JOURNAL OF CATALYSIS 134, 691–701 (1992)

Kinetic Analysis of a Generalized Catalytic Selective Oxidation Reaction

HAROLD H. KUNG

Ipatieff Laboratory and Department of Chemical Engineering, Northwestern University, Evanston, Illinois 60208-3120

Received April 29, 1991; revised November 21, 1991

A kinetic model is presented for a generalized catalytic selective oxidation reaction in which lattice oxygen is the proximate source of oxygen. The model takes into account the effects on the overall kinetics due to finite residence time of intermediates on the surface, diffusional rate of lattice oxygen, and overall stoichiometry of the reaction. It is shown that except under the condition when adsorption of the hydrocarbon reactant is the slow step, the rate expression derived from this model differs from that obtained with a model in which these effects are neglected. One important consequence of the model is that the rate of consumption of hydrocarbon can be changed if the selectivity of the reaction is changed, even when reoxidation of the catalyst is the rate-limiting step. In such a circumstance, the rate might show an order dependence in oxygen partial pressure, the apparent activation energy reflects that of reoxidation and the temperature dependence of the selectivity, and the apparent preexponential factor is also influenced by the stoichiometry of the reaction. The implications of these to the interpretation of substituent effects and deuterium kinetic isotope effects are discussed.

INTRODUCTION

It has always been of interest to obtain information on the mechanism of a catalytic reaction. The reversibility of individual steps, the nature of rate-limiting steps, the nature of the surface species, their interaction with the active sites, and the details of molecular transformation of surface intermediates are some of the valuable information needed to fully understand a reaction. Over the years, many techniques have been invented to generate these types of information. Among them are kinetic and *in situ* spectroscopic measurements and the use of isotope labeling. Whereas *in situ* spectroscopy directly probes the surface species, additional evidence is needed to show that the species are in the reaction pathway of interest. On the other hand, isotopic labeling provides information specific to the species relevant to the reaction. From the distribution of isotopically labeled atoms in the products and their redistribution in the reactants, information such as reversibility of a surface step and the identity of the bonds that are broken or formed can be obtained (*1–3*). Of course, conclusions from these measurements regarding a reaction mechanism should be consistent with the measured kinetics.

The measurement of kinetic isotope effect has also been used to provide supplementary mechanistic information. For this purpose, molecules are labeled with deuterium atoms to make use of the large difference in the zero point energy of the bonds containing the isotope. It is often assumed that if the observed reaction rate differs significantly between the two isotopes, the isotopically labeled bond must be involved in the rate-limiting step or the slow step, that is, the step with the smallest rate constant. Only when it is clear that the reaction does not involve the labeled bond, such as in the epoxidation of deuteroethene, then other interpretations are invoked (*4, 5*).

There have been many studies on the re-

0021-9517/92 $3.00

action mechanisms of selective oxidation reactions utilizing these techniques and others (*4–7*). For example, Table 1 lists a number of studies in which kinetics and kinetic isotope effects were determined. In contrast, there have been only a few analyses of the detailed kinetics of these reactions (*4, 7*). Except for the oxidation of ethene on Ag, the analyses of these reactions commonly assumed that the Mars–van Krevelen mechanism in which the oxide catalyst undergoes a reduction–reoxidation cycle during the reaction applies (*8*). The surface was assumed to be made up of oxidized (SO) and reduced sites (SR) (see Fig. 1). A hydrocarbon molecule, such as propene, reacts on the SO site by reducing the site with a rate constant, k_R, and a SR site is reoxidized by gaseous oxygen with a rate constant k_{OX}. At steady state, the reaction rate, defined as the rate of disappearance of propene was found to be (*7*)

$$\frac{-d[C_3H_6]}{dt} = \frac{k_{OX}P_O^Y}{1 + (k_{OX}P_O^Y/k_RP_C^X)} \quad (1)$$

where P_O and P_C are the partial pressures of oxygen and propene, respectively. If $k_{OX}P_O^Y \gg k_RP_C^X$, Eq. (1) can be reduced to

$$\text{Rate} = k_RP_C^X. \quad (2)$$

In this case, the observed rate would be first order in propene and zeroth order in oxygen, and the apparent rate constant would be the same as that of the reaction of propene on the oxidized site, which could involve the breaking of a C–H bond in the hydrocarbon molecule. Therefore one expects to observe a normal deuterium kinetic isotope effect. These are indeed often observed at higher temperatures.

Although this model explains a large amount of data, it is not satisfactory in a number of aspects:

(1) The model does not address the relationship between the observed kinetics and the rate of diffusion of lattice oxygen in the solid. In the Mars–van Krevelen mechanism, gaseous oxygen is incorporated in the solid at a site different from the reaction site of the surface hydrocarbon intermediate. Thus diffusion of lattice oxygen is necessary. The model implicitly assumes that lattice diffusion is infinitely fast compared to k_R and k_{OX}. This assumption may not be valid in solids where only a small fraction of the lattice oxygen is involved in the reaction, such as in V–P–O (*9, 10*) and USb_3O_{10} (*11*) or when the temperature is low.

