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## ON THE STEADY OXIDATION OF ETHYLENE OVER SILVER CATALYSTS

By

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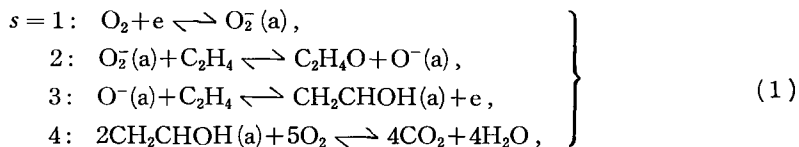
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A method for studying mechanisms of heterogeneous catalysis by determining the stoichiometric numbers of their rate-determining steps<sup>1)</sup> or by investigating the "structure" of reactions<sup>2)</sup> has been developed by HORIUTI and coworkers on the basis of his theory of steady reaction<sup>3)</sup> and applied successfully to various catalytic reactions. The method is, however, applicable only to reactions with a single reaction route<sup>3)</sup>, 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 1946<sup>4)5)</sup>.

A reaction mechanism proposed by LYUBARSKII<sup>6)</sup> 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 reaction<sup>3)</sup>, 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,

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

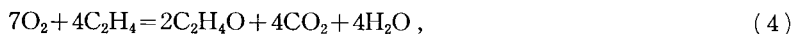
The number of linearly independent solutions of this equation is the number of independent reaction routes<sup>3)</sup> of the ethylene oxidation and equals the degeneracy of the square matrix  $\mathbf{a}$ , which is unity. The solution is

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

where  $A$  is an arbitrary constant. The set,  $[\nu_s]$ , of integers,  $\nu_s$ , 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



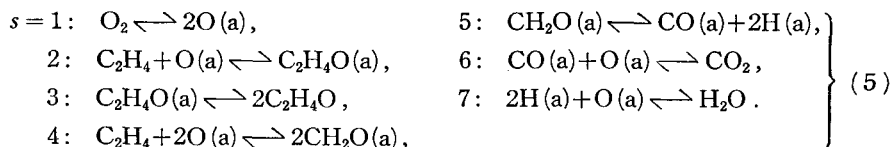
where  $B_m$  denotes the coefficient of  $m$ -th chemical species in the chemical equation of the route, the element,  $b_{ms}$ , of the matrix  $\mathbf{b}$  is the number of molecules of  $m$ -th species produced or consumed by one act of step  $s$ , and  $m=1, 2, 3, 4$  or  $5$  denotes  $\text{O}_2$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

Eq. (4) indicates that the relative amounts of  $\text{C}_2\text{H}_4\text{O}$ ,  $\text{C}_2\text{O}$  and  $\text{H}_2\text{O}$  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  $\text{O}_2$  and  $\text{C}_2\text{H}_4$  and the reaction temperature, and thus LYUBARSKII's scheme (1) is denied.

TWIGG<sup>4)</sup> has, on the other hand, proposed the following scheme\*):

\*)  $\text{C}_3\text{HCHO}$  (a) proposed by TWIGG<sup>4)</sup> as an intermediate of the complete oxidation of ethylene is omitted here on account of the experimental fact of MARGOLIS and ROGIN-SKII<sup>7)</sup> that intentional addition of  $\text{CH}_3\text{CHO}$  to the mixture of  $\text{O}_2$  and  $\text{C}_2\text{H}_4$  slightly accelerated the formation of  $\text{C}_2\text{H}_4\text{O}$  but not of  $\text{CO}_2$ , against TWIGG's expectation.

