of these three possibilities that must be taken into account are $(3^9 - 1)$ or 19 682, even if the network comprises only nine elementary reactions. This can readily give rise to more than 100 plausible networks, from which the feasible candidate pathways are to be identified; by any measure, this is a daunting or almost insurmountable mathematical task. Hence, it is not surprising that this phase of reaction-pathway determination has attracted relatively few researchers, most of whom come from the fields of system science, mathematics, computer science, and chemical information. Naturally, the number of publications resulting from their works is correspondingly small (see, e.g. Aris, 1965; Sellers, 1971; Temkin, 1971, 1973; Sellers, 1972; Happel and Sellers, 1982, 1983; Sellers, 1984; Happel and Sellers, 1989; Sellers, 1989; Happel and Sellers, 1990; Mavrovouniotis and Stephanopoulos, 1992a,b; Mavrovouniotis et al., 1990, 1992; Pethő, 1990; Szalkai, 1991; Valdes-Perez, 1992; Mavrovouniotis, 1995, 1996).

Those who are engaged in the second phase come mainly from the fields of catalysis, biochemistry, and combustion science. In contrast to the first phase, their number is vast and increasing. This is attributable not only to the academic and theoretical importance, but also to the industrial and practical significance of the subject matter. Enormous investments have been made in this phase in terms of both monetary and human resources. These investments together with the advent of modern precision sensors and instrumentation, as well as high-speed computing methods and devices have rendered it possible for the researchers to mitigate the difficulties encountered in performing accurate measurements of the experimental parameters, efficient spectroscopic determination, speedy simulation of mechanistic reaction-rate equations, reliable molecular dynamic and quantum mechanical calculations, and robust multi-steady state or stability analysis (see, e.g. Feinberg, 1988; Huff and Schmidt, 1994a,b, 1996; Huff et al., 1994; Schmidt and Huff, 1994; Schmidt et al., 1994; Balakos and Chuang, 1995; Krishnamurthy and Chuang, 1995; Neurock and Manzer, 1996; Chuang and Tan, 1997; Neurock, 1997). Consequently, the number of publications pertaining to the second phase far exceeds that pertaining to the first phase (see, e.g. Happel, 1972; Boudart and Djega-Mariadassou, 1984; Happel, 1986, 1988; Feinberg, 1988, 1991; Dumesic et al., 1993; van Santen, 1995; van Santen and Niemantsverdriet, 1995; Huff and Schmidt, 1996, 1996; van Santen and Neurock, 1997). Moreover, the spectacular success in the second phase has been achieved seemingly without much aid or benefit from the contributions of the first phase.

In the second phase, a limited number of candidate pathways or mechanisms is selected on the basis of the huge knowledge and data bases accumulated in the field and in-depth heuristics compiled by individual researchers usually working in focused areas. Such pathways or mechanisms are adaptively modified in the light of experimental and computational results; nevertheless, a valid pathway or mechanism may be overlooked. Often, it is inordinately difficult, if not impossible, to statistically discriminate among various analogous mechanisms on the basis of experimental or computational results. This indicates that all the valid candidate mechanisms should be rigorously identified in the first phase. In reality, therefore, the two phases of reaction-pathway determination probably need be undertaken systematically not only in series, but also interactively as mentioned at the outset, The work performed in the second phase, more likely than not, could detect a previously unknown active species in-

$$M=\{C_4H_{10},\ C_4H_8\lambda,\ C_4H_6\lambda,\ H_2,\ \ell\}$$

$$O=\{1\rightarrow,\ 3\rightarrow\}=\{(\{C_4H_{10},\ \lambda\},\{C_4H_8\lambda,\ H_2\}),\ (\{C_4H_8\lambda\ \},\{C_4H_6\lambda,\ H_2\})\}$$

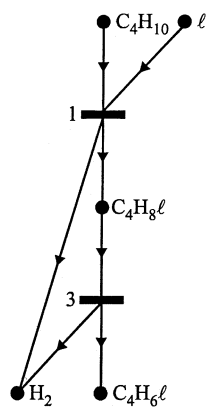

Fig. 1. P-graph representation of the network comprising elementary-reaction steps $1\rightarrow$ and $3\rightarrow$ in the pathway of the dehydrogenation of butane to butene.

```
inputs: RPI problem (E, M, O);
output: maximal structure (m, o);

begin
    comment: reduction part of the algorithm;
    repeat
        M:= Ψ(O);
        exc:=∅;
        for all x∈M
        begin
            comment: Case 1
            if x∉ω(E) and υ⁻(x)=∅ then exc:=exc∪υ⁺(x);
            comment: Case 2
            if x∉ω(E) and υ⁺(x)=∅ then exc:=exc∪υ⁻(x);
            comment: Case 3
            if x∉ω(E) and |υ⁻(x)|=1 and υ⁺(x)=X(υ⁻(x)) then exc:=exc∪υ(x);
            comment: Case 4
            if x∉ω⁻(E) and |υ⁻(x)|=1 then exc:=exc∪X(υ⁻(x));
            comment: Case 5
            if x∉ω⁺(E) and |υ⁺(x)|=1 then exc:=exc∪X(υ⁺(x));
        end;
        O:=O\exc;
    until exc=∅;

    comment: composition part of the algorithm;
    m:=ω⁺(E);
    o:=∅;
    repeat
        add:=φ⁻(m)\o;
        o:=o∪add;
        m:=m∪Ψ⁻(o);
    until add=∅;
    if ω⁻(E)\m≠∅ or ω⁺(E)\m≠∅ then stop; comment: There is no maximal structure.
    write (m, o);
end.
```

Fig. 2. Algorithm RPIMSG.

volved in the reaction of concern, thereby indicating the need to include an additional elementary reaction or reactions in the first phase. In fact, it is very common that the sources of elementary reactions necessary to initiate the first phase are the vast information and data bases generated by those engaged in the second phase.

The most rational approach for accomplishing the first phase of reaction-pathway determination is probably through the synthesis of feasible candidate networks from all plausible elementary reactions (see, e.g. Aris, 1965; Sellers, 1971, 1972, 1984, 1989; Happel and Sellers, 1982, 1983, 1989, 1990; Szalkai, 1991; Mavrovouniotis, 1995). A problem of utmost significance, however, remains unresolved for accomplishing this synthesis, it is to axiomatically and mathematically establish a rigorous algorithmic method for constructing such networks, in each of which an active intermediate generated by any step is totally consumed by others. The difficulties in developing the algorithmic method for constructing a network of chemical reactions, including elementary reactions giving rise to a reaction mechanism, are attributable to "the combinatorial explosion of answers" (see, e.g. Mavrovouniotis, 1995) and the complexity involved in rendering a computer program for the algorithm effective "both synthetically (from precursors towards targets) and retrosynthetically (from targets towards precursors)" (Corey et al., 1985; Mavrovouniotis, 1995).

The current work presents a novel algorithmic method for synthesizing a network of elementary chemical reactions, which corresponds to the reaction pathway or mechanism of a given overall reaction. The method is capable of rapidly yielding a complete network, the maximal structure with minimal complexity,

for a given set of candidate elementary reactions. A complete set of feasible subnetworks corresponding to feasible pathways, in turn, can be extracted from the maximal structure. The feasible pathways or mechanisms are to be explored experimentally, computationally and/or theoretically for the final selection of reaction pathways, i.e. mechanism identification, which is outside the scope of the this work. The present method is firmly rooted in a set of axioms and expressed in the parlance of process graph or P-graph, in brief (Friedler et al., 1992, 1993, 1995; Blázsik and Imreh, 1996; Friedler et al., 1996; Imreh et al., 1996; Friedler et al., 1998). The efficacy of the method has been demonstrated through application to well-known examples.

Whenever deemed desirable or necessary, what follows in the current discourse will be illustrated with the dehydrogenation of butane (C_4H_{10}) to butene (C_4H_8). Given below are the overall reaction and the five elementary reactions in the pathway proposed by Temkin (1971).

Overall reaction:

$$C_4H_{10} \rightleftarrows C_4H_8 + H_2$$

Elementary reactions:

$$C_4H_{10} + \lambda \rightleftarrows C_4H_8\lambda + H_2 \quad (1)$$

$$C_4H_8\lambda \rightleftarrows C_4H_8 + \lambda \quad (2)$$

$$C_4H_8\lambda \rightleftarrows C_4H_6\lambda + H_2 \quad (3)$$

$$C_4H_6\lambda \rightleftarrows C_4H_6 + \lambda \quad (4)$$

$$C_4H_{10} + \lambda + C_4H_6\lambda \rightleftarrows 2C_4H_8\lambda \quad (5)$$

2. Axioms

At the outset, it is assumed that the concentrations of all chemical species designated as active intermediates, i.e. those that are neither starting reactants (precursors) nor final products (targets), remain invariant and stationary without exhibiting transient or oscillatory behavior (Happel and Sellers, 1983). Moreover, the overall reaction and the plausible elementary reactions are defined a priori. According to the classical chemical thermodynamics, the overall reaction and all elementary reactions in any mechanism are reversible, and each reaction step, either forward or reverse, is stoichiometrically exact (see, e.g. Aris, 1965; Berry et al., 1980; Boudart and Djega-Mariadassou, 1984; Ross, 1993).

In the light of the reversibility of all the reactions and the stoichiometric exactness of all the reaction steps, the pathway leading from the starting reactants (precursors) through a series of the steps of elementary reactions to the final products (targets) of the overall reaction can be traced backward through every step. Thus, it suffices to determine the pathway only in one direction, e.g. $C_4H_{10} \rightarrow C_4H_8 + H_2$. Naturally, the complete mechanism is recovered trivially by supplementing the opposite step to each step of the pathway. Moreover, the principle of microscopic reversibility prohibits the inclusion of any cycle in a pathway (Happel and Sellers, 1983). These first principles and conditions give

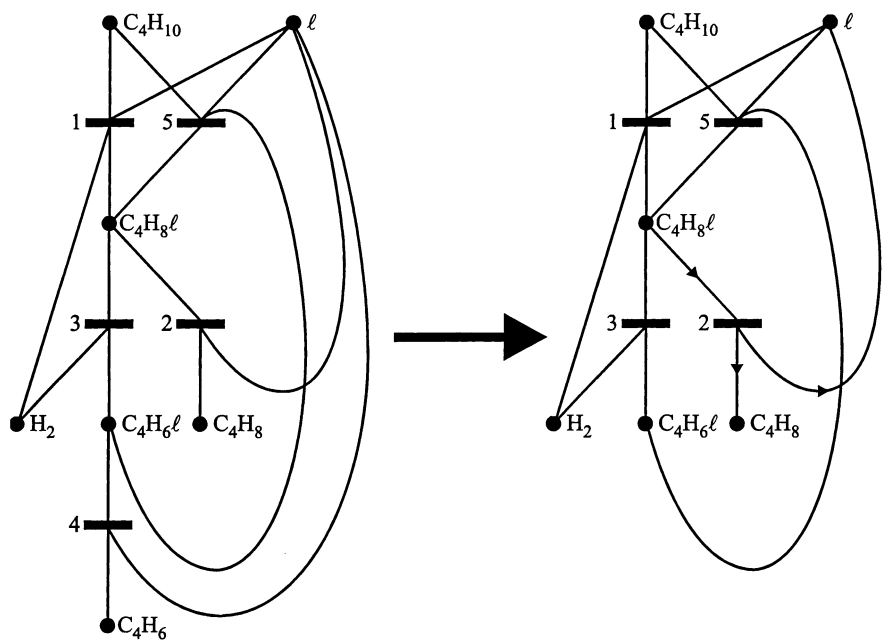

Fig. 3. Reduction part of algorithm RPIMSG for the dehydrogenation of butane to butene.

rise to the following set of six *axioms of feasible reaction pathways for any given overall reaction.*

(R1) Every final product (target) is totally produced by the reaction steps represented in the pathway.

(R2) Every starting reactant (precursor) is totally consumed by the reaction steps represented in the pathway.

(R3) Every active intermediate produced by any reaction step represented in the pathway is totally consumed by one or more reaction steps in the pathway, and every active intermediate consumed by any reaction step represented in the pathway is totally produced by one or more reaction steps in the pathway.

(R4) All reaction steps represented in the pathway are defined a priori.

(R5) The network representing the pathway is acyclic.

(R6) At least one elementary-reaction step represented in the pathway activates a starting reactant (precursor).

Since every elementary reaction is reversible, it comprises both forward and reverse steps. As a result, at most either the forward or reverse step of any elementary reaction can be in a pathway to circumvent the formation of a cycle or cycles within it. The directions of the forward and reverse steps of a given elementary reaction are opposite to each other. Hence, they can be simply indicated by the opposite arrows, $\rightarrow$ and $\leftarrow$, respectively, as illustrated below with the forward reaction of C_4H_{10} dehydrogenation to C_4H_8, and the reaction steps in the proposed set of the plausible elementary reactions.

input: reaction pathway identification problem (E, O, M)
output: all combinatorially feasible structures (m, o)

begin
  RPISSG($\omega^+(E)$, $\varnothing$, $\varnothing$, $\varnothing$);
end.

procedure RPISSG(p, dp, inc, exc)
begin
  exc:=RPIRSG(exc);
  if ($inc \cap exc \neq \varnothing$) **then return**;
  if $\omega^-(E) \backslash \Psi^-(O \backslash exc) \neq \varnothing$ **or** $\omega^+(E) \backslash \Psi^+(O \backslash exc) \neq \varnothing$ **then return**;

  inc:=NX(inc, exc);
  for all $x \in p$
  if ($\upsilon^-(x) \backslash exc \backslash inc = \varnothing$) **then**
  begin
    $dp := dp \cup \{x\}$;
    $p := (\, p \cup \Psi^-(\upsilon^-(x) \cap inc)\,) \backslash dp$;
  end;

  if $p = \varnothing$ **then**
  begin
    $o := inc$; $m := \Psi(o)$;
    print (m, o);
    return;
  end;

  let $x \in p$;
  $o_x := \upsilon^-(x) \backslash exc$;
  $o_{xb} := \upsilon^-(x) \cap inc$;
  $C := \wp(o_x \backslash o_{xb})$;
  if $o_{xb} = \varnothing$ **and** $x \notin \omega^-(E)$ **then** $C := C \backslash \{\varnothing\}$;
  for all $c \in C$
    RPISSG($(p \cup \Psi^-(c \cup o_{xb})) \backslash (dp \cup \{x\})$, $dp \cup \{x\}$, $inc \cup c$, $exc \cup (o_x \backslash o_{xb} \backslash c) \cup X(c)$);
end;

Fig. 4. Algorithm RPISSG.

```
function RPIRSG(exc)
begin
    repeat
        m:= Ψ(O\exc);
        ex:=∅;
        for all x∈m
        begin
            comment: Case 1
            if x∉ω(E) and υ⁻(x)\exc=∅ then ex:=ex∪υ⁺(x);
            comment: Case 2
            if x∉ω(E) and υ⁺(x)\exc=∅ then ex:=ex∪υ⁻(x);
            comment: Case 3
            if x∉ω(E) and |υ⁻(x)\exc|=1 and υ⁺(x)\exc=X(υ⁻(x)\exc) then ex:=ex∪υ(x);
            comment: Case 4
            if x∉ω⁻(E) and |υ⁻(x)\exc|=1 then ex:=ex∪X(υ⁻(x)\exc);
            comment: Case 5
            if x∉ω⁺(E) and |υ⁺(x)\exc|=1 then ex:=ex∪X(υ⁺(x)\exc);
        end;
        ex:=ex\exc;
        exc:=exc∪ex;
    until ex=∅;
    return exc;
end;
```

Fig. 5. Algorithm RPIRSG.