(2) The model implicitly assumes that the reaction of the surface intermediate is very fast compared to the reduction (k_R) and the reoxidation (k_{OX}) processes. Thus the surface only consists of SO and SR sites, and the amount of surface being covered by adsorbed intermediates is negligible. This assumption may not always be valid, such as at conditions where infrared spectroscopic investigation of the adsorbed species under reaction conditions could be made (*12, 13*).

(3) The model does not adequately explain situations in which the observed kinetics show zeroth order dependence in hydrocarbon and nearly first order in oxygen, and yet a deuterium isotope effect is observed (see Table 1). This can be seen by applying the limit of $k_RP_C^X \gg k_{OX}P_O^Y$ to Eq. (1) to obtain

$$\text{Rate} = k_{OX}P_O^Y. \quad (3)$$

Then the rate is controlled by the kinetics of reoxidation of the catalyst. It shows an order dependence in oxygen. The apparent rate constant is k_{OX}, and the apparent activation energy in this regime may be different from the other regime described by Eq. (2). Since the slow step is now the reoxidation of the catalyst, which does not involve the hydrocarbon molecule, there will be no deuterium kinetic isotope effect on the rate of consumption of hydrocarbon.

The purpose of this paper is to describe a more detailed kinetic model to address these points. The model takes into account the diffusion of lattice oxygen, the possibility that a substantial fraction of the surface is covered by reaction intermediates, and the influence of product selectivity of the reaction on the overall kinetics. It will be shown

TABLE 1

Reaction Orders and Deuterium Kinetic Isotope Effects in Some Selective Oxidation Reactions[a]

Catalyst[b]	Temp. (°C)	Reaction	$\text{Rate}_H/\text{Rate}_D$	Order in		Comment
				HC	O_2	
		Propene oxidation				
$Bi_2Mo_3O_{12}$	450	C_3H_4O formation	1.8	1	0	
(*6, 7*)		CO_2 formation	1.8	1	0.4	
	350	C_3H_4O formation	1.7	0	0	
		CO_2 formation	1.4	0	0.4	
Bi_2MoO_6	450	C_3H_4O formation	1.7	1	0	Higher Ea below 420°C
(*6, 7*)		CO_2 formation	1.7	1	0.4	
	350	C_3H_4O formation	1.5	0	0.4	
		CO_2 formation	1.5	0	0.4	
$Bi_3FeMo_2O_{12}$	450	C_3H_4O formation	1.7	1	0	Higher Ea below 375°C
(*6, 7*)		CO_2 formation	1.2	1	0.4	
	350	C_3H_4O formation	2.2	0.5	1	
		CO_2 formation	1.2	0.7	1	
$Bi_2Mo_2O_9$	450	C_3H_4O formation	1.65	1	0	Higher Ea below 440°C
(*16*)		CO_2 formation	1.65	1.5	0.3	
	350	C_3H_4O formation	1.4	0–0.85	0–0.4	Order depends on C_3H_6 pressure
		CO_2 formation	1.4	0.4–1	0–0.5	
USb_3O_{10}	450	C_3H_4O formation	1.5	1	0	Higher Ea below 410°C
(*11*)		CO_2 formation	1.3	0.9	0.3	
	351	C_3H_4O formation	2.5	0.4	0.3	
		CO_2 formation	1.2	0	0.8	
Fe–Sb–O	450	C_3H_4O formation	1.8	0.8	0.3	
(*17*)		CO_2 formation	1.8	0.7	0.7	
	350	C_3H_4O formation	2.25	0.5	0.4	
		CO_2 formation	1.9	0.4	0.6	
		Methanol oxidation (18–20)				
$Fe_2(MoO_4)_3$	200	CH_3OH consumption	3.3	0.5	0.5	
	250		3.57			
Fe–Mo–O	230		3.84	0.5	0.5	
MoO_3	300		3.22			
		Butene oxidation (21)				
$MgFe_2O_4$	300	Butene consumption	3.9	1	0	
	400		2.6			
		Ethene oxidation				
Ag (*4*)	145	C_2H_4O formation	0.56	Fractional orders		
		CO_2 formation	1.54	Fractional orders		
Ag/Cl (*5*)	200	C_2H_4O formation	0.75	—	—	
		CO_2 formation	1.45	—	—	

[a] The selectivities to selective oxidation products can be deduced from the kinetic isotope effects. If $\text{rate}_H/\text{rate}_D$ is the same for both selective products and CO_x, the selectivity is the same for both H-labeled and D-labeled reactants. If this ratio is higher for selective products than for CO_x, the reaction is more selective with an H-labeled reactant than with a D-labeled reactant.

