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(Note)

ON THE STEADY OXIDATION OF ETHYLENE OVER SILVER CATALYSTS

By

Koshiro MIYAHARA^{*)}

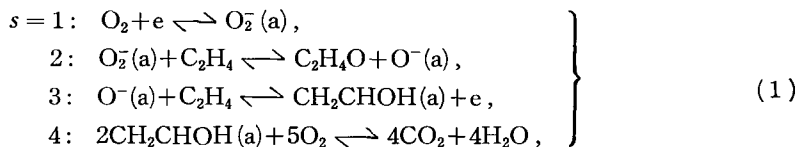
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A method for studying mechanisms of heterogeneous catalysis by determining the stoichiometric numbers of their rate-determining steps¹⁾ or by investigating the "structure" of reactions²⁾ has been developed by HORIUTI and coworkers on the basis of his theory of steady reaction³⁾ and applied successfully to various catalytic reactions. The method is, however, applicable only to reactions with a single reaction route³⁾, so that it is highly desirable to extend the theory to cover reactions with two or more reaction routes, the relative rates of which are directly related to the selectivity of catalyst.

In this note the oxidation of ethylene over silver catalyst is discussed on the basis of the theory of steady reaction as an example of catalytic reactions with two reaction routes.

The products of this reaction are ethylene oxide by partial oxidation and water and carbon dioxide by complete oxidation, and many mechanisms have been proposed for it since 1946⁴⁾⁵⁾.

A reaction mechanism proposed by LYUBARSKII⁶⁾ for instance, is



where (a) denotes the adsorbed state of the chemical species to which it is attached. Let us denote the intermediates, $\text{O}_2^-(a)$, $\text{O}^-(a)$ and $\text{CH}_2\text{CHOH}(a)$, by $i=1, 2$ and 3 respectively. According to HORIUTI's theory of steady reaction³⁾, the following relations are given for $i=1, 2$ and 3 respectively as the steady state condition of the reaction:

$$n_1 - n_2 = 0, \quad n_2 - n_3 = 0 \quad \text{and} \quad n_3 - 2n_4 = 0,$$

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where n_s means the number of acts of step s in a specified time of reaction.

These relations can be summarized by the matrix representation,

$$\mathbf{an} \equiv \begin{bmatrix} 1 & -1 & 0 & 0 \\ 0 & 1 & -1 & 0 \\ 0 & 0 & 1 & -2 \\ 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} n_1 \\ n_2 \\ n_3 \\ n_4 \end{bmatrix} = 0.$$

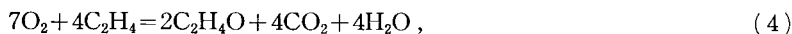
The number of linearly independent solutions of this equation is the number of independent reaction routes³⁾ of the ethylene oxidation and equals the degeneracy of the square matrix \mathbf{a} , which is unity. The solution is

$$\mathbf{n} = A[2, 2, 2, 1], \quad (2)$$

where A is an arbitrary constant. The set, $[\nu_s]$, of integers, ν_s , obtained by dividing the elements of \mathbf{n} by their greatest common factor is that of the stoichiometric numbers of steps constituting an overall reaction given by a chemical equation with the simplest set of coefficients for respective reactants and resultants. The $[\nu_s]$ in this case is \mathbf{n} of Eq. (2) with $A=1$ and the chemical equation of this route is given, according to the equation,

$$\mathbf{B} \equiv [B_m] = \mathbf{bn} = \begin{bmatrix} -1 & 0 & 0 & -5 \\ 0 & -1 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 4 \\ 0 & 0 & 0 & 4 \end{bmatrix} \begin{bmatrix} 2 \\ 2 \\ 2 \\ 1 \end{bmatrix} = \begin{bmatrix} -7 \\ -4 \\ 2 \\ 4 \\ 4 \end{bmatrix}, \quad (3)$$

as



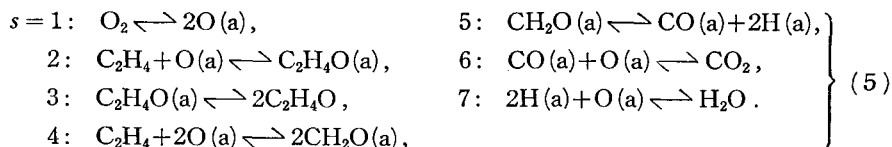
where B_m denotes the coefficient of m -th chemical species in the chemical equation of the route, the element, b_{ms} , of the matrix \mathbf{b} is the number of molecules of m -th species produced or consumed by one act of step s , and $m=1, 2, 3, 4$ or 5 denotes O_2 , C_2H_4 , $\text{C}_2\text{H}_4\text{O}$, CO_2 or H_2O respectively.

