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Evidence for Direct *Cis–Trans* Isomerization of Dideuteroethylene on Nickel Catalyst

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The "anomalous" increase of *cis*-ethylene-d_2 in the equilibration of *trans*-ethylene-d_2 reported by Flanagan and Rabinovitch (1956) is explained quantitatively on the basis of direct isomerization between both species. Rates of both exchange via the half-hydrogenated state and isomerization are calculated according to an analytical method given by the present authors. It could be shown that the introduction of the kinetic isotope effect proposed by them is not necessary and further that there is evidence for direct-isomerizing mechanism via a distortedly adsorbed ethylene.

The formulation obtained here is applicable also to ethylene hydrogenation and would give information on kinetic details of each elementary step in the reaction.

INTRODUCTION

Attempts to calculate elementary-reaction rates from deuterium distribution in reaction products were made by Keii (*1*) and by Kemball and Wells (*2*) in ethylene hydrogenation, and also by Yasuda and Hirota (*3*) in olefin hydrogenation. The methods by Keii and by Kemball and Wells, however, are applicable to the deuterium distribution only at the initial stage, while ours is applicable at every conversion.

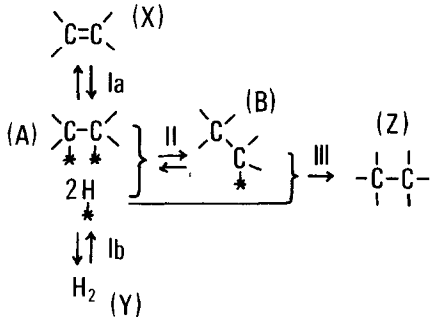
Detailed investigations of the nickel-catalyzed exchange and isomerization of deuteroethylene were undertaken by Flanagan and Rabinovitch (*4, 5*) assuming the existence of an intimate relation between the exchange associated with the isomerization and hydrogenation reactions of olefins. The time course of the equilibration of *trans*-ethylene-d_2 was studied and the anomalous increase of *cis*-ethylene-d_2 as compared with its expectation, was explained on the basis of an isotope effect in the rupture of the carbon–"hydrogen" bond. The fact that ethylene-d_1 and -d_3 (and also -d_0 and -d_4) are produced in the same amount from *trans*-ethylene-d_2, however, appears to afford evidence against the isotope effect. It seems, therefore, that some inconsistency is contained in the assumptions adopted to derive their equations that fit the experimental results. The results have been criticized by Miyahara (*6*) already.

In this paper their experimental results are analyzed as an extension of the method proposed by us (*3*). Thereby, the isotope effect which was ignored for simplicity in the original treatment is considered but it turns out that a direct-isomerizing process between *cis*- and *trans*-ethylene-d_2 on the nickel surface may be more important.

The exchange and isomerization can be regarded as a special case of ethylene hydrogenation, and general equations to give information on elementary-reaction rates in ethylene hydrogenation will be derived in the present formulation.

NOTATION

Both hydrogenation, exchange, and also isomerization, in part, of ethylene may proceed via the half-hydrogenated state proposed by Horiuti and Polanyi (7):



Capital letters X, Y, and Z represent total numbers of ethylene, hydrogen, and ethane molecules in the gas phase, respectively, irrespective of isotopic content; A and B, total numbers of chemisorbed ethylene and half-hydrogenated ethyl radicals, respectively.

The elementary steps are named Ia, Ib, II, and III; numbers of molecules transforming forward and backward through step K in a unit time are denoted by V_{K} and $V_{-\mathrm{K}}$, respectively.

A single subscript, i, is added to a quantity concerned with the isotopic species containing i deuterium atoms. Isotopic subspecies belonging to the same kind of isotopic species are distinguished from each other by a supplementary subscript, j. Their mole fractions are represented further by corresponding small letters; in the case of ethylene in the gas phase, for instance, the following relations exist among the representations defined above:

$$X = \sum_{i=0}^{4} X_i,\ X_i = \sum_{j} X_{i(j)};$$

$$x_i = X_i/X,\ x_{i(j)} = X_{i(j)}/X. \quad (1)$$

A set of x_i, $\{x_i\}$, is called the fine deuterium distribution and $\{x_{i(j)}\}$, the hyperfine deuterium distribution.

