HOKKAIDO UNIVERSITY

Title	COMMENT ON MILNER'S PAPER ON "THE POSSIBLE MECHANISMS OF COMPLEX REACTIONS"
Author(s)	MIYAHARA, Koshiro
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 17(3), 219-222
Issue Date	1969-12
Doc URL	https://hdl.handle.net/2115/24899
Type	departmental bulletin paper
File Information	17(3)_P219-222.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

J. Res. Inst. Catalysis, Hokkaido Univ., Vol. 17, No. 3, pp. 219 to 222 (1969)

COMMENT ON MILNER'S PAPER ON "THE POSSIBLE MECHANISMS OF COMPLEX REACTIONS"

By

Koshiro MIYAHARA*)

(Received September 9, 1969)

It will be shown in this note that the method proposed by MILNER[1] for generating "complete sets of reaction mechanisms" was no more than a bad change of the theory of the steady rate of reaction developed by HORIUTI *et al.*[2] with an unnecessary assumption of a single overall reaction and some confusions in the dependence among possible mechanisms. DESPIĆ *et al.*[3] have, furthermore, proposed a method to list up possible steps and mechanisms for a single overall reaction on the basis of MILNER's method, which was erroneously treated by the formers as "a formal method to obtain a list of all reaction paths of a single overall reaction, each of which cannot be obtained by superposition of any other members of the list."

MILNER[1] has started his discussion by solving the equations,

$$\sum_s a_{is}\nu_s = 0\,, \qquad (i = 1, 2, \cdots, I;\ s = 1, 2, \cdots, S) \tag{1}$$

with respect to the stoichiometric number, ν_s, of step s with reference to a special value of a coefficient,

$$B_r = \sum_s b_{ms}\nu_s\,, \tag{2}$$

of m-th reactant or product in the stoichiometric equation of a single overall reaction, where a_{is} or b_{ms} is the coefficient of i-th intermediate or the m-th reactant or product in the stoichiometric equation of step s respectively. According to this method, a value inconveniently differring from integer may be obtained for ν_s depending upon the stoichiometric equations assumed for step s and the overall reaction, and, furthermore, such a restriction as Eq. (2) is unnecessary to solve Eqs. (1) as follows.

Eq. (1) is a special form of the steady state condition of a reaction system, which states that the amounts of respective intermediates are kept constant during the progress of reaction, and are grenerally given as

$$\sum_s a_{is}n_s = 0 \qquad (s = 1, 2, \cdots, S \text{ and } i = 1, 2, \cdots, I') \tag{3}$$

or $\mathbf{an}=0$ in its matrix representation, where n_s is the number of acts of step s in

*) Research Institute for Catalysis, Hokkaido Univ., Sapporo, Japan.

a specified time of reaction. On the basis of a specified set of S steps and I' intermediates, we can solve Eqs. (3) with respect to n_s's and obtain $P(=S-I)$ independent sets of $n_s^{(p)}$-values ($p=1,2,\cdots,P$), where I is the rank of the largest nonsingular matix of $\mathbf{a}\equiv[a_{is}]$, called by HORIUTI and NAKAMURA[2] as the number of *independent intermediates**). The sets of $n_s^{(p)}$-values thus obtained are not unique because $n_s^{(p)}$'s may have a common factor, and HORIUTI and NAKAMURA[2] have defined the p-th *independent route* of reaction by a set, $\mathbf{n}^{(p)}=[\nu_1^{(p)}, \nu_2^{(p)}, \cdots, \nu_s^{(p)}]$, of the so-called *stoichiometric numbers*, $\nu_s^{(p)}$'s, which are the simplest integers given by the $n_s^{(p)}$-values aside from their comon factor. The set, $\mathbf{B}^{(p)}$, of coefficients, $B_m^{(p)}$'s, of the m-th species in the stoichimetric equation of route p is now determined by an equation, similar to Eqs. (2),

$$\mathbf{B}^{(p)} \equiv [B_m^{(p)}] = [b_{ms}]\mathbf{n}^{(p)}, \tag{4}$$

where b_{ms} and $B_m^{(p)}$ are negative or positive integers according to m-th species being reactant or product respectively. The coefficients, $B_m^{(p)}$'s, and hence the sorts of overall reactions able to occur in the specified reaction system are thus necessarily determined by Eqs. (4) on the basis of $\mathbf{n}^{(p)}$, as illustrated by HORIUTI[2] by RICE–HERZFELD–mechanism for the pyrolysis of ethane.