Overall reaction:

$C_4H_{10} \rightarrow C_4H_8 + H_2$

Elementary reaction steps:

$(1\rightarrow)$ $C_4H_{10} \rightarrow C_4H_8 + H_2$

$(1\leftarrow)$ $C_4H_8\ell + H_2 \rightarrow C_4H_{10} + \ell$

$(2\rightarrow)$ $C_4H_8\ell \rightarrow C_4H_8 + \ell$

$(2\leftarrow)$ $C_4H_8 + \ell \rightarrow C_4H_8\ell$

$(3\rightarrow)$ $C_4H_8\ell \rightarrow C_4H_6\ell + H_2$

$(3\leftarrow)$ $C_4H_6\ell + H_2 \rightarrow C_4H_8\ell$

$(3\leftarrow)$ $C_4H_6\ell + H_2 \rightarrow C_4H_8\ell$

$(4\rightarrow)$ $C_4H_6\ell \rightarrow C_4H_6 + \ell$

$(4\leftarrow)$ $C_4H_6 + \ell \rightarrow C_4H_6\ell$

$(5\rightarrow)$ $C_4H_{10} + \ell + C_4H_6\ell \rightarrow 2C_4H_8\ell$

$(5\leftarrow)$ $2C_4H_8\ell \rightarrow C_4H_{10} + \ell + C_4H_6\ell$

To focus on the combinatorial properties of the network comprising the feasible reaction pathways, the condition imposed by Axiom (R5) is relaxed except for the cycles formed by the forward and reverse steps of individual elementary reactions. The condition imposed by Axiom (R6) is totally relaxed: this axiom does not have any direct bearing on the generation of combinatorially feasible networks. Then, Axioms (R1) through (R5) can be recast as the seven axioms of the *combinatorially feasible reaction networks*, leading from the starting reactants (precursors) to the final products (targets) of any given overall reaction; this set of axioms is given in the following.

(T1) Every final product (target) is represented in the network.

(T2) Every starting reactant (precursor) is represented in the network.

```
function NX(inc, exc)
begin
    repeat
        m:= Ψ(inc)∪ω(E);
        in:=∅;
        for all x∈m
        begin
            if x∉ω⁻(E) and |υ⁻(x)\exc|=1
            then in:=in∪υ⁻(x)\exc;
            if x∉ω⁺(E) and |υ⁺(x)\exc|=1
            then in:=in∪υ⁺(x)\exc;
        end;
        in:=in\inc;
        inc:=inc∪in;
    until in=∅;
    return inc;
end;
```

Fig. 6. Algorithm NX.

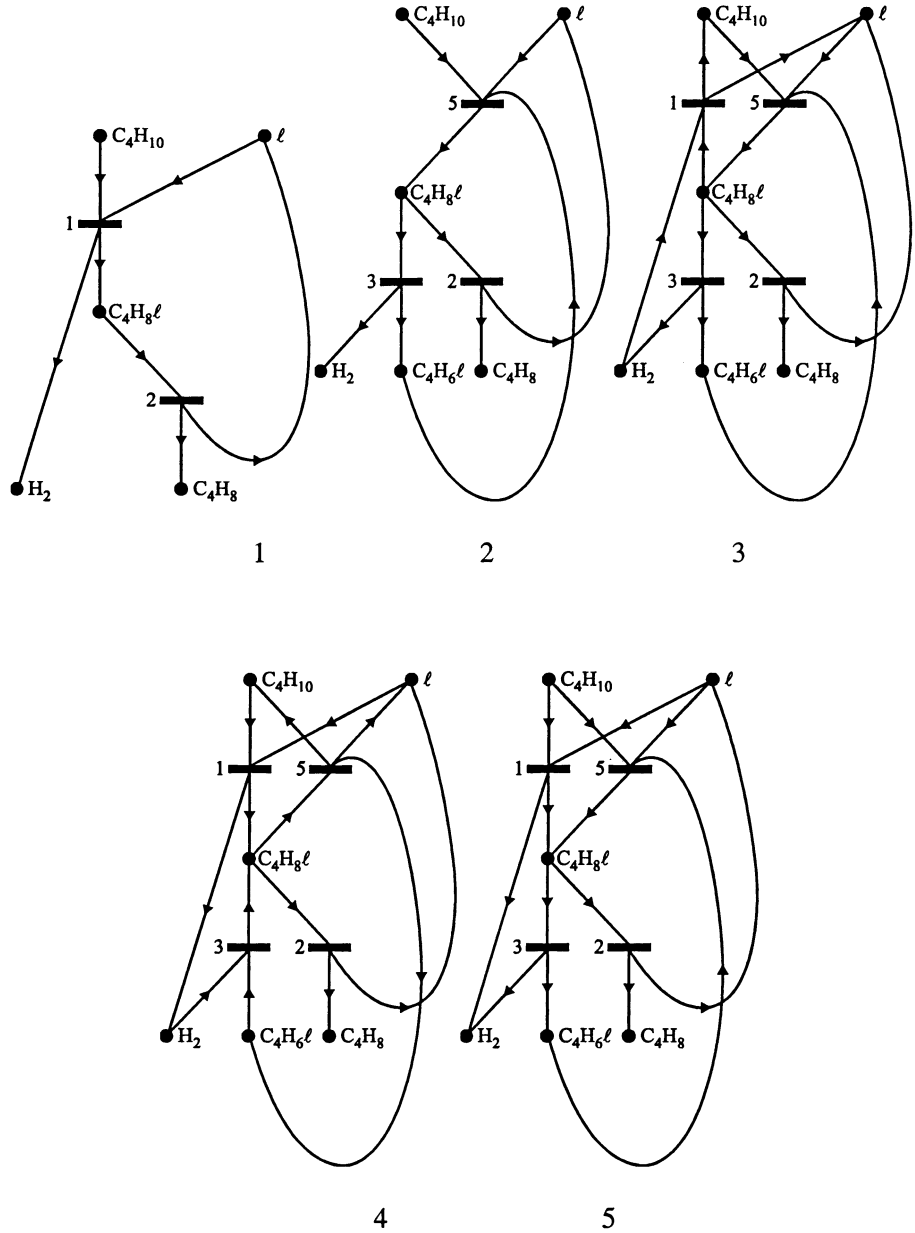

Fig. 7. Combinatorially feasible reaction networks for the dehydrogenation of butane to butene.

(T3) Each reaction step represented in the network is defined a priori.

(T4) Every active species represented in the network has at least one path leading to a final product (target) of the overall reaction.

(T5) Every chemical or active species represented in the network must be a reactant for or a product from at least one reaction step represented in the network.

(T6) A reactant of any elementary reaction represented in the reaction network is a starting reactant (precursor), if it is not produced by any reaction step represented in the network.

(T7) The network includes at most either the forward or reverse step of each elementary reaction represented in the network.

Naturally, the last axiom, i.e. Axiom (T7), is a consequence of Axiom (R5), the two steps of an elementary reaction automatically form a cycle, thereby violating the latter axiom; the inclusion of only one of them is needed to generate a valid pathway from the starting

reactants (precursors) to the final products (targets). Nevertheless, Axiom (R5) is disregarded for other cyclic loops, exclusion of which may prematurely eliminate combinatorially feasible networks in the algorithmic implementation of the axioms, as will be elaborated later.

It is indeed worth noting that Axioms (T1) through (T6) straightforwardly reduce to Axioms (S1) through (S5) established for process-network synthesis (Friedler et al., 1992, 1993). The phrase, 'every active species', at the outset of Axiom (T4) can be replaced with the phrase, 'any reaction step', since every active species generated by any reaction step is totally consumed by one or more of other reaction steps represented in the network.

3. P-graphs

An unambiguous network representation is required in the reaction-pathway determination through the synthesis of elementary reactions if the resultant networks are to be mathematically exact so that they can be analyzed formally. The elementary-reaction steps are directed; thus, every network representing a reaction pathway including these steps can be represented by

input: reaction pathway identification problem (E, O, M)
output: all feasible pathways (m, o)

begin
  PBT($\omega^+(E)$, $\omega^-(E)$, $\varnothing$, $\varnothing$, $\varnothing$, $\varnothing$);
end.

procedure PBT(p, c, dp, dc, inc, exc)
begin
  exc:=RPIRSG(exc);
  if ($inc \cap exc \neq \varnothing$) **then return**;
  if $\omega^-(E) \setminus \Psi^-(O \setminus exc) \neq \varnothing$ **or** $\omega^+(E) \setminus \Psi^+(O \setminus exc) \neq \varnothing$ **then return**;
  inc:=NX(inc, exc);
  for all $x \in p$
    if ($\upsilon^-(x) \setminus exc \setminus inc = \varnothing$) **then begin**
      $dp := dp \cup \{x\}$; $p := (p \cup \Psi^-(\upsilon^-(x) \cap inc)) \setminus dp$; **end**;
  for all $y \in p$
    if ($\upsilon^+(y) \setminus exc \setminus inc = \varnothing$) **then begin**
      $dc := dc \cup \{y\}$; $c := (c \cup \Psi^+(\upsilon^+(y) \cap inc)) \setminus dc$; **end**;
  if $\exists (m, o)$ $((m, o) \in avoid, o \subseteq inc)$ **then return**;
  if $p = \varnothing$ **and** $c = \varnothing$ **then begin**
    $o := inc$; $m := \Psi(o)$;
    if $dp = dc$ **and** Solution((m, o)) **then print** (m, o);
    return;
  end;
  if ($inc \setminus sol \neq \varnothing$) **or** ($exc \setminus (O \setminus sol) \neq \varnothing$) **or** ($sol = \varnothing$) **then** sol=CandidateSolution(inc, exc);
  if ($sol = \varnothing$) **then return**;
  if $p \neq \varnothing$ **then let** $x \in p$, where pFreedom(x, inc, exc) is minimal;
  if $c \neq \varnothing$ **then let** $y \in c$, where cFreedom(y, inc, exc) is minimal;
  If $c = \varnothing$ **or** ($p \neq \varnothing$ **and** pFreedom(x, inc, exc)<cFreedom(y, inc, exc)) **then begin**
    $o_x := \upsilon^-(x) \setminus exc$; $o_{xb} := \upsilon^-(x) \cap inc$; $C := \wp(o_x \setminus o_{xb})$;
    if $o_{xb} = \varnothing$ **and** $x \notin \omega^-(E)$ **then** $C := C \setminus \{\varnothing\}$;
    for all $q \in C$
      PBT($(p \cup \Psi^-(q \cup o_{xb})) \setminus (dp \cup \{x\})$, c, $dp \cup \{x\}$, dc, $inc \cup q$, $exc \cup (o_x \setminus o_{xb} \setminus q) \cup X(q)$);
  end;
  else begin
    $o_y := \upsilon^+(y) \setminus exc$; $o_{yb} := \upsilon^+(y) \cap inc$; $C := \wp(o_y \setminus o_{yb})$;
    if $o_{yb} = \varnothing$ **and** $y \notin \omega^+(E)$ **then** $C := C \setminus \{\varnothing\}$;
    for all $c \in C$
      PBT(p, $(c \cup \Psi^+(q \cup o_{yb})) \setminus (dc \cup \{y\})$, dp, $dc \cup \{y\}$, $inc \cup q$, $exc \cup (o_y \setminus o_{yb} \setminus q) \cup X(q)$);
  end;
end;

Fig. 8. Algorithm PBT.

directed graphs. In contrast, conventional graphs are incapable of uniquely representing such networks. The P-graphs, which are bipartite graphs, serve this purpose as mentioned in the preceding section (see, e.g. Friedler et al., 1992, 1993, 1995, 1996; Blázsik and Imreh, 1996). What follows is a brief description of the P-graphs for representing a network of elementary reactions.

Let O be the set of elementary-reaction steps and M be the set of chemical or active species under consideration; then, $O \subseteq \mathscr{P}(M) \times \mathscr{P}(M)$, where $O \cap M = \varnothing$. If (α, β) is a reaction step, i.e. $(\alpha, \beta) \in O$, then α is called the input set, and β, the output set of this step. Pair (M, O) is termed a P-graph with the set of vertices $M \cup O$, and the set of arcs $\{(x, y): y = (\alpha, \beta) \in O \text{ and } x \in \alpha\} \cup \{(y, x): y = (\alpha, \beta) \in O \text{ and } x \in \beta\}$. P-graph (M, O) is identified to be a subgraph of (M', O'), i.e. $(M, O) \subseteq (M', O')$, if $M \subseteq M'$ and $O \subseteq O'$. The union of P-graphs (M_1, O_1) and (M_2, O_2) results in P-graph $(M_1 \cup M_2, O_1 \cup O_2)$.

