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Author(s)	HAPPEL, John; ATKINS, Richard S.; TANAKA, Kazunori
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# STOICHIOMETRIC NUMBER OF THE RATE- DETERMINING STEP FOR DEHYDROGENATION OF BUTANE AND BUTENES OVER CHROMIA AND CHROMIA-ALUMINA CATALYSTS

Analysis of Data of Balandin and His Collaborators

By

John HAPPEL<sup>\*)</sup>, Richard S. ATKINS<sup>\*)</sup>  
and Kazunori TANAKA<sup>\*\*)</sup>

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## Abstract

Using carbon-14 as a tracer, Balandin and his collaborators investigated the dehydrogenation of butane-butene mixtures over chromia and chromia-alumina catalysts. From this study it was concluded that butadiene comes from butene but not directly from butane. In the present work their data have been analyzed to evaluate  $\nu_r$  (the stoichiometric number of the rate-determining step) for both butane and butene dehydrogenations in a conventional manner in which a single rate-controlling step and no side reaction are assumed. The  $\nu_r$  values derived on this basis were close to two for butane dehydrogenation and three to four for butene dehydrogenation. The stoichiometric number of two for butane dehydrogenation may be accounted for, although probably unlikely, on the basis of an intermediate with two carbon atoms. More likely, contrary to the above conventional assumption, the reaction is either controlled by two rate-controlling steps or accompanied by a side reaction giving rise to the C<sup>14</sup> exchange between butane and butene. It is demonstrated that under these conditions the apparent  $\nu_r$  value evaluated in the above way may be two or more even if the reaction consists only of elementary steps with a stoichiometric number of one. The unusually great stoichiometric number observed for butene dehydrogenation might also be interpreted as due to two rate-controlling steps or a side reaction of similar type.

## Introduction

WATSON, DODD, and BECKBERGER<sup>1,2)</sup> made a pioneer study on butane

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<sup>\*)</sup> Department of Chemical Engineering, School of Engineering and Science, New York University, Bronx, N. Y., U.S.A. Present address of R.S.A.: Shell Oil Company, New York, N. Y., U.S.A..

<sup>\*\*)</sup> Associate research scientist at New York University, 1966-1967, from Research Institute for Catalysis, Hokkaido University, Sapporo, Japan. Present address: Institute of Physical and Chemical Research, Saitama Pref., Japan.

and butene dehydrogenations over chromia-alumina and No. 1707 catalysts\*). The kinetic data observed were treated by the fundamental rate equations developed by HOUGEN and WATSON<sup>4,5</sup>). The so-called dual-site mechanism rather than the single-site mechanism correlated well with their data. A Russian school headed by BALANDIN<sup>6,7</sup>) also extensively investigated the same reactions over chromia and chromia-alumina catalysts. In contrast with the results of WATSON and his co-workers the Russian data were best explained by the single-site mechanism. However, more recent data obtained over chromia-alumina by one of the present authors and his co-workers<sup>8</sup>) indicate that neither of these mechanisms affords satisfactory correlation. They correlated their data by developing a more generalized rate expression in which  $\nu_r$ , the stoichiometric number of the rate-controlling step, is involved. This expression includes the HOUGEN and WATSON equation as a special case when  $\nu_r$  is one. The value for  $\nu_r$  was two in the recent data. This could be interpreted as involving the formation of an intermediate with two carbon atoms, e.g. adsorbed ethylene for both butane and butene dehydrogenations. Then it would be very likely that in butene dehydrogenation for example, ethylene, if involved in the mechanism, would be incorporated into product butadiene. However, this was not observed in experiments made by the use of C<sup>14</sup>-tagged ethylene<sup>9</sup>).

It is to be noted that the more generalized rate expression as well as that of HOUGEN and WATSON involves adsorption terms which can hardly be determined exactly. Conventionally these terms have been treated on the basis of the Langmuir adsorption isotherm, which might be open to question. The  $\nu_r$  values for butane and butene dehydrogenations are thus worth measuring by other methods without assuming any rate expression. This has been done by two of the present authors<sup>10</sup>), who determined  $\nu_r$  for butane dehydrogenation and its reverse by measuring simultaneously the forward and backward rates of the overall reaction by the use of C<sup>14</sup> as a tracer. The  $\nu_r$  values obtained were close to one rather than to two, suggesting that the single rate-controlling step consists in the transformation of an unruptured C<sub>4</sub> skeleton. Similar experimental work on the butene-butadiene system is now in progress in our laboratory.

Prior to this C<sup>14</sup> work, the Russian school<sup>11,12</sup>) also made a C<sup>14</sup> tracer study for these reactions. Since  $\nu_r$  determination was not their direct intention, some quantities needed for the  $\nu_r$  determination were left unmeasured. These quantities, however, may be estimated based on some plausible assump-

\*) The Standard Oil Development Co. developed this catalyst consisting of oxides of Mg, Fe, Cu and K (cf. Reference 3).

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tions. The present work aims to analyze the Russian data to evaluate  $\nu_r$  for butane and butene dehydrogenations.

