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Resolution of Kinetic Models by Steady State Tracing

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The technique of steady state isotopic tracing of heterogeneous catalytic reactions is examined to provide a procedure for determining to what extent it is possible to determine individual step velocities for a given mechanism. The experimental data required to obtain such information is also discussed using recent studies as illustrations.

The use of steady state tracing in which rate of passage of an isotopic species from one reactant or product to another is observed, while at the same time the overall reaction itself is maintained constant has proven to be a useful tool in characterizing heterogeneous catalysis systems (*1*). The purpose of this note is to outline the general procedure employed in this type of study to show when individual step velocities of a mechanistic model can be determined and what information is required for this purpose.

Except for the instrumentation needed to monitor tracer concentrations, the experimental equipment employed is the same as that usually used in kinetic studies of heterogeneous catalysis. So-called gradientless reactors in which the reacting gases are rapidly recirculated while feed is introduced and product withdrawn are most useful. For reactions in which rapid deterioration of catalyst occurs, once through differential conversion reactors are sometimes employed. In either case the overall reaction rate V is maintained constant at a given temperature, pressure and concentration of reacting species and products. For a recirculating reactor a tracer experiment then consists in setting tracer concentrations at fixed levels in the feed for all components and observing the corresponding tracer concentrations in the product. The transfer rate of tracer to the traced species in the gas phase is then directly calculated as follows:

$$-a_e^i = m^i\left(\frac{F_0^i z_{0e}^i}{W} - \frac{F^i z_e^i}{W}\right), \qquad (1)$$

where

a_e^i	transfer rate of traced element e to species i, g·atoms/sec/g catalyst.
F_0^i	rate of feed of species i to reactor, moles/sec.
F^i	rate of removal of species i from reactor, moles/sec.
z_{0e}^i	fraction of tracer element e in feed of component i which is marked.
z_e^i	fraction of tracer element e in effluent of component i which is marked.
W	weight of catalyst, g.
m^i	number of atoms of tracer element in a molecule of i.

In the case of a different reactor in which *both* the reaction rate and the rate of tracer transfer are differential

$$a_e^i = m^i \frac{\Delta(F^i z_e^i)}{W}. \qquad (2)$$

In either a recirculating or differential reactor the rate of tracer transfer to each species will be a function of all the z_e^i involved. Often the subscript e is omitted when only a single tracer is used.

Interpretation of the data obtained from tracer experiments is concerned with estimation of velocities of intermediate steps in an assumed mechanism. In order to accomplish this the functional relationship between the a^i and z^i must first be derived from material balances involving tracer transfer. Since there is no change in the number of tracer atoms, one of these material balances is given for the n marked species in a given traced reaction by the following:

$$\sum_{i=1}^{i=n} a^i = 0. \qquad (3)$$

The remaining $n - 1$ balances are obtained by making material balances of transfer of a given tracer between steps assuming no isotopic kinetic effects. If there are k intermediates involved $k + n - 1$ such balances will be required. Elimination of the markings of intermediate species results in the required $n - 1$ structural equations. In view of Eq. (3) one of the z^i and a^i could be eliminated from these balances so that actually $n - 1$ of each of these variables is also involved. The maximum number of constants which can be specified in these equations is $(n - 1)^2$ since they are linear and homogeneous, and the corresponding number of experiments would be $(n - 1)$. These constants contain the desired step velocities as parameters, either alone or in groups. It is next necessary to ascertain whether the parameters are themselves independent of each other. Such determination is facilitated by considering the groupings which result from passage of tracer in paths connecting the reacting species as has been previously discussed (*1*, *2*). Once the number of independent velocity parameters is established they can be treated as unknowns in the $n - 1$ simultaneous structural equations.

The values of these parameters give the information obtainable by tracer experimentation conducted in this fashion and are used to compute the individual step velocities. It is possible in some cases to compute all the mechanistic step velocities from this information. If this is not possible velocities can often be grouped so that the available parameters will suffice for their estimation. A useful additional relationship not related to the tracer technique was developed by Horiuti (*3*) and its use in the present context has been discussed (*2*).

$$\prod_{r=1}^{r=i} (v_{+r}/v_{-r})^{\nu_r} = \exp(-\Delta G/RT), \qquad (4)$$

where ΔG is the total Gibbs free energy change for overall reaction, R is the gas constant and T is the absolute temperature. ν_r is the stoichiometric number of each step in the overall reaction, i.e., the number of times it occurs each time the overall reaction occurs once. Other supplementary information related to step velocities can sometimes be derived from tracer experiments which involve changes in the type of tracing within traced molecules. Also, if more than a single tracer element can be employed for a given system, it is possible to reduce the number of experiments required for a single determination of the parameters.