[b] Numbers in parentheses are reference numbers.

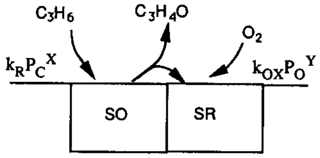

FIG. 1. Schematic drawing showing the reduction–reoxidation cycle during the selective oxidation of propene as proposed previously.

that under appropriate conditions, this more detailed model can be reduced to the simpler one described earlier, as it should. However, under other conditions, different rate expressions are obtained.

THE KINETIC MODEL

The model assumes that there are four different types of active sites on the surface: sites in the oxidized form, SO (site-oxidized); sites in the reduced form, SR (site-reduced); and sites that are covered with surface reaction intermediates (I–O$_i$'s) and they can be either in the oxidized, SCO (site-covered-oxidized) or reduced, SCR (site-covered-reduced), form. There are different SCR and SCO sites depending on the degree of oxidation of the adsorbed intermediate. These different sites are labeled by subscript i if the intermediate has taken up i number of lattice oxygen atoms. Figure 2 shows a possible manner with which these different sites interconvert. The processes involved are

(1) A reduced site SR can be oxidized by gaseous oxygen to form an oxidized SO site with a rate constant k_{OX}.

(2) A reactant molecule A reacts with a SO site to form a SCO site with a rate constant k_A. Since only one species of hydrocarbon reactant is considered, the model implicitly assumes the condition of low conversions.

(3) A SCO site is converted to a SCR site when the surface intermediate I abstracts a lattice oxygen atom from the surface. The rate of conversion of a surface intermediate I–O$_i$ to I–O$_{i+1}$ is $k_{el}\theta_{SCO_i}$, which can also be written as $k_X\theta_{I-O_i}$, where θ_{SCO_i} is the surface coverage of I–O$_i$ on a SCO site, and θ_{I-O_i} is the surface coverage of I–O$_i$ counting both SCO and SCR sites. For simplicity, it is assumed that the values of k_{el} and k_X are independent of the degree of oxidation of the intermediate, that is, independent of i.

(4) The reduced SCR site can be reoxidized to form a SCO site by diffusion of lattice oxygen from neighboring SO sites and leaves a SR site. However, since it is covered by a surface intermediate I–O$_i$, it cannot be reoxidized directly by gaseous oxygen.

(5) An oxidized SCO site can be converted

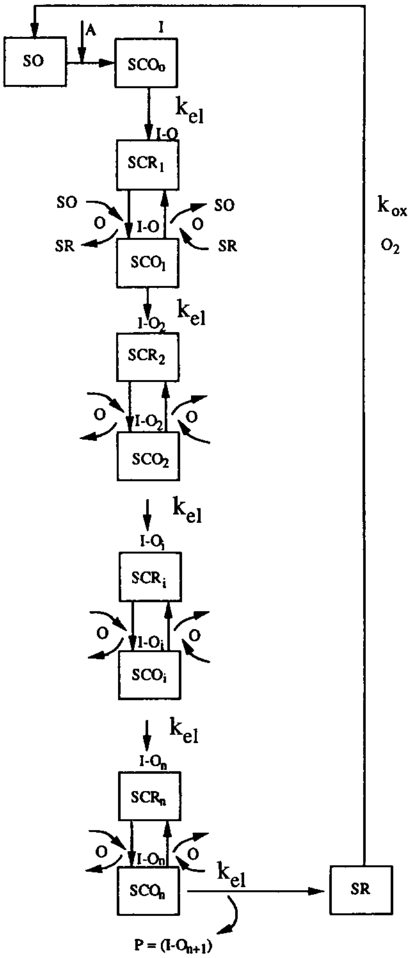

FIG. 2. A generalized scheme of oxidation reaction.

to a SCR site by diffusion of lattice oxygen to a reduced SR site.

(6) The observed gaseous product P is formed when $(n + 1)$ number of lattice oxygen atoms are incorporated into the molecule.

There are two points that should be noted here. One is that k_X is not a rate constant for an elementary step but an effective rate constant. This is because it is defined based on $\theta_{I\text{-}O_i}$, which is the sum of θ_{CO_i} and θ_{CR_i}. The second point is that the diffusion of lattice oxygen between an SR and an SO site does not result in any net change of the surface and thus has no kinetic consequence. Likewise, diffusion of lattice oxygen between a SCO$_i$ and a SCR$_i$ site has no kinetic consequence.

