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(Note)

SELECTIVITY IN THE REACTIONS OF ETHYLENE
AND DEUTERIUM ON TUNGSTEN:
EFFECT OF TEMPERATURE*)

By

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Due to low activity¹⁾ the hydrogenation of ethylene on tungsten has not been as extensively studied as the same reaction on metals such as nickel and platinum, but the work that has been reported points out the unusual features of tungsten as a catalyst. Recently MIYAHARA *et al.* reported on the reaction of ethylene with deuterium and hydrogen²⁾. Along with a low hydrogenation activity these authors observe an unusually low optimum temperature (T_m) of 293°K. The values of T_m for Pt and Ni tabulated by BOND range between 333°K and 438°K³⁾. Comparison of the products obtained from the reaction of deuterium and ethylene by Kimball at 173°K⁴⁾ and those obtained by MIYAHARA *et al.* above 228°K²⁾ show surprising differences. KIMBALL observed predominantly d_2 -ethane (~70%) and only trace amounts of deuterated ethylenes. At 173°K hydrogenation is much faster than olefin exchange, and, as pointed out by KIMBALL, the ratio of the hydrogenation rate on tungsten to that on rhodium is over 200 times greater at 173°K than at 273°K. Thus, relative to rhodium, tungsten is a better catalyst at low temperatures. With a 55° increase in temperature, however, MIYAHARA *et al.* observed the opposite results²⁾. Extensive olefin exchange was observed with only slight hydrogenation; the yield of deuterated ethanes was not sufficient for mass spectrometric analysis.

In light of recent flash dehydrogenation⁵⁾ and hydrogenation⁶⁾ studies these observations are more easily understood. The spectrum resulting from flash dehydrogenation of an ethylene monolayer formed at 95°K is shown in Fig. 1⁵⁾. Mass spectrometric analysis shows this spectrum to be entirely hydrogen resulting from a two step dehydrogenation.

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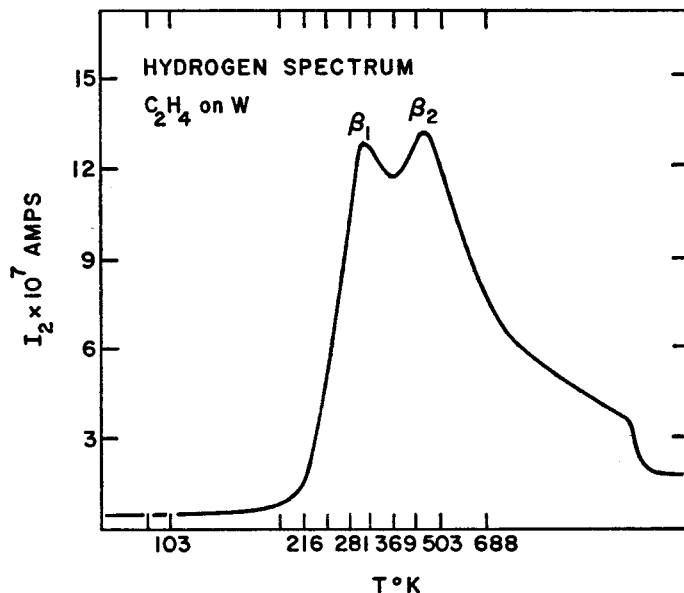


Fig. 1. Hydrogen spectrum resulting from the flash decomposition of an ethylene monolayer formed at 95°K. Ordinate is mass spectrometer ion current (proportional to hydrogen partial pressure).



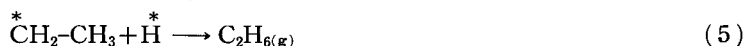
Reaction 1 has an appreciable rate above 200°K and reaction 2 has an appreciable rate ~300°K. For a monolayer of ethylene, as in Fig. 1, Reaction 3 is fast due to a lack of stable surface sites. Ethylene occupies the most stable β_2 hydrogen sites leaving at most low energy sites from which hydrogen rapidly desorbs.

The optimum temperature reported by MIYAHARA *et al.* is identical with the temperature at which Reaction 2 first has an appreciable rate²⁾. Thus the decrease in hydrogenation activity above T_m can be correlated with dehydrogenation to a carbon residue. Previous explanations for an optimum temperature cannot be operative in the case of tungsten. Olefin desorption was suggested by ZUR STRASSEN⁷⁾, but the flash filament results show that desorption of chemisorbed ethylene does not occur⁵⁾. Horiuti, in his half hydrogenation state mechanism suggests that T_m occurs as a result of a shift in rate limiting step with increasing temperature from adsorption of hydrogen to hydrogenation of the ethyl radical⁸⁾.