In the following discussion of applications of this method we will restrict consideration to systems in which the number of marked species involved $n \leq 3$.

Simple Reactions

Paradoxically, steady state tracing will not enable step velocities to be determined for what is probably the simplest case, though this can be accomplished by unsteady state tracing (*4*):

$$A = B, \tag{5}$$

with the reaction mechanism

$$\begin{aligned} \mathrm{A} + l &\underset{v_{-1}}{\overset{v_{+1}}{\rightleftharpoons}} \mathrm{A}l, \\ \mathrm{A}l &\underset{v_{-2}}{\overset{v_{+2}}{\rightleftharpoons}} \mathrm{B} + l, \end{aligned} \tag{6}$$

where l is a catalyst site and Al is a chemisorbed species. Let us suppose that A and B each contain only a single atom of traced element. There are $n = 2$ species involved and $k = 1$ intermediate. Hence there will be $n + k - 1 = 2$ material balance equations:

$$\begin{aligned} -a^{\mathrm{A}} &= z^{\mathrm{A}}v_{+1} - z^{\mathrm{A}l}v_{-1}, \\ -a^{\mathrm{A}} &= z^{\mathrm{A}l}v_{+2} - z^{\mathrm{B}}v_{-2}. \end{aligned} \tag{7}$$

Elimination of $z^{\mathrm{A}l}$ and use of the relationship $V = v_{+i} - v_{-i}$ results in the equation

$$\frac{V_+^{1,2}}{V_-^{1,2}} = \frac{v_{+1}v_{+2}}{v_{-1}v_{-2}} = \frac{z^{\mathrm{B}} + (a^{\mathrm{A}}/V)}{z^{\mathrm{A}} + (a^{\mathrm{A}}/V)}. \tag{8}$$

Tracing will provide no more information than to establish the ratio $v_{+1}v_{+2}/v_{-1}v_{-2}$. Since $V = V_+^{1,2} - V_-^{1,2}$ this corresponds to only one parameter in Eq. (8). Two additional equations $V = v_{+1} - v_{-1} = v_{+2} - v_{-2}$ result in a total of three independent equations to determine the four unknowns $v_{\pm 1,2}$. Therefore, they cannot be established.

It is readily shown that for any reaction governed by Eq. (5) and following a sequence

$$\mathrm{A} \underset{v_{-1}}{\overset{v_{+1}}{\rightleftharpoons}} X'l \cdots X^n l \underset{v_{-n}}{\overset{v_{+n}}{\rightleftharpoons}} \mathrm{B}, \tag{9}$$

a relationship similar to Eq. (8) is obtained by tracing

$$\frac{V_+^{1,2,\ldots,n}}{V_-^{1,2,\ldots,n}} = \frac{v_{+1}v_{+2}\cdots v_{+n}}{v_{-1}v_{-2}\cdots v_{-n}} = \frac{z^{\mathrm{B}} + (a^{\mathrm{A}}/V)}{z^{\mathrm{A}} + (a^{\mathrm{A}}/V)}. \tag{10}$$

The path velocities are useful in establishing kinetic equations for reactions of this type, but it is not possible to determine separate step velocities by tracing in this fashion. The discussion of this problem by Happel and Hnatow (*1*) contains the incorrect statement that reactions of the type shown in Eq. (9) can be resolved by multiple level steady state tracing.

For more complicated cases, however, single and double level tracing will often enable step velocities to be determined. Consider the reaction

$$\mathrm{A} = \mathrm{B} + \mathrm{C}, \tag{11}$$

where it is assumed that a single tracer element is employed that contains two atoms of tracer element in A and one atom each in B and C. Assume the mechanism

$$\begin{aligned} \mathrm{A} + l &\underset{v_{-1}}{\overset{v_{+1}}{\rightleftharpoons}} \mathrm{A}l, \\ \mathrm{A}l &\underset{v_{-2}}{\overset{v_{+2}}{\rightleftharpoons}} \mathrm{B} + \mathrm{C} + l. \end{aligned} \tag{12}$$

