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EXCHANGE REACTION BETWEEN ETHANE AND DEUTERIUM ON EVAPORATED METAL FILMS

Reply to Comments of KEMBALL

By

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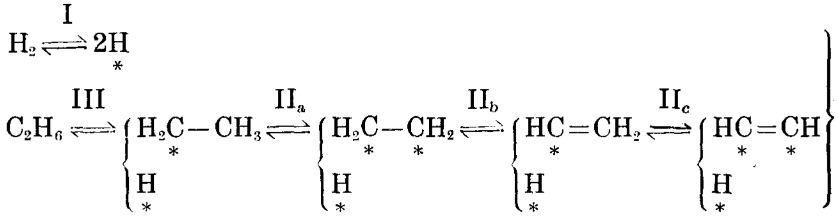
The present author[1] has previously analysed the catalysed exchange reaction between ethane and deuterium in the presence of various evaporated metal films, as observed by ANDERSON and KEMBALL[2], on the basis of the Scheme,



$$\left.\begin{array}{l} H_2 \overset{I}{\rightleftharpoons} 2\underset{*}{H} \\ C_2H_6 \overset{III}{\rightleftharpoons} \left\{\begin{array}{l} H_2\underset{*}{C}-CH_3 \\ \underset{*}{H} \end{array}\right. \overset{II_a}{\rightleftharpoons} \left\{\begin{array}{l} H_2\underset{*}{C}-\underset{*}{CH_2} \\ \underset{*}{H} \end{array}\right. \overset{II_b}{\rightleftharpoons} \left\{\begin{array}{l} H\underset{*}{C}=CH_2 \\ \underset{*}{H} \end{array}\right. \overset{II_c}{\rightleftharpoons} \left\{\begin{array}{l} H\underset{*}{C}=\underset{*}{CH} \\ \underset{*}{H} \end{array}\right. \end{array}\right\} \quad (1)$$

where H stands for protium P or deuterium D and * signifies a bond of chemisorption. KEMBALL[3] has commented upon the analysis, objecting i) the likelihood of the existence of further dissociation of the chemisorbed ethylene in the Scheme (1), especially of the step II_c assumed quick enough to be in the exchange equilibrium and ii) that of the validity of the concluded slowest step I especially in the case of tungsten catalyst.

The present note replies to his comments with reference to his own theory[2] on the above exchange reaction.

§ 1. Existence of Further Dissociation of Chemisorbed Ethylene.

KEMBALL maintains on one hand that the 'relative strength of adsorption'

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$$C_2H_6 : C_2H_4 : C_2H_2 = 1 : 10^{15} : 10^{30}, \qquad (2)$$

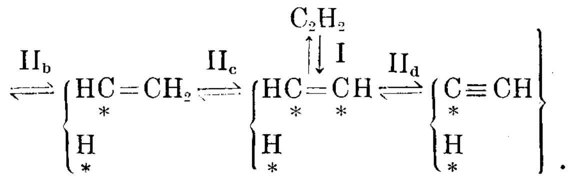
which sufficiently accounts for the heavy coverage of $H\underset{*}{C}=\underset{*}{C}H$ identified with "acetylenic complex" at the experimental condition of Beeck[4] and more recently of Jenkins and Rideal[5], leads to an insufficient amount of $H\underset{*}{C}=\underset{*}{C}H$ for the Scheme (1) to proceed at the condition of the experiment in question, and that the sufficient 'relative strength of adsorption' at the latter condition must be such that

$$C_2H_6 : C_2H_4 : C_2H_2 = 1 : 10^{23} : 10^{39}. \qquad (2')$$

It may be pointed out that the latter 'relative strength' (2′) accounts for the heavy coverage of $H\underset{*}{C}=\underset{*}{C}H$ at the former experimental condition as well, and in consequence that the objection based on (2), equally purely hypothetical as (2′), is not grounded at all.

§ 2. Quick Step II_c.

We might note with regard to the Kemball's objection to the quick step of II_c that this is the necessary conclusion of the recent analysis[6] of the experimental results of the catalysed exchange reaction between acetylene and deuteroacetylene on nickel observed by Bond *et al.*[7] on the basis of the Scheme



$$\left.\overset{\mathrm{II_b}}{\rightleftharpoons}\left\{\begin{matrix}H\underset{*}{C}=CH_2\\ \underset{*}{H}\end{matrix}\right. \overset{\mathrm{II_c}}{\rightleftharpoons}\left\{\begin{matrix}\overset{C_2H_2}{\overset{\uparrow\downarrow\ \mathrm{I}}{H\underset{*}{C}=\underset{*}{C}H}}\\ \underset{*}{H}\end{matrix}\right. \overset{\mathrm{II_d}}{\rightleftharpoons}\left\{\begin{matrix}\underset{*}{C}\equiv CH\\ \underset{*}{H}\end{matrix}\right.\right]. \qquad (3)$$

Kwan[8] has moreover observed that the rates of ethane formation from acetylene or ethylene in the presence of nickel are almost coincident with each other as shown in Fig. 1, from which it is concluded that the acetylene hydrogenation is rapid enough compared with the ethylene hydrogenation in conformity with the assumption of the quick step of II_c. Beeck[4] has reported that the acetylene hydrogenation to ethylene is slower than that of ethylene but the rate of the latter hydrogenation is appreciably reduced by treating the catalyst preliminarily by acetylene[9]. It is hence reasonable to assume the quick step of II_c, since such a state of catalyst may exist according to the above facts depending on the condition. Kemball objects the latter assumption on the ground of extremely slow hydrogenation of the "acetylenic complex" reported by Jenkins and Rideal[5] but the intermediate $H\underset{*}{C}=\underset{*}{C}H$ may be physically different[*] from the latter.