DERIVATION OF EQUATIONS

1. *Relations Between Fine Deuterium Distributions*

As a typical example, let us consider the change in species B_i with time. It follows that

$$\dot{B}_i = V_{\mathrm{II}}(pa_i + da_{i-1}) - (V_{-\mathrm{II}} + V_{\mathrm{III}})b_i, \quad (2)$$

where p or d is the probability of a "hydrogen" atom being an H or D atom, respectively, when the atom and an A species are combined in a B species. Hence, obviously,

$$p + d = 1. \quad (3)$$

On the other hand, the definitions $B_i = b_i B$ and $V_{\pm\mathrm{K}}$ lead to

$$\dot{B}_i = \dot{b}_i B + (V_{\mathrm{II}} - V_{-\mathrm{II}} - V_{\mathrm{III}})\, b_i. \quad (4)$$

Comparison of Eq. (2) with Eq. (4) gives

$$\dot{b}_i = (V_{\mathrm{II}}/B)\{(pa_i + da_{i-1}) - b_i\}. \quad (5)$$

If the amount of adsorbed ethylene on catalyst is negligible compared with that of ethylene in the whole system, the inequality $|\dot{b}_i| \ll V_{\mathrm{II}}/B$ is valid (3). Since this condition is usually satisfied, Eq. (5) becomes

$$b_i = pa_i + da_{i-1}. \quad (6)$$

After similar consideration on $\dot{X}_i$ and $\dot{Z}_i$, we find

$$a_i = x_i + \dot{x}_i/v_{-\mathrm{Ia}},\ v_{-\mathrm{Ia}} \equiv V_{-\mathrm{Ia}}/X, \quad (7)$$

and

$$w_i = pb_i + db_{i-1}, \qquad w_i \equiv z_i + (Z/\dot{Z})\dot{z}_i, \quad (8)$$

respectively. The probabilities p and d at step III are assumed here to be identical with those at step II. Simple elimination of the fine deuterium distributions, $\{a_i\}$ and $\{b_i\}$ which could scarcely be observed, gives

$$w_1 = p^2x_i + 2pdx_{i-1} + d^2x_{i-2} + (p^2\dot{x}_i + 2\,pd\dot{x}_{i-1} + d^2\dot{x}_{i-2})/v_{-\mathrm{Ia}}. \quad (9)$$

Another elimination of them from Eqs. (6), (7), and (8) gives (Appendix)

$$d = d_\infty - \frac{1}{2}\left(\sum_{i=1}^{4} i\dot{x}_i\right) \Big/ v_{-\mathrm{Ia}},$$

$$d_\infty \equiv \frac{1}{2}\left(\sum_{i=1}^{6} iw_i - \sum_{i=1}^{4} ix_i\right). \quad (10)$$

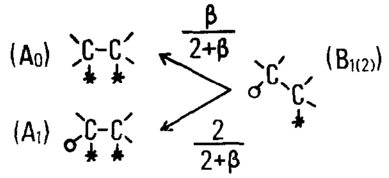
Substituting Eq. (10) to Eq. (9) where i is chosen to be zero, we have

$$\left\{\frac{1}{v_{-\mathrm{Ia}}} + \frac{2(1-d_\infty)}{\Sigma i\dot{x}_i}\right\}^2 \left(\frac{1}{v_{-\mathrm{Ia}}} + \frac{x_0}{\dot{x}_0}\right) + \frac{4\,w_0}{(-\dot{x}_0)(\Sigma i\dot{x}_i)^2} = 0. \quad (11)$$

This equation would be useful in analyzing fine deuterium distributions in an ethylene hydrogenation reaction.

2. *Relations Between Hyperfine Deuterium Distributions*

Let β be the ratio of the C–D to C–H bond rupture probability in the transformation of a B species into an A on removal of an H or D atom. Then species A_0 and A_1, for instance, arise from species $B_{1(2)}$ at rates proportional to $\beta/(2+\beta)$ and $2/(2+\beta)$, respectively:



Here the small circles denote deuterium atoms.