### 1. Theoretical

For any chemical reaction which is controlled by a single rate-controlling step,  $\nu_r$ , the stoichiometric number of the rate-controlling step, may be expressed as<sup>13)</sup>

$$\nu_r = \frac{-\Delta G}{RT \ln(V_+/V_-)}, \quad (1)$$

where  $-\Delta G$  is the chemical affinity associated with the overall reaction,  $R$  is the gas constant,  $T$  is the reaction temperature, and  $V_+$  and  $V_-$  are the unidirectional forward and backward rates of the overall reaction respectively. This equation will be developed here for butane dehydrogenation



and butene dehydrogenation



The chemical affinity of reaction (2. I) may be given in terms of its equilibrium constant  $K_A$  and the pressures  $P_A$ ,  $P_E$ , and  $P_H$  respectively of butane, butene and hydrogen as

$$-\Delta G = RT \ln(P_A K_A / P_E P_H). \quad (3. 1)$$

The chemical affinity of reaction (2. II) is expressed in a similar form,

$$-\Delta G = RT \ln(P_E K_E / P_I P_H), \quad (3. II)$$

where  $K_E$  is the equilibrium constant for reaction (2. II) and  $P_I$  is the pressure of butadiene.

Suppose that a mixture of butane, butene, and hydrogen is continuously fed to a reactor with a fixed catalyst bed. Either the butane or butene is labeled with  $\text{C}^{14}$ . Let the flow rate of butane be  $F_A$ . Then  $V_\alpha$ , the net rate of butane dehydrogenation, can be given as

$$V_\alpha = V_{+\alpha} - V_{-\alpha} = -\frac{dF_A}{dW}, \quad (4)$$

where  $V_{+\alpha}$  and  $V_{-\alpha}$  are the unidirectional forward and backward rates of reaction (2.I) respectively and  $W$  is the catalyst weight. Let the mole fraction of the labeled butane to the total butanes be  $Y_A$ , and that of butene be  $Y_E$ , and assume that the exchange of  $\text{C}^{14}$  atoms between butane and butene takes

place through the rate-controlling step of butane dehydrogenation. Then the rate of  $C^{14}$  transfer from butane to butene, neglecting the kinetic isotope effect, may be expressed by

$$-\frac{d(Y_A F_A)}{dW} = -Y_A \frac{dF_A}{dW} - F_A \frac{dY_A}{dW} = -Y_E V_{-\alpha} + Y_A V_{+\alpha}. \quad (5)$$

Combining Eqs. (4) and (5), we obtain

$$V_{-\alpha} = F_A dY_A / (Y_E - Y_A) dW \quad (6. V_{-\alpha})$$

and

$$V_{+\alpha} = -dF_A / dW + F_A dY_A / (Y_E - Y_A) dW \quad (6. V_{+\alpha})$$

Substituting  $-dG$ ,  $V_{-\alpha}$  and  $V_{+\alpha}$  from Eqs. (3.I) and (6) into Eq. (1) we finally obtain, as an expression for  $\nu_r$ ,

$$\nu_r = \frac{RT \ln (P_A K_A / P_E P_H)}{RT \ln [1 - (Y_E - Y_A) dF_A / F_A dY_A]}. \quad (7)$$

Similar consideration of the butene dehydrogenation system gives

$$V_\varepsilon = V_{+\varepsilon} - V_{-\varepsilon} = \frac{dF_I}{dW} \quad (8)$$

and

$$\frac{d(Y_I F_I)}{dW} = Y_I \frac{dF_I}{dW} + F_I \frac{dY_I}{dW} = Y_E V_{+\varepsilon} - Y_I V_{-\varepsilon}. \quad (9)$$

In these equations,  $V_\varepsilon$  is the net rate of butene dehydrogenation,  $V_{+\varepsilon}$  and  $V_{-\varepsilon}$  are the unidirectional forward and backward rates,  $F_I$  is the flow rate of butadiene, and  $Y_I$  is the mole fraction of the labeled butadiene to the total butadienes. These equations, combined with Eqs. (1) and (3.II), give an expression for  $\nu_r$ ,

$$\nu_r = \frac{RT \ln (P_E K_E / P_I P_H)}{RT \ln [1 / \{1 - (Y_E - Y_I) dF_I / F_I dY_I\}]}. \quad (10)$$

For the sake of the analysis below, Eqs. (7) and (10) are rewritten in a different form such as

$$\nu_r = \frac{RT \ln (P_A K_A / P_E P_H)}{RT \ln [1 - (Y_E - Y_A) (dF_A / F_A d\tau) / (dY_A / d\tau)]} \quad (11. I)$$

and

$$\nu_r = \frac{RT \ln (P_E K_E / P_I P_H)}{RT \ln [1 / \{1 - (Y_E - Y_I) (dF_I / F_I d\tau) / (dY_I / d\tau)\}]} \quad (11. II)$$

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respectively, where  $\tau$  is the contact time.

## 2. Data of Balandin and His Co-workers

Using  $C^{14}$  as a tracer Balandin and his co-workers<sup>11,12)</sup> conducted three series of experiments on the dehydrogenation of butane-butene mixtures. The catalyst used was chromia in two series among them, referred to subsequently as series 1 and 2, and chromia-alumina in the other (series 3). The reactor employed was of integral type with a fixed catalyst bed. In each series, several runs were carried out at various feed rates or various contact times.

In series 1, an equimolar mixture of ordinary butane and  $C^{14}$ -labeled butene was fed into the reactor with water vapor in the ratio of 9 moles of water per mole of hydrocarbons. The catalyst temperature was 635°C. The total pressure is supposed, although not explicitly stated, to have been atmospheric since on their paper there is no description suggestive of any elevated or reduced pressure. The compositions of the exit gas and the radioactivities measured are shown in Table 1.