In P-graphs, elementary-reaction steps are represented by horizontal bars; chemical and active species, by circles. If a chemical or active species is an input to an elementary-reaction step, the vertex representing this species is linked by an arc to the vertex representing the elementary-reaction step. Similarly, if a chemical or active species is an output from an elementary-reaction step, the vertex representing this step is linked by an arc to the vertex representing the chemical or active species as illustrated in Fig. 1, with a network composed of the forward steps of two elementary reactions of the dehydrogenation of C_4H_{10} to C_4H_8 (Temkin, 1971).

P-graph (M, O) representing a reaction network leading from the starting reactants (precursors) to the final products (targets) of the overall reaction of interest is *combinatorially feasible*, if it satisfies Axioms (T1) through (T7). Moreover, P-graph (M, O) representing a reaction pathway is *feasible*, if it satisfies Axioms (R1) through (R6).

```
function pFreedom(x, inc, exc)
begin
    if x∈ω⁻(E) or υ⁻(x)∩inc=∅
        then return |υ⁻(x)\inc\exc|
        else return |υ⁻(x)\inc\exc| -1;
end;

function cFreedom(y, inc, exc)
begin
    if y∈ω⁺(E) or υ⁺(y)∩inc=∅
        then return |υ⁺(y)\inc\exc|
        else return |υ⁺(y)\inc\exc| -1;
end;
```

Fig. 9. Algorithms pFreedom and cFreedom.

```
function CandidateSolution(inc, exc)
begin
    LP problem:
        ∀ v_i ≥ ε
        e_i∈inc
        ∀ v_i ≥ 0
        e_i∈O\exc
        Σ v_i e_i = E
        e_i∈O\exc
        ---------------
        Σ v_i → min
        e_i∈O\exc
    if LP problem is not feasible
        then return ∅;
        else begin
            Solve LP problem;
            sol := {e_i: e_i∈O\exc, v_i > 0};
            return sol;
        end;
end;
```

Fig. 10. Algorithm Candidate Solution.

```
function Solution( (m, o) )
begin
    LP problem:
        ∀ v_i ≥ ε
        e_i∈o
        ∀ v_i ≤ 1/ε²
        e_i∈o
        Σ v_i e_i = E
        e_i∈o
        ---------------
        Σ v_i → max
        e_i∈o
    if LP problem is not feasible
        then return FALSE;
        else begin
            Solve LP problem;
            if ∀ (v_i ≤ 1/ε)
               e_i∈o
                then begin
                    avoid := avoid ∪ {(m, X(o))};
                    return TRUE;
                end;
                else begin
                    o := {e_i: v_i > 1/ε}; m := Ψ(o);
                    avoid := avoid ∪ {(m, o), (m, X(o))};
                    return FALSE;
                end;
        end;
end;
```

Fig. 11. Algorithm Solution.

function Solution((m, o))
begin
LP problem:

$$\forall_{e_i \in o} \; v_i \geq \varepsilon$$

$$\forall_{e_i \in o} \; v_i \leq \frac{1}{\varepsilon^2}$$

$$\sum_{e_i \in o} v_i e_i = E$$

$$\sum_{e_i \in o} v_i \rightarrow \max$$

if LP problem is not feasible
then return FALSE;
else begin
Solve LP problem;
if $\forall_{e_i \in o}\left(v_i \leq \frac{1}{\varepsilon} \right)$
then begin
$avoid := avoid \cup \{(m, o), (m, \mathrm{X}(o))\}$;
return TRUE;
end;
else begin
$o := \left\{ e_i : v_i > \frac{1}{\varepsilon} \right\}$; $m := \Psi(o)$;
$avoid := avoid \cup \{(m, o), (m, \mathrm{X}(o))\}$;
return FALSE;
end;
end;
end;

Fig. 12. Modified algorithm Solution.

To maintain consistency, the current work follows the well-established convention of placing the starting reactants (precursors) and final products (targets) of any overall reaction at the left-hand and right-hand sides of the stoichiometric equation of the reaction, respectively.

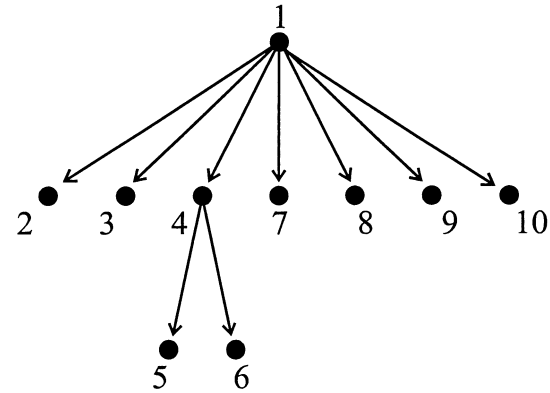

Fig. B.1. Search (enumeration) tree for algorithm RPISSG.

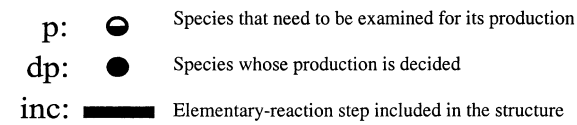

Fig. B.2. Graphical symbols representing the elements of the sets in algorithm RPISSG.

4. Algorithms

The axioms presented in the preceding section naturally give rise to efficient algorithms necessary for carrying out the synthesis of a feasible network of elementary reactions.

4.1. Maximal structure generation (algorithm RPIMSG)

To minimize the computational difficulty encoun-

Table 1
Summary of computational results from the determination of reaction pathways for ammonia synthesis and the corresponding computational requirements

	Number of elementary reactions	Number of LPs	Computation time[a]	Number of combinatorially independent pathways
Independent pathways				
Problem #1	11	13	0.06 s	6
Problem #2	14	581	1.1 s	35
				Number of acyclic pathways
Acyclic pathways (*independent and combined*)				
Problem #1	11	35	0.06 s	17
Problem #2	14	984	1.7 s	367

[a] Pentium II Celeron 450 MHz PC, 128 MB RAM.

tered in synthesizing feasible networks of elementary reactions, the mathematical formulation for it should be of minimum complexity. In the framework of the current approach, this is accomplished by generating the maximal structure of the reaction network of interest. The maximal structure contains all combinatorially feasible structures, i.e. reaction networks or pathways, each leading from the starting reactants (precursors) to the final products (targets), without violating Axioms (T1) through (T7) presented in the preceding section; note that not every combinatorially feasible structure constitutes a feasible pathway. Moreover, such a structure must satisfy the elementary balances, as expressed by Axioms (R1) through (R3); must not contain a cycle satisfying the principle of microscopic reversibility, as expressed by Axiom (R5); and must contain at least one elementary-reaction step activating a starting reactant (precursor), as expressed by Axiom (R6).

A mathematically rigorous algorithm for the maximal structure generation, algorithm RPIMSG, systematically places all the candidate reaction steps and examines their feasibility in the light of Axioms (T1) through (T7); algorithm RPIMSG represents a slight but judicious adaptation of algorithm MSG originally conceived for the synthesis of a network for the transformation of material species (Friedler et al., 1992). Fig. 2 contains the computer program for implementing algorithm RPIMSG, compactly written in PIDGIN ALGOL in terms of the formal graph-theoretic description of the reaction-pathway-identification problem

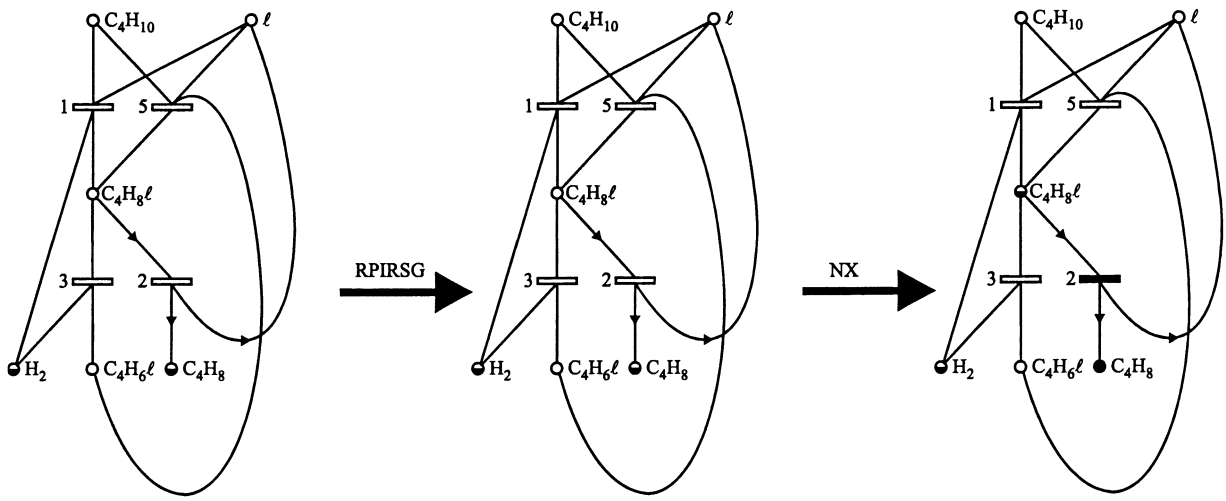

Fig. B.3. Step 1.

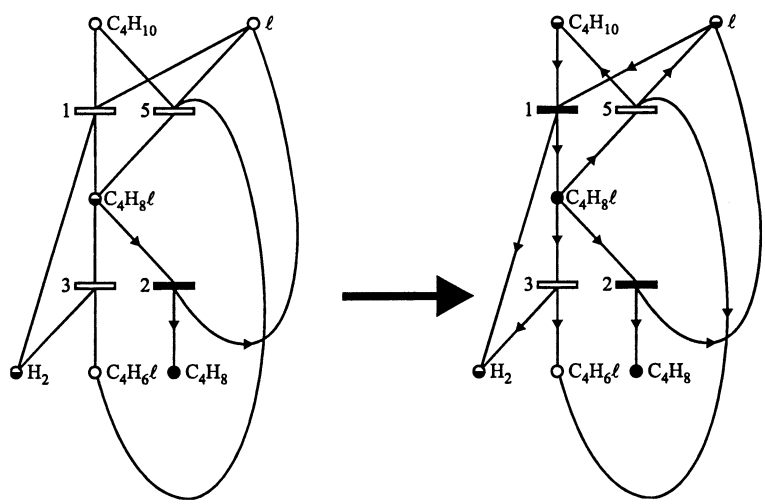

Fig. B.4. Generation of subproblem 2 at step 1.

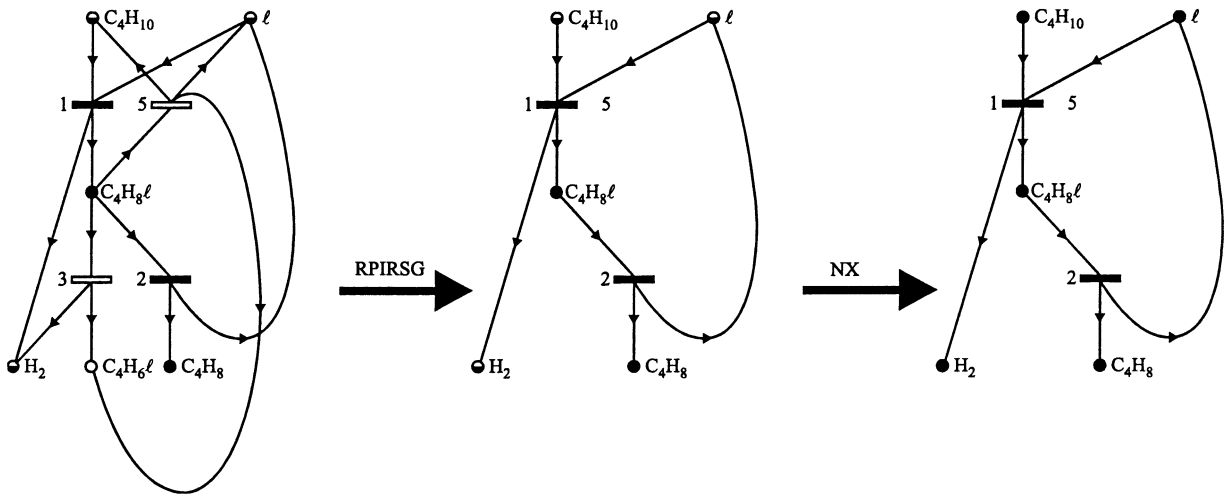

Fig. B.5. Step 2 resulting in combinatorially feasible structure 1.

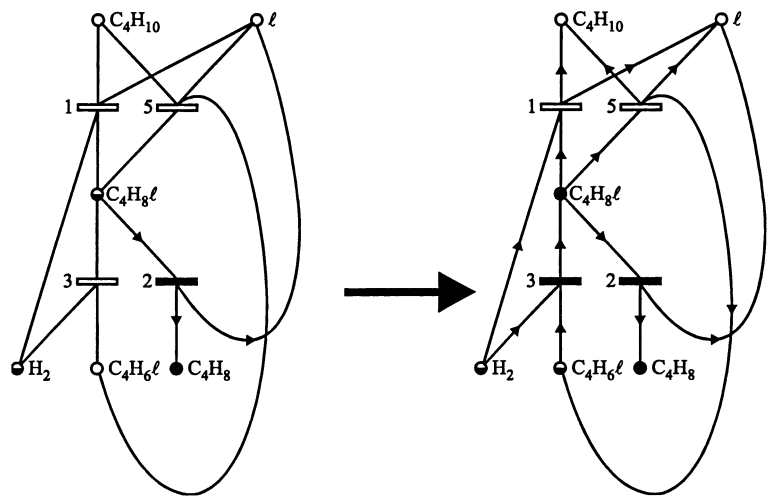

Fig. B.6. Generation of subproblem 3 at step 1.

analogous to that established for the process-network-synthesis problem (Friedler et al., 1992, 1993; Imreh et al., 1996; also see Appendix A).