The equations that apply to this scheme are:

(1) The total fraction of sites equals unity:

$$\begin{aligned} 1 &= \theta_O + \theta_R + \Sigma\theta_{CO_i} + \Sigma\theta_{CR_i} \\ &= \theta_O + \theta_R + (1 - r)\theta_C + r\theta_C, \quad (4) \end{aligned}$$

where θ_O, θ_R, θ_{CO_i}, and θ_{CR_i} are fractions of the surface being in the SO, SR, SCO$_i$, and SCR$_i$ states, respectively. We further define θ_C as the total fraction of surface sites covered by intermediates; that is, $\theta_C = \Sigma\theta_{CO_i} + \Sigma\theta_{CR_i}$, and r is the fraction of it in the reduced form.

(2) Assuming that the reactions denoted by rate constants k_A, k_{OX}, and k_{el} are irreversible, the observed rate of reaction, which is defined to be the rate of consumption of reactant A and is equal to that of each surface oxidation step, is

$$\text{Rate} = k_A P_A \theta_O = k_{el}\theta_{SCO_i} = k_S\theta_C. \quad (5)$$

This equation defines k_S, which represents the rate constant of the oxidation of the surface intermediate based on the total covered sites, θ_C. It can be shown readily that, if for simplicity, $\theta_C = (n + 1)\theta_{I\text{-}O_i}$, then $k_S = k_X/(n + 1)$, where k_X is defined by $k_S\theta_C = k_X\theta_{I\text{-}O_i}$ (and $\theta_{I\text{-}O_i} = \theta_{COi} + \theta_{CRi}$). Using this, the scheme shown in Fig. 2 can be simplified to that shown in Fig. 3.

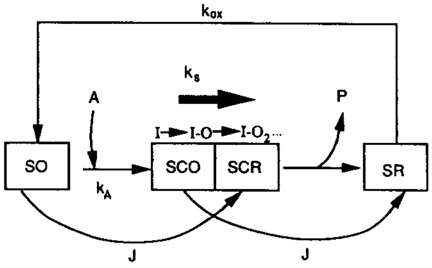

FIG. 3. A simplified version of the generalized scheme of oxidation reaction.

(3) The total number of oxygen atoms consumed by a surface intermediate, $n + 1$, is given by

$$(n + 1) = 1 + \tau J r\theta_o - \tau J(1 - r)\theta_R \quad (6)$$

in which it is assumed that each SCO site supplies only one oxygen atom to be inserted into the surface intermediate. The unity on the right-hand side represents the first oxygen atom inserted to species I. τ is the total surface residence time of the intermediate, and J is the jump frequency of lattice oxygen from a neighboring SO site to a SCR site, or from a SCO site to a SR site. Equation (6) says that the number of oxygen atoms picked up by a molecule equals what it picks up on adsorption plus the net number of oxygen diffused to the adsorption site within the surface residence time of the surface intermediate.

Equation (6) can be rearranged to express n, the net number of oxygen diffused to the surface intermediate, as

$$n = \tau J r\theta_O - \tau J(1 - r)\theta_R. \quad (7)$$

Since $\tau = (n + 1)\tau_i$, $\tau_i = 1/k_X$, and $k_S = k_X/(n + 1)$, therefore $\tau = 1/k_S$. Then Eq. (7) can be rewritten as

$$nk_S/J = r\theta_O - (1 - r)\theta_R. \quad (8)$$

The material balance equations for θ_O, θ_R, or θ_C can be written using the scheme in Fig. 2 or 3. The equation for θ_O at steady state reads

$$d\theta_O/dt = k_{OX}P_O\theta_R + k_AP_A\theta_O + J\theta_R(\Sigma\theta_{CO_i}) - J\theta_O(\Sigma\theta_{CR_i}) = 0. \quad (9)$$

In this equation and those before it, it is assumed without loss of generality that every reaction is first order in the reactants for that step. By substituting Eq. (8) for the last two terms in this equation and θ_R in terms of θ_O using Eqs. (4) and (5), one obtains

$$\theta_O = k_{OX}P_O/[k_{OX}P_O + k_AP_A(1 + n) + k_AP_Ak_{OX}P_O/k_S]. \quad (10a)$$

Likewise, θ_C and θ_R can be expressed as

$$\theta_C = k_AP_Ak_{OX}P_O/k_S[k_{OX}P_O + k_AP_A(1 + n) + k_AP_Ak_{OX}P_O/k_S] \quad (10b)$$

$$\theta_R = k_AP_A(1 + n)/[k_{OX}P_O + k_AP_A(1 + n) + k_AP_Ak_{OX}P_O/k_S]. \quad (10c)$$

The observed rate of consumption of reactant A is then

$$\text{Rate} = k_AP_A\theta_O = \frac{k_AP_A}{1 + k_AP_A/k_S + (1 + n)k_AP_A/k_{OX}P_O}. \quad (11)$$

This equation can be simplified further depending on the relative magnitudes of the various rate constants.