TABLE 1. The observations in series 1 and 2

Series		1						2				
Run	Contact time in sec. ( $\tau$ )	B-B <sup>a)</sup>	17	19	18	16	20	B-B <sup>a)</sup>	22	23	21	
		0	0.74	1.20	1.89	2.32	3.22	0	1.11	1.74	2.56	
	CH <sub>4</sub>		0.56	0.76	1.03	1.07	1.17		0.72	0.96	1.10	
	C <sub>2</sub> H <sub>4</sub>		0.49	0.54	0.58	0.61	0.65		0.54	0.56	0.63	
	C <sub>2</sub> H <sub>6</sub>		0.77	1.68	2.11	2.35	2.64		1.61	2.06	2.46	
Composi- tion of <sup>b)</sup>	C <sub>3</sub>		0.63	0.85	1.21	1.39	1.66		0.81	1.14	1.48	
	C <sub>4</sub> H <sub>6</sub> (N <sub>I</sub> )		5.55	6.50	7.25	7.75	9.00		6.28	7.10	8.10	
	C <sub>4</sub> H <sub>8</sub> (N <sub>E</sub> )	22.35	14.7	13.9	13.0	12.9	12.3	22.35	14.1	13.0	13.0	
	C <sub>4</sub> H <sub>10</sub> (N <sub>A</sub> )	22.35	22.1	21.9	21.5	21.2	20.5	22.35	21.9	21.6	21.0	
	CO <sub>2</sub>		2.24	3.02	3.85	4.04	4.56		2.89	3.72	4.33	
	CH <sub>4</sub>				0.335			0.320		0.0503	0.085	0.0595
	C <sub>2</sub> H <sub>4</sub>				0.157			0.320		0.222	0.252	0.232
Specific radio- activity of <sup>c)</sup>	C <sub>2</sub> H <sub>6</sub>											
	C <sub>3</sub>			0.180			0.247		0.311	0.246	0.261	
	C <sub>4</sub> H <sub>6</sub> (Y <sub>I</sub> )		0.970	0.985	0.985	0.970	0.994		0.0039	0.0029	0.0048	
	C <sub>4</sub> H <sub>8</sub> (Y <sub>E</sub> )	1.00	1.005	0.980	0.980	1.000	0.954	0.00	0.0048	0.0077	0.0097	
	C <sub>4</sub> H <sub>10</sub> (Y <sub>A</sub> )	0.00	0.005	0.005	0.005	0.0075	0.0115	1.00	0.998	0.997	0.988	
CO <sub>2</sub>		0.350	0.322	0.338		0.334		0.0069	0.0046	0.0057		

a) The original butane-butene mixture before being diluted with water vapor.

b) In millimoles per liter of original B-B mixture.

c) Taking the specific activity of either butane or butene of the original B-B mixture as unity.

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In series 2 an equimolar mixture of C<sup>14</sup>-labeled butane and ordinary butene, instead of ordinary butane and C<sup>14</sup>-labeled butene in series 1, was used as a reactant. The reaction was carried out otherwise under the same conditions as in series 1. The results are listed in Table 1.

TABLE 2. The observations in series 3

Series		3						
Run		B-B <sup>a)</sup>	31	41	38	40	29	33
Contact time in sec. ( $\tau$ )		0	0.56	0.60	1.05	1.27	1.88	1.94
Composition of <sup>b)</sup>	C <sub>4</sub> H <sub>10</sub> ( $N_A$ )	22.3	21.4	21.0	18.6	18.9	17.2	
	C <sub>4</sub> H <sub>8</sub> ( $N_B$ )	22.3	18.0	16.9	15.7	15.7	15.1	
	C <sub>4</sub> H <sub>6</sub> ( $N_I$ )			3.5	4.1	3.9	6.1	3.9
	Coke <sup>d)</sup>			1.1	1.33	1.3	2.1	2.2
	Total	44.6		42.5	39.7	39.9	40.5	
Run		B-B	35	42	36	43	34	37
Contact time in sec. ( $\tau$ )		0	0.57	0.75	1.26	1.49	1.72	2.69
Specific radioactivity for <sup>c)</sup>	C <sub>4</sub> H <sub>10</sub> ( $Y_A$ )	1.00		0.97	0.97	0.97	0.935	0.925
	C <sub>4</sub> H <sub>8</sub> ( $Y_B$ )	0.00	0.07		0.10	0.124	0.175	0.12
	C <sub>4</sub> H <sub>6</sub> ( $Y_I$ )		0.068	0.072	0.093	0.136	0.165	0.116
	Coke <sup>d)</sup>		0.115	0.14	0.19		0.130	

a, b, c) See Table 1.

d) Carbonaceous deposits on the catalyst in millimoles of C<sub>4</sub> hydrocarbons.

In series 3, an equimolar mixture of ordinary butane and ordinary butene or of C<sup>14</sup>-labeled butane and ordinary butene was fed without diluting it with water vapor. The reaction temperature and total pressure were kept at 600 ± 3°C and 250 ± 5 mmHg. The compositions of the exit gas were determined for the non-radioisotope runs, while the specific radioactivities were measured for the radioisotope runs. The results are summarized in Table 2.