For the convenience of executing algorithm RPIMSG, the initial network structure is constructed by linking all common nodes representing the chemical or active species in the form of solid circles; the nodes for elementary reactions are in the form of horizontal bars. Moreover, the direction of any arc linking a pair of these two different nodes, one succeeding the other, is not indicated in the initial structure. Every elementary reaction is bi-directional, and at this juncture, no decision can be made as to which step of this elementary reaction, forward or reverse, should be included in the network.

Algorithm RPIMSG consists of two major parts, reduction and composition. In the former, the chemical species, i.e. starting reactants (precursors), final products (targets), or active species, i.e. intermediates, and the reaction steps that must not belong to the maximal structure are excluded from the initial structure to the maximum extent possible on the basis of Axioms (T1) through (T7). To initiate the latter, every step of each elementary reaction, which has survived the elimination and is deemed plausible for inclusion, is properly identified on the basis of Axiom (T3), and each final product (target) is correctly specified on the basis of Axiom (T1). Hereafter, the maximal structure is constructed stepwisely by collecting the reaction steps so as to satisfy Axioms (T4) and (T5).

For simplicity, only the reduction part of the maximal-structure generation is delineated. This is done by listing below the situations leading to the elimination of chemical or active species or reaction steps.

Situation 1. Every active species not produced by elementary-reaction steps in the network must not be included in a combinatorially feasible pathway on the basis of Axiom (T6), and thus is eliminated together with the elementary-reaction steps consuming this species.

Situation 2. Every active species not consumed by elementary-reaction steps in the network must not be included in a combinatorially feasible pathway on the basis of Axiom (T4), and thus is eliminated together with the elementary-reaction steps producing this species.

Situation 3. Every active species consumed and produced by the opposite steps of a single elementary reaction in the network is eliminated. Upon excluding either the forward or reverse step of this elementary reaction on the basis of Axiom (T7), this situation reduces to either situation 1 or 2.

Situation 4. If a final product (target) is produced by only one elementary-reaction step in the network, this step must be contained in every combinatorially feasible structure, which includes this final product (target) on the basis of Axioms (T1), (T5), and (T6); consequently, the opposite of the reaction step of concern is eliminated on the basis of Axiom (T7). An essentially identical statement can be made with respect to an active species.

Situation 5. If a starting reactant (precursor) is consumed by only one elementary-reaction step in the

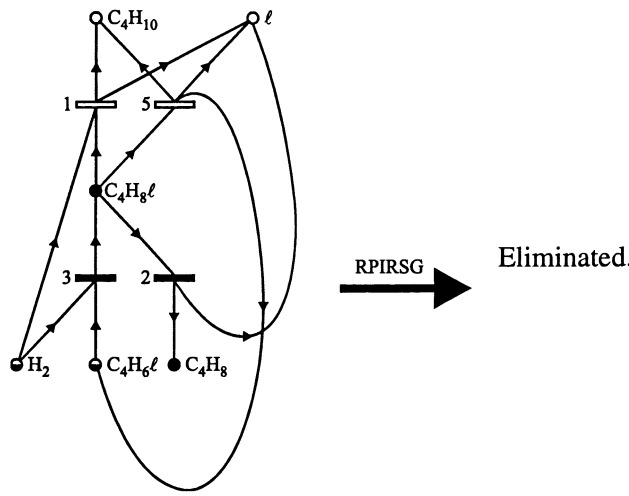

Fig. B.7. Step 3 identifying a combinatorially infeasible subproblem.

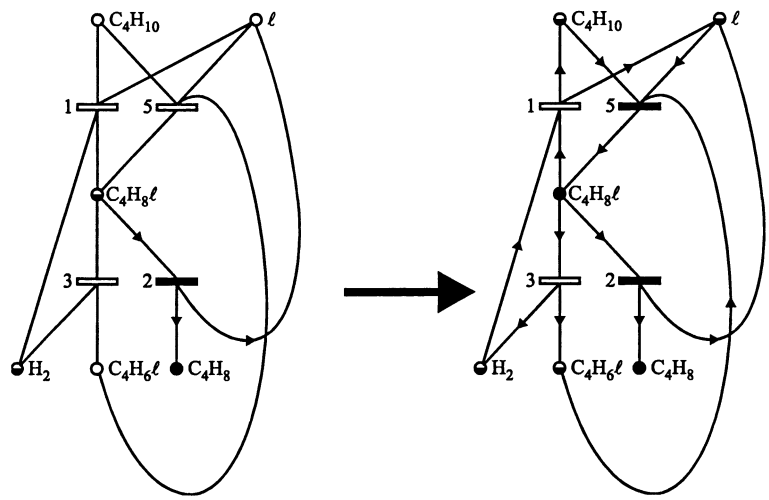

Fig. B.8. Generation of subproblem 4 at step 1.

network, this step must be included in every combinatorially feasible structure including the starting reactant (precursor) on the basis of Axioms (T2), (T5), and (T6), and thus, the opposite of this reaction step can be eliminated by virtue of Axiom (T7). Again as in Situation 4, an essentially identical statement can be made with respect to an active species.

The reduction part of algorithm RPIMSG is illustrated in Fig. 3 with the dehydrogenation of C_4H_{10} to C_4H_8. Elementary reaction (Eq. (4)) and the reverse step of elementary reaction (Eq. (2)) have been eliminated, thereby illustrating situations 3 and 4, respectively. The initial structure appears in the left-hand side, and the resultant structure, in the right-hand side. This structure can be proven to be indeed the maximal structure in the construction part of algorithm RPIMSG.

4.2. Solution structure generation (algorithm RPISSG)

The algorithm for the solution structure generation, algorithm RPISSG, yields the set of all combinatorially feasible reaction networks from the maximal structure of reaction networks. The search (enumeration) tree for this algorithm and the steps of the algorithm represented on P-graphs, as applied to the dehydrogenation of C_4H_{10} to C_4H_8, are illustrated in Appendix B. This algorithm is generated through the adaptation of algorithm SSG (Friedler et al., 1992) developed for process-network synthesis. Such adaptation has been

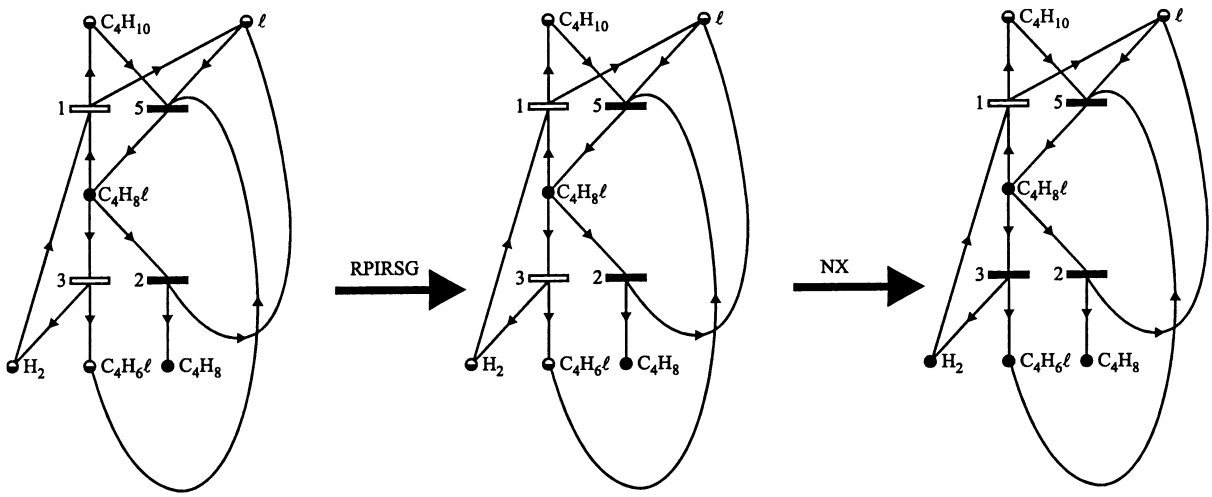

Fig. B.9. Step 4.

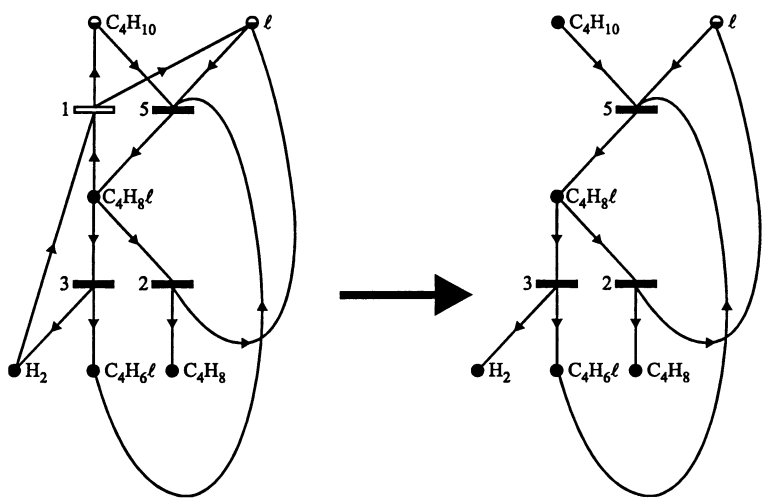

Fig. B.10. Generation of subproblem 5 at step 4.

executed by prudently rewriting algorithm in the parlance of the graph-theoretic description of the reaction-pathway-identification based on the P-graphs mentioned earlier (Appendix A) and in the light of the axioms of the combinatorially feasible reaction networks, i.e. Axioms (T1) through (T7). Algorithm RPISSG is further accelerated by algorithms RPIRSG and NX. Algorithm RPIRSG is similar to the reduction part of algorithm RPIMSG; and algorithm NX is for neutral extension conceived for minimizing the complexity and the number of the sub-problems. Algorithms RPISSG, RPIRSG and NX are given in Figs. 4–6, respectively.

When applied to the dehydrogenation of C_4H_{10} to C_4H_8, these algorithms yield the combinatorially feasible reaction networks illustrated in Fig. 7. Note that the order of the generation of the combinatorially feasible networks may be effected by the implementation of the algorithms; however, the resultant set of networks is obviously invariant. Moreover, it is remarkable that algorithm RPISSG reduces the search space of $(3^5 - 1) = 242$ combinations of the five elementary reactions for the dehydrogenation of C_4H_{10} to C_4H_8 to only five feasible combinations, i.e. networks, of elementary-reaction steps. Nevertheless, assessing exhaustively each of these feasible combinations, i.e. combinatorially feasible networks, on the basis of Axioms (R1) through (R6), to finally identify the feasible reaction pathways can be computationally laborious unless the number of candidate elementary reactions proposed is modest. In

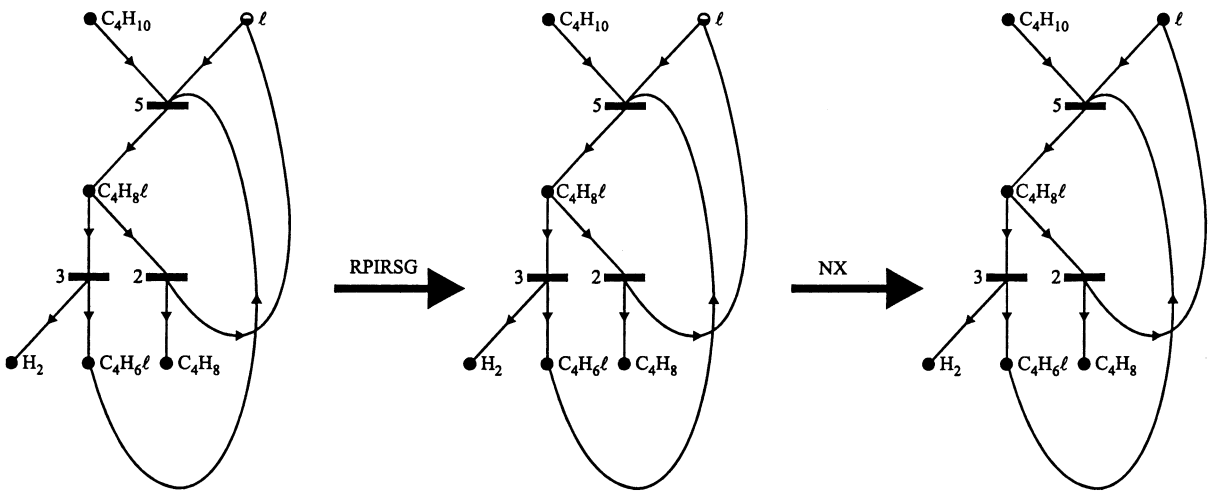

Fig. B.11. Step 5 resulting in combinatorially feasible structure 2.

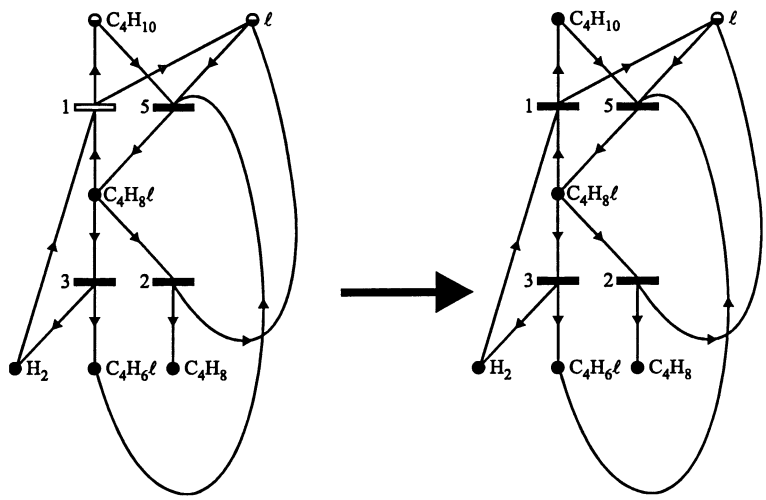

Fig. B.12. Generation of subproblem 6 at step 4.