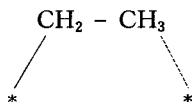
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However, above 300°K the adsorption of hydrogen would be a highly unfavored process, and hydrogenation would be limited by the fast competitive dehydrogenation reaction. Previous work with ethylene on iridium⁹⁾ suggests that surface dehydrogenation may also be the source of T_m on more active metals. On iridium Reaction 1 does not have an appreciable rate until $\sim 400^\circ\text{K}$ suggesting that T_m should be quite high. No values of T_m on Ir have been reported that this author is aware of, but BOND obtains good hydrogenation activity at temperatures as high as 425°K¹⁰⁾.

Below 200°K Reaction 1 is slow and the surface is covered predominately with associatively adsorbed ethylene. At 173°K as in the case of KIMBALL's deuteration experiments⁴⁾, the main reactions that occur are probably those proposed by HORIUTI⁸⁾.



The reverse of Reaction 4 should occur through a transition state of the form



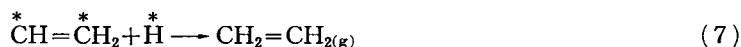
with the probability of formation of this transition state decreasing with increasing metal-metal distance^{5,6)}. The distribution of deuterated ethanes is controlled by this reverse step. Predominantly d_2 -ethane should be obtained on metals with long metal-metal spacings, and ethane containing more extensive deuterium should result on metals with short metal-metal spacings. KIMBALL⁴⁾ observed $\sim 70\%$ d_2 -ethane in the case of tungsten (bcc with a high density of long spacings), and much broader distribution of deuterated ethanes in the case of Rh, Ni and Fe. (fcc with a high density of short spacings).

Above 228°K, however, MIYAHARA *et al.* observed quite different results on tungsten. These authors report extensive olefin exchange with very little hydrogenation activity²⁾. This shift in observed products with a 55°K increase in temperature reflects the effect of Reaction 1. At temperatures above 200°K, Reaction 1 is rapid on a time scale of seconds and results in a surface covered with acetylenic species. In the case of KIMBALL's work below 200°K⁴⁾ the active surface species is associatively adsorbed ethylene. If hydrogenation occurs by Reactions 4 and 5 and olefin exchange occurs through reactions involving the acetylenic species, one would see a shift in the main reaction from hydrogenation to olefin exchange as the temperature increases from 173°K to above 228°K.

Since ethylene is tenaciously bound to tungsten^{1,5)}, it is highly improbable

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that olefin exchange occurs as a result of a surface reaction followed by olefin desorption, but most probably occurs as a result of reactive desorption. A possible sequence of reaction leading to olefin exchange could be



Reactions 6 and 7 could give at most d_2 -ethylene since the reverse of 6 removes the same hydrogen inserted by the forward reaction. Reaction 8 would give a path for more extensive olefin exchange as well as maintain a low concentration of associative ethylene for hydrogenation to ethane. Since Reaction 8 requires the simultaneous addition of two hydrogen atoms to surface acetylene, the concentration of associative ethylene, and as a result the rate of hydrogenation, should be low. During the formation of the initial monolayer, however, where a competition exists between Reaction 1, and Reactions 4 and 5, hydrogenation activity is initially very large⁶⁾.

The distribution of deuterated olefins, however, will also be a function of the isotopic composition of adsorbed hydrogen. Under conditions as used by MIYAHARA *et al.* the deuterium content of adsorbed hydrogen could be constantly changing. Even with admission of a mixture of equal parts of ethylene and deuterium, initial adsorption could lead to a surface predominantly covered with acetylenic species and hydrogen resulting from Reaction 1. This hydrogen would be slowly replaced by deuterium as a result of the slow hydrogen exchange observed by MIYAHARA *et al.*²⁾ As a result d_1 -ethylene would be the major initial product since the insertion of more than one deuterium would be highly improbable with an excess of surface hydrogen. Interpretation of the deuterated olefin distribution obtained by MIYAHARA *et al.* is further complicated by multiple exchange resulting from re-adsorption of product olefin. That this occurs is indicated by the maximum in percentage of d_1 -ethylene. The large amount of d_2 and d_4 -ethylene relative to d_3 -ethylene may be, as suggested by MIYAHARA *et al.*, a result of multiple adsorption. However, the same relative high percentage of d_2 and d_4 -ethylene in the initial products must require reactions such as 6, 7 and 8 that yield multiple exchange with a single residence on the surface.

In the case of tungsten, a major controlling factor in catalytic activity is surface dehydrogenation. Below 200°K, where dehydrogenation of adsorbed ethylene has a negligibly slow rate, tungsten is a relatively good hydrogenation catalyst^{4,5)} and a poor olefin exchange catalyst⁴⁾. Above 200°K, as in the experiments of MIYAHARA *et al.*,²⁾ Reaction 1 has an appreciable rate, and the main

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reaction shifts from hydrogenation to olefin exchange with exchange occurring through the acetylenic species. Above 300°K complete dehydrogenation to a carbon residue occurs. This process poisons the surface and leads to a decrease in activity. The unusually low hydrogenation activity of tungsten results from the unusually low temperature at which Reaction 1 occurs.

Acknowledgment

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