Case 1. If $k_{OX}P_O$, $k_S \gg k_AP_A$, that is, the rate of activation of A is much slower than the rates of reoxidation of the catalyst and the rate of surface reaction, then Eq. (11) can be reduced to

$$\text{Rate} = k_AP_A. \quad (12)$$

The reaction rate will depend on the partial pressure of A, and the apparent rate constant equals the rate constant of the activation of A. This is equivalent to Eq. (2). Furthermore, θ_O is approximately unity and the surface is mostly in the oxidized state.

Case 2. If k_AP_A, $k_S \gg k_{OX}P_O$, that is, the rate of reoxidation of the catalyst is slow, then Eq. (11) becomes

$$\text{Rate} = k_{OX}P_O/(1 + n). \quad (13)$$

In this case, the observed rate of reaction of A will depend on the partial pressure of oxygen, and the apparent rate constant equals the rate constant for reoxidation of the catalyst modified by the term $(1 + n)$. If the deuterium kinetic isotope effect is being measured, the *apparent* kinetic isotope effect is the ratio of the rates for the H-labeled and D-labeled molecules. Since k_{OX} is independent of the molecule, this ratio is

$$\text{Rate}_H/\text{Rate}_D = (1 + n)_D/(1 + n)_H \quad (14)$$

which is

$$>1 \text{ if } n_D > n_H$$

$$= 1 \text{ if } n_D = n_H$$

and

$$< 1 \text{ if } n_D < n_H.$$

Under this condition, both θ_O and θ_C are small and θ_R is nearly unity. The surface is mostly in the reduced state.

Case 3. If k_AP_A, $k_{OX}P_O \gg k_S$; that is, the reaction of the surface intermediates is slow. Then Eq. (11) is reduced to

$$\text{Rate} = k_S. \quad (15)$$

The observed rate equals the apparent rate constant for the overall surface reaction, and θ_C is nearly unity. The reaction sites are nearly fully covered by surface intermediates.

DISCUSSION

The model presented here incorporates three features not considered in the earlier simpler model. They are (i) diffusion of lattice oxygen; (ii) residence time of the intermediates on the surface; and (iii) stoichiometry of the overall reaction expressed as the number of oxygen atoms consumed per hydrocarbon molecule. The consequence of considering these features is that a generalized rate expression, Eq. (11), that includes the parameters that characterize these features is obtained. It is significant to note that of the three limiting cases considered for this equation, only Case 1 results in a simplified rate expression (Eq. (12)) that is the same as that (Eq. (2)) from a simpler model described in the Introduction. It is particularly interesting that in the second limiting case, Case 2, in which reoxidation of the catalyst is slow, the simplified rate expression (Eq. (13)) differs from the corresponding one (Eq. (3)) of the simpler model by a term $(1 + n)$ that reflects the stoichiometry of the reaction.

Effect of Diffusion of Lattice Oxygen and Surface Residence Time

The effects of diffusion of lattice oxygen and residence time of surface intermediates on the kinetic expression appear in determining the magnitudes of the apparent overall surface reaction rate constant, k_S, and the apparent individual step rate constant, k_X. This can be more easily seen when the components of k_X are expressed explicitly. In the statement following Eq. (5), k_X is defined as: Rate $= k_X\theta_{I-O_i}$. k_X can be related to the rate constant, k_{el}, for the elementary steps involving the reaction of intermediate $I - O_i$ on a SCO site:

$$k_{el}\theta_{SCO_i} = k_X\theta_{I-O_i}. \qquad (16)$$

Recalling that $\theta_{I-O_i} = \theta_{CO_i} + \theta_{CR_i}$, one obtains

$$k_X = k_{el}[\theta_{CO_i}/(\theta_{CO_i} + \theta_{CR_i})]. \qquad (17)$$

At steady state, a material balance equation for θ_{CO_i} leads to

$$\begin{aligned} d\theta_{CO_i}/dt = k_{el}\theta_{CO_i} + J\theta_{CO_i}\theta_R + J\theta_{CO_i}(\Sigma\theta_{CR_i}) \\ - J\theta_{CR_i}\theta_O - J\theta_{CR_i}(\Sigma\theta_{CO_i}) = 0 \end{aligned}$$

Or,

$$\frac{\theta_{CO_i}}{\theta_{CR_i}} = \frac{J[\theta_O + (1 - r)\theta_C]}{k_{el} + J[\theta_R + r\theta_C]}. \qquad (18)$$

Equation (18) can be combined with Eq. (17) to yield

$$\begin{aligned} k_X &= \frac{k_{el}J[\theta_O + (1 - r)\theta_C]}{k_{el} + J[\theta_R + r\theta_C] + J[\theta_O + (1 - r)\theta_C]} \\ &= \frac{k_{el}J[\theta_O + (1 - r)\theta_C]}{k_{el} + J}. \qquad (19) \end{aligned}$$