§ 3. The Slowest Step.

Kemball's points against ii) are that tungsten is a well-known catalyst extremely efficient for the hydrogen-deuterium exchange reaction and that the chemisorption of ethane on this metal could not be sufficient to inhibit the step I to such an extent as to reduce it to the rate-determining one.

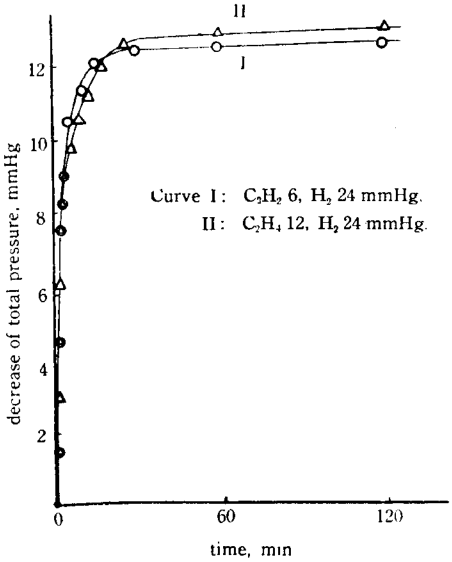


Fig. 1. Courses of hydrogenation of acetylene and ethylene on nickel catalyst at 20°C observed by Kwan[3].

It has been found by reinvestigation of the previous analysis[1] that the set of values of parameters α, β and y^D [**] given in the previous paper and reproduced in the first line in the Table below is not an unique solution of fitting the Scheme (1) to the observation of Anderson and Kemball[2] for molybdenum, tantalum and oriented nickel as well as for tungsten, but those

Table. Values of parameters α, β and y^D fitted to the initial rates of deuteroethane formation observed on Mo, Ta, W and oriented Ni films.

Values of parameters			Relative rates of initial formation of deuteroethanes, %.						Rates of steps relative to that of II_a		
y^D	α	β	C_2P_5D	$C_2P_4D_2$	$C_2P_3D_3$	$C_2P_2D_4$	C_2PD_5	C_2D_6	I	III	II_b
0.05	0.6	0.6	90.6	8.6	0.8	0	0	0	0.23	0.67	0.6
0.50	0.3	0	82.9	14.6	2.3	0.2	0	0	1.50	2.0	0
0.90	0.2	0	81.6	15.7	2.5	0.3	0	0	22.3	4.0	0

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[*] The present author carelessly identified the intermediate $H\underset{*}{C}=\underset{*}{C}H$ with the "acetylenic complex" in this respect in his previous paper (Ref. 1).

[**] These parameters are defined as that $\alpha=V(II_a)/\{V(II_a)+V(III)\}$, $\beta=V(II_b)/V(II_a)$ and y^D is the fraction of the number of $\underset{*}{D}$ over the sum of those of $\underset{*}{P}$ and $\underset{*}{D}$, where $V(II_a)$ *etc.* denote the balanced overall forward or backward rates of steps II_a *etc.* respectively.

in the second and third lines do as well, which imply, as shown in the Table, that I is not the slowest but even the quickest among I, II_a, II_b and III.

It is readily seen from these results that the unique set of values of parameters and hence the relative rates of respective steps in the presence of above metals cannot be determined from the above observation of ANDERSON and KEMBALL; this point may be decided by simulaneous measurements of the relative initial formation rates V^{P_2} and V^{PD} respectively of P_2 and PD, from which the value of y^D and hence the set of parameters is decided according to the equation

$$y^D = V^{PD}/(2V^{P_2}+V^{PD}) \qquad (4)$$

derived in the previous paper[1].

§ 4. Neglect of the Surface Heterogenuity of the Catalysts.

KEMBALL[2][3] maintains the surface heterogenuity against the single reaction route adopted by the present author, principally on the grounds that the film of nickel reveals the catalysis of the molybdenum or chromium type according as oriented or unoriented, besides that metals of molybdenum or of palladium type catalysts are respectively of body-centred or face-centred cubic lattice. However, no argument is put forward by ANDERSON and KEMBALL, which would base the surface heterogenuity necessarily or even plausibly on the latter fact. That oriented nickel film, evidently of face-centred cubic lattice, is molybdenum type in catalysis would speak against any correlation of these facts as the ground of the surface heterogenuity, as metals of molybdenum type are exclusively of body-centred cubic lattice. Moreover he does not give any consistent interpretation for the different values of his parameter on the basis of dual types of reaction proposed by him.

It would hence be quite worthwhile to study other possible mechanisms, e.g. the single reaction route of the present author, which account for the experimental results alternatively by assuming II_b and II_c instead of the dual types of reaction preferred by ANDERSON and KEMBALL.

A few points might be advanced, which would settle the appropriate mechanism. ANDERSON and KEMBALL[2] assume *a priori* that adsorbed hydrogen which attacks adsorbed ethane, ethyl or ethylene consists of deuterium alone. This leads to the conclusions that D_2 or PD is but none of P_2 is formed on one hand and that $P_3C\text{–}CPD_2$ and $P_3C\text{–}CD_3$ are absent in deuteroethanes initially formed. The single route mechanism of the present author predicts on the other hand that P_2 as well as $P_3C\text{-}CPD_2$ and $P_3C\text{-}CD_3$ exist in the initial product and even how much they exist from the values of parameters deduced. Experiments will decide the alternatives.

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