In consideration of $\dot{A}_{i(j)}$ in much the same fashion as $\dot{B}_i$, we obtain the following equations;

$$\frac{1}{2+\beta}\left(\frac{\beta}{2}pa_1 - 2\,da_0\right)V_{-\mathrm{II}} = \dot{x}_0 X V_{\mathrm{Ia}}/V_{-\mathrm{Ia}}, \quad (12)$$

$$\left[\frac{2}{2+\beta}da_0 + \frac{\beta}{1+2\beta}pa_{2(1)} + \frac{\beta}{2+\beta}pa_{2(2)} + \left\{\frac{4+\beta}{2(2+\beta)}p + \frac{5+4\beta}{2(1+2\beta)(2+\beta)} \times d - 1\right\}a_1\right]V_{-\mathrm{II}} = \dot{x}_1 X V_{\mathrm{Ia}}/V_{-\mathrm{Ia}}, \quad (13)$$

$$\frac{1}{2}\left\{\frac{d}{1+2\beta}a_1 + \left(\frac{p}{1+2\beta} + \frac{\beta}{2+\beta}d - 1\right)a_{2(1)} + \frac{\beta}{2+\beta}pa_3\right\}V_{-\mathrm{II}} = \dot{x}_{2(1)} X V_{\mathrm{Ia}}/V_{-\mathrm{Ia}}, \quad (14)$$

$$\left\{\frac{d}{2+\beta}a_1 + \left(\frac{2}{2+\beta}p + \frac{2\beta}{1+2\beta}d - 1\right)a_{2(2)} + \frac{\beta}{1+2\beta}pa_3\right\}V_{-\mathrm{II}} = \dot{x}_{2(2)} X V_{\mathrm{Ia}}/V_{-\mathrm{Ia}}, \quad (15)$$

$$\left[\frac{d}{2+\beta}a_{2(1)} + \frac{d}{1+2\beta}a_{2(2)} + \left\{\frac{4+5\beta}{2(1+2\beta)(2+\beta)}p + \frac{1+4\beta}{2(1+2\beta)}d - 1\right\}a_3 + \frac{2\beta}{1+2\beta}pa_4\right]V_{-\mathrm{II}} = \dot{x}_3 X V_{\mathrm{Ia}}/V_{-\mathrm{Ia}}, \quad (16)$$

$$\frac{1}{1+2\beta}\left(\frac{d}{2}a_3 - 2\beta pa_4\right)V_{-\mathrm{II}} = \dot{x}_4 X V_{\mathrm{Ia}}/V_{-\mathrm{Ia}}, \quad (17)$$

where $x_{2(1)}$ and $x_{2(2)}$, as well as $a_{2(1)}$ and $a_{2(2)}$, correspond to CH_2CD_2 and CHDCHD, respectively.

When discrimination between *cis*- and *trans*-CHDCHD is required, Eq. (15) is divided into

$$\left\{\frac{1}{2}\frac{d}{2+\beta}a_1 + \left(\frac{p}{2+\beta} + \frac{\beta}{1+2\beta}d - 1\right){}^{c}a_{2(2)} + \left(\frac{1}{2+\beta}p + \frac{\beta}{1+2\beta}d\right){}^{t}a_{2(2)} + \frac{1}{2}\frac{\beta}{1+2\beta}pa_3\right\}V_{-\mathrm{II}} = {}^{c}\dot{x}_{2(2)} X V_{\mathrm{Ia}}/V_{-\mathrm{Ia}}, \quad (15c)$$

and

$$\left\{\frac{1}{2}\frac{d}{2+\beta}a_1 + \left(\frac{p}{2+\beta} + \frac{\beta}{1+2\beta}d\right){}^{c}a_{2(2)} + \left(\frac{p}{2+\beta} + \frac{\beta}{1+2\beta}d - 1\right){}^{t}a_{2(2)} + \frac{1}{2}\frac{\beta}{1+2\beta}pa_3\right\}V_{-\mathrm{II}} = {}^{t}\dot{x}_{2(2)} X V_{\mathrm{Ia}}/V_{-\mathrm{Ia}}. \quad (15t)$$

APPLICATION

Flanagan and Rabinovitch (*5*) studied the time course of the equilibration of 99% *trans*-ethylene-d_2 on nickel wire at 75°C.