This equation shows that the apparent rate constant for the surface reaction, k_x, depends on the rate constant of the elementary step of oxygen insertion into a surface intermediate, k_{el}, the lattice oxygen jump frequency, J, and the fraction of the surface being in the oxidized state. It shows that

$$\text{When } k_{el} \gg J, \quad k_X = J[\theta_O + (1 - r)\theta_C] \qquad (20)$$

$$\text{When } J \gg k_{el}, \quad k_X = k_{el}[\theta_O + (1 - r)\theta_C]. \qquad (21)$$

Equation (20) shows that when the lattice diffusion term is small, the apparent rate constant for the surface reaction is determined by the rate of reoxidation of the surface reaction site by lattice diffusion. This rate, however, is not a constant but depends on the overall degree of oxidation of the surface, i.e., $\theta_O + \Sigma\theta_{CO_i}$. Interestingly, when the elementary reaction rate constant, k_{el}, is small compared to the diffusional term, Eq. (21) shows that k_X does not equal k_{el} but differs from it by the fraction of the surface in the oxidized state. The reason for this is that further oxidation of the intermediate is possible only when the site the intermediate occupies is in the oxidized state but not in the reduced state. Thus, as can be seen from Eq. (17), k_X differs from k_{el} by a term that shows the fraction of the intermediate-covered sites being in the oxidized state. When lattice diffusion is fast compared to oxidation of the intermediate, the ratio of the oxidized to reduced states for the covered sites equals the same ratio for the uncovered sites, i.e., $\theta_{CO_i}/\theta_{CR_i} = \theta_O/\theta_R$. This latter point can be deduced from Eq. (18) by finding the relationship between $\Sigma\theta_{CO_i}$ and $\Sigma\theta_{CR_i}$.

Effect of Overall Reaction Stoichiometry

Since the rates of consumption of hydrocarbon and oxygen must be related by the overall stoichiometry of the reaction, it is reasonable that their relative rates would change when the selectivity of the reaction changes. The term $(1 + n)$ in Eq. (11) specifies the relationship between selectivity and the observed rate of consumption of hydrocarbon. A significant consequence of this, illustrated by Eq. (13), is that the relative reactivities of two hydrocarbon molecules can be different if their selectivities are different, even when reoxidation of the catalyst is the slow step. For example, there have been studies in which the relative rates of reactions of molecules containing primary, secondary, or tertiary C–H bonds were compared with the relative strengths of these bonds to conclude that the breaking of the C–H bond was the rate-limiting step (*14*). Equation (13) states that one needs to examine the effect due to different selectivities of the different molecules before conclusions about rate-limiting steps can be made. The same caution applies to the interpretation of deuterium kinetic isotope effects, which is discussed further.

The physical meaning of Eq. (13) can be stated as follows. Although both the rates of adsorption of hydrocarbon and of reaction between a lattice oxygen atom and a surface intermediate at site SCO can be fast, the observed rate of consumption of the hydrocarbon is still limited by the rate of availability of oxygen to the site, which in turn is limited by the rate of reoxidation of site SCR. If the overall stoichiometry requires more oxygen atoms because of lower selectivity, the surface residence time of the intermediate will be longer because more time is needed to supply the desired number of oxygen atoms to the sites. Then the observed turnover frequency of hydrocarbon will be lower.

That the rates of reaction of the different reactants are related by stoichiometry is apparent not only in the limit when reoxidation rate is slow. It is present under all conditions, including the situation of the limit described by Case 1 when the rate of activation of the hydrocarbon is slow. It can be shown readily using Eq. (9) that the rate of consumption of oxygen is

$$\text{Rate}_\text{O} = k_\text{OX}P_\text{O}\theta_\text{R} = (1+n)k_AP_A\theta_\text{O}$$
$$= \frac{(1+n)k_AP_A}{[1 + k_AP_A/k_\text{S} + (1+n)k_AP_A/k_\text{OX}P_\text{O}]}. \tag{22}$$

In the limit of Case 1, where $k_\text{OX}P_\text{O}$, $k_\text{S} \gg k_AP_A$, the equation is reduced to

$$\text{Rate}_\text{O} = (1+n)k_AP_A \tag{23}$$

In other words, even in the limit when the rate of activation of hydrocarbon is the slow step, a change in the selectivity of the reaction when the hydrocarbon contains a different substituent or is isotopically labeled will result in a change in the rate of consumption of oxygen.

When reoxidation is the slow step, Eq. (13) shows that the apparent rate constant equals $k_\text{APP} = k_\text{OX}/(1 + n)$. Thus the apparent activation energy equals the activation energy for reoxidation plus the temperature dependence of the selectivity. The exponential factor equals that for reoxidation modified by the $(1 + n)$ term.