Let us consider an another example, which is the system of catalytic oxidation[4] of C_2H_4 by O_2 assumed to proceed by the following steps proposed by TWIGG[5].

$$\left.\begin{array}{ll} s=1: \ O_2 \rightleftharpoons 2O(a), & 5: \ CH_2O(a) \rightleftharpoons CO(a)+2H(a), \\ 2: \ C_2H_4+O(a) \rightleftharpoons C_2H_4O(a), & 6: \ CO(a)+O(a) \rightleftharpoons CO_2, \\ 3: \ C_2H_4O(a) \rightleftharpoons C_2H_4O, & 7: \ 2H(a)+O)a) \rightleftharpoons H_2O. \\ 4: \ C_2H_4+2O(a) \rightleftharpoons 2CH_2O(a), & \end{array}\right\} \tag{5}$$

Denoting the intermediates, O(a), $C_2H_4O(a)$, $CH_2O(a)$, CO(a) and H(a) by $i=$ 1, 2, 3, 4 and 5 respectively, we have the steady state condition,

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

*) With respect to, for instance, the formation of HCl from H_2 and Cl_2 through steps, 1: $Cl+H_2 \rightleftharpoons HCl+H$ and 2: $H+Cl_2 \rightleftharpoons HCl+Cl$, of NERNST chain, we have, according to Eqs. (3), that $-n_1+n_2=0$ for Cl and $n_1-n_2=0$ for H, which are linearly dependent with each other, and thus the independent intermediate in this case is either of two intermediates, H and Cl.

The rank of the matrix **a** is 5 and $S=7$ as seen from scheme (5) and hence we have two independent routes of reaction, which are

$$\mathbf{n}^{(1)}=(1, 2, 2, 0, 0, 0, 0) \text{ and } \mathbf{n}^{(2)}=(3, 0, 0, 1, 2, 2, 2). \quad (7)$$

Introducing Eqs. (7) and the matrix,

$$[b_{ms}]=\begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix},$$

into Eqs. (4), where O_2, C_2H_4, C_2H_4O, CO_2 and H_2O are assigned by $m=1$, 2, 3, 4 and 5 respectively, we have

$$\mathbf{B}^{(1)}=(-1,-2, 2, 0, 0) \quad \text{and} \quad \mathbf{B}^{(2)}=(-3,-1, 0, 2, 2)$$

and thus find the two independent routes can be represented by the stoichiometric equations,

$$2C_2H_4+O_2=2C_2H_4O \quad \text{and} \quad C_2H_4+3O_2=2CO_2+2H_2O,$$

i.e. the partial and the complete oxidations of C_2H_4 respectively.

It is now pointed out that MILNER[1] has introduced some confusions into his list of possible mechanisms by leaving the dependence among the routes of reaction out of consideration.

Let us consider the hydrogen electrode reaction, $2H^++2e=H_2$, which was exemplified by MILNER as comprising three steps, 1: $H^++e \rightleftharpoons H$, 2: $H^++H+e \rightleftharpoons H_2$ and 3: $2H \rightleftharpoons H_2$. We have $S=3$ and $I=1$ in this case, and hence two independent routes of reaction, which are $\mathbf{n}^{(1)}=(1, 1, 0)$ and $\mathbf{n}^{(2)}=(2, 0, 1)$, assigned by MILNER as mechanisms A and B, respectively. MILNER has listed up another one, C ($=\mathbf{n}^{(3)}=(0, 2,-1)$), and discussed that this mechanism is possible only on some specific electrode material, which forms H atoms only through step 1 but not step 3, and necessarily behaves a phenomenon of induction period. The mechanism C is, however, as pointed out by HORIUTI *et al.*,[2] no more than one of linear combinations of A and B, *i.e.* 2A–B, which corresponds to the so-called 'slow discharge mechanism' where step 1 is the slowest and consequently H_2 is evolved predominantly through steps, 2 and 3.

With respect to the other two overall reactions, $Cu^{2+}+2e=Cu$ and $4OH^-=O_2+2H_2O+4e$, illustrated by MILNER,[1] we can easily see $P=4$ and 5 respectively on the basis of steps assumed by MILNER and that only four or five mechanisms from those, A, B, C *etc.*, listed up by MILNER are linearly independent with each other and the other mechanisms are all given as linear combinations of these

independent ones as follows:

For $Cu^{2+}+2e=Cu$, it follows

$A=\frac{1}{2}(D+E)$, $B=2A-F$, $C=\frac{1}{2}(D+J)$, $F=\frac{1}{2}(E+H)$, $G=\frac{1}{2}(H+J)$ and $I=2G-F$

as linear combinations of D, E, H and J,

For $4OH^{-}=O_2+2H_2O+e$, we have

$B=2(A-D)+H$, $C=2D-H$, $F=E+D-G$, $I=2(E-D)+H$, $J=2(E-G)+H$ and $K=2(G-D)+H$

as linear combinations of A, D, E, C and H.

These dependent routes of reaction are just the "combinations of simultaneous mechanisms" of MILNER and omitted by him from his list of the possible mechanisms. We see thus, sofar as MILNER's analysis concerns, that it is sufficient for the discussion of possible mechanisms to list up independent routes of reactions, which has already been done by HORIUTI *et al.*[2]

References

1) P. C. MILNER, J. Electrochem. Soc. **111**, 228 (1964).
2) J. HORIUTI and T. NAKAMURA, Z. Physik. Chem. (Neue Folge) **11**, 358 (1959); Advances in Catalysis **17**, 1 (1967), J. HORIUTI, This Journal **5**, 1 (1957) *etc.*
3) A. R. DESPIĆ *et al.*, Private communication to T. NAKAMURA (1969).
4) K. MIYAHARA, This Journal, the preceding paper.
5) G. T. TWIGG, Trans. Faraday Soc. **42**, 284 (1946).