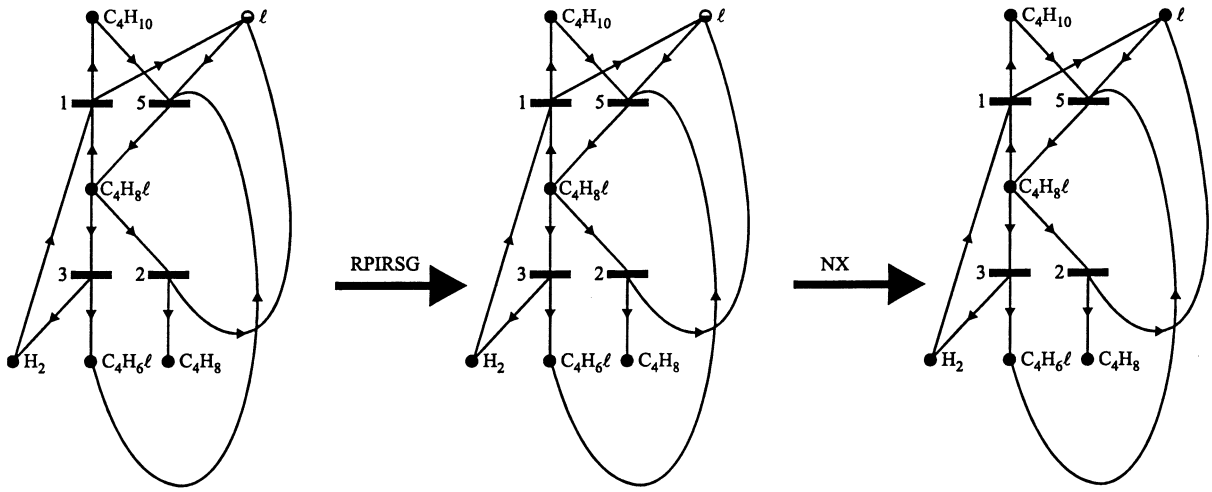

Fig. B.13. Step 6 resulting in combinatorially feasible structure 3.

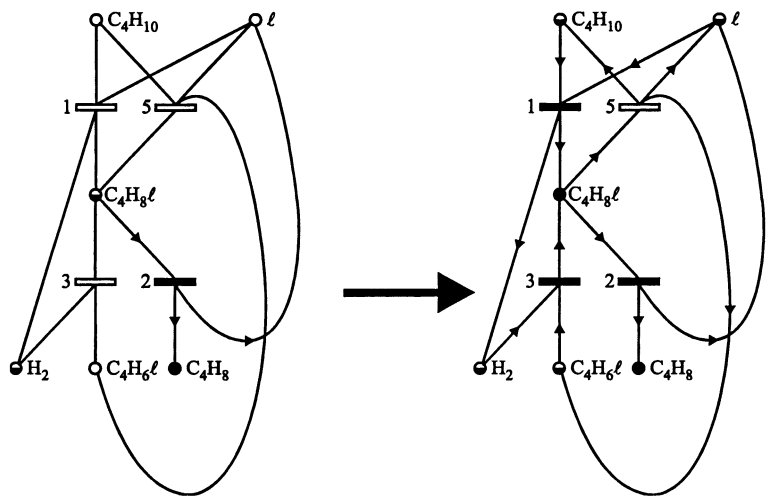

Fig. B.14. Generation of subproblem 7 at step 1.

addition to the combinational exploration, this effort involves repeated applications of linear programming to every resultant network for determining the multiplier, i.e. stoichiometric number, for each elementary reaction such that the pathway meets the elementary-balance constraint as dictated by Axiom (R1) through (R3) (Temkin, 1971, 1973; Horiuti, 1973; Boudart and Djega-Mariadassou, 1984) and for detecting the pathways containing cycles. Recall that Axiom (R6) is totally relaxed at the outset; it is brought into consideration for the final selection of the feasible networks from those preselected based on Axioms (R1) through (R5).

4.3. Feasible pathway generation (algorithm PBT)

To drastically reduce the computational time necessary to ascertain if each combinatorially feasible reaction network or pathway is indeed a feasible pathway in the light of Axioms (R1) through (R5), a branch-and-bound-like algorithm termed Pathway-Back-Tracking algorithm (algorithm PBT) has been developed (Fig. 8). The search (enumeration) tree for this algorithm and the steps of the algorithm represented on P-graphs, as applied to the dehydrogenation of C_4H_{10} to C_4H_8, are illustrated in Appendix C. The procedure for implementing algorithm PBT, or equivalently the search through the tree, is initiated at the maximal structure of reaction networks obtained by virtue of algorithm RPIMSG; this structure is at the root of the tree. Algorithm PBT, facilitated by the subsidiary algorithms, eventually generates the complete set of feasible pathways for a given reaction-pathway-identification problem.

Algorithm PBT involves three types of steps, i.e. synthetic, retrosynthetic and back-tracking steps. The synthetic steps deciding on the consumption of chemical or active species and retrosynthetic steps deciding on the production of chemical or active species alternate until they result either in a feasible solution or in an infeasible subproblem. The back-tracking steps are invoked if the subproblem examined is infeasible. During the implementation of the algorithm, the elementary-reaction steps are classified into three sets. Set *inc* contains those included in the network; set *exc*, those excluded from the network; and the set of free steps, comprising the steps neither in set *inc* nor in set *exc*. The selection rule for the subproblems, implemented by algorithm pFreedom and algorithm cFreedom, is based on the number of these free steps producing or consuming certain species; see Fig. 9. Every subproblem is assessed according to the combinatorial axioms by algorithm RPIRSG in Fig. 5 for exclusion and by algorithm NX in Fig. 6 for inclusion. The multipliers or stoichiometric numbers are evaluated by solving linear programming problems (LP-s), minimizing their sum so as to satisfy the elementary balances for each subproblem in algorithm CandidateSolution; see Fig. 10.

The multipliers, i.e. stoichiometric numbers, of the elementary-reaction steps in any acyclic pathway are bounded by the numbers of starting reactants (precursers) and final products (targets) in the overall reaction through the stoichiometric equations and mass-balance constraints in the light of Axioms (R1) through (R3). Thus, cycles are determined by maximizing the sum of these multipliers by means of LP. Those elementary-re-

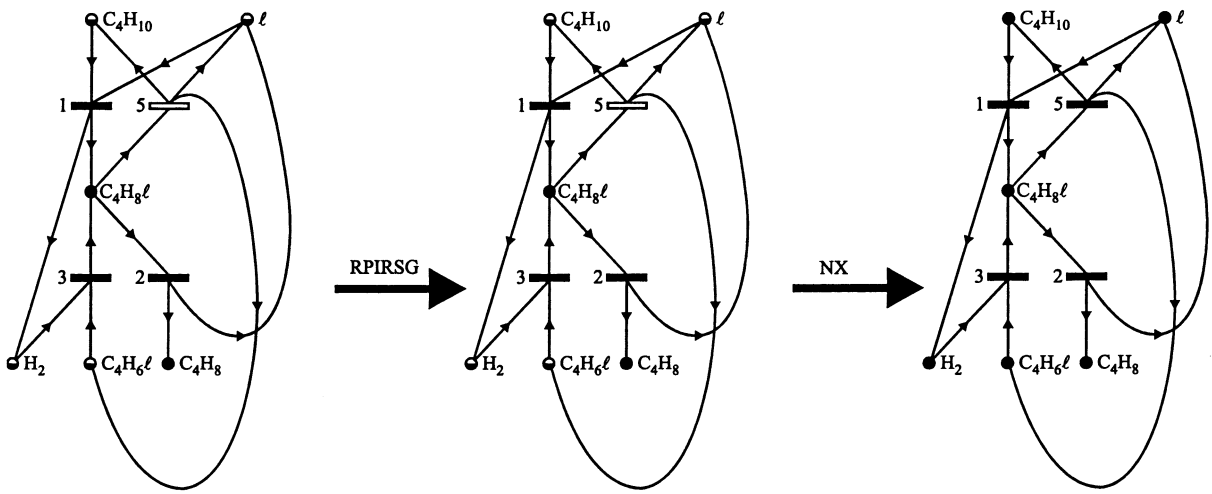

Fig. B.15. Step 7 resulting in combinatorially feasible structure 4.

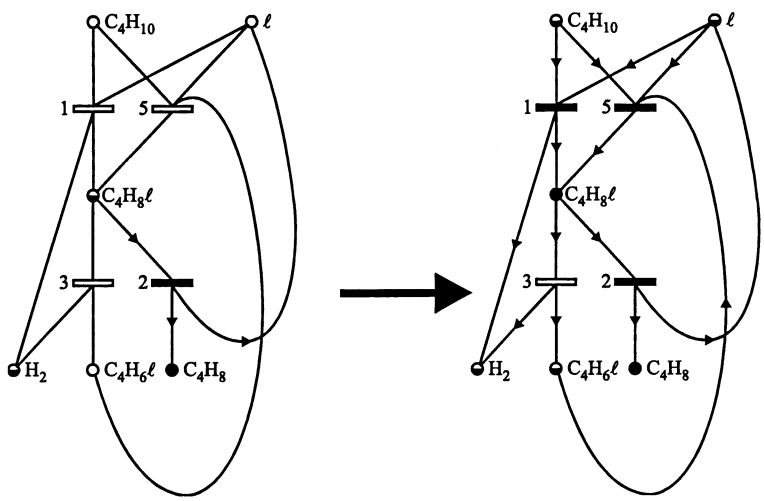

Fig. B.16. Generation of subproblem 8 at step 1.

action steps for which the corresponding multipliers are not bounded by the LP model of the pathway are contained in a cycle. For instance,

$$U = \sum_{a_j \in M} |E_j| \prod_{e_i \in O} \left(\sum_{a_j \in M} |e_{j,i}| \right) \qquad \text{and} \qquad \varepsilon = \frac{1}{U}$$

are the appropriate upper and lower limits for the multipliers of the elementary reaction steps in a feasible reaction pathway, respectively; note that the upper limit, U, is denoted by $1/\varepsilon$. The pathways containing cycles, which have been determined, are stored in the set *avoid* to prevent the algorithm to generate the pathways or networks containing cycles already found; see Fig. 11 presenting algorithm Solution.

Algorithm PBT is capable of generating directly all acyclic feasible pathways; nevertheless, it is more convenient to identify only the independent feasible pathways first when the number of such pathways is large (Happel and Sellers, 1982). Suppose that the elements of powerset C, which are all possible combinations of elementary-reaction steps in each feasible subproblem, i.e. combinatorially feasible pathway, are generated in the increasing order of their cardinality and that the feasible pathways already generated are placed into set *avoid*. Thus, algorithm PBT will not generate an independent feasible pathway already identified. As such, the algorithm generates any independent feasible pathway only once; see Fig. 12 presenting modified algorithm Solution.

For the dehydrogenation of C_4H_{10} to C_4H_8, algorithm PBT, together with the subsidiary algorithms, generates directly from the maximal reaction network

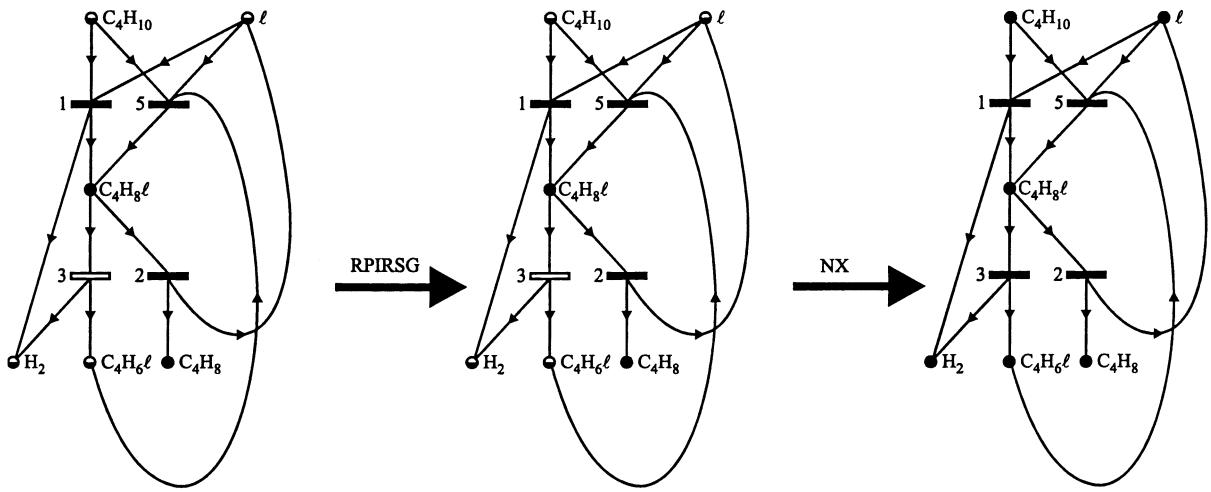

Fig. B.17. Step 8 resulting in combinatorially feasible structure 5.

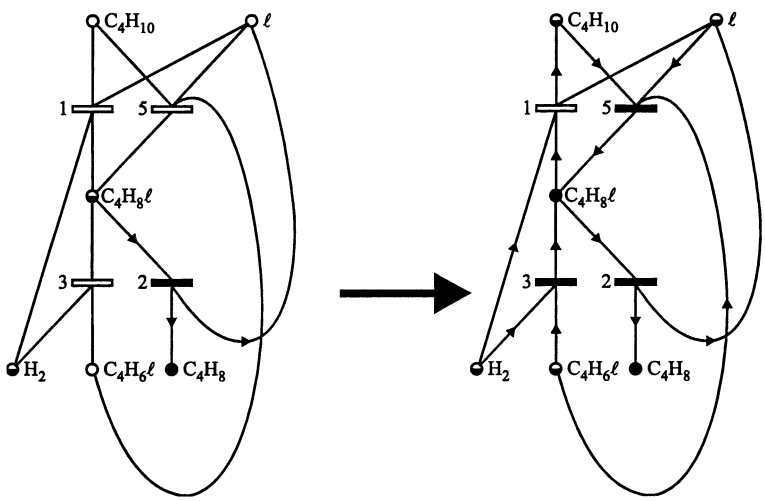

Fig. B.18. Generation of subproblem 9 at step 1.

obtained by algorithm PRIMSG, given in Fig. 3, combinatorially feasible independent pathways 1 and 2, and acyclic combined pathway 5 in Fig. 7 as feasible pathways. Nevertheless, pathway 2 is deemed infeasible by visual inspection by virtue of Axiom (R6). This gives rise to two feasible pathways, pathway 1 which is independent and pathway 2 which is acyclic combined, as summarized below.