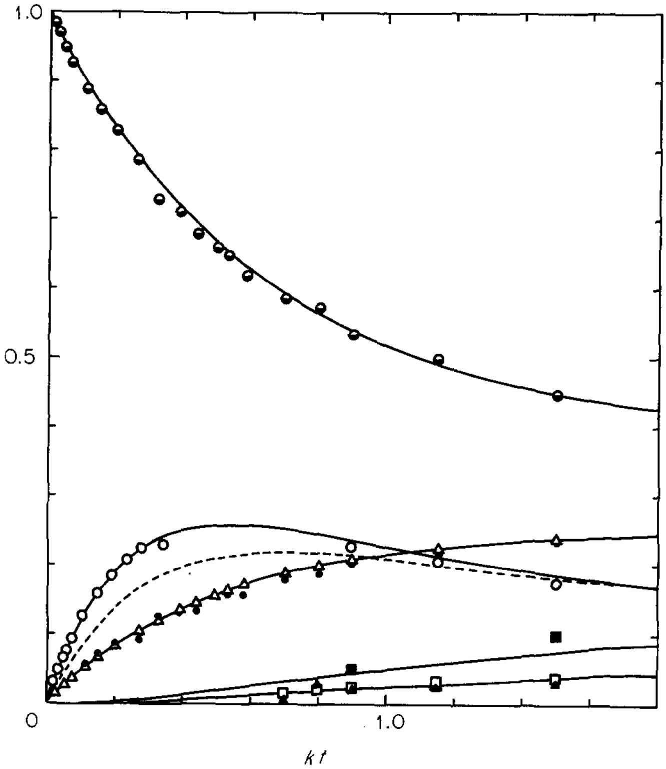


FIG. 1. Equilibration of *trans*-ethylene-d_2 at 75°C (5). The solid lines correspond to the values of equations in Eqs. (18) and (19): ◒ represents mole fraction of total $C_2H_2D_2$, x_2; ○, that of *cis*-CHD-CHD, ${}^cx_{2(2)}$; △, that of C_2HD_3, x_3: ●, that of C_2H_3D, x_1; ■, that of *asym*-CD_2CH_2, $x_{2(1)}$: ▲, that of C_2H_4, x_0; □, that of C_2D_4, x_4.

The results are plotted in Fig. 1; they are expressed well by the solid lines of the following equations except for *cis*-CHDCHD;

$$\left.\begin{aligned} x_2 &= \frac{1}{8}(3 + 2e^{-kt} + 3e^{-2kt}), \\ x_{2(1)} &= \frac{1}{8}(1 - e^{-kt})^2, \\ x_1 = x_3 &= \frac{1}{4}(1 - e^{-2kt}), \\ x_0 = x_4 &= \frac{1}{16}(1 - e^{-kt})^2. \end{aligned}\right\} \quad (18)$$

These expressions were also derived by analytical treatment on the basis of their reaction model.

The amount of *cis*-CHDCHD was derived also as

$${}^cx_{2(2)} = \frac{1}{8}\{1 + 2e^{-kt} + e^{-2kt} - 4e^{-(\alpha+1/\alpha+1)kt}\}, \quad (19)$$

where α is a new parameter, whose meaning will be discussed below. By choosing 0.27 for α the experimental values coincide well with the calculated ones. However, the same agreement can be obtained by our following treatment, on the basis of a more reasonable model.

According to the results shown by Eq. (18), there are experimental relations of $x_1 = x_3$ and $x_0 = x_4$ at every conversion. Thus we have Eq. (20) from Eq. (7)

$$a_1 = a_3, \qquad a_0 = a_4. \quad (20)$$

Comparison of Eq. (12) with Eq. (17), therefore, leads to

$$\frac{1}{2+\beta}\left(\frac{\beta}{2}pa_1 - 2da_0\right) = \frac{1}{1+2\beta}\left(\frac{d}{2}a_1 - 2\beta pa_0\right), \quad (21)$$

which is rewritten as

$$\{\beta(1+2\beta) - 2(1+\beta+\beta^2)d\}a_1 + 4\{\beta(2+\beta) - (1+4\beta+\beta^2)d\}a_0 = 0. \quad (22)$$