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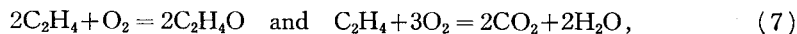
Denoting the intermediates, O(a), C<sub>2</sub>H<sub>4</sub>O(a), CH<sub>2</sub>O(a), CO(a) and H(a), by  $i=1, 2, 3, 4$  and 5 respectively, we have the steady state condition of the overall reaction,

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

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 NAKAMURA<sup>8)</sup> 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 NAKAMURA<sup>8)</sup>,

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

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

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

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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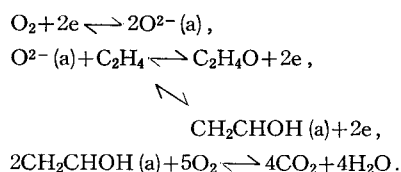
net rate,  $v_1$ , of step 1, and this conclusion coincides with the fact observed by KUMMER<sup>9)</sup> that the rate of decrease of oxygen partial pressure was nearly equal to the rate of oxygen chemisorption.

ii) Eq. (13) shows that decrease of the chemical affinity,  $-\Delta^{(2)}G$ , of the complete oxidation caused, for instance, by intentional addition of  $\text{CO}_2$  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.*<sup>10)</sup> that the reactions were strongly inhibited by addition  $\text{CO}_2$ .

iii) The activation heats of the partial and complete oxidations of ethylene have been observed<sup>11)</sup> 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.*<sup>12)</sup> by improving scheme (1) as



According to LANGWELL<sup>13)</sup> the selectivity of silver catalyst to form ethylene oxide was increased by addition of  $\text{Cl}_2$  *etc.* With reference to scheme (5) and the experimental fact that the rate of ethylene oxidation was strongly inhibited by the intentional addition of  $\text{CO}_2$  as mentioned above but scarcely by  $\text{H}_2\text{O}$ <sup>12)</sup>, it may be assumed that step 6 in scheme (5) is practically reversible, but step 7 is not, and thus the coexistence of  $\text{Cl}_2$  *etc.* on the catalyst surface may retard the formation of  $\text{CO}(\text{a})$ . If so, the addition of  $\text{Cl}_2$  *etc.* may cause the decrease of the retardation by  $\text{CO}_2$  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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**References**

- 1) J. HORIUTI and M. IKUSHIMA, Proc. Imp. Acad. Tokyo **15**, 39 (1936); J. HORIUTI, This Journal **5**, 1 (1956); A. MATSUDA and J. HORIUTI, This Journal **10**, 14 (1962).
- 2) K. TANABE, Shokubai (Catalyst) No. **14**, 17 (1957); J. HORIUTI and K. TANABE, Proc. Japan Acad. **27**, 404 (1951); J. HORIUTI and K. MIYAHARA, "Hydrogenation of Ethylene on Metallic Catalysts" NSRDS-NBS-13, National Bureau of Standards, U.S.A. (1968).
- 3) J. HORIUTI and T. NAKAMURA, Advances in Catalysis **17**, 1 (1967).
- 4) G. H. TWIGG, Trans. Faraday Soc. **42**, 284 (1946).
- 5) An example of the reviews: E. ECHIGOYA, *Shokubai-Kōgaku Kōza* (in Japanese), Chijin Book Co. Tokyo, **7**, 56 (1964).
- 6) G. D. LYUBARSKII, Doklady Nauk **110**, 112 (1956).
- 7) L. YA. MARGOLIS and S. Z. ROGINSKII, Izvest. Akad. Nauk, Otdel Khim. Nauk No. 3, 282 (1956).
- 8) T. NAKAMURA, This Journal **7**, 224 (1959); **9**, 87 (1961).
- 9) J. T. KUMMER, J. Phys. Chem. **60**, 666 (1956).
- 10) L. G. NAULT, D. W. BOLME and L. N. JOHANSON, Ind. Eng. Chem. Process Design and Development **1**, 285 (1962).
- 11) K. E. MURRAY, Chemical Abstract **45**, 6573 (1951).
- 12) A. I. KRUILENKO, N. V. KUL'KOVA, N. A. RYBAKOVA and M. I. TEMKIN, Zhur. Fiz. Khim. **32**, 797, 1043 (1958).
- 13) W. H. LANGWELL, General Discussion supplemented to the paper of Ref. 9.