In this case the number of terminal species $n = 3$, the number of intermediates $k = 1$, so there will be $n + k - 1 = 3$ material balances:

$$\begin{aligned} -a^{\mathrm{A}} &= 2z^{\mathrm{A}}v_{+1} - 2z^{\mathrm{A}l}v_{-1}, \\ a^{\mathrm{B}} &= z^{\mathrm{A}l}v_{+2} - z^{\mathrm{B}}v_{-2}, \\ a^{\mathrm{C}} &= z^{\mathrm{A}l}v_{+2} - z^{\mathrm{C}}v_{-2}. \end{aligned} \tag{13}$$

Upon elimination of $z^{\mathrm{A}l}$ from these equations, we obtain the required two equations to determine a^i as functions of z^i.

$$\left.\begin{aligned} &\frac{V_+^{1,2}}{V_-^{1,2}} z^{\mathrm{A}} - z^{\mathrm{B}} - \frac{a^{\mathrm{B}}}{V_-^{1,2}} + \frac{[(a^{\mathrm{A}}/2) + a^{\mathrm{B}}]}{v_{+1}} \times \frac{V_+^{1,2}}{V_-^{1,2}} = 0, \\ &\frac{V_+^{1,2}}{V_-^{1,2}} z^{\mathrm{A}} - z^{\mathrm{C}} - \frac{a^{\mathrm{C}}}{V_-^{1,2}} + \frac{[(a^{\mathrm{A}}/2) + a^{\mathrm{C}}]}{v_{+1}} \times \frac{V_+^{1,2}}{V_-^{1,2}} = 0, \end{aligned}\right\} \tag{14}$$

where

$$V_+^{1,2} = v_{+1}v_{+2}/(v_{-1} + v_{+2})$$

and

$$V_-^{1,2} = v_{-1}v_{-2}/(v_{-1} + v_{+2}).$$

Since

$$V = V_+^{1,2} - V_-^{1,2} = v_{+1} - v_{-1} = v_{+2} - v_{-2},$$

we can specify a selection of two independent parameters, i.e., one from each of two of the following three groups, $V_+^{1,2}$ and $V_-^{1,2}$, v_{+1} and v_{-1}, v_{+2}, and v_{-2}. For convenience if we choose $V_+^{1,2}$ and v_{+1}, it is easy to eliminate v_{+1} from Eqs. (14). A single level experiment will establish $V_+^{1,2}$ using the remaining equation and in turn the four $v_{\pm 1,2}$ from the above equalities.

Sulfur Dioxide Oxidation

The oxidation of sulfur dioxide using a gradientless recirculating reactor has been treated by Happel *et al.* (5) using oxygen (^{18}O) and sulfur (^{35}S) isotopes for the following reaction and mechanism:

$$2\,\mathrm{SO_2} + \mathrm{O_2} = 2\,\mathrm{SO_3}. \qquad (15)$$

Step No.	Partial reaction	Stoichiometric No., ν	
1	$\mathrm{O_2} + 2l \underset{v_{-1}}{\overset{v_{+1}}{\rightleftharpoons}} 2\mathrm{O}l$	1	
2	$\mathrm{SO_2} + l \underset{v_{-2}}{\overset{v_{+2}}{\rightleftharpoons}} \mathrm{SO_2}l$	2	(16)
3	$\mathrm{SO_2}l + \mathrm{O}l \underset{v_{-3}}{\overset{v_{+3}}{\rightleftharpoons}} \mathrm{SO_3}l + l$	2	
4	$\mathrm{SO_3}l \underset{v_{-4}}{\overset{v_{+4}}{\rightleftharpoons}} \mathrm{SO_3}l + l$	2	

For this mechanism, employing oxygen as the tracer element, the number of terminal species containing oxygen is $n = 3$ and the number of intermediates $k = 3$ so the number of material balances is $n + k - 1 = 5$. They may be written as follows:

$$\left.\begin{aligned}
-a_\mathrm{O}^{\mathrm{O_2}} &= 2(z_\mathrm{O}^{\mathrm{O_2}}v_{+1} - z_\mathrm{O}^{\mathrm{O}l}v_{-1})/\nu_1,\\
-a_\mathrm{O}^{\mathrm{SO_2}} &= 4(z_\mathrm{O}^{\mathrm{SO_2}}v_{+2} - z_\mathrm{O}^{\mathrm{SO_2}l}v_{-2})/\nu_2,\\
-a_\mathrm{O}^{\mathrm{O_2}} &= 2(z_\mathrm{O}^{\mathrm{O}l}v_{+3} - z_\mathrm{O}^{\mathrm{SO_2}l}v_{-3})/\nu_3,\\
-a_\mathrm{O}^{\mathrm{SO_2}} &= 4(z_\mathrm{O}^{\mathrm{SO_2}l}v_{+3} - z_\mathrm{O}^{\mathrm{SO_3}l}v_{-3})/\nu_3,\\
a_\mathrm{O}^{\mathrm{SO_3}} &= 6(z_\mathrm{O}^{\mathrm{SO_3}l}v_{+4} - z_\mathrm{O}^{\mathrm{SO_3}}v_{-4})/\nu_4.
\end{aligned}\right. \qquad (17)$$

The subscript O is added to designate oxygen in the tracer element. $z_\mathrm{O}^{\mathrm{O}l}$, $z_\mathrm{O}^{\mathrm{SO_2}l}$ and $z_\mathrm{O}^{\mathrm{SO_3}l}$ may be eliminated to obtain the following:

$$\left.\begin{aligned}
&\frac{V_-^{1,3,4}}{V_+^{1,3,4}} z_0^{\mathrm{SO_3}} - z_0^{\mathrm{O_2}} - \frac{a_0^{\mathrm{O_2}}}{2V_+^{1,3,4}} + \frac{V_-^{1,3,4}}{V_+^{1,3,4}}\\
&\qquad \times \frac{\nu_4}{v_{-4}}\left(\frac{a_0^{\mathrm{SO_3}}}{6} + \frac{a_0^{\mathrm{O_2}}}{2}\right) = 0,\\
&\frac{V_-^{2,3,4}}{V_+^{2,3,4}} z_0^{\mathrm{SO_3}} - z_0^{\mathrm{SO_2}} - \frac{a_0^{\mathrm{SO_2}}}{4V_+^{2,3,4}} + \frac{V_-^{2,3,4}}{V_+^{2,3,4}}\\
&\qquad \times \frac{\nu_4}{v_{-4}}\left(\frac{a_0^{\mathrm{SO_3}}}{6} + \frac{a_0^{\mathrm{SO_2}}}{4}\right) = 0,
\end{aligned}\right\} \qquad (18)$$

where

$$V_+^{1,3,4} = 1\bigg/\left[\frac{\nu_1}{v_{+1}} + \frac{v_{-1}\nu_3}{v_{+1}v_{+3}} + \frac{v_{-1}v_{-3}\nu_4}{v_{+1}v_{+3}v_{+4}}\right], \qquad (19)$$

$$V_-^{1,3,4} = 1\bigg/\left[\frac{\nu_4}{v_{-4}} + \frac{v_{+4}\nu_3}{v_{-4}v_{-3}} + \frac{v_{+4}v_{+3}\nu_1}{v_{-4}v_{-3}v_{-1}}\right], \qquad (20)$$

with similar expressions for $V_\pm^{2,3,4}$. $\nu_4 = 2$ from Eqs. (16).

Equations (18) are the required two relationships expressing a_0^i in terms of z_0^i. There are three independent parameters, which may be chosen as $V_+^{1,3,4}$, $V_+^{2,3,4}$, and v_{-4}. Either of the Eqs. (18) contains two of these parameters. Two experiments at different tracing levels using one of these relationships will provide two equations with the two parameters as unknowns. The other parameter can then be calculated from the remaining Eq. (18). Alternatively by tracing with a sulfur isotope independent determination of $V_\pm^{2,3,4}$ is possible, thus requiring only a single experimental set of oxygen tracer values for each determination of the parameters.

For this system, determination of the parameters will not enable determination of $v_{\pm 1,2,3,4}$ separately without resort to additional relationships such as the transition state theory Eq. (4) which becomes in this case

$$\exp(-\Delta G/RT) = \frac{K_P p_{\mathrm{SO_2}}{}^2 p_{\mathrm{O_2}}}{p_{\mathrm{SO_3}}{}^2} = \frac{v_{+1}}{v_{-1}}\left(\frac{v_{+2}v_{+3}v_{+4}}{v_{-2}v_{-3}v_{-4}}\right)^2, \quad (21)$$

where K_P is the equilibrium constant and p_i (i = SO_2, O_2, and SO_3) the partial pressure. Use of $V_+{}^{2,3,4}/V_-{}^{2,3,4}$ in conjunction with Eq. (21) enables $v_{\pm 1}$ to be determined. Then from a knowledge of $V_\pm{}^{1,3,4}$ and of $v_{\pm 4}$, it is possible to establish $v_{\pm 3}$ and finally $v_{\pm 4}$ can be calculated. In the experimental study of this system (*5*), both two level tracing with oxygen and single level tracing with isotopic sulfur and oxygen were employed.