Since Eq. (22) holds at every conversion, it is required that

$$\begin{aligned} \beta(1+2\beta) - 2(1+\beta+\beta^2)d &= 0, \\ \beta(2+\beta) - (1+4\beta+\beta^2)d &= 0. \end{aligned} \quad (23)$$

Consequently, the following results are obtained:

$$\beta = 1, \quad (24)$$

and

$$d = 0.5. \quad (25)$$

In the present case of exchange and isomerization, the ethylene pressure must be constant. It then follows that

$$V_{\mathrm{Ia}}/V_{-\mathrm{Ia}} = 1. \quad (26)$$

Equation (12) combined with Eq. (7) is rewritten, therefore, after substitution of the conclusions in Eqs. (24), (25), and (26) after consideration of the experimental results in Eq. (18), by

$$(1 - e^{-kt})(V_{-\mathrm{II}} - 3kX) - k(1 - 2e^{-kt})V_{-\mathrm{II}}/v_{-\mathrm{Ia}} = 0. \quad (27)$$

In order that Eq. (27) may hold at every time, it is required that

$$V_{-\mathrm{II}} = 3kX, \quad (28)$$

and

$$V_{-\mathrm{Ia}} = \infty. \quad (29)$$

Substituting the various conclusions of Eqs. (24), (25), (26), (28), and (29) into Eqs. (15c) and (15t), we have

$$\frac{1}{k}\frac{d}{dt}{}^{c}x_{2(2)} = \frac{1}{8}(1 - e^{-2kt}) - 2{}^{c}x_{2(2)} + {}^{t}x_{2(2)}, \quad (30c)$$

$$\frac{1}{k}\frac{d}{dt}{}^{t}x_{2(2)} = \frac{1}{8}(1 - e^{-2kt}) - 2{}^{t}x_{2(2)} + {}^{c}x_{2(2)}, \quad (30t)$$

where x_1 is replaced by the experimental result given in Eq. (18). The solution for ${}^{c}x_{2(2)}$, under the initial conditions of ${}^{t}x_{2(2)} = 1$ and ${}^{c}x_{2(2)} = 0$, is given by

$${}^{c}x_{2(2)} = \frac{1}{8}(1 + 2e^{-kt} + e^{-2kt} - 4e^{-3kt}), \quad (31)$$

which is shown in Fig. 1 by the dashed line. This does not agree with the experimental values.* Modification of the equations is attempted, therefore, by adding a term which corresponds to direct transformation between *cis*- and *trans*-ethylene; i.e.,

$$\frac{1}{k}\frac{d}{dt}{}^{c}x_{2(2)} = \left\{\frac{1}{8}(1 - e^{-2kt}) - 2{}^{c}x_{2(2)} + {}^{t}x_{2(2)}\right\} + \zeta({}^{t}x_{2(2)} - {}^{c}x_{2(2)}), \quad (32c)$$

$$\frac{1}{k}\frac{d}{dt}{}^{t}x_{2(2)} = \left\{\frac{1}{8}(1 - e^{-2kt}) - 2{}^{t}x_{2(2)} + {}^{c}x_{2(2)}\right\} - \zeta({}^{t}x_{2(2)} - {}^{c}x_{2(2)}), \quad (32t)$$

whose solutions are described generally as

$${}^{c}x_{2(2)} = \frac{1}{8}(1 + e^{-2kt}) + C_1e^{-kt} + C_2e^{-(3+2\zeta)kt}, \quad (33c)$$

$${}^{t}x_{2(2)} = \frac{1}{8}(1 + e^{-2kt}) + C_1e^{-kt} - C_2e^{-(3+2\zeta)kt}, \quad (33t)$$

where C_1 and C_2 are constants.

Taking account of the initial conditions again, we have

$${}^{c}x_{2(2)} = \frac{1}{8}\{1 + 2e^{-kt} + e^{-2kt} - 4e^{-(3+2\zeta)kt}\}. \quad (34)$$

By choosing 0.54 for ζ in Eq. (34) the solid line of *cis*-CHDCHD in Fig. 1 can be derived.