### 3. Analysis of Data

Using (Eq. 11. I) it is possible to calculate  $\nu_r$  for butane dehydrogenation from the data of Table 1 or 2. The values of  $\nu_r$  for butene dehydrogenation can also be calculated from these Tables using Eq. (11. II). As  $K_E$  for the  $\nu_r$  calculation, if the isomerization of the three n-butenes is assumed much faster than their dehydrogenation<sup>9,14</sup>, may be employed an apparent equilibrium constant referring to an equilibrium mixture of the three n-butenes, *i.e.*

$$K_E = \frac{P_I P_H}{P_{E,cis-2} + P_{E,trans-2} + P_{E,1}}, \quad (12)$$

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where the denominator is the sum of the partial pressures of the n-butenes in equilibrium with each other. Denoting the equilibrium constants for the dehydrogenation of each single butene as  $K_{E,cis-2}$ ,  $K_{E,trans-2}$ , and  $K_{E,1}$ , we have from Eq. (12)

$$\frac{1}{K_E} = \frac{1}{K_{E,cis-2}} + \frac{1}{K_{E,trans-2}} + \frac{1}{K_{E,1}}. \quad (13. K_E)$$

Similar consideration to butane dehydrogenation leads to

$$K_A = K_{A,cis-2} + K_{A,trans-2} + K_{A,1}, \quad (13. K_A)$$

where  $K_{A,cis-2}$  etc. are the equilibrium constants for butane dehydrogenation to the corresponding single butene. On the basis of spectroscopic data, ASTON and SZASZ<sup>15)</sup> calculated at a set of temperatures these six equilibrium constants referred to a single butene. By using Eq. (13.  $K_A$ ) and assuming a linear relation between  $\log K_A$  and  $1/T$ , the  $K_A$  values in atmos. at 600 and 635°C were interpolated to yield 0.730 and 1.40 respectively. The values of  $K_E$  worked out in a similar way was 0.0897 atmos. at 635°C.

For the calculation of  $-\Delta G$ , the amounts of butane etc. given in millimoles in Tables 1 and 2 were converted into pressure by multiplying the appropriate mole fraction by the total pressure. In series 1 and 2 the mole fractions can be evaluated by assuming that the components of the exit gas except hydrogen are all listed in Table 1 and that there is no significant accumulation on the catalyst. In support of these assumptions, Table 3 shows that the feed (B-B) and exit gases are in close agreement in the number of gram-atoms of carbon added up for all the components listed in Table 1. The amount of molecular hydrogen produced was evaluated from a hydrogen balance between the feed and exit by further assuming the origin of  $CO_2$  produced and the average H-C atomic ratio for the  $C_3$  hydrocarbons. Suppose that  $CO_2$  was produced by the hydrolysis of hydrocarbons according to the stoichiometric relation

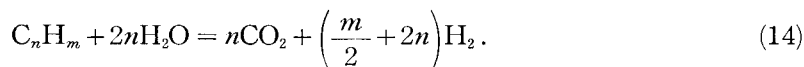


TABLE 3. The number of gram-atoms of carbon added up for all the components listed in Table 1

Series	1					2				
Run	B-B	17	19	18	16	20	B-B	22	23	21
Amount of C*)	179	177	178	181	183	184	179	179	180	184

\*) in milligram-atom.

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Then the number of moles of  $H_2$  coming from water is twice as great as  $CO_2$  produced. Since the feed and exit must agree in number of hydrogen atoms involved, we have

$$\sum_i m_i^f n_i^f = \sum_i m_i^e n_i^e + 2n_{H_2} - 4n_{CO_2}, \quad (15)$$

where  $m_i$  is the number of hydrogen atoms involved in the  $i$ -th hydrocarbon molecule of Table 1 and  $n_i$  is its number of moles, the superscripts  $f$  and  $e$  signify the feed and exit respectively,  $n_{H_2}$  is the number of moles of hydrogen, and  $n_{CO_2}$  is that of carbon dioxide. Among  $C_3$  hydrocarbons, propane is greatest in H-C atomic ratio (8:3) and propadiene or propyne is lowest (4:3). The upper bound of  $n_{H_2}$ , therefore, was evaluated from Eq. (15) by setting  $m_i^e$  equal to 4 for the  $C_3$  hydrocarbons, while  $m_i^f=8$  gave the lower bound. The  $n_{H_2}$  values thus determined, coupled with the composition listed in Table 1, were used in turn to calculate the upper and lower bounds of  $P_H$ ,  $P_A$ ,  $P_E$ , and  $P_I$ .

Also in series 3, the partial pressures of hydrogen etc. were evaluated by means of a hydrogen balance. In contrast with the foregoing series, as is seen from Table 2, there was an appreciable amount of coke on the catalyst. According to Vogé<sup>16)</sup> the average atomic H-C ratio in coke may vary from about 0.3 to 1.0 or even higher, depending on the conditions of its formation. The greatest hydrogen content of coke so far reported seems to be 13 wt. per cent<sup>17)</sup> approximating an H-C atomic ratio of 1.8. Table 2 indicates that the feed (B-B), on the one hand, and the exit gas and coke, on the other, are not in agreement in total number of carbon atoms if only the  $C_4$  hydrocarbons listed are taken into account. The balance is likely to exist in the exit gas as  $C_1$ - $C_3$  hydrocarbons, among which methane is greatest in H-C atomic ratio (4) while acetylene is lowest (1). Therefore the upper bound of  $n_{H_2}$  and hence that of  $P_H$  were calculated by taking an H-C atomic ratio as 1 for the  $C_1$ - $C_3$  hydrocarbons and as 0.3 for the coke. An H-C atomic ratio of 4 for the  $C_1$ - $C_3$  hydrocarbons and 1.8 for the coke would give the lower bound of  $P_H$  instead.