Isobutane Dehydrogenation

A still more complicated case was recently studied by us (*6*, *7*) using a once through differential reactor (and assuming differential transfer of tracer), namely the catalytic dehydrogenation of isobutane. For this reaction,

$$iC_4H_{10} = iC_4H_8 + H_2, \quad (22)$$

deuterium can be employed as a tracer present in all three species. The following general mechanism was assumed:

Step No.	Elementary reaction	Stoichiometric No., ν	
1	$iC_4H_{10} + l \underset{v_{-1}}{\overset{v_{+1}}{\rightleftharpoons}} iC_4H_{10}l$	1	
2	$iC_4H_{10}l + l \underset{v_{-2}}{\overset{v_{+2}}{\rightleftharpoons}} iC_4H_9l + Hl$	1	
3	$iC_4H_9l + l \underset{v_{-3}}{\overset{v_{+3}}{\rightleftharpoons}} iC_4H_8l + Hl$	1	(23)
4	$iC_4H_8l \underset{v_{-4}}{\overset{v_{+4}}{\rightleftharpoons}} iC_4H_8 + l$	1	
5	$2Hl \underset{v_{-5}}{\overset{v_{+5}}{\rightleftharpoons}} H_2l + l$	1	
6	$H_2l \underset{v_{-6}}{\overset{v_{+6}}{\rightleftharpoons}} H_2 + l$	1	

With this mechanism the number of terminal species $n = 3$, and the number of intermediates $k = 5$. Therefore $n + k - 1 = 7$ step material balances are required. The two structural equations obtained after elimination of the 5 intermediate tracer markings contain four independent velocity groupings which may be chosen as $V_+{}^{1,2}$, v_{+3}, v_{+4}, $V_+{}^{5,6}$. Here $V_+{}^{1,2} = (v_{+1}v_{+2})/(v_{-1} + v_{+2})$, $V_-{}^{1,2} = (v_{-1}v_{-2})/(v_{-1} + v_{+2})$ with an analogous definition for $V_{\pm 5,6}$. In principle a 2 level experiment with deuterium would enable these parameters to be established.

In the actual experimental study (*6*) isotopic carbon (^{14}C) data and the transition state relationship were used to provide two independent additional relationships giving $V_\pm{}^{1,2,3,4}$ and $V_\pm{}^{5,6}$, respectively so that the four parameters could be reduced to two and established by single level experiments. This program thus enabled the determination of $V_\pm{}^{1,2}$, $v_{\pm 3}$, $v_{\pm 4}$ and $V_\pm{}^{5,6}$.

More recent studies involving this reaction have been conducted on the assumption that deuterium tracing is integral (*8*) rather than differential, using the same once through flow reactor under conditions where the overall reaction is differential. Instead of algebraic equations relating tracer transfer to marking, a set of linear first order differential equations results. The same velocity parameters can be determined by solution of these equations.

DISCUSSION

A general procedure has been outlined for conducting tracer experiments at multiple levels and with more than one tracer to resolve step velocities in a reaction mechanism. The procedure is illustrated for two systems which have been studied experimentally and application to other systems should be straightforward. For single overall reactions where a tracer does not follow all species, similar equations will apply. Thus for the water gas shift reaction involving four species, $n = 3$ for ^{18}O transfer. The procedure should be applicable to reaction networks involving more than one overall reaction, since the step velocities will also all be fixed in this case. For example, in dehydrogenation of the three *n*-butenes to produce butadiene and hydrogen $n = 4$ for ^{13}C transfer and $n = 5$ for D transfer. Since steady state experiments represent the terminal conditions for transient studies, an understanding of steady state behavior is useful as a guide for the latter.

The steady state tracing procedure will not be useful for reaction paths which involve irreversible reactions. However, transient studies involving tracers will enable step velocities to be obtained in these cases and concentrations of surface species can be determined as well (*4*).

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