Discussion

The second term on the right in Eq. (32c) equals

$$\zeta({}^{t}a_{2(2)} - {}^{c}a_{2(2)})$$

because $v_{-\mathrm{Ia}} = \infty$ in this case, which suggests a direct-isomerizing mechanism via species A besides that via the half-hydrogenated state.

The temperature dependence of the *cis*-CHDCHD product in the nickel-catalyzed isomerization of *trans*-CHDCHD was investigated in detail by Flanagan and

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* When α is chosen to be unity in Eq. (19), the equation coincides with Eq. (31). The unity means that the C–D rupture probability equals that of C–H. This fact is a reason why a kinetic isotope effect is considered by Flanagan and Rabinovitch in their analytical treatment.

Rabinovitch (*4*) over a temperature range as large as -78–$429°\mathrm{C}$, which is expressed by Eq. (19) with an appropriate value of α. Comparison of Eq. (34) with Eq. (19) shows that ζ is connected with α by the relation

$$3 + 2\zeta = \alpha + (1/\alpha) + 1. \qquad (35)$$

The experimental results of α are shown in Fig. 2 together with the corresponding values of ζ calculated from Eq. (35). The contribution of the direct-isomerizing mechanism increases as the temperature decreases. This fact may be understood by taking account of the decrease in the amount of species $\underset{*}{\overset{}{\mathrm{H}}}$ yielded by dissociatively adsorbed ethylene with decreasing temperature. Thus, a possible mechanism for the direct isomerization via a dissociatively adsorbed ethylene such as $\underset{*}{\mathrm{C}}\mathrm{H{-}CH_2}$ may be rejected.

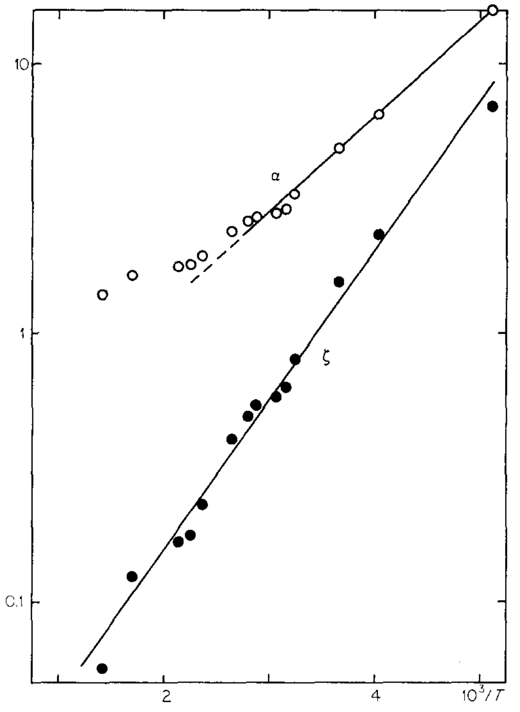

FIG. 2. Temperature dependence of α and ζ.

Hansen *et al.* (*8*) proposed *trans*-diadsorbed ethylene on tungsten by flash-filament spectroscopy and field emission methods. By analogy, the isomerization might occur via a distortedly adsorbed ethylene.

On the other hand, the present procedure concludes that $\beta = 1$ and $d = 0.5$; there is no isotope effect. The surprising result reminds us of a dimerization mechanism of ethylene on nickel proposed by Whalley, Davis, and Moss (*9*) by the field emission method or a concerted reaction mechanism in ethylene hydrogenation on metals proposed by Gardner and Hansen (*8c*). If the exchange occurs between a pair of adsorbed species only, the isotope effect would be quenched because the C–D rupture always associates with the C–H rupture. The latter mechanism is unlikely in this case, however, because the exchange is stepwise as will be shown below.

The absolute values of the exchange and isomerization could be evaluated if the absolute values of k be given. Flanagan and Rabinovitch did not show them because the catalyst activity decreased progressively with continued exposure to ethylene. According to the present treatment, however, the raw data of k would be able to give certain information upon the catalyst poisoning in such reaction.