Eq. (4) indicates that the relative amounts of $\text{C}_2\text{H}_4\text{O}$, C_2O and H_2O in the product should remain constant against the experimental fact that the selectivity to form $\text{C}_2\text{H}_4\text{O}$ changed depending upon the initial partial pressures of O_2 and C_2H_4 and the reaction temperature, and thus LYUBARSKII's scheme (1) is denied.

TWIGG⁴⁾ has, on the other hand, proposed the following scheme*):

*) C_3HCHO (a) proposed by TWIGG⁴⁾ as an intermediate of the complete oxidation of ethylene is omitted here on account of the experimental fact of MARGOLIS and ROGINSKII⁷⁾ that intentional addition of CH_3CHO to the mixture of O_2 and C_2H_4 slightly accelerated the formation of $\text{C}_2\text{H}_4\text{O}$ but not of CO_2 , against TWIGG's expectation.

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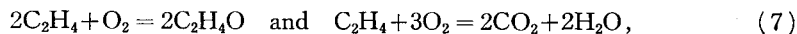
Denoting the intermediates, O(a), C₂H₄O(a), CH₂O(a), CO(a) and H(a), by $i=1, 2, 3, 4$ and 5 respectively, we have the steady state condition of the overall reaction,

$$\mathbf{an} \equiv \begin{bmatrix} 2 & -1 & 0 & -2 & 0 & -1 & -1 \\ 0 & 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 0 & 2 & 0 & -2 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{matrix} n_1 \\ n_2 \\ n_3 \\ n_4 \\ n_5 \\ n_6 \\ n_7 \end{matrix} = 0,$$

where the degeneracy of the square matrix \mathbf{a} is 2. We have hence two independent reaction routes, which are defined by the stoichiometric numbers $[\nu_s^{(1)}]$ and $[\nu_s^{(2)}]$:

$$[\nu_s^{(1)}] = [1, 2, 2, 0, 0, 0, 0] \quad \text{and} \quad [\nu_s^{(2)}] = [3, 0, 0, 1, 2, 2, 2]. \quad (6)$$

Thus we see that the two independent reaction routes can be represented by the following stoichiometric equations,



i. e., the partial oxidation of ethylene to ethylene oxide and the complete one to water and carbon dioxide, respectively.

Now let us see that there exists a coupling between these two routes because they comprise step 1 in common. For reasons of simplicity we shall limit our discussion to the case where each of the steps in scheme (5) is nearly in equilibrium and thus linear relations such as Eq. (8) below hold. Many of conclusions to be drawn below should, however, remain qualitatively correct in more general cases where the linearity breaks down.

According to NAKAMURA⁸⁾ the chemical affinity, $-\mathcal{A}^{(p)}G$, of the reaction of route p is given by a linear combination of the rates, $V^{(q)}$'s, of routes q 's as

$$-\mathcal{A}^{(p)}G = \sum_q \kappa_{qp} V^{(q)}, \quad (8)$$

where

$$\kappa_{pq} = \sum_s \kappa_s \nu_s^{(p)} \nu_s^{(q)}, \quad (9)$$

$$\kappa_s = kT/v_{+s,e} \quad (10)$$

and $v_{+s,e}$ is the unidirectional forward rate of step s in its equilibrium. From

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Eq. (9) and the set of stoichiometric numbers, $[\nu_s^{(1)}]$ and $[\nu_s^{(2)}]$, given by Eqs. (6) it follows for the oxidation of ethylene that

$$[\kappa_{pq}] \cong \begin{bmatrix} \kappa_1 + 4(\kappa_2 + \kappa_3) & 3\kappa_1 \\ 3\kappa_1 & 9\kappa_1 + \kappa_4 + 4(\kappa_5 + \kappa_6 + \kappa_7) \end{bmatrix}. \quad (11)$$

Eq. (11) can be specialized as follows:

a) If $\kappa_1 \gg \kappa_s$ ($s \neq 1$), *i.e.* the step $O_2 \rightleftharpoons 2O(a)$ is extremely slower than the other steps, it follows from Eq. (11) that

$$[\kappa_{pq}] \cong \begin{bmatrix} \kappa_1 & 3\kappa_1 \\ 3\kappa_1 & 9\kappa_1 \end{bmatrix}, \quad (12)$$

which results with reference to Eq. (8) in

$$-\mathcal{A}^{(1)}G = \kappa_1(V^{(1)} + 3V^{(2)}) = -\mathcal{A}^{(2)}G/3. \quad (13)$$

b) If $\kappa_j \gg \kappa_s$ ($j=4, 5, 6$ or $7, s \neq j$), we have

$$[\kappa_{pq}] \cong \begin{bmatrix} 0 & 0 \\ 0 & \sum \kappa_j \end{bmatrix}, \text{ hence } \mathcal{A}^{(1)}G = 0 \text{ and } -\mathcal{A}^{(2)}G/\sum \kappa_j = V^{(2)},$$

where $\sum \kappa_j = \kappa_4, 4\kappa_5, 4\kappa_6$ or $4\kappa_7$ for $j=4, 5, 6$ or 7 respectively. We see, furthermore, in this case that

$$V^{(2)} = v_4, v_5/2, v_6/2 \text{ or } v_7/2$$

for $j=4, 5, 6$ or 7 respectively, according to the general relation between $V^{(p)}$ and the net rate v_s ($=v_{+s} - v_{-s}$), derived by NAKAMURA⁸⁾,

$$v_s = \sum_p \nu_s^{(p)} V^{(p)}. \quad (14)$$

c) If $\kappa_j \gg \kappa_s$ ($j=2$ or $3, s \neq j$), it follows that

$$[\kappa_{pq}] \cong \begin{bmatrix} 4\kappa_j & 0 \\ 0 & 0 \end{bmatrix}, \text{ hence } \mathcal{A}^{(2)}G = 0 \text{ and } -\mathcal{A}^{(1)}G/4\kappa_j = V^{(1)} = v_j/2 \\ (j=2 \text{ or } 3).$$

In the case of b) or c) the partial or the complete oxidation of ethylene is in equilibrium, hence, C_2H_4O or $CO_4 + H_4O$ should be formed practically exclusively under the usual experimental condition^{*)} against the experimental fact that C_2H_4O , CO_2 and H_2O are formed with rates comparable with each other, and thus only the case of a), where the rate of oxidation of ethylene is determined by the step of oxygen chemisorption, is probable among these three cases and conforms to the observed results as follows.

i) We see according to Eq. (14), that, the rate $V^{(1)} + 3V^{(2)}$ in Eq. (13) is just the

*) The logarithmic equilibrium constant, $\log_{10} K_P (= \mathcal{A}G_B^\circ/T)$, is evaluated at 210°C, on the basis of values given in LANDOLT-BERNSTEIN Tabellen, 6 Aufgabe, II Band, 4 Teil, as -15.7 or -129.5 for the partial or the complete oxidation of ethylene of Eq. (7) respectively.

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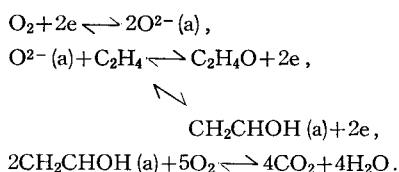
net rate, v_1 , of step 1, and this conclusion coincides with the fact observed by KUMMER⁹⁾ that the rate of decrease of oxygen partial pressure was nearly equal to the rate of oxygen chemisorption.

ii) Eq. (13) shows that decrease of the chemical affinity, $-\Delta^{(2)}G$, of the complete oxidation caused, for instance, by intentional addition of CO_2 into the reaction system gives rise to a decrease of the chemical affinity, $-\Delta^{(1)}G$, of ethylene oxide formation as well as that of the rate of ethylene oxidation. This conclusion coincides with the observed result of NAULT *et al.*¹⁰⁾ that the reactions were strongly inhibited by addition CO_2 .

iii) The activation heats of the partial and complete oxidations of ethylene have been observed¹¹⁾ to be 12 and 15 kcal/mole respectively. The similarity between these activation heats can be expected in the case where the rate-determining step is common to these two oxidations.

To discuss the rate law of the oxidation is difficult for the present because of the lack of knowledges of the occupation of catalyst surface and interactions among adsorbates, however, the observed positive order of the rate with respect to oxygen partial pressure may be expected in the case of the chemisorption oxygen being the slowest.

Much the same conclusions as above are similarly derivable from the scheme proposed by KRUILENKO *et al.*¹²⁾ by improving scheme (1) as



According to LANGWELL¹³⁾ the selectivity of silver catalyst to form ethylene oxide was increased by addition of Cl_2 *etc.* With reference to scheme (5) and the experimental fact that the rate of ethylene oxidation was strongly inhibited by the intentional addition of CO_2 as mentioned above but scarcely by H_2O ¹²⁾, it may be assumed that step 6 in scheme (5) is practically reversible, but step 7 is not, and thus the coexistence of Cl_2 *etc.* on the catalyst surface may retard the formation of $\text{CO}(\text{a})$. If so, the addition of Cl_2 *etc.* may cause the decrease of the retardation by CO_2 as well as the increase of selectivity of catalyst for formation of ethylene oxide.

Experiments along with the present analysis are now in progress.

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