Independent feasible pathway

Pathway 1
$(1\rightarrow)\quad C_4H_{10}+\lambda\rightarrow C_4H_8\lambda+H_2$
$(2\rightarrow)\quad C_4H_8\lambda\rightarrow C_4H_8+\lambda$

Overall: $C_4H_{10}\rightarrow C_4H_8+H_2$

Acyclic combined feasible pathway

Pathway 2
$(1\rightarrow)\quad C_4H_{10}+\lambda\rightarrow C_4H_8\lambda+H_2$
$(2\rightarrow)\quad 2C_4H_8\lambda\rightarrow 2C_4H_8+2\lambda$
$(3\rightarrow)\quad C_4H_8\lambda\rightarrow C_4H_6\lambda+H_2$
$(5\rightarrow)\quad C_4H_{10}+\lambda+C_4H_6\lambda\rightarrow 2C_4H_8\lambda$

Overall: $2C_4H_{10}\rightarrow 2C_4H_8+2H_2$

Note that combinatorially feasible pathways 3 and 4 each contains a cyclic loop, thereby rendering them infeasible in view of Axiom (R5). Upon supplementing the opposite step to each reaction step, the two feasible pathways above give rise to the stoichiometrically exact

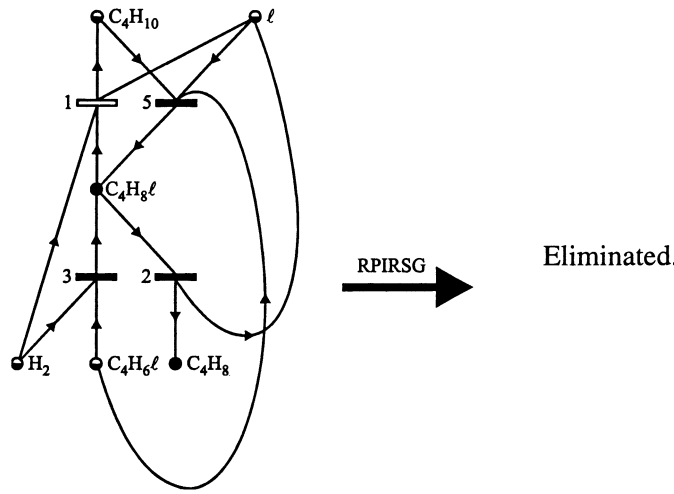

Fig. B.19. Step 9 identifying a combinatorially infeasible subproblem.

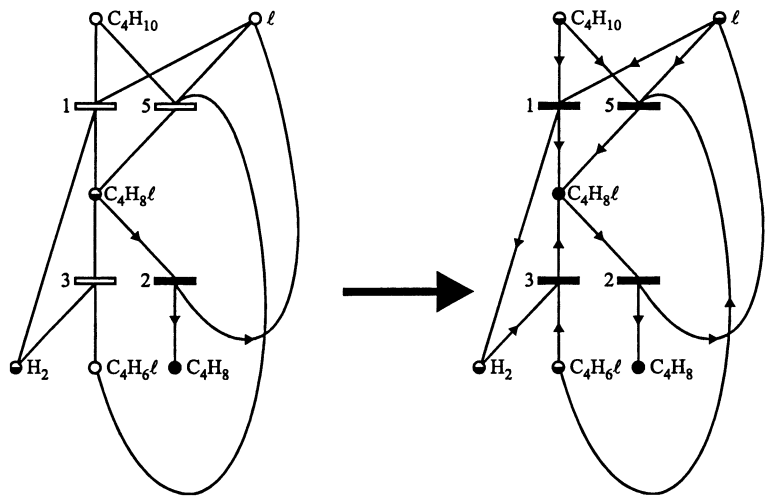

Fig. B.20. Generation of subproblem 10 at step 1.

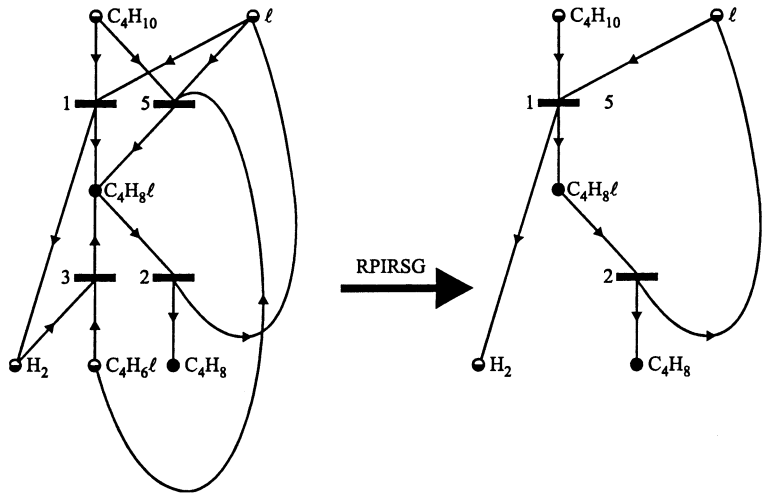

Fig. B.21. Step 10 identifying a combinatorially infeasible subproblem.

and thus valid mechanisms. Temkin (1971) has reported only one mechanism, which corresponds to pathway 1.

5. Application

The efficacy of the current method has been ascertained through the ammonia-synthesis reaction

$N_2 + 3H_2 \rightleftarrows 2NH_3$

The mechanism for catalytic synthesis of ammonia has been under investigation for many years because of its theoretical importance and its enormous economic implication.

When applied to a set of 11 elementary reactions appearing frequently in the open literature (Happel, 1972; Horiuti, 1973; Boudart and Djega-Mariadassou, 1984; Happel and Sellers, 1990), the method has recovered a set of six well-established independent reaction pathways. Moreover, it has yielded a set of (17–6) or 11 acyclic combined reaction pathways, among which only one has been known (Happel and Sellers, 1990). Notice that the number of elementary reactions actually reported in the literature is eight instead of 11; this increase is a result of splitting each initiation step into two and adding the desorption step for NH_3 in the light of the modern paradigm logically favoring involvement of a single active site in each elementary reaction (Hei, 1997).

When applied to a set of 14 elementary reactions, generated by adding three elementary reactions which have become known more recently (Hei, 1997), the method has yielded 35 independent reaction pathways and (367–35) or 332 acyclic combined pathways. These pathways contain all the pathways obtained with the 11 elementary reactions discussed in the preceding paragraph.

Table 1 summarizes the results described above. It comprises two subtables, one for independent pathways and the other for acyclic pathways which are either independent or combined.

6. Discussion

For any given overall reaction and a set of plausible elementary reactions, the proposed method exactly yields all feasible mechanisms, each containing a set of elementary reactions with varied multipliers, i.e. stoichiometric numbers. Obviously, these elementary reactions individually and collectively satisfy the stoichiometric requirement (Ross, 1993). Nevertheless, the final selection of valid mechanisms from the set of feasible mechanisms, i.e. correct identification, must await the comparison of the rate expressions derived from them with the experimental data; these rate ex-

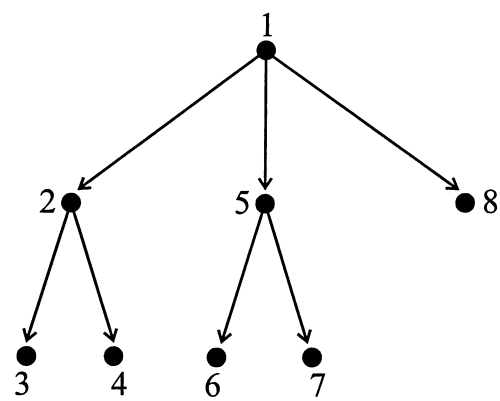

Fig. C.1. Search (enumeration) tree for algorithm PBT.

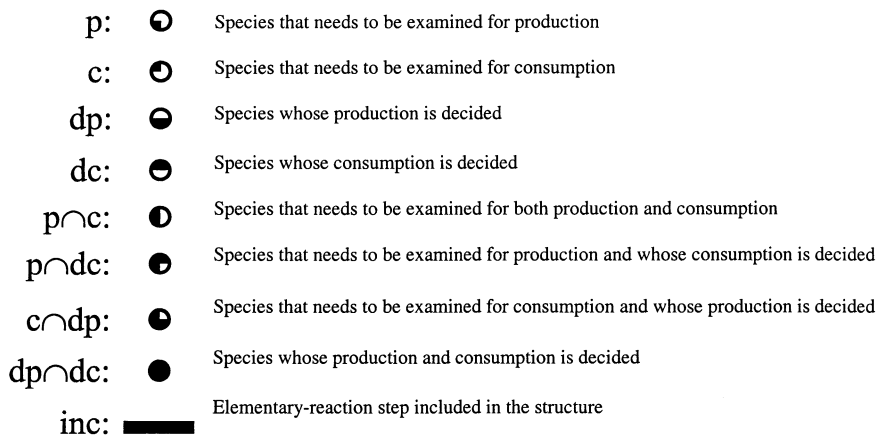

Fig. C.2. Graphical symbols representing the elements of the sets appearing in algorithm PBT.

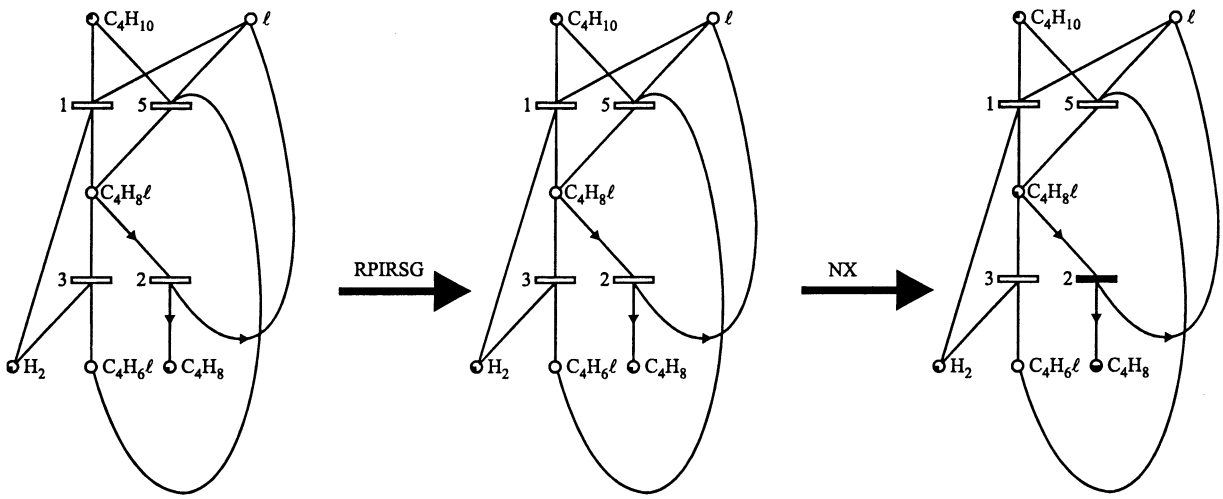

Fig. C.3. Step 1.

pressions or laws are almost always obtained under some assumptions, e.g. the existence of rate-controlling and/or equilibrium steps. The final rate law of any chemical reaction should emerge from one of the stoichiometrically exact mechanisms identified by the current method. Naturally, this selection is greatly facilitated by in-situ spectroscopic identification and measurement of active intermediates (see, e.g. Chuang and Tan, 1997).

7. Concluding remarks

A mathematically exact, graph-theoretic method is proposed for the identification, i.e. determination, of the mechanisms of chemical reactions through the synthesis of networks of pathways. A set of computer programs has been established to implement the method. Each step of the method is elucidated with the aid of a relatively simple example; moreover, the efficacy of the method is demonstrated by revisiting the well-known example of ammonia synthesis. The method should be useful not only for reassessing the existing mechanisms but also for discovering new ones.

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Appendix A. Formal graph—theoretic description of the reaction-pathway-identification problem

Here, a formal description is given of the problem of reaction-pathway identification. It is couched in the parlance of graph theory in general and that of P-graph in particular (Friedler et al., 1992, 1993; Imreh et al., 1996).

A.1. Problem definition

Let a reaction-pathway-identification problem be defined by triplet (E, O, M), where E is the overall reaction; $O = \{e_1, e_2, \ldots, e_n\}$, the finite ordered set of elementary reactions; $M = \{a_1, a_2, \ldots, a_l\}$, the finite ordered set of chemical and active species; $E = [E_1, E_2, \ldots, E_l]^T \in \mathbf{Z}^l$, where E_j is the difference between the number of moles of the j-th chemical produced and that consumed by the overall reaction; and $e_i = [e_{1,i}, e_{2,i}, \ldots, e_{l,i}]^T \in \mathbf{Z}^l$, where $e_{j,i}$ is the difference between the number of moles the j-th chemical or active species produced and that consumed by the i-th elementary-reaction step. Since every elementary reaction is reversible, both its forward and reverse steps are included in set O, i.e.

$$\forall e_i (e_i \in O \Rightarrow -e_i \in O)$$

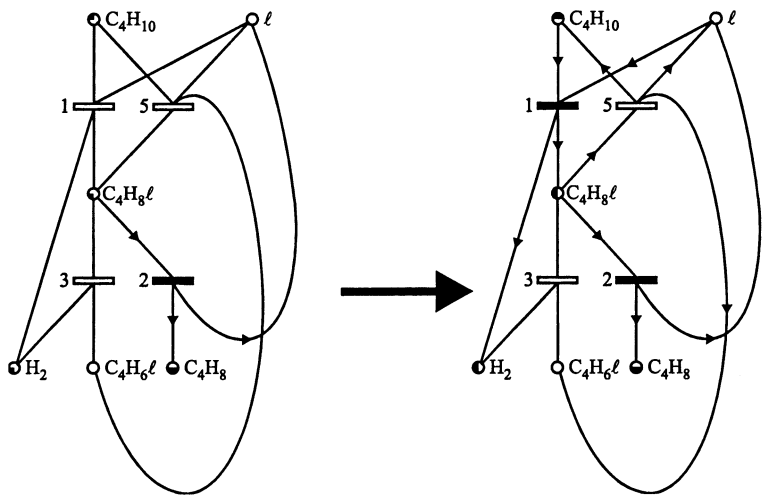

Fig. C.4. Generation of subproblem 2 at step 1.

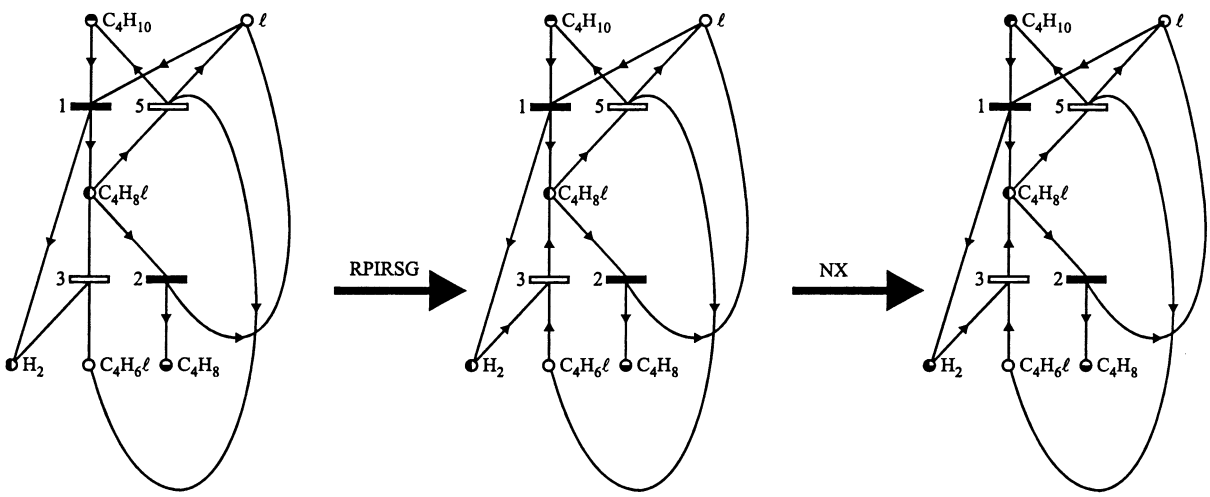

Fig. C.5. Step 2.

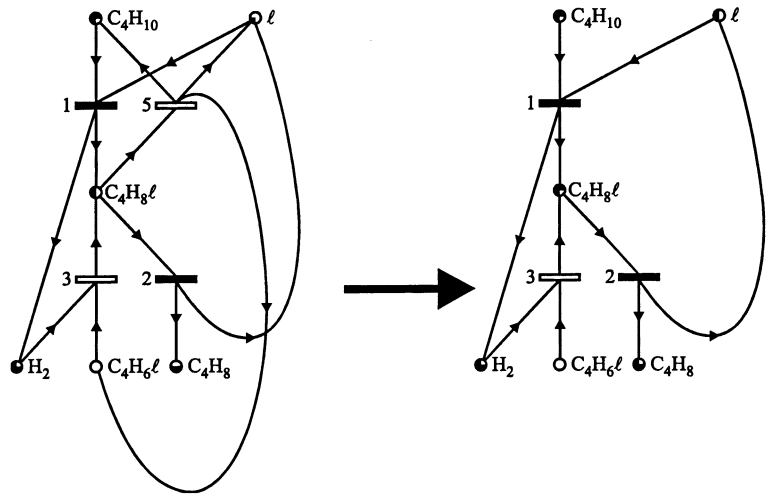

Fig. C.6. Generation of subproblem 3 at step 2.

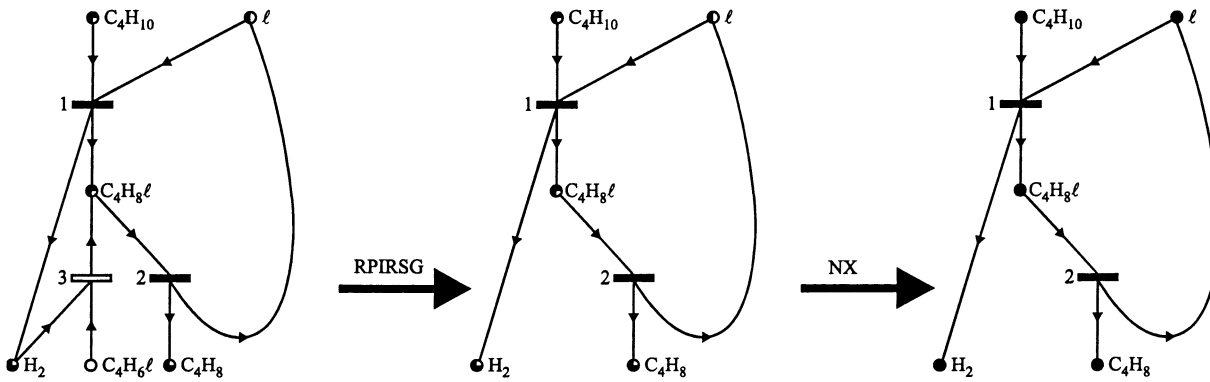

Fig. C.7. Step 3 resulting in feasible pathway 1.

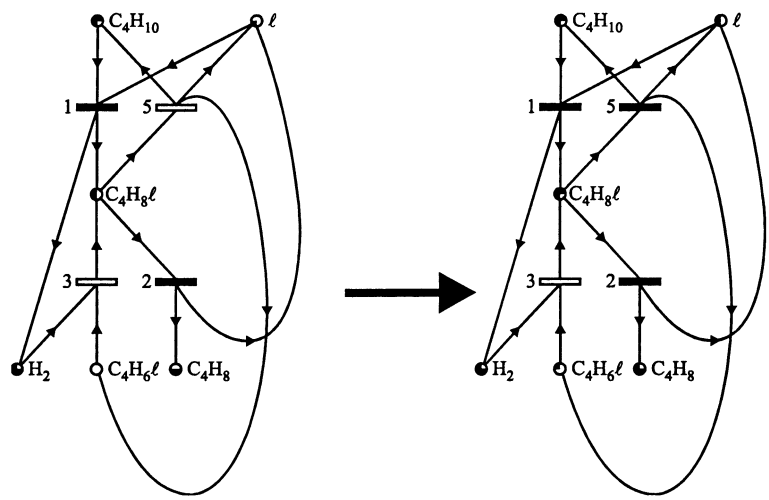

Fig. C.8. Generation of subproblem 4 at step 2.

In other words, for any elementary-reaction step e_i defined, its opposite step, denoted by $-e_i$, is also defined in the problem. It is assumed that

$$M \cap O = \varnothing \text{ and } E \notin O \cup M$$

A.2. Representation

Elementary reactions, chemical and active species are represented by P-graphs as follows:

For the overall reaction, E, let $\omega^-(E)$ and $\omega^+(E)$ denote the set of starting reactants (precursors) and final products (targets), respectively; it follows that

$$\omega^-(E) = \{a_j : a_j \in M,\ E_j < 0\}$$

$$\omega^+(E) = \{a_j : a_j \in M,\ E_j > 0\}$$

If $\omega(E)$ is the set of chemical species consumed or produced by the overall reaction, E, we have

$$\omega(E) = \omega^-(E) \cup \omega^+(E)$$

For any elementary-reaction step $e_i \in O$, let $\omega^-(e_i)$ and $\omega^+(e_i)$ denote the set of reactants and products of e_i, respectively; it follows that

$$\omega^-(e_i) = \{a_j : a_j \in M,\ e_{j,i} < 0\}$$

and

$$\omega^+(e_i) = \{a_j : a_j \in M,\ e_{j,i} > 0\}$$

If $\omega(e_i)$ denotes the set of chemical and active species consumed or produced by the elementary-reaction step e_i, we have

$$\omega(e_i) = \omega^-(e_i) \cup \omega^+(e_i)$$

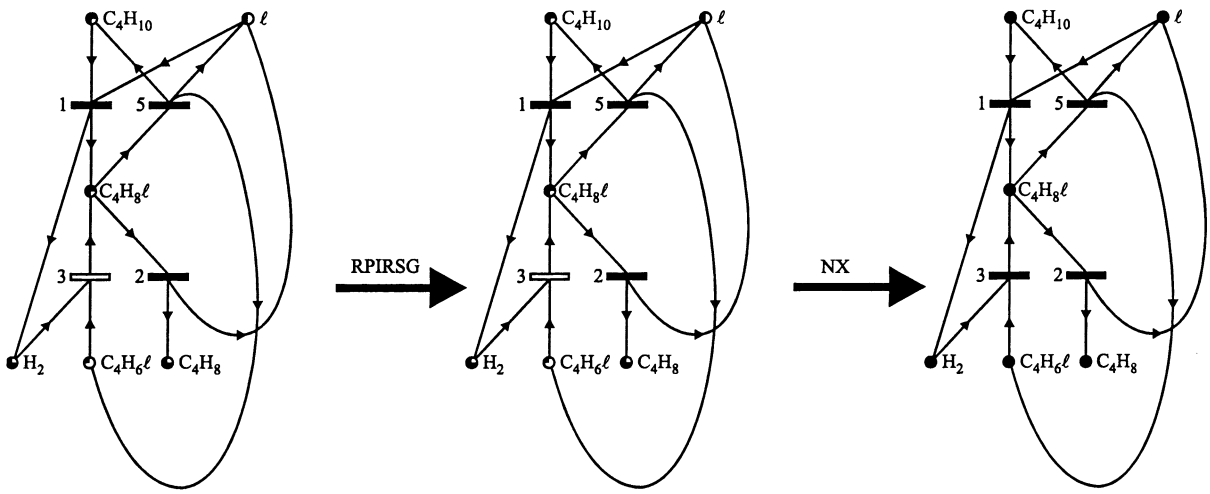

Fig. C.9. Step 4 identifying a cyclic pathway by solving an LP problem.

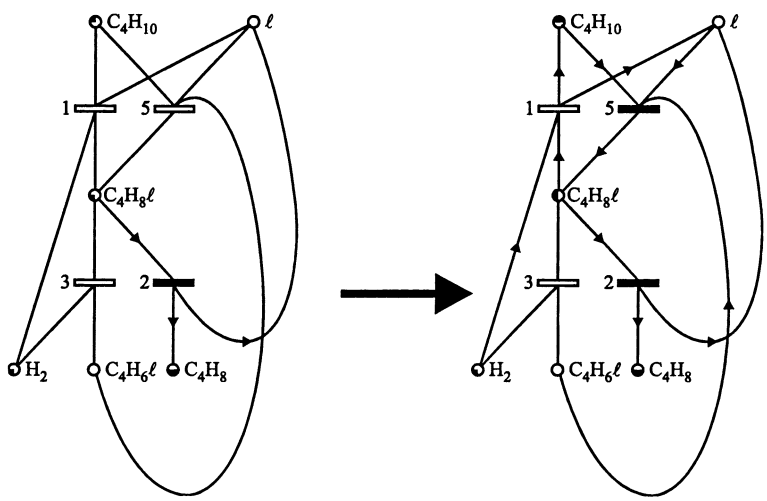

Fig. C.10. Generation of subproblem 5 at step 1.

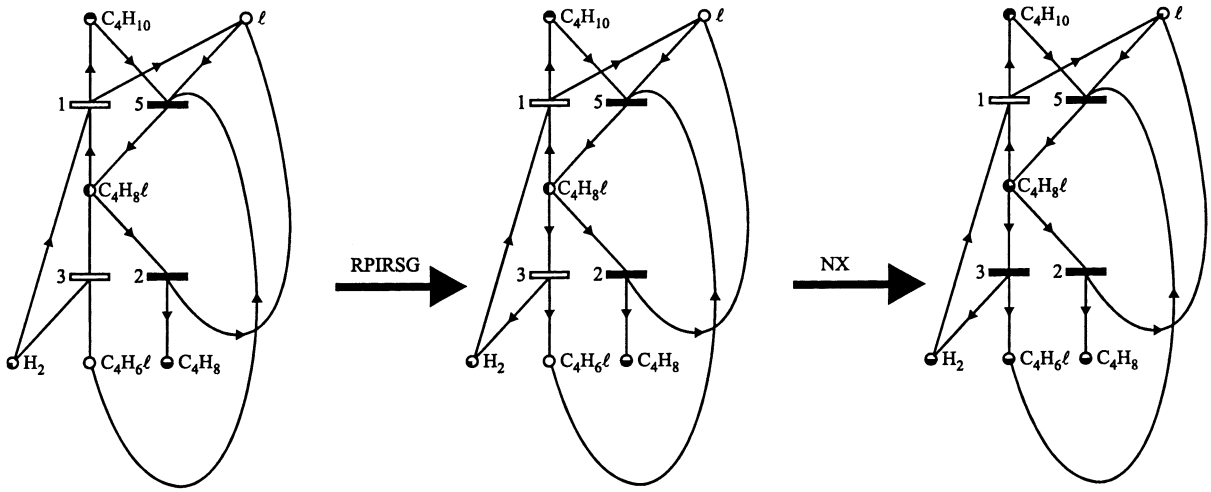

Fig. C.11. Step 5.

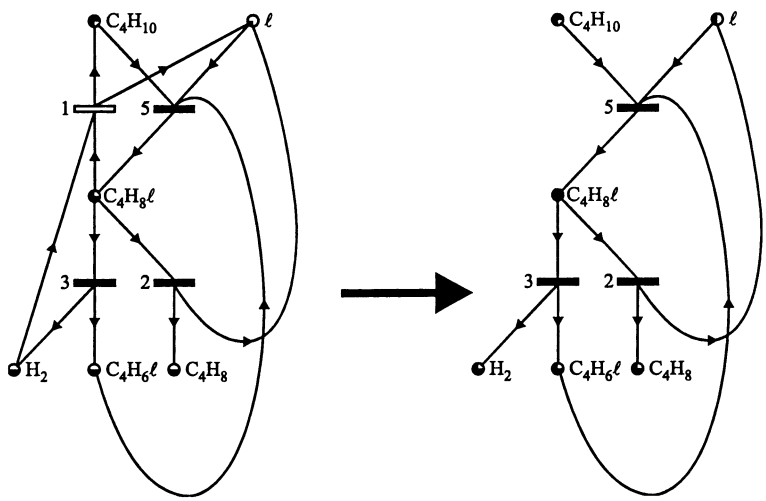

Fig. C.12. Generation of subproblem 6 at step 5.

For any chemical or active species $a_j \in M$, let $\upsilon^-(a_j)$ and $\upsilon^+(a_j)$ denote the set of elementary-reaction steps consuming and producing a_j, respectively; it follows that

$$\upsilon^-(a_j) = \{e_i : e_i \in O,\ a_j \in \omega^+(e_i)\}$$

and

$$\upsilon^+(a_j) = \{e_i : e_i \in O,\ a_j \in \omega^-(e_i)\}$$

If $\upsilon(a_j)$ denotes the set of elementary-reaction steps consuming or producing a_j, we have obviously

$$\upsilon(a_j) = \upsilon^-(a_j) \cup \upsilon^-(a_j)$$

For any set of the elementary-reaction steps, $o \subseteq O$, let $\Psi^-(o)$ and $\Psi^+(o)$ denote the set of chemical and active species consumed and produced by any element of o, respectively; it follows that

$$\Psi^-(o) = \bigcup_{e_i \in o} \omega^-(e_i)$$

and

$$\Psi^+(o) = \bigcup_{e_i \in o} \omega^+(e_i)$$

If $\Psi(o)$ is the set of chemical and active species consumed or produced by any element of o, we have

$$\Psi(o) = \Psi^-(o) \cup \Psi^+(o)$$

For any set of chemical or active species $m \subseteq M$, let $\varphi^-(m)$ and $\varphi^+(m)$ denote the set of elementary-reaction steps producing and consuming any element of m, respectively; it follows that

$$\varphi^{-}(m) = \bigcup_{a_j \in m} \upsilon^{-}(a_j)$$

and

$$\varphi^{+}(m) = \bigcup_{a_j \in m} \upsilon^{+}(a_j)$$

If $\varphi(m)$ is the set of elementary-reaction steps producing or consuming any element of m, we have

$$\varphi(m) = \varphi^{-}(m) \cup \varphi^{+}(m)$$

For any set of elementary-reaction steps $o \subseteq O$, let $X(o)$ denote the set of opposite steps of the elementary-reaction steps included in set o; then,

$$X(o) = \{e_i : -e_i \in o\}$$

Any P-graph representing a set of chemical or active species and elementary-reaction steps is given by pair (m, o), where $o \subseteq O$ is the set of the elementary-reaction steps, and $m \subseteq M$ is the set of chemical and active species, where

$$\Psi(o) \subseteq m$$

The set of vertices of the graph is

$$V = o \cup m$$

where any vertex corresponding to set m is termed M-type, and any vertex corresponding to set o is termed O-type. The set of arcs is

$$A = A_1 \cup A_2$$

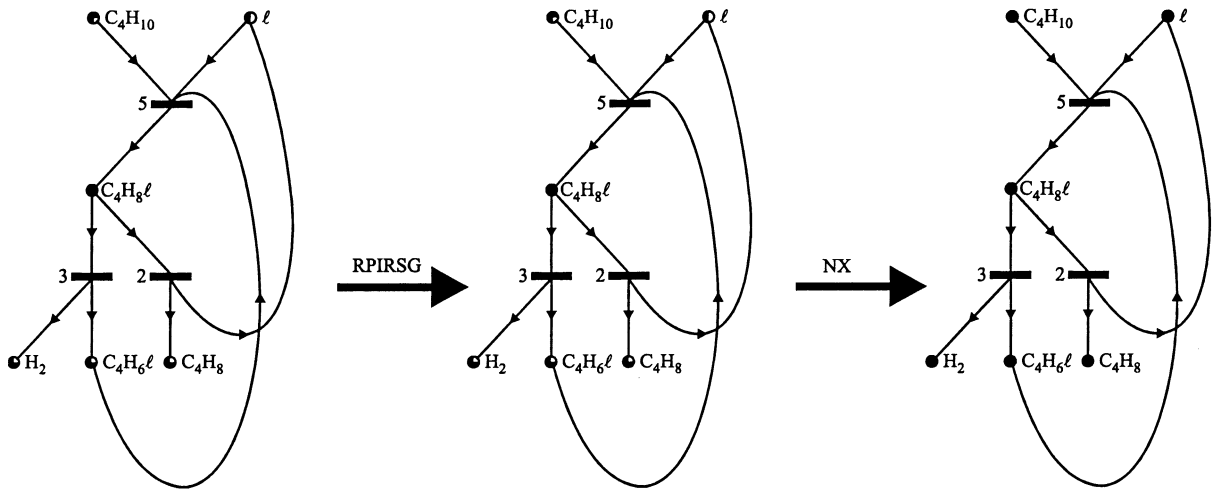

Fig. C.13. Step 6 resulting in feasible pathway 2.

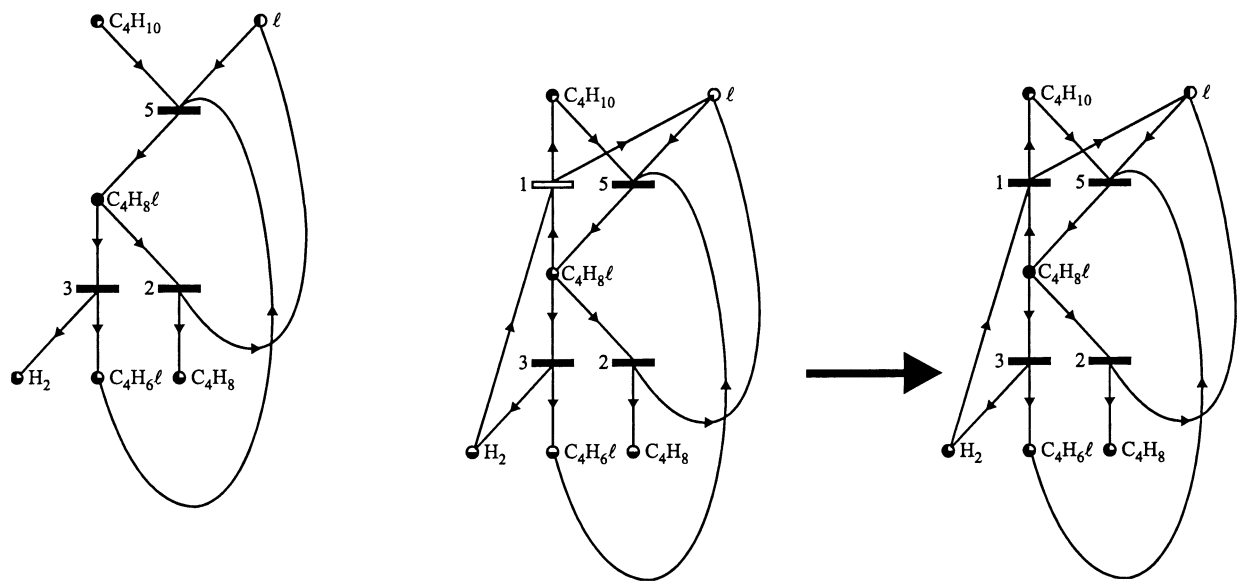

Fig. C.14. Generation of subproblem 7 at step 5.

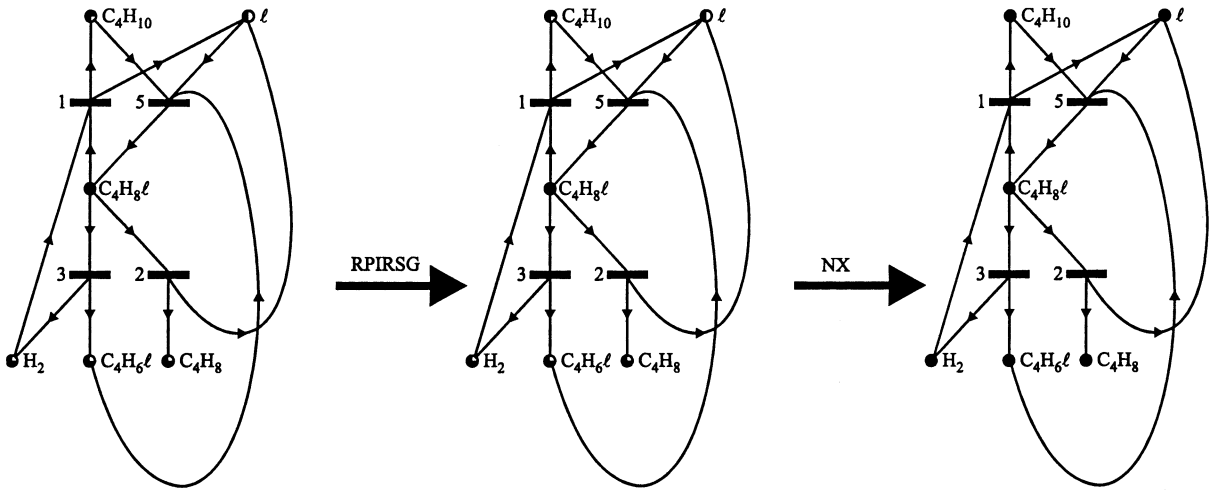

Fig. C.15. Step 7 identifying a cyclic pathway with the aid of set *avoid*.

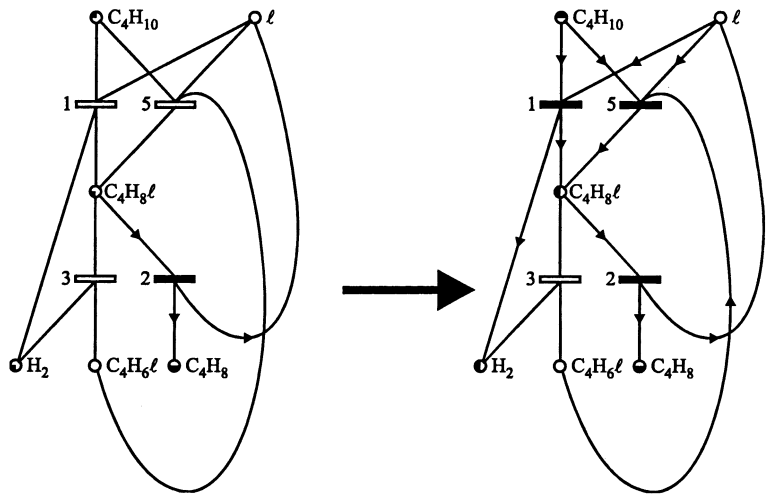

Fig. C.16. Generation of subproblem 8 at step 1.

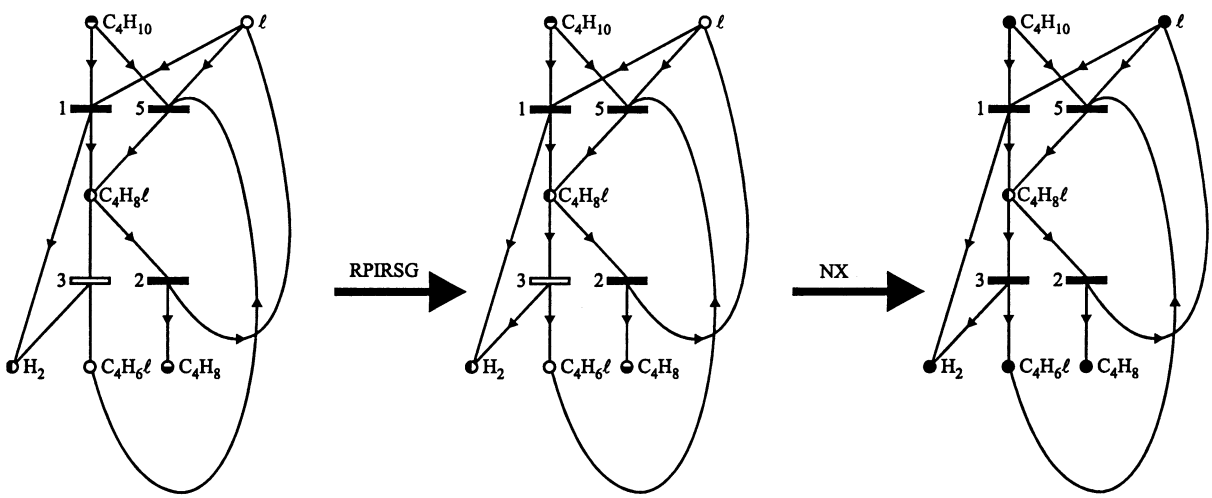

Fig. C.17. Step 8 resulting in feasible pathway 2.

where

$A_1 = \{(a_j, e_i): a_j \in m,\ e_i \in o,\ a_j \in \omega^-(e_i)\}$

and

$A_2 = \{(e_i, a_j): e_i \in o,\ a_j \in m,\ a_j \in \omega^+(e_i)\}$

In graphical representation, vertices of the O-type are denoted by horizontal bars, and vertices of the M-type are denoted by solid circles.

Appendix B

Search (Enumeration) tree for algorithm RPISSG and steps of the algorithm illustrated with the dehydrogenation of butane (C_4H_{10}) to butene (C_4H_8)

Appendix C

Search (enumeration) tree for algorithm PBT and steps of the algorithm illustrated with the dehydrogenation of butane (C_4H_{10}) to butene (C_4H_8)

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