The result that $v_{-\mathrm{Ia}} = \infty$, leads also to

$$V_{\mathrm{Ia}} = V_{-\mathrm{Ia}} = \infty, \qquad (36)$$

and then

$$a_1 = x_1. \qquad (37)$$

It appears, therefore, that the discrimination between species X and A is apparently unnecessary, corresponding to the Twigg–Rideal mechanism in ethylene hydrogenation. However, species A plays a more important role in the isomerization as shown above. The result of Eq. (36) shows further that the exchange is stepwise as estimated by Flanagan and Rabinovitch.

They derived a differential equation similar in form to Eq. (32) where isotope effect defined by

$$\alpha = \frac{\text{prob. of C–H rupture}}{\text{prob. of C–D rupture}}$$

was introduced. Referring to the deviation from unity of the values of α (Fig. 2), Kemball and Wells (2b) proposed their revised theory. However, no alteration would be necessary in the formulation by Flanagan and Rabinovitch even if α were defined by

$$\alpha = \frac{\text{prob. of C–D rupture}}{\text{prob. of C–H rupture}}$$

because α is always associated with $1/\alpha$. The uncertainty of the value is clear. This is another ambiguous point in their assumptions besides the ones mentioned in the introduction.

ACKNOWLEDGMENT

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APPENDIX

Let us take a summation of Eq. (9) such as

$$\sum_{i=1}^{6} iw_i = d^2 \sum i(x_i - 2x_{i-1} + x_{i-2}) - 2d \sum i(x_i - x_{i-1}) + \sum ix_i + v_{-\mathrm{Ia}}^{-1} \left\{ d^2 \sum i(\dot{x}_i - 2\dot{x}_{i-1} + \dot{x}_{i-2}) - 2d \sum i(\dot{x}_i - \dot{x}_{i-1}) + \sum i\dot{x}_i \right\}, \qquad \text{(A1)}$$

which is simplified to

$$\Sigma iw_i = 2d + \Sigma ix_i + (\Sigma i\dot{x}_i)/v_{-\mathrm{Ia}}, \qquad \text{(A2)}$$

by making use of the identities

$$\begin{aligned} \Sigma i(x_i - x_{i-1}) &= \Sigma ix_i - \Sigma(j+1)\,x_j \\ &= -\Sigma x_j \\ &= -1, \end{aligned} \qquad \text{(A3)}$$

and

$$\begin{aligned} &\Sigma i(x_i - 2x_{i-1} + x_{i-2}) \\ &= \Sigma ix_i - 2\Sigma(j+1)x_j + \Sigma(k+2)x_k = 0. \end{aligned} \qquad \text{(A4)}$$

Thus, Eq. (A2) leads to a sum rule of Eq. (10) which is applicable to olefin hydrogenation.

REFERENCES

1. KEII, T., *J. Res. Inst. Catal., Hokkaido Univ.* **3,** 36 (1953).
2. (a) KEMBALL, C., *J. Chem. Soc.* 735 (1956); (b) KEMBALL, C., AND WELLS, P. B., 444 (1968).
3. YASUDA, Y., AND HIROTA, K., *Z. Phys. Chem. Neue Folge* **71,** 181 (1970).
4. FLANAGAN, T. B., AND RABINOVITCH, B. S., *J. Phys. Chem.* **60,** 724 (1956).
5. FLANAGAN, T. B., AND RABINOVITCH, B. S., *J. Phys. Chem.* **60,** 730 (1956).
6. MIYAHARA, K., *J. Res. Inst. Catal., Hokkaido Univ.* **5,** 87 (1957).
7. HORIUTI, J., AND POLANYI, M., *Trans. Faraday Soc.* **30,** 1164 (1934).
8. (a) RYE, R. R., AND HANSEN, R. S., *J. Chem. Phys.* **50,** 3585 (1969); (b) HANSEN, R. S., AND GARDNER, N. C., *J. Phys. Chem.* **74,** 3646 (1970); (c) GARDNER, N. C., AND HANSEN, R. S., **74,** 3298 (1970).
9. WHALLEY, L., DAVIS, B. J., AND MOSS, R. L., *Trans. Faraday Soc.* **66,** 3143 (1970).