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Reply to Rooney *in re* Isotopic Exchange of Ethane and Microscopic Reversibility

In Ref. (*1*), Hegarty and Rooney (HR) proposed a general mechanism for the isotopic exchange between D_2 and ethane on certain noble metals which involved two sets of independent sites, A and B. The following quotation would be presumed to give the essence of the mechanism.

> (i) Ethane is activated on A sites which are few in number and only generate a limited $\alpha\beta$ process. (ii) There is essentially irreversible transfer of a significant portion of intermediates, either adsorbed ethyls or ethene from A sites to B sites. (iii) The B sites are much more numerous than the A sites, they give rise to an extensive $\alpha\beta$ process, but are basically incapable of activating ethane, although they generate desorbed ethane by addition of a D atom to adsorbed ethyl. In reality, of course all steps are reversible, but in mathematical modelling it is quite permissible to assign minor steps as having zero rates.

We proposed the following as one realization of the HR mechanism (*2*). The presence of surface D is assumed and H represents either H or D:

$$\begin{tikzcd}
 & C_2H_6(g) \arrow[d, shift left, "a"] & \\
X & CH_3{-}CH_2^* \arrow[u, shift left] \arrow[r, shift left, "b"] \arrow[d, "c"] & CH_2^*{-}CH_2^* \arrow[l, shift left] \\
Y & CH_3{-}CH_2^* \arrow[r, shift left, "d"] \arrow[d, "e"] & CH_2^*{-}CH_2^* \arrow[l, shift left] \\
 & C_2H_6(g) &
\end{tikzcd}$$

We noted that if the system was C_2H_6 + H_2, the gas phase and all surface species would be in equilibrium and that the principle of microscopic reversibility would require the forward and reverse rates of each step, including steps c and e, to be identical. Now substitute D for H. The rate of adsorption of ethane on sites Y can be changed only by a kinetic isotope effect and, at low conversions, the rate of adsorption of C_2H_6 would be essentially unchanged. Thus, item (iii) in the quotation above must be impossible.

Rooney states that the "assertion" of the preceding sentence is incorrect and "that the confusion has arisen from placing a wrong kinetic construction on the schemes and equations in our paper," but he does not identify or discuss what or where the error is or show why the argument of the previous paragraph is incorrect (*3*). The first set of equations in Ref. (*3*) is a mechanistic formulation equivalent to that quoted above from Ref. (*2*) for reaction in the presence of H_2 (no D_2). This formulation was not in HR. He states that ethane is predominantly activated on A sites, reversibly (in item (ii) of HR, "essentially irreversible"), transferred to B sites where extensive exchange occurs, and then C_2X_5 is eliminated from the surface as C_2X_6 from both A and B sites. (How can C_2X_6 desorb from sites B if sites B are "basically incapable of activating ethane" (item (iii) in HR)?) Further, "direct adsorption of C_2H_6 on B sites is kinetically and statistically of minor importance and is statistically ignored to a good approximation." However, if desorption from B sites is significant, why is not adsorption?

If the mechanism is really one involving the following sequence of steps—adsorption on A sites, spillover of intermediates onto B sites, respillover onto A sites, desorption from A sites—and if adsorption and desorption from B sites are negligible, then problems of microscopic reversibility

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do not arise. Reference (*3*) presents fewer problems with microscopic reversibility than Ref. (*1*), in particular, *in re* step c, but it is not clear that problems with step e have been eliminated.

REFERENCES

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