In series 1 and 2, there was a marked difference between the upper and lower bounds of  $P_H$  thus calculated, but little with  $P_A$ ,  $P_E$  and  $P_I$ . These values are plotted against contact time in Figs. 1 and 2. In series 3, the lower bound of  $n_{H_2}$  and in turn that of  $P_H$  were negative. Therefore, in Fig. 3 are plotted only the upper bounds of  $P_H$  together with the appropriate lower bounds of  $P_A$ ,  $P_E$ , and  $P_I$ . The values of  $N_A$ ,  $Y_A$ , etc. (Tables 1 and 2) are also plotted in Figs. 1 to 3.

For the calculation of  $\nu_r$  from Eq. (11.I), the values of  $Y_A$ ,  $Y_E$ ,  $P_A$ , and

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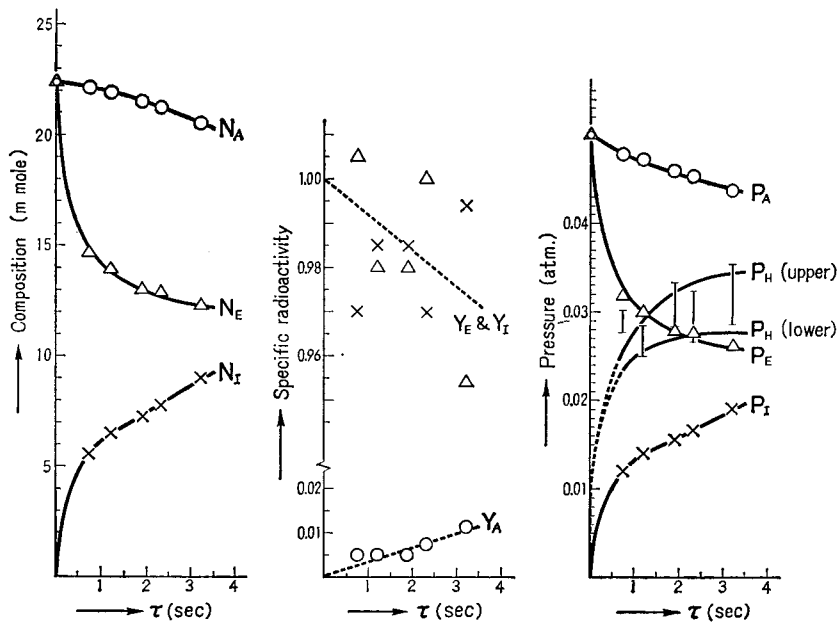


Fig. 1. Graphic presentation of kinetic data of series 1.

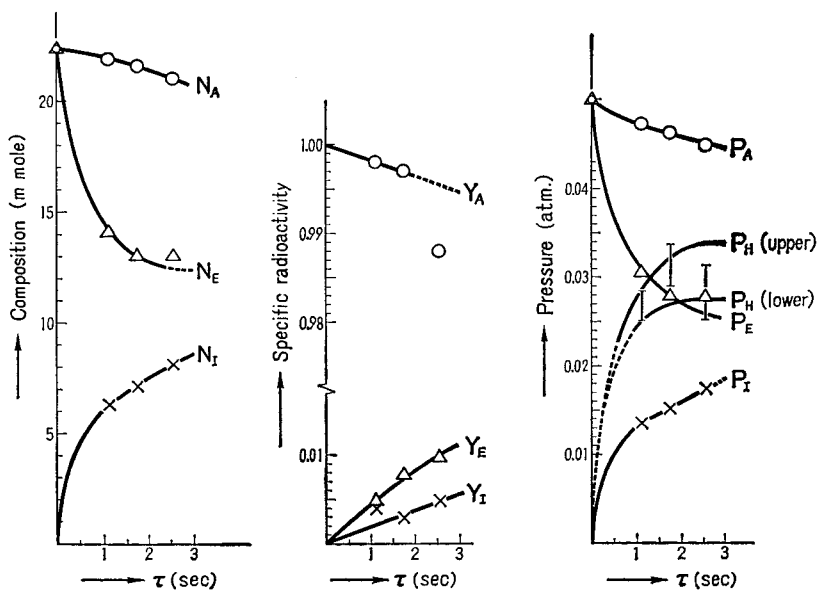


Fig. 2. Graphic presentation of kinetic data of series 2.

