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# COMMENTS ON ISOMERIZATION AND EXCHANGE OF DEUTEROETHYLENES

By

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MIYAHARA<sup>1)</sup> has interpreted recent results on the equilibration of  $C_2D_4-C_2H_4$  mixtures and *trans*- $C_2D_2H_2$  on nickel catalysts in the absence of added hydrogen<sup>2)</sup> by the theory which he has applied earlier to the reaction of deuterium and ethane.<sup>3)</sup> MIYAHARA's reaction scheme differs from earlier ones<sup>4)</sup> in that the intermediates  $\overset{H}{C}=\overset{H}{CH}$  and  $\overset{H}{C}=\overset{H}{C}$  are considered as an integral part of the reaction. KEMBALL<sup>5)</sup> has questioned the role of such intermediates in the system  $D_2-C_2H_6$ . FLANAGAN and RABINOVITCH<sup>2)</sup> interpreted their results by considering that reaction takes place effectively *via* ethyl radicals only. The ethyl radicals are formed from reaction of ethylene with chemisorbed hydrogen (or deuterium) arising from dissociative adsorption of ethylene. In order to explain the observed ratios of isomerization to exchange when *trans*- $C_2D_2H_2$  was exposed to a catalyst in the absence of hydrogen, the (C-H)/(C-D) bond rupture isotope effect was considered.

The purpose of this note is to discuss these two interpretations and the effect of the neglect of the isotope effect in MIYAHARA's treatment.

MIYAHARA criticized the rate equations developed by FLANAGAN and RABINOVITCH on the ground that the hydrogen (or deuterium) necessary to catalyze the reaction sequence arises from initial dissociative processes which then "cease", implying according to MIYAHARA an abrupt change in the catalyst activity. In fact this implies only that the hydrogen or deuterium-producing reactions like II<sub>b</sub> or II<sub>c</sub> (MIYAHARA's notation) are essentially irreversible and are relatively unimportant as a source of exchange or isomerization. It has been pointed out that acetylenic complexes are rehydrogenated more slowly than ethylene.<sup>6)</sup> MIYAHARA's reaction scheme includes the possibility of initial formation

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of  $C_2H_4$ ,  $C_2D_4$  and *asym*- $C_2D_2H_2$  from *trans*- $C_2H_2D_2$ , and  $C_2H_2D_2$  from  $C_2H_4$ - $C_2D_4$  mixtures; and although he has extrapolated our data to find initial, small rates of formation of these species, in practice *none were observed* by us in the early stages of reaction.<sup>2),6)</sup> The insignificance of reactions II<sub>b</sub> and II<sub>c</sub> as a source of exchange and isomerization is reflected by the small values of MIYAHARA's  $\alpha$  and  $\beta$ .

MIYAHARA remarks that the rate equations of FLANAGAN and RABINOVITCH are valid for the Rideal mechanism but not for the associative mechanism, except where there is a rapid equilibration between associatively adsorbed surface ethylenes and gas phase ethylenes. We have pointed out earlier<sup>2),6)</sup> that from our results we are unable to distinguish between a Rideal mechanism and an associative mechanism with rapid surface-gas equilibrium, and furthermore, if an associative mechanism were operative it must be one with such a rapid equilibrium, because only singly exchanged olefins were observed initially. At low temperatures, e. g.,  $-100^\circ C$  where multi-exchanged products were observed initially,<sup>7)</sup> we have already pointed out that mechanