How catalytic mechanisms reveal themselves in multiple steady-state data: II. An ethylene hydrogenation example

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Abstract

Many mechanisms have been proposed for ethylene hydrogenation on catalytic surfaces. In a companion article we discussed how isothermal multiple steady-state data can be used to discriminate between rival candidate mechanisms. While most catalytic mechanisms have the capacity to support some pair of steady states, they will not usually have the capacity to support a particular pair of steady states observed in the laboratory. The companion article described how chemical reaction network theory can be used to determine whether multiple steady-state data are consistent with a given mechanism. Multiple steady-state data had been obtained previously for ethylene hydrogenation over a rhodium catalyst in an isothermal CFSTR. In this article, these data are used to discriminate between a total of 80 single- and multiple-pathway mechanisms. Given certain assumptions, it will be seen that only nine of the 80 mechanisms are consistent with the data. The purpose of this article is not to favor one mechanism over another, but to demonstrate the type of refined mechanism discrimination that is possible using even fragmentary multiple steady-state data. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Ethylene hydrogenation on a variety of catalytic surfaces has been extensively studied over the years [1]. However, no single operative mechanism has been universally accepted, even for the same catalytic material. Thus, good discrimination tools are needed when elucidating the behavior of a given catalyst. In a companion article [2] we discussed how, when isothermal multiple steady-state data are available, chemical reaction network theory can be used to discriminate between different candidate mechanisms in a very refined way. In that article only hypothetical examples were used in order to demonstrate the general methods and uses of the theory. In this article we apply those same techniques to actual laboratory data for ethylene hydrogenation on a rhodium surface.

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In the early 1980's, a similar experimental study was performed for ethylene hydrogenation over a platinum catalytic surface by Mullins and Rumschitzki [3,4]. When studying ethylene hydrogenation over platinum in an isothermal CFSTR, Mullins obtained partial multiple steady-state data at a single temperature. Mullins and Rumschitzki were able to discriminate between a number of candidate mechanisms for ethylene hydrogenation using chemical reaction network theory techniques similar to those discussed here. The candidate mechanisms they examined are included in the mechanisms considered in this article. Here, however, we are able to apply more recent developments in chemical reaction network theory, in particular developments that permit analysis of catalytic mechanisms with multiple pathways.

Section 2 contains a brief summary of the facets of chemical reaction network theory that are applied in this article. For a more in-depth introduction to the theory, see [2,5–7]. Section 3 describes the experimental set-up and procedure that were used to obtain the multiple steady-state data examined in this article. In Sections 4 and 5 the data are used to discriminate between 80 distinct mechanisms for ethylene hydrogenation.

The application of the theory in this article is algorithmic in nature. Although the theory could, in principle, be applied by hand, computer implementation is easier, faster and less error-prone. All of the results in this article were found using the CHEMICAL REACTION NETWORK TOOLBOX Version 1.1[1], a stand-alone freely distributed public program that is suitable for use on both DOS- and WINDOWS-based personal computers. Only a basic understanding of the ideas found in the companion article is necessary for use of this program.

2. Chemical reaction network theory overview

When the underlying mechanism of a catalytic process can only be conjectured, rate constants for the elementary reactions are unlikely to be known precisely. One of the goals of chemical reaction network theory is to determine whether a given candidate mechanism has the *qualitative* capacity to explain behavior observed in the laboratory — that is, whether there exists *any* set of positive rate constants such that the corresponding differential equations produce the observed behavior. If no such set of rate constants exists, then that mechanism cannot be considered viable. In this way, laboratory data — in this article, partial multiple steady-state data — can be used to discriminate between different candidate mechanisms.

In order to illustrate the questions we are exploring, consider the ethylene hydrogenation mechanism:

$$H_2 + 2S \underset{\beta}{\overset{\alpha}{\rightleftharpoons}} 2H - S$$

$$C_2H_4 + H - S \underset{\varepsilon}{\overset{\gamma}{\rightleftharpoons}} C_2H_5 - S \qquad (M2)$$

$$C_2H_5 - S + H - S \overset{\nu}{\rightarrow} C_2H_6 + 2S$$

In this mechanism, the symbol S represents an empty catalytic site and the symbols $H - S$ and $C_2H_5 - S$ represent H and C_2H_5 adsorbed onto a single catalytic site. Suppose that this mechanism is

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[1] The toolbox is available at http://www.che.eng.ohio-state.edu/ ∼ FEINBERG/CRNT

occurring in an isothermal CFSTR whose feed contains only H_2, C_2H_4 and an inert carrier gas. In addition, it will be assumed in this article that all mechanistic reactions are governed by mass action kinetics, that the gas phase and the surface compositions are each spatially uniform and that there is no change in gas phase density between the reactor inlet and the reactor outlet. (In the experiment under consideration, the gas phase was composed largely of the inert carrier, argon.) In this context, mechanism (M2) gives rise to the following differential equations for the species concentrations:

$$
\begin{aligned}
\dot{c}_{H_2} &= (1/\tau)\left(c_{H_2}^f - c_{H_2}\right) - \alpha c_{H_2} c_S^2 + \beta c_{H-S}^2 \\
\dot{c}_{C_2H_4} &= (1/\tau)\left(c_{C_2H_4}^f - c_{C_2H_4}\right) - \gamma c_{C_2H_4} c_{H-S} + \varepsilon c_{C_2H_5-S} \\
\dot{c}_{C_2H_6} &= (-1/\tau)c_{C_2H_6} + \nu c_{C_2H_5-S} c_{H-S} \\
\dot{c}_S &= -2\alpha c_{H_2} c_S^2 + 2\beta c_{H-S}^2 + 2\nu c_{C_2H_5-S} c_{H-S} \\
\dot{c}_{H-S} &= 2\alpha c_{H_2} c_S^2 - 2\beta c_{H-S}^2 - \gamma c_{C_2H_4} c_{H-S} + \varepsilon c_{C_2H_5-S} - \nu c_{C_2H_5-S} c_{H-S} \\
\dot{c}_{C_2H_5-S} &= \gamma c_{C_2H_4} c_{H-S} - \varepsilon c_{C_2H_5-S} - \nu c_{C_2H_5-S} c_{H-S}
\end{aligned}
\tag{1}
$$

where τ is the residence time, $c_{H_2}^f$ and $c_{C_2H_4}^f$ are the feed concentrations of H_2 and C_2H_4 respectively, and the overdot represents differentiation with respect to time. The concentrations for the gas phase species are expressed per unit volume, while the concentrations for the surface species are expressed per unit area.

At steady state all of the derivatives in (1) must equal zero; this condition leads to the following equations that any steady state composition must satisfy:

$$
\begin{aligned}
0 &= (1/\tau)\left(c_{H_2}^f - c_{H_2}\right) - \alpha c_{H_2} c_S^2 + \beta c_{H-S}^2 \\
0 &= (1/\tau)\left(c_{C_2H_4}^f - c_{C_2H_4}\right) - \gamma c_{C_2H_4} c_{H-S} + \varepsilon c_{C_2H_5-S} \\
0 &= (-1/\tau)c_{C_2H_6} + \nu c_{C_2H_5-S} c_{H-S} \\
0 &= -2\alpha c_{H_2} c_S^2 + 2\beta c_{H-S}^2 + 2\nu c_{C_2H_5-S} c_{H-S} \\
0 &= 2\alpha c_{H_2} c_S^2 - 2\beta c_{H-S}^2 - \gamma c_{C_2H_4} c_{H-S} + \varepsilon c_{C_2H_5-S} - \nu c_{C_2H_5-S} c_{H-S} \\
0 &= \gamma c_{C_2H_4} c_{H-S} - \varepsilon c_{C_2H_5-S} - \nu c_{C_2H_5-S} c_{H-S}
\end{aligned}
\tag{2}
$$

Let a pair of compositions be given as:

$$
\{c_1^*, c_2^*, \ldots, c_N^*\} \quad \text{and} \quad \{c_1^{**}, c_2^{**}, \ldots, c_N^{**}\}
\tag{3}
$$

where N is the number of species in the network, c_i^* is the concentration of the ith species in the first composition and c_i^{**} is the concentration of the ith species in the second composition. In addition, suppose that the compositions are compatible with the conservation of catalytic sites; for example, site conservation for mechanism (M2) requires that:

$$
c_S^* + c_{H-S}^* + c_{C_2H_5-S}^* = c_S^{**} + c_{H-S}^{**} + c_{C_2H_5-S}^{**}
\tag{4}
$$

The question we are exploring in this article is: *do there exist positive rate constants such that the pair of compositions, (3), are compatible with the corresponding steady state equations and with the conservation of catalytic sites?*

Two theories from chemical reaction network theory that answer this question are the deficiency one theory and the (broader) advanced deficiency theory [2]. Both theories determine a network's capacity to support multiple steady states through the construction of systems of inequalities and equalities, called *signatures*, for the network under consideration. These signatures provide information on which pairs of steady states the network has the capacity to support.

Recall from the companion article that these signatures contain a set of numbers

$$\{\mu_1, \mu_2, \ldots, \mu_N\} \tag{5}$$

which are related to a pair of compositions, (3), by the equation:

$$\mu_i = \ln\left(\frac{c_i^{**}}{c_i^*}\right) \qquad i = 1, \ldots, N. \tag{6}$$

Deficiency one theory and advanced deficiency theory state that a reaction network will have the capacity to support a pair of steady states, (3), consistent with site conservation if and only if the set of μ's, defined by Eq. (6), satisfies one of the signatures constructed for the network. If a network does not have the capacity to support multiple steady states, then the theories will also indicate this fact and will produce no signatures for that network.

Deficiency one theory produces the following signature[2] for mechanism (M2), in a CFSTR context[3]:

$$\mu_{C_2H_5-S} + \mu_{H-S} = \mu_{C_2H_6} > 0 > \{\mu_{H_2}, \mu_{C_2H_4}\}$$
$$2\mu_{H-S} > \mu_{H_2} + 2\mu_S > \mu_{C_2H_6} > \mu_{C_2H_4} + \mu_{H-S} > \mu_{C_2H_5-S} \tag{7}$$

In this signature, the notation $0 > \{\mu_{H_2}, \mu_{C_2H_4}\}$ indicates that both μ_{H_2} and $\mu_{C_2H_4}$ are less than zero. The fact that a signature can be found for this mechanism indicates that the mechanism has the capacity to support *some* pair of steady states. Thus, there exist some pair of distinct compositions, (3), consistent with site conservation, and positive rate constants, α, β, γ, ε and ν, such that the equations of (2) are satisfied. Again, this signature was found using the CHEMICAL REACTION NETWORK TOOLBOX; it is not necessary to understand the underlying theory in order to use the methods in this article.

In an isothermal CFSTR context, most catalytic mechanisms have the capacity to support some pair of steady states. Thus, the mere existence of multiple steady states does not provide a good means for discrimination. However, signatures provide more information than just the qualitative capacity to support multiple steady states; the signatures tell us which *particular* pairs of steady states a network has the capacity to support. Multiple steady-state data, even partial data, lead to restrictions on at least some of the μ's through Eq. (6). Although a signature may have a solution, it is not guaranteed that there exists a set of μ's consistent with *both* the signature *and* the given data. Methods for constructing these data restrictions are discussed in the companion article and are demonstrated using actual laboratory data in Section 4 of this article.

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[2] For every signature of a reaction network there is an equivalent signature that is formed by reversing all of the inequality signs. These new signatures correspond to reversing the roles of the two steady states in Eq. (6). These equivalent signatures are not written explicitly, but they still must be considered when testing a signature against multiple steady-state data.

[3] Recall from the companion article that, when modeling a CFSTR, the pseudo-reaction $A_i \to 0$ must be added to a mechanism for each species in the effluent and the pseudo-reaction $0 \to A_i$ must be added to the mechanism for each species in the feed. These reactions account for the changes in concentrations due to the presence of the effluent and feed streams.

More examples of signatures can be found in the companion article [2]. The algorithms for finding the signatures of a reaction network can be found in [6,8]; however, knowledge of these algorithms is not necessary for an understanding of this article. In fact, the use of a computer is both faster and more reliable. The CHEMICAL REACTION NETWORK TOOLBOX [9] will apply both deficiency one theory and advanced deficiency theory. The toolbox will find the signatures for a given reaction network. In addition, if multiple steady-state data are available, the program can test that data against the signatures. When multiple steady states consistent with the data are possible, the toolbox constructs sample rate constants such that the corresponding differential equations admit a pair of distinct steady states consistent with the data.

3. Experimental set-up

Yue and Saltsburg examined multiple steady state behavior for ethylene hydrogenation on a rhodium surface. This section briefly describes their experimental set-up and procedure. A more detailed description of the apparatus, the preparation of the catalyst and the experimental results can be found in Yue's PhD thesis [10].

Ethylene hydrogenation was studied in a β''-alumina reactor tube (Ceramatec) with one end closed. The closed end was coated with a thin porous rhodium film with a thickness of about 1000 Å. The tube had an inner diameter of 1.34 cm and was made to approximate a CFSTR by placing a circular ceramic piece approximately 2 cm above the catalytic surface. This ceramic piece had a clearance of 0.5 mm around its edge to allow the escape of the effluent. Two holes were cut through the ceramic piece for the insertion of an inlet tube and of a thermocouple. This reaction chamber is illustrated in Fig. 1.
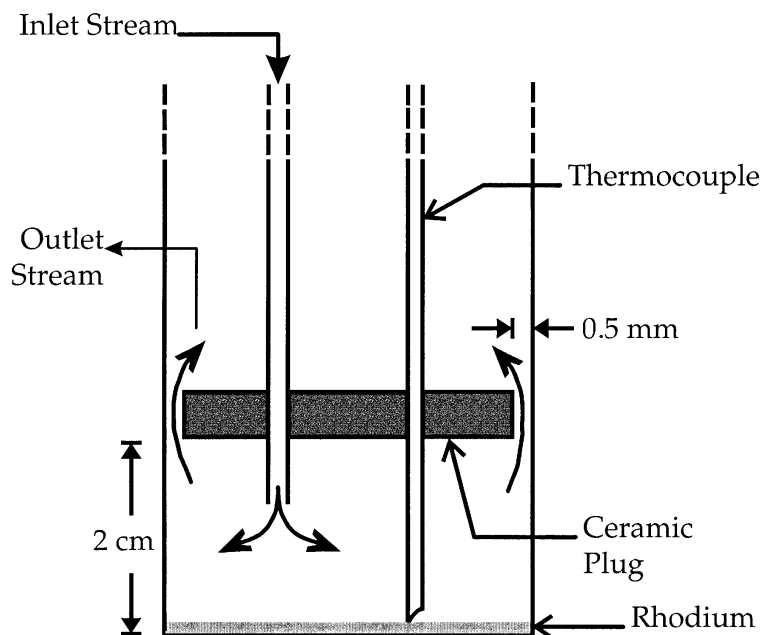
Fig. 1. Reaction chamber set-up.

The concentrations of ethylene and ethane in the effluent stream were measured using a GOW-MAC series 750 gas chromatograph with a flame ionization detector. The concentration of hydrogen in the effluent stream was measured using a GOWMAC series 550 thermal conductivity gas chromatograph with a silica gel column at room temperature.

A solid electrolyte cell was used to measure the thermodynamic activity of hydrogen on the catalytic surface using a technique developed by Vayenas and Saltsburg [11]. When an electrolyte cell is a proton conductor, the potential difference between the two sides of the cell depends on the activity of hydrogen adsorbed on one side of the cell (as compared to the hydrogen activity on the other side of the cell). In this experiment the catalytic surface acted as one side of the electrolyte cell; the other side of the cell was exposed to a reference chamber containing hydrogen and argon. In this way the activity of hydrogen on the catalytic surface was determined by measuring the potential difference in the electrolyte cell.

The advantage of this method is that measurements can be taken while the experiment is running. Thus surface data can be obtained without disturbing the operation of the reactor and without risking the contamination of the hydrogen surface concentration during the measurement process. While exact measurements of the concentration of hydrogen absorbed on the catalytic surface were not possible in this experiment, it was still possible to determine which steady state had the higher concentration of hydrogen adsorbed on the catalytic surface.

The feed for the Saltsburg–Yue experiments contained hydrogen, ethylene and a high concentration of argon, which acted as an inert carrier. Precautions were taken to keep oxygen out of both the feed stream and the reaction chamber.

Multiple steady states were observed by Yue using two different procedures. First, for a fixed feed, the temperature of the reactor was incrementally increased. A new steady state was reached after each increase in temperature. As the temperature was increased, the steady state reaction rate increased gradually; however, at a certain temperature the reaction rate jumped sharply in value. At this point, Yue decreased the temperature of the reactor incrementally; again, at each temperature, he allowed the reactor to reach a steady state. The reaction rate did not drop sharply from one temperature to the next, but rather, decreased slowly, and completely different steady state reaction rates were exhibited at each of the revisited temperatures. Eventually, when the reactor was reduced to a low enough temperature, the steady state reaction rate jumped back to a previously exhibited lower rate[4]. By use of this method it was possible to find two distinct steady states at the same temperature. These results were highly reproducible and it was possible to switch back and forth between distinct steady states at the same temperature during a single experimental run. The catalytic surface was rejuvenated between experimental runs.

In the second procedure the temperature was kept constant and the concentration of hydrogen in the feed was varied incrementally to obtain a succession of steady states. The same type of reaction rate behavior was observed for this method. As the hydrogen feed concentration was increased, the reaction rate also gradually increased until, at a certain concentration, the reaction rate jumped to a markedly higher value. When the hydrogen concentration in the feed was then decreased, a new set of steady states could be obtained. Again, it was possible, using this procedure, to find two distinct steady states at the same temperature and feed composition.

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[4] Readers familiar with the usual reaction-rate vs. temperature hysteresis picture will recognize that Yue's experiment were traversing the high- and low-rate branches.

For the data discussed in this article the feed stream had a flow rate of about 2.2 cm^3/s. The partial pressures of hydrogen and ethylene in the feed were 0.28 atm and 0.046 atm, respectively. The reaction chamber was kept at a temperature of 343 K. Under these conditions two steady states were observed. For the first steady state, the partial pressures of hydrogen, ethylene and ethane were measured to be 0.26, 0.028, and 0.018 atm, respectively. For the second steady state, the partial pressures of hydrogen, ethylene and ethane were measured to be 0.25, 0.018, and 0.028 atm, respectively. In addition, the hydrogen surface activity measurements indicated that more hydrogen was adsorbed on the catalytic surface in the second steady state than in the first steady state.

It is prudent at this point to examine how well this experimental set-up conforms to the assumptions, such as those stated in Section 2, that underlie the presumed differential equations. All mechanistic reactions discussed in this article occur on the catalytic surface; thus the differential equations are only affected by the surface temperature. Since the catalytic surface consisted of a pure metallic material, it had a high thermal conductivity and thermal spatial uniformity is reasonable to assume. In addition, once steady state had been achieved, the temperature did not change with time. It is difficult to determine if surface concentration uniformity was achieved. However, the experimental results were highly reproducible, both within individual experimental runs and from one run to another following rejuvenation of the catalyst; such reproducibility suggests that surface uniformity was likely. Moreover, the design of the chamber would seem conducive to reasonably good mixing in the gas phase. Finally, any density change can be detected by comparing the feed and effluent flow rates. For the data analyzed in this article, the discrepancy between the feed and effluent flow rates was less than 2%.

It is possible to account in the theory for deviations from some of these assumptions [10,12]. However, the purpose of this case study is to demonstrate the power of the techniques of chemical reaction network theory, not to make any definitive statements about the operative mechanism of ethylene hydrogenation. Ideally, an experimenter using these techniques will want to take steps to ensure that the assumptions of the theory are satisfied.

4. Mechanism analysis

The gas phase steady state concentrations were calculated from the partial pressures using an ideal gas assumption. These converted multiple steady-state data (at 343 K) are summarized in Table 1. The main question addressed in this article is: *for what mechanisms do there exist positive rate constants such that the corresponding CFSTR differential equations support multiple steady states consistent with the data in Table 1?*

Testing mechanisms against multiple steady-state data is one of the major applications of deficiency one theory and advanced deficiency theory. A given mechanism has the capacity to support a pair steady state compositions, (3), if and only if the μ's, defined by Eq. (6), satisfy one of the

Table 1
Multiple steady-state data

	c_{H_2} mol/m^3	$c_{C_2H_4}$ mol/m^3	$c_{C_2H_6}$ mol/m^3	c_{H-S}
Steady state #1	9.24	0.99	0.64	Lower
Steady state #2	8.89	0.64	0.99	Higher

signatures of that mechanism. The data in Table 1 impose certain restrictions on the μ's. A mechanism will be consistent with the data if and only if there exists a set of μ's satisfying one of the signatures of the mechanism and these data restrictions. From the gas phase data, values for μ_{H_2}, $\mu_{C_2H_4}$ and $\mu_{C_2H_6}$ can be calculated as follows:

$$\mu_{H_2} = \ln(8.89/9.24) \approx -0.04$$
$$\mu_{C_2H_4} = \ln(0.64/0.99) \approx -0.44 \tag{8}$$
$$\mu_{C_2H_6} = \ln(0.99/0.64) \approx 0.44$$

Although numerical values for the μ's related to the surface species cannot be calculated, some information on the signs of these μ's can be gained from the data. First, since there is more hydrogen adsorbed on the catalytic surface in steady state #2 than in steady state #1, Eq. (6) produces the condition:

$$\mu_{H-S} = \ln(c^{**}_{H-S}/c^{*}_{H-S}) > 0 \tag{9}$$

Second, by site conservation, only certain sign patterns for the μ's are allowed by the data[5]: at least one of the μ's related to the surface species must be positive and at least one must be negative[6]. Thus, from Eq. (9), the final data restriction on the μ's is:

$$\text{At least one of the remaining } \mu\text{'s related to the surface species must be negative} \tag{10}$$

Remark. Recall from the companion article that, in order to model a CFSTR, pseudo-reactions corresponding to the effluent and feed stream must be added to each catalytic mechanism. For the reactor in this article the reactions

$$H_2 \rightleftharpoons \quad 0 \quad \rightleftharpoons C_2H_4$$
$$\uparrow$$
$$C_2H_6$$
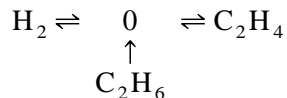
must be added to each mechanism in order to get the corresponding reaction network. In this article only catalytic mechanisms will be given; the addition of the pseudo-reactions will be assumed and not shown explicitly.

When Yue originally obtained the data in Table 1, he tested the data against 13 mechanisms found in literature for ethylene hydrogenation. These 13 mechanisms are given in Table 2.

Mechanisms (M1) through (M7) are reaction mechanisms of Eley–Rideal type [10]. Mechanisms (M1) and (M2) were suggested by Jenkins and Rideal [13]. Mechanisms (M3) thru (M6) were proposed by Mullins and Rumschitzki [3,4]. Mechanism (M9) is the Horiuti–Polanyi reaction mechanism [14]. Mechanisms (M8) and (M10) are variations of (M9); all three are of Langmuir–Hinshelwood type. Mechanism (M11) is the Twigg–Rideal mechanism [16]. Mechanism (M12) was suggested by chemisorption studies of ethylene [17]. Finally, mechanism (M13) was proposed by Godbey et al. [18].

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[5] Both deficiency one theory and advanced deficiency theory contain procedures for finding these sign pattern restrictions. The CHEMICAL REACTION NETWORK TOOLBOX apply these sign restrictions automatically.

[6] Site conservation can also be satisfied if all of the μ's related to surface species are equal to zero. In this case the surface compositions for both steady states are the same.

Table 2
Original 13 mechanisms

$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S \quad (M1)$	Jenkins and Rideal [13]
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + H-S \rightleftharpoons C_2H_5-S,$ $C_2H_5-S + H-S \rightarrow C_2H_6 + 2S \quad (M2)$	Jenkins and Rideal [13]
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$ $C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S \quad (M3)$	Mullins and Rumschitzki [3,4]
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$ $C_2H_4 + H-S \rightleftharpoons C_2H_5-S,$ $C_2H_5-S + H-S \rightarrow C_2H_6 + 2S \quad (M4)$	Mullins and Rumschitzki [3,4]
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + S \rightleftharpoons C_2H_4-S,$ $C_2H_4-S + S \rightleftharpoons C_2H_3-S + H-S,$ $C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S \quad (M5)$	Mullins and Rumschitzki [3,4]
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + S \rightleftharpoons C_2H_4-S,$ $C_2H_4-S + S \rightleftharpoons C_2H_3-S + H-S,$ $C_2H_4 + H-S \rightleftharpoons C_2H_5-S,$ $C_2H_5-S + H-S \rightarrow C_2H_6 + 2S \quad (M6)$	Mullins and Rumschitzki [3,4]
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$ $C_2H_4-S_2 + H_2 \rightarrow C_2H_6 + 2S \quad (M7)$	Yue [10]
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + S \rightleftharpoons C_2H_4-S,$ $C_2H_4-S + H-S \rightleftharpoons C_2H_5-S + S,$ $C_2H_5-S + H-S \rightarrow C_2H_6 + 2S \quad (M8)$	Horiuti–Polanyi [14,15]
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$ $C_2H_4-S_2 + H-S \rightleftharpoons C_2H_5-S + 2S,$ $C_2H_5-S + H-S \rightarrow C_2H_6 + 2S \quad (M9)$	Horiuti–Polanyi [14,15]
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$ $C_2H_4-S_2 + H-S \rightleftharpoons C_2H_5-S_2 + S,$ $C_2H_5-S_2 + H-S \rightarrow C_2H_6 + 3S \quad (M10)$	Horiuti–Polanyi [14,15]
$C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$ $C_2H_4-S_2 + H_2 \rightleftharpoons C_2H_5-S + H-S,$ $C_2H_5-S + 2S \rightleftharpoons C_2H_4-S_2 + H-S,$ $C_2H_5-S + H-S \rightarrow C_2H_6 + 2S \quad (M11)$	Twigg [16]
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$ $C_2H_4-S_2 + H-S \rightleftharpoons C_2H_5-S + 2S,$ $C_2H_4-S_2 + 2S \rightleftharpoons C_2H_3-S_3 + H-S,$ $C_2H_5-S + H-S \rightarrow C_2H_6 + 2S \quad (M12)$	Yue [10,17]
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$ $C_2H_4-S_2 + 2S \rightleftharpoons C_2H_3-S_3 + H-S,$ $C_2H_4 + 2C_2H_4-S_2 + 2S \rightarrow C_2H_6 + 2C_2H_3-S_3 \quad (M13)$	Godbey et al. [18]

All 13 of these mechanisms fall within the scope of deficiency one theory. Of these 13 mechanisms, only mechanism (M1) cannot support multiple steady states; deficiency one theory produces signatures for each of the other mechanisms. However, there does not exist any set of μ's that satisfies one of the signatures produced by the theory for these mechanisms *when taken with the data restrictions* (8)–(10). Thus, none of the mechanisms has the capacity to support a pair of steady states consistent with the data in Table 1; that is, for no mechanism do there exist positive rate constants such that the corresponding differential equations support multiple steady states consistent with the steady states that Yue observed in the laboratory. New mechanisms are needed to explain the data in Table 1.

5. New mechanisms

Each of the mechanisms in Table 2 has only a single pathway for the production of ethane. One way to produce new candidate mechanisms is to combine these to form new multiple-pathway mechanisms. For example, mechanisms (M1) and (M4) could be combined to produce the mechanism:

$$H_2 + 2S \rightleftharpoons 2H - S,$$
$$C_2H_4 + 2S \rightleftharpoons C_2H_3 - S + H - S,$$
$$C_2H_4 + H - S \rightleftharpoons C_2H_5 - S,$$
$$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S,$$
$$C_2H_4 + 2H - S \rightarrow C_2H_6 + 2S \tag{M1_4}$$

Most multiple-pathway mechanisms fall outside the scope of deficiency one theory; for such mechanisms it is necessary to use advanced deficiency theory[7].

There are 78 ways of combining the 13 mechanisms, two at a time. However, these 78 combinations give only 67 distinct multiple-pathway mechanisms. Five of the combinations produce one of the original 13 mechanisms; for example, the combination of mechanism (M2) and (M4) gives mechanisms (M4) back again. Six of the combinations produce mechanisms duplicated by another combination; for example, the combination of mechanisms (M2) and (M3) also gives mechanism (M1_4). These 67 distinct mechanisms are given in Table 3.

Advanced deficiency theory produces signatures for all of the reaction networks associated with the 67 multiple-pathway mechanisms. Thus, all of these mechanisms have the capacity to support multiple steady states. However, only nine mechanisms, {(M2_11), (M4_11), (M6_11), (M7_13), (M8_11), (M9_13), (M10_11), (M10_13), (M11_13)} have signatures consistent with the data restrictions (8)–(10). Thus, out of the 68 multiple-pathway mechanisms, only these nine mechanisms, indicated by a check mark in Table 3, have the capacity to support multiple steady states *consistent with the data in Table 1*.

For each of these nine mechanisms, advanced deficiency theory provides procedures for finding sample rate constants that give rise to full steady state compositions consistent with the data in Table 1. Again, the CHEMICAL REACTION NETWORK TOOLBOX will find these rate constants and steady states automatically.

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[7] At the time Yue obtained the data in Table 1 advanced deficiency theory had not been developed yet and so this analysis could not be done.

Table 3
Multiple-pathway mechanisms

$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$ $C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S,$ $C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M1_2)	$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$ $C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H-S,$ $C_2H_4 + 2C_2H_4 - S_2 + 2S \rightarrow C_2H_6 + 2C_2H_3 - S_3,$ $C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M1_13)
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_3 - S + H-S,$ $C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$ $C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S,$ $C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M1_4)	$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$ $C_2H_4 - S_2 + H_2 \rightarrow C_2H_6 + 2S,$ $C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$ $C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M2_7)
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + S \rightleftharpoons C_2H_4 - S,$ $C_2H_4 - S + S \rightleftharpoons C_2H_3 - S + H-S,$ $C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$ $C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S,$ $C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M1_6)	$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + S \rightleftharpoons C_2H_4 - S,$ $C_2H_4 - S + H-S \rightleftharpoons C_2H_5 - S + S,$ $C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$ $C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M2_8)
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$ $C_2H_4 - S_2 + H_2 \rightarrow C_2H_6 + 2S,$ $C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M1_7)	$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$ $C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5 - S + 2S,$ $C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$ $C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M2_9)
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + S \rightleftharpoons C_2H_4 - S,$ $C_2H_4 - S + H-S \rightleftharpoons C_2H_5 - S + S,$ $C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S,$ $C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M1_8)	$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$ $C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5 - S_2 + S,$ $C_2H_5 - S_2 + H-S \rightarrow C_2H_6 + 3S,$ $C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$ $C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M2_10)
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$ $C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5 - S + 2S,$ $C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S,$ $C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M1_9)	$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$ $C_2H_4 - S_2 + H_2 \rightleftharpoons C_2H_5 - S + H-S,$ $C_2H_5 - S + 2S \rightleftharpoons C_2H_4 - S_2 + H-S,$ $C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M2_11)✔
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$ $C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5 - S_2 + S,$ $C_2H_5 - S_2 + H-S \rightarrow C_2H_6 + 3S,$ $C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M1_10)	$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$ $C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5 - S + 2S,$ $C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H-S,$ $C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$ $C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M2_12)
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2H-S \rightarrow C_2H_6,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$ $C_2H_4 - S_2 + H_2 \rightleftharpoons C_2H_5 - S + H-S,$ $C_2H_5 - S + 2S \rightleftharpoons C_2H_4 - S_2 + H-S,$ $C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M1_11)	$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$ $C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H-S,$ $C_2H_4 + 2C_2H_4 - S_2 + 2S \rightarrow C_2H_6 + 2C_2H_3 - S_3,$ $C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$ $C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M2_13)
$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$ $C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5 - S + 2S,$ $C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H-S,$ $C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S,$ $C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M1_12)	$H_2 + 2S \rightleftharpoons 2H-S,$ $C_2H_4 + S \rightleftharpoons C_2H_4 - S,$ $C_2H_4 - S + S \rightleftharpoons C_2H_3 - S + H-S,$ $C_2H_4 + 2S \rightleftharpoons C_2H_3 - S + H-S,$ $C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M3_5)

Table 3 (*continued*)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + S \rightleftharpoons C_2H_4-S,$
$C_2H_4 - S + S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + H-S \rightleftharpoons C_2H_5-S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M3_6)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$
$C_2H_4 - S_2 + H_2 \rightarrow C_2H_6 + 2S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M3_7)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + S \rightleftharpoons C_2H_4-S,$
$C_2H_4 - S + H-S \rightleftharpoons C_2H_5-S + S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M3_8)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$
$C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5-S + 2S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M3_9)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$
$C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5-S_2 + S,$
$C_2H_5 - S_2 + H-S \rightarrow C_2H_6 + 3S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M3_10)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$
$C_2H_4 - S_2 + H_2 \rightleftharpoons C_2H_5-S + H-S,$
$C_2H_5 - S + 2S \rightleftharpoons C_2H_4-S_2 + H-S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M3_11)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$
$C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5-S + 2S,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3-S_3 + H-S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M3_12)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3-S_3 + H-S,$
$C_2H_4 + 2C_2H_4 - S_2 + 2S \rightarrow C_2H_6 + 2C_2H_3-S_3,$
$C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M3_13)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + S \rightleftharpoons C_2H_4-S,$
$C_2H_4 - S + S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + H-S \rightleftharpoons C_2H_5-S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M4_6)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$
$C_2H_4 - S_2 + H_2 \rightarrow C_2H_6 + 2S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + H-S \rightleftharpoons C_2H_5-S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M4_7)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + S \rightleftharpoons C_2H_4-S,$
$C_2H_4 - S + H-S \rightleftharpoons C_2H_5-S + S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + H-S \rightleftharpoons C_2H_5-S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M4_8)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$
$C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5-S + 2S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + H-S \rightleftharpoons C_2H_5-S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M4_9)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$
$C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5-S_2 + S,$
$C_2H_5 - S_2 + H-S \rightarrow C_2H_6 + 3S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + H-S \rightleftharpoons C_2H_5-S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M4_10)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + H-S \rightleftharpoons C_2H_5-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$
$C_2H_4 - S_2 + H_2 \rightleftharpoons C_2H_5-S + H-S,$
$C_2H_5 - S + 2S \rightleftharpoons C_2H_4-S_2 + H-S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M4_11)✔

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$
$C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5-S + 2S,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3-S_3 + H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + H-S \rightleftharpoons C_2H_5-S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M4_12)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4-S_2,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3-S_3 + H-S,$
$C_2H_4 + 2C_2H_4 - S_2 + 2S \rightarrow C_2H_6 + 2C_2H_3-S_3,$
$C_2H_4 + 2S \rightleftharpoons C_2H_3-S + H-S,$
$C_2H_4 + H-S \rightleftharpoons C_2H_5-S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M4_13)

Table 3 (*continued*)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H_2 \rightarrow C_2H_6 + 2S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + S \rightleftharpoons C_2H_3 - S + H-S,$
$C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M5_7)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + H-S \rightleftharpoons C_2H_5 - S + S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S,$
$C_2H_4 - S + S \rightleftharpoons C_2H_3 - S + H-S,$
$C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M5_8)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5 - S + 2S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + S \rightleftharpoons C_2H_3 - S + H-S,$
$C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M5_9)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5 - S_2 + S,$
$C_2H_5 - S_2 + H-S \rightarrow C_2H_6 + 3S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + S \rightleftharpoons C_2H_3 - S + H-S,$
$C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M5_10)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + S \rightleftharpoons C_2H_3 - S + H-S,$
$C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H_2 \rightleftharpoons C_2H_5 - S + H-S,$
$C_2H_5 - S + 2S \rightleftharpoons C_2H_4 - S_2 + H-S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M5_11)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5 - S + 2S,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H-S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + S \rightleftharpoons C_2H_3 - S + H-S,$
$C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M5_12)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H-S,$
$C_2H_4 + 2C_2H_4 - S_2 + 2S \rightarrow C_2H_6 + 2C_2H_3 - S_3,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + S \rightleftharpoons C_2H_3 - S + H-S,$
$C_2H_4 + 2H-S \rightarrow C_2H_6 + 2S$ (M5_13)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H_2 \rightarrow C_2H_6 + 2S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + S \rightleftharpoons C_2H_3 - S + H-S,$
$C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M6_7)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + H-S \rightleftharpoons C_2H_5 - S + S,$
$C_2H_4 - S + S \rightleftharpoons C_2H_3 - S + H-S,$
$C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M6_8)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5 - S + 2S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + S \rightleftharpoons C_2H_3 - S + H-S,$
$C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M6_9)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5 - S_2 + S,$
$C_2H_5 - S_2 + H-S \rightarrow C_2H_6 + 3S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + S \rightleftharpoons C_2H_3 - S + H-S,$
$C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M6_10)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + S \rightleftharpoons C_2H_3 - S + H-S,$
$C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H_2 \rightleftharpoons C_2H_5 - S + H-S,$
$C_2H_5 - S + 2S \rightleftharpoons C_2H_4 - S_2 + H-S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M6_11)✔

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H-S \rightleftharpoons C_2H_5 - S + 2S,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H-S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + S \rightleftharpoons C_2H_3 - S + H-S,$
$C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M6_12)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H-S,$
$C_2H_4 + 2C_2H_4 - S_2 + 2S \rightarrow C_2H_6 + 2C_2H_3 - S_3,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + S \rightleftharpoons C_2H_3 - S + H-S,$
$C_2H_4 + H-S \rightleftharpoons C_2H_5 - S,$
$C_2H_5 - S + H-S \rightarrow C_2H_6 + 2S$ (M6_13)

Table 3 (*continued*)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + H - S \rightleftharpoons C_2H_5 - S + S,$
$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H_2 \rightarrow C_2H_6 + 2S$ (M7_8)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H - S \rightleftharpoons C_2H_5 - S + 2S,$
$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S,$
$C_2H_4 - S_2 + H_2 \rightarrow C_2H_6 + 2S$ (M7_9)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H - S \rightleftharpoons C_2H_5 - S_2 + S,$
$C_2H_5 - S_2 + H - S \rightarrow C_2H_6 + 3S,$
$C_2H_4 - S_2 + H_2 \rightarrow C_2H_6 + 2S$ (M7_10)

$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H_2 \rightleftharpoons C_2H_5 - S + H - S,$
$C_2H_5 - S + 2S \rightleftharpoons C_2H_4 - S_2 + H - S,$
$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S,$
$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4S_2 + H_2 \rightarrow C_2H_6 + 2S$ (M7_11)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H - S \rightleftharpoons C_2H_5 - S + 2S,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H - S,$
$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S,$
$C_2H_4 - S_2 + H_2 \rightarrow C_2H_6 + 2S$ (M7_12)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H - S,$
$C_2H_4 + 2C_2H_4 - S_2 + 2S \rightarrow C_2H_6 + 2C_2H_3 - S_3,$
$C_2H_4 - S_2 + H_2 \rightarrow C_2H_6 + 2S$ (M7_13)✔

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H - S \rightleftharpoons C_2H_5 - S + 2S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + H - S \rightleftharpoons C_2H_5 - S + S,$
$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S$ (M8_9)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H - S \rightleftharpoons C_2H_5 - S_2 + S,$
$C_2H_5 - S_2 + H - S \rightarrow C_2H_6 + 3S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + H - S \rightleftharpoons C_2H_5 - S + S,$
$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S$ (M8_10)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + H - S \rightleftharpoons C_2H_5 - S + S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H_2 \rightleftharpoons C_2H_5 - S + H - S,$
$C_2H_5 - S + 2S \rightleftharpoons C_2H_4 - S_2 + H - S,$
$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S$ (M8_11)✔

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H - S \rightleftharpoons C_2H_5 - S + 2S,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H - S,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + H - S \rightleftharpoons C_2H_5 - S + S,$
$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S$ (M8_12)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H - S,$
$C_2H_4 + 2C_2H_4 - S_2 + 2S \rightarrow C_2H_6 + 2C_2H_3 - S_3,$
$C_2H_4 + S \rightleftharpoons C_2H_4 - S,$
$C_2H_4 - S + H - S \rightleftharpoons C_2H_5 - S + S,$
$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S$ (M8_13)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H - S \rightleftharpoons C_2H_5 - S_2 + S,$
$C_2H_5 - S_2 + H - S \rightarrow C_2H_6 + 3S,$
$C_2H_4 - S_2 + H - S \rightleftharpoons C_2H_5 - S + 2S,$
$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S$ (M9_10)

$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H_2 \rightleftharpoons C_2H_5 - S + H - S,$
$C_2H_5 - S + 2S \rightleftharpoons C_2H_4 - S_2 + H - S,$
$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S$ (M9_11)

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H - S,$
$C_2H_4 + 2C_2H_4 - S_2 + 2S \rightarrow C_2H_6 + 2C_2H_3 - S_3,$
$C_2H_4 - S_2 + H - S \rightleftharpoons C_2H_5 - S + 2S,$
$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S$ (M9_13)✔

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H - S \rightleftharpoons C_2H_5 - S_2 + S,$
$C_2H_5 - S_2 + H - S \rightarrow C_2H_6 + 3S,$
$C_2H_4 - S_2 + H_2 \rightleftharpoons C_2H_5 - S + H - S,$
$C_2H_5 - S + 2S \rightleftharpoons C_2H_4 - S_2 + H - S,$
$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S$ (M10_11)✔

$H_2 + 2S \rightleftharpoons 2H-S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H - S \rightleftharpoons C_2H_5 - S + 2S,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H - S,$
$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S,$
$C_2H_4 - S_2 + H - S \rightleftharpoons C_2H_5 - S_2 + S,$
$C_2H_5 - S_2 + H - S \rightarrow C_2H_6 + 3S$ (M10_12)

Table 3 (*continued*)

$H_2 + 2S \rightleftharpoons 2H - S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H - S,$
$C_2H_4 + 2C_2H_4 - S_2 + 2S \rightarrow C_2H_6 + 2C_2H_3 - S_3,$
$C_2H_4 - S_2 + H - S \rightleftharpoons C_2H_5 - S_2 + S,$
$C_2H_5 - S_2 + H - S \rightarrow C_2H_6 + 3S$ (M10_13)➘

$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + H_2 \rightleftharpoons C_2H_5 - S + H - S,$
$C_2H_5 - S + 2S \rightleftharpoons C_2H_4 - S_2 + H - S,$
$H_2 + 2S \rightleftharpoons 2H - S,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H - S,$
$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S$ (M11_12)

$H_2 + 2S \rightleftharpoons 2H - S,$
$C_2H_4 + 2S \rightleftharpoons C_2H_4 - S_2,$
$C_2H_4 - S_2 + 2S \rightleftharpoons C_2H_3 - S_3 + H - S,$
$C_2H_4 + 2C_2H_4 - S_2 + 2S \rightarrow C_2H_6 + 2C_2H_3 - S_3,$
$C_2H_4 - S_2 + H_2 \rightleftharpoons C_2H_5 - S + H - S,$
$C_2H_5 - S + 2S \rightleftharpoons C_2H_4 - S_2 + H - S,$
$C_2H_5 - S + H - S \rightarrow C_2H_6 + 2S$ (M11_13)➘

In summary, nine of the 80 mechanisms have been found to be consistent with the data in Table 1. It is interesting to note that all nine of these mechanisms have either (M11) or (M13) as a component.

All of the constituent mechanisms considered here were proposed by others; we make no judgments about their efficacy. Indeed, it is certainly possible that other mechanisms can also explain the data or that the experimental set-up did not satisfy one of the assumptions of the theory. For example, it is likely that the final reaction step of mechanism (M13) is not governed by mass action kinetics. It is also possible that either the gas phase or surface concentrations were not uniform[8]. Still, this example has demonstrated the type of refined discrimination results possible using the information carried by multiple steady-state data.

Remark. Recall from the companion article that, for advanced deficiency theory, there are conditions that determine whether a mechanism's signatures are linear. If a mechanism fails one of the linearity conditions, then the mechanism's signatures will contain some non-linear equalities; for such a mechanism, non-linear techniques are required for a *full* analysis. However, as will be seen, the linear part of these signatures often contain enough information to produce definitive answers.

Of the 67 multiple pathway mechanisms, nine fail the linearity conditions of advanced deficiency theory: {(M2_11), (M3_11), (M4_11), (M5_11), (M6_11), (M8_11), (M10_11), (M11_13)}. The signatures produced by advanced deficiency theory for these nine mechanisms contain non-linear equalities. However, before using non-linear analysis, the linear portions of the signatures can be tested against the data restrictions. For example, for the signatures of mechanism (M1_11), none of the linear portions is consistent with the data restrictions; thus none of the full signatures can be consistent with the data restrictions either. Similarly, it turns out that mechanisms (M3_11) and (M5_11) are also not consistent with data in Table 1.

For mechanism (M2_11) a set of μ values can be found that satisfies both the linear portion of one of its signatures and the data restrictions. This set of μ values can be used to try to find rate constants and steady state compositions consistent with the data in Table 1. However, this technique is not guaranteed to produce definitive results. The CHEMICAL REACTION NETWORK TOOLBOX is programmed to make one attempt at finding a consistent multiple steady state example in this manner. If an example is not found, then this test is inconclusive and non-linear analysis is necessary. However, the

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[8] It should be noted, though, that the results Yue obtained were extremely reproducible. This suggests that surface uniformity was likely.

toolbox successfully found sample rate constants and two steady state compositions for mechanism (M2_11) consistent with the data in Table 1. In fact, the toolbox found rate constants and two steady state compositions consistent with the data for mechanisms (M4_11), (M6_11), (M8_11), (M10_11) and (M11_13) as well. Thus, even for mechanisms that might, in principle, require nonlinear analysis, the advanced deficiency theory produced, for this case study, definitive results, both positive and negative, using linear methods.

6. Conclusion

Multiple steady-state data had been reported for ethylene hydrogenation on a rhodium catalyst in an isothermal CFSTR. In this article, 80 mechanisms have been examined in an attempt to elucidate the operative mechanism for this reactor using these data. Out of these 80 mechanisms it was determined, using reaction network theory, that only nine of the mechanisms have the capacity to support multiple steady states consistent with the data obtained.

The purpose of this article is not to determine the ''true'' operative mechanism for ethylene hydrogenation. Instead, this article demonstrates the power of reaction network theory as a mechanism discrimination tool. On the basis of only fragmentary multiple steady-state data, it was possible, granted certain assumptions, to eliminate 71 out of 80 candidate mechanisms. In addition, these results can be obtained without any knowledge of underlying theory by using the CHEMICAL REACTION NETWORK TOOLBOX. Such refined results suggest that the theory has the potential to be a valuable tool for mechanism discrimination.

Acknowledgements

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