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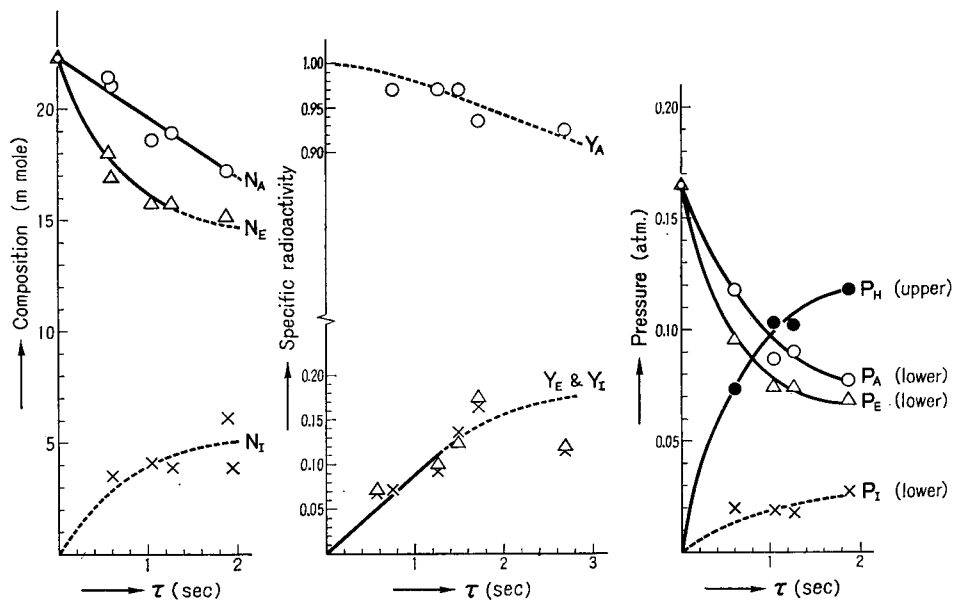


Fig. 3. Graphical presentation of kinetic data of series 3.

$P_E$  as well as the upper or lower bound of  $P_H$  were directly read from Figs. 1, 2 or 3 at several values of  $\tau$ . The upper and lower bounds of  $P_H$  lead to the lower and upper bounds of  $\nu_r$ , respectively. The derivative  $dY_A/d\tau$  was taken as the slope of the tangent to the  $Y_A \sim \tau$  curve. The other derivative  $dF_A/d\tau$  divided by  $F_A$  can be rewritten as  $d(kF_A)/kF_Ad\tau$ , where  $k$  is an arbitrary constant. For a certain value of  $k$ ,  $kF_A$  would be equal to  $N_A$  of Table 1 or 2. Therefore,  $dF_A/F_Ad\tau$  was evaluated from the  $N_A \sim \tau$  curves of Figs. 1 to 3. Table 4 lists the upper and lower bounds of  $\nu_r$  thus calculated for butane dehydrogenation at several values of  $\tau$ . It is seen that in series 1 and 2 the  $\nu_r$  values are close to two rather than to one. Although in series 3 the lower bounds of  $\nu_r$  fall closer to one, ranging from 1.3 to 1.5, it is to be recalled that the calculation was based on the assumption that the average atomic H-C ratio of the  $C_1$ - $C_3$  hydrocarbons was 1:1, that of acetylene. In view of the  $C_4$  hydrocarbon compositions of the other series, it appears very unlikely that the  $C_1$ - $C_3$  constituents of series 3 would really be dehydrogenated to that extent. If the atomic H-C ratio is taken as 2, that of ethylene, then the pressure profiles of hydrogen etc. are represented by Fig. 4, and the  $\nu_r$  values derived increase to 1.6 or even higher (Table 5). The greater the assumed atomic H-C ratio, the greater the  $\nu_r$  value. Therefore, it seems that also in series 3 the true  $\nu_r$  value is two rather than one.

In principle the value of  $\nu_r$  for butene dehydrogenation can be calculated

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TABLE 4. Upper and lower bounds of  $\nu_r$  for butane dehydrogenation

$\tau$ (sec)		0.25	0.50	0.75	1.00	1.25	1.50	1.75	2.00	2.50	3.00
Series 1	$\nu_r$ (U)		2.7		2.2		2.0		1.9	1.8	1.8
	$\nu_r$ (L)		2.6		2.1		1.9		1.8	1.7	1.7
	$-\Delta G$ (U)		8.14		8.05		8.03		8.03	8.02	8.02
	$-\Delta G$ (L)		8.01		7.86		7.75		7.70	7.66	7.64
Series 2	$\nu_r$ (U)		1.9		1.7		1.6		1.5	1.5	
	$\nu_r$ (L)		1.9		1.7		1.5		1.5	1.4	
	$-\Delta G$ (U)		8.24		8.02		8.02		8.06	8.09	
	$-\Delta G$ (L)		8.07		7.81		7.73		7.71	7.72	
Series 3	$\nu_r$ (L)	1.3	1.3	1.3	1.4	1.5	1.4	1.4			
	$-\Delta G$ (L)	5.05	4.39	4.10	3.86	3.66	3.54	3.44			

(U) and (L) signify the upper and lower bounds respectively.  $-\Delta G$  is in kcal per mole.

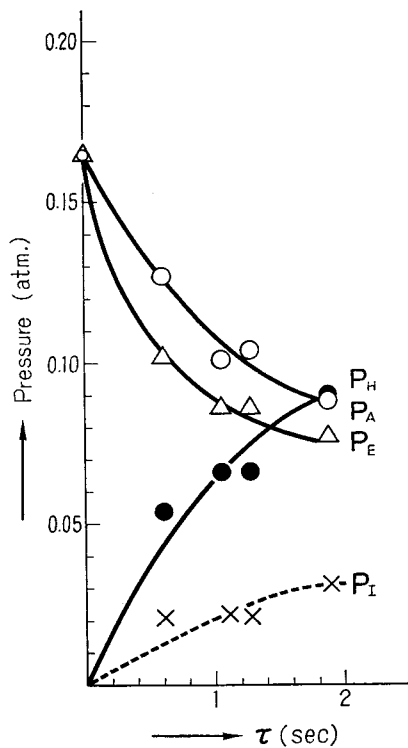


Fig. 4. Pressure profile of series 3 obtained on the basis of an assumed H-C atomic ratio of 2 for  $C_1$ - $C_3$  hydrocarbons.

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TABLE 5. The  $\nu_r$  values for butane dehydrogenation derived on the basis of an assumed H-C atomic ratio of 2 for C<sub>1</sub>-C<sub>2</sub> hydrocarbons

$\tau$ (sec)		0.25	0.50	0.75	1.00	1.25	1.50	1.75
Series 3	$\nu_r$	1.6	1.6	1.6	1.6	1.7	1.6	1.6
	$-\Delta G$	6.50	5.51	4.94	4.57	4.30	4.10	3.95

$-\Delta G$  is in kcal per mole. An H-C atomic ratio for coke was taken as 0.3 as in the calculation of Table 4.

for each of series 1 through 3 using Eq. (11.II) in a similar manner to the above case in butane dehydrogenation. The actual calculations, however, were made only for series 2, because  $Y_I$  was much scattered in series 1 and  $Y_E$  and  $Y_I$  were too close to each other in series 3. Most of the values calculated fell from three to four (Table 6).

TABLE 6. Upper and lower bounds of  $\nu_r$  for butene dehydrogenation

$\tau$ (sec)		0.5	1.0	1.5	2.0	2.5
Series 2	$\nu_r$ (U)	3.3	3.7	4.3	3.8	3.6
	$\nu_r$ (L)	3.2	3.5	3.9	3.3	3.1
	$-\Delta G$ (U)	5.12	3.94	3.45	3.13	2.88
	$-\Delta G$ (L)	4.96	3.73	3.16	2.78	2.51

(U) and (L) signify the upper and lower bounds respectively.  $-\Delta G$  is in kcal per mole.

#### 4. Discussion

The obtained  $\nu_r$  value of two for butane dehydrogenation might be accounted for by assuming that an intermediate with two carbon atoms is involved in the rate controlling step. This can be exemplified by the following mechanism,



where (a) signifies the adsorbed state. If step (II) is rate-determining in the

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above sequence,  $\nu_r$  is two in agreement with the data observed. This sequence, however, seems very unlikely in view of the results of the C<sup>14</sup>-ethylene experiments referred to in Introduction. In order to explain on a similar basis the observed  $\nu_r$  values of three and four for butene dehydrogenation, we would be forced to speculate regarding more dubious mechanisms. Therefore, the unexpectedly large  $\nu_r$  values are discussed below in other terms.

It is to be recalled that Eqs. (11), the expressions for evaluating  $\nu_r$ , have been derived by assuming a single rate-controlling step and no side reaction resulting in C<sup>14</sup>-exchange between butane and butene. Were either one of these assumptions not the case, the apparent  $\nu_r$  value derived from Eq. (11) might be greater than one even if the stoichiometric numbers of the steps involved in the reaction are all one. Apparent  $\nu_r$  values in the presence of two or more rate-controlling steps have been discussed in general by MATSUDA and HORIUTI<sup>18</sup>. Their argument will be applied to butane dehydrogenation in what follows. When the overall rate of butane dehydrogenation is controlled by any two steps 1 and 2, the chemical affinity for the overall reaction is divided between them. Therefore

$$-\Delta G = -\nu_1 \Delta g_1 - \nu_2 \Delta g_2, \quad (17)$$

where  $\nu$  is the stoichiometric number,  $-\Delta g$  is the chemical affinity associated with the elementary step, and the suffix signifies the step 1 or 2. If these two steps are taken tentatively as



then radioactive C<sup>14</sup> atoms are exchanged between butane and butene by-passing step 2. Under these circumstances the right side of Eq. (5) must be replaced by  $Y_A v_{+1} - Y_E v_{-1}$ , where  $v_{+1}$  and  $v_{-1}$  are the forward and backward rates of step 1 respectively. Thus we have

$$Y_A \frac{dF_A}{dW} + F_A \frac{dY_A}{dW} = Y_E v_{-1} - Y_A v_{+1}. \quad (19)$$

The steady state equation for butane dehydrogenation may be written as

$$V_\alpha = v_{+1} - v_{-1} = -\frac{dF_A}{dW} \quad (20)$$

along with Eq. (4). Eqs. (19) and (20) lead to the expression in the square brackets of Eq. (7), thus indicating that the right side of Eq. (7) represents the ratio of  $-\Delta G$  to  $RT \ln(v_{+1}/v_{-1})$  rather than the real  $\nu_r$  defined by Eq. (1). The ratio is referred to subsequently as  $\nu_{app}$ . In view of Eq. (17) we

have

$$\nu_{\text{app}} = \frac{-\nu_1 \Delta g_1 - \nu_2 \Delta g_2}{RT \ln (v_{+1}/v_{-1})}. \quad (21. A)$$

As is demonstrated in Appendix,  $RT \ln (v_{+1}/v_{-1})$  is equivalent to  $-\Delta g_1$ . Therefore Eq. (21. A) reduces to

$$\nu_{\text{app}} = \frac{\nu_1 \Delta g_1 + \nu_2 \Delta g_2}{\Delta g_1}. \quad (21. B)$$

From Eq. (18), it is seen that  $\nu_1 = \nu_2 = 1$ . Therefore, if  $\Delta g_1 \simeq \Delta g_2$ , then  $\nu_{\text{app}} \simeq 2$  as was actually obtained for butane dehydrogenation. The above argument is also applicable to butene dehydrogenation, for which the actually observed  $\nu_r$  value, *i.e.*  $\nu_{\text{app}}$  of 3 or 4, can be well accounted for by setting the ratio  $\Delta g_2/\Delta g_1$  equal to 2 or 3.