Deuterium Kinetic Isotope Effect

The deuterium kinetic isotope effect has been used extensively to help identify slow steps in a reaction. For selective oxidation reactions considered here, Eq. (14) shows that even when reoxidation is the slow step, the reaction still exhibits an apparent kinetic isotope effect when the hydrocarbon molecule is labeled, if such labeling also changes the selectivity of the reaction (i.e., $n_\text{D} \neq n_\text{H}$). When $n_\text{D} > n_\text{H}$, the D-labeled molecule consumes on average a larger number of oxygen atoms than the normal isotope molecule, and an apparent normal kinetic isotope effect will be observed. This corresponds to the case when there is a decrease in the selectivity for partial oxidation products and an increase in combustion using the D-labeled molecule. On the other hand, if $n_\text{D} < n_\text{H}$, then the D-labeled molecule shows a higher selectivity for partial oxidation products, and an apparent inverse kinetic isotope effect will be observed.

The magnitude of the apparent kinetic isotope effect as described by Eq. (14) depends on the value of n, which in turn depends on the reaction and the selectivity. Using the selective oxidation of propene to acrolein as an example, the two relevant reactions are

$$C_3H_6 + O_2 \rightarrow C_3H_4O + H_2O \qquad \text{selective oxidation}$$

$$C_3H_6 + 9/2\ O_2 \rightarrow 3\ CO_2 + 3\ H_2O \qquad \text{combustion.}$$

To form acrolein, a total of two oxygen atoms are needed for the reaction, $(n + 1) = 2$. Thus n for this reaction is unity. For combustion, a total of nine oxygen atoms are needed. Thus $n = 8$. If the selectivity is 90% for the production of acrolein with the H-labeled molecule and 60% with the D-labeled molecule, then $n_H = 1.7$ ($= 0.9 \times 1 + 0.1 \times 8$), and $n_D = 3.8$ ($= 0.6 \times 1 + 0.4 \times 8$). The apparent isotope effect for the consumption of propene is 1.78.

It is interesting to note that under this condition (i.e., Case 2), the surface active sites are almost all in the reduced state (SR). The rate of reoxidation of the catalyst, which is independent of the isotopic label of the hydrocarbon, limits the rate of consumption of the hydrocarbon. Thus if deuterium labeling decreases the rate of reaction in a certain pathway that results in a decrease of the selectivity of propene to acrolein, there will be a normal isotope effect for the formation of acrolein. Since fewer lattice oxygen atoms are consumed for acrolein formation, more is available for the combustion reaction for which an inverse kinetic isotope effect is expected.

The kinetic model described here provides an alternate explanation for the propene oxidation data listed in Table 1. In cases where normal kinetic isotope effects are observed and the reaction rates are zeroth order in oxygen and positive order in hydrocarbon, the condition of Case 1 is sufficient as an explanation. The rate of dissociative adsorption of the reactant is the slow step. These cases are observed at the higher temperatures. In some other cases such as at lower temperatures, the rates show a positive order in oxygen. To explain this order dependence, the rate of reoxidation of the oxide catalyst cannot be much faster than the other rates. However, it is unlikely that the condition of case 2 is approached because then the reaction should be zeroth order in hydrocarbon, and the kinetic isotope effect for acrolein and CO_2 formation would be inverse of each other. Neither of these conditions are observed. These results can be explained by the two possibilities below:

(i) $k_A P_A \gg k_S, k_{OX} P_O$. Then Eq. (11) becomes

$$\text{Rate} = \frac{k_S k_{OX} P_O}{k_{OX} P_O + (1 + n) k_S} \tag{24}$$

and

$$\frac{\text{Rate}_H}{\text{Rate}_D} = \frac{(k_S)_H [k_{OX} P_O + (1 + n) k_S]_D}{(k_S)_D [k_{OX} P_O + (1 + n) k_S]_H}. \tag{25}$$

When $n_D > n_H$, i.e., lower selectivity of acrolein for deuterated propene, and $(k_S)_H \geq (k_S)_D$, i.e., the surface reaction rate constant shows either a normal kinetic isotope effect or no effect, then $\text{Rate}_H/\text{Rate}_D > 1$ will result.

(ii) $k_S \gg k_A P_A, k_{OX} P_O$, then

$$\text{Rate} = \frac{k_A P_A k_{OX} P_O}{k_{OX} P_O + (1 + n) k_A P_A} \tag{26}$$

and

$$\frac{\text{Rate}_H}{\text{Rate}_D} = \frac{(k_A P_A)_H [k_{OX} P_O + (1 + n) k_A P_A]_D}{(k_A P_A)_D [k_{OX} P_O + (1 + n) k_A P_A]_H}. \tag{27}$$

When $n_D > n_H$ and $(k_A)_H \geq (k_A)_D$, a normal kinetic isotope effect will also be observed.