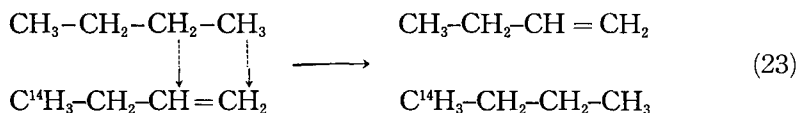
In the presence of a side reaction which just results in the exchange of  $\text{C}^{14}$  atoms between butane and butenes, the right side of Eq. (5) becomes  $Y_A(V_{+\alpha} + V_{\text{ex}}) - Y_B(V_{-\alpha} + V_{\text{ex}})$ , where  $V_{\text{ex}}$  is the rate of the side reaction. The expression in square brackets of Eq. (7) is then regarded as the ratio  $(V_{+\alpha} + V_{\text{ex}})/(V_{-\alpha} + V_{\text{ex}})$ . Therefore we have

$$\nu_{\text{app}} = \frac{-\Delta G}{RT \ln [(V_{+\alpha} + V_{\text{ex}})/(V_{-\alpha} + V_{\text{ex}})]}. \quad (22. A)$$

For butene dehydrogenation a similar consideration leads to

$$\nu_{\text{app}} = \frac{-\Delta G}{RT \ln [(V_{+\varepsilon} + V_{\text{ex}})/(V_{-\varepsilon} + V_{\text{ex}})]}. \quad (22. E)$$

These equations account for the observed stoichiometric number of two or more because  $\nu_{\text{app}}$  can take any value from the real  $\nu_r$  to infinity as  $V_{\text{ex}}$  increases from zero to infinity. In this connection, it is interesting to note that BALANDIN and his coworkers<sup>11)</sup> suggested a new reaction of simultaneous catalytic hydrogenation and dehydrogenation between two adjacently adsorbed molecules such as



In this scheme, two hydrogen atoms transfer from butane to butene as is shown by the broken arrows.  $\text{C}^{14}$  atoms are thus exchanged apparently, although not really, between butane and butane. A similar scheme is conceivable for the butene-butadiene system.

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The  $\nu_r$  values of 2 and over derived above from the Russian data do not coincide with the  $\nu_r$  values close to one observed by us<sup>10</sup>. Attention is now to be called to the difference in reaction temperature between these two works; 390 to 560°C in our work and higher temperatures of 600 and 635°C by the Russian workers. The side reaction as exemplified in Eq. (23), if any, might be more predominant at higher temperatures, thus giving rise to a  $\nu_{app}$  value of two or even higher. Another significant difference between these two studies is in the proportion of hydrogen present. We always used feeds containing substantial proportions of butane, butenes and hydrogen while the Russian investigators started with feeds containing no hydrogen. Since the rate of dehydrogenation does not seem to be markedly affected by the presence of hydrogen, it would seem that the rate of desorption of hydrogen must be rapid even at very low hydrogen concentrations. Under these conditions the concentration gradients of hydrogen would necessarily be small, so that even with high adsorption rate constants a point would be reached where equilibrium could not be maintained between adsorbed and gaseous hydrogen. If so,  $\Delta g_2$  (for step 2 of Eq. (18)) would not be zero, thus resulting in  $\nu_{app}$  of greater than unity. Further studies will be necessary to completely assess the importance of hydrogen chemisorption and desorption rates on the kinetics of butane and butene dehydrogenation at low hydrogen concentrations. Tentatively, from the Russian data, one might conclude that the effect is relatively more important in the dehydrogenation of butene than of butane.

### Appendix

According to HORIUTI's general theory of reaction rate<sup>13</sup>, the forward and backward rates  $v_{+1}$  and  $v_{-1}$  of step 1 (Eq. (18)) can be expressed as

$$v_{+1} = \frac{kT \exp(-\mu_{\ddot{x},1}/RT)}{h \exp(-\mu_{I,1}/RT)}$$

and

$$v_{-1} = \frac{kT \exp(-\mu_{\ddot{x},1}/RT)}{h \exp(-\mu_{F,1}/RT)},$$

where  $k$  is the Boltzman constant,  $h$  is the Planck constant,  $\mu$  is the chemical potential,  $R$  is the gas constant, and the suffixes  $\ddot{x},1$ ;  $I,1$ , and  $F,1$  denote the activated complex, reactants and products respectively of step 1. Combining these two equations, we have

$$RT \ln \frac{v_{-1}}{v_{+1}} = \mu_{I,1} - \mu_{F,1}.$$

Since the right side of this equation is the difference in chemical potential between the reactants and products of step 1, it can be equated to  $\Delta g_1$ . Eq. (21. A) is thus converted into Eq. (21. B).

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