Generalization of the Model

Although the model is developed using examples of selective oxidation reactions that proceed with reduction and reoxidation of the catalyst, it is likely that it can be generalized to include other reactions in which one reactant reacts with more than one atoms of another reactant and which involves diffusion of one reactant to another on the surface. This is because the two most important equations in the model, Eqs. (6) and (9), are not specific to the redox mechanism. They can be used to describe any reaction processes in general that involve diffusion (including surface diffusion) of one reactant to the active site SC that contains the surface intermediate. Thus it is quite possible that this model applies to reactions such as hydrogenolysis of alkanes in which a hydrocarbon molecule reacts with a number of hydrogen atoms to form a range of products, Fischer–Tropsch synthesis that involves CO reacting with hydrogen atoms, as well as ethene epoxidation, which does not involve C–H bond breaking. In fact, it is possible that the exceptionally large apparent kinetic isotope effect in ethylene oxide formation reported in a study using low partial pressures of oxygen and ethene (*15*) may be a result of the effect of the slow rate of adsorption of oxygen on the overall reaction kinetics.

CONCLUSION

An analysis is presented on a generalized kinetic model of selective oxidation reactions in which lattice oxygen is consumed as the source of oxygen. The analysis takes into account the effect of lattice oxygen diffusion, finite surface residence time of intermediates, and overall stoichiometry of the reaction on the observed kinetics. However, the model does not address what determines selectivity. Instead, it addresses the consequence on the kinetics when the reaction rates to certain products are changed and result in changes in selectivity. The result is that a rate expression that contains rate parameters for all the processes including lattice diffusion is obtained. The dependence of the rate on the degree of oxidation of the catalyst is explicitly stated. The result also suggests that when one interprets the observed effect on the kinetics due to changes in hydrocarbons such as by the use of substituents or isotopes, it is important to take into consideration possible effects associated with changes in the overall stoichiometry of the reaction due to changes in the selectivities of the reaction. It is also important to check if the partial pressure or concentration dependence of the rate is consistent with the interpretation and the assumption of the slow step.

ACKNOWLEDGMENT

Support of this work by the U.S. Department of Energy, Division of Basic Energy Sciences is gratefully acknowledged.

REFERENCES

1. Burwell, Jr., R. L., *in* "Catalysis: Science and Technology" (J. R. Anderson and M. Boudart, Eds.), Vol. 9. Springer-Verlag, Berlin/New York, 1991.
2. Ozaki, A., "Isotopic Studies of Heterogeneous Catalysis." Academic Press, New York, 1977.
3. Happel, J., "Isotopic Assessment of Heterogeneous Catalysis." Academic Press, New York, 1986.
4. Cant, N. W., and Hall, W. K., *J. Catal.* **52,** 81 (1978).
5. van Santen, R. A., Moolhuysen, J., and Sachtler, W. M. H., *J. Catal.* **65,** 478 (1980).
6. Krenzke, L. D., and Keulks, G. W., *J. Catal.* **61,** 316 (1980).
7. Krenzke, L. D., and Keulks, G. W., *J. Catal.* **64,** 295 (1980).
8. Mars, P., and van Krevelen, D., *Chem. Eng. Sci. Suppl.* **3,** 41 (1954).
9. Centi, G., Fornasari, G., and Trifirò, F., *J. Catal.* **89,** 44 (1984).
10. Pepera, M. A., Callahan, J. L., Desmond, M. J., Milberger, E. C., Blum, P. R., and Bremer, N. J., *J. Am. Chem. Soc.* **107,** 4883 (1985).
11. Keulks, G. W., Yu, Z., and Krenzke, L. D., *J. Catal.* **84,** 38 (1983).
12. Wenig, R. W., and Schrader, G. L., *J. Phys. Chem.* **90,** 6480 (1986).
13. Force, E. L., and Bell, A. T., *J. Catal.* **38,** 440 (1975); **40,** 356 (1975).
14. For example, Patel, D., Kung, M. C., and Kung, H. H., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 4, p. 1554. Chem. Institute of Canada, Ottawa, 1988.
15. Grant, R., and Lambert, R. M., *J. Catal.* **92,** 364 (1985).
16. Monier, J. R., and Keulks, G. W., *J. Catal.* **68,** 51 (1981).
17. Keulks, G. W., and Lo, M.-Y., *J. Catal.* **90,** 4768 (1986).

18. Michaels, C. J., and Sleight, A. W., *J. Catal.* **76,** 238 (1982).

19. Pernicone, N., Lazzerin, F., Liberti, G., and Lanzarecchia, G., *J. Catal.* **14,** 293 (1969).

20. Jiru, P., Wichterlova, B., and Tichy, J., *in* "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964," p. 199. Wiley, New York, 1965.

21. Gibson, M., and Hightower, J., *J. Catal.* **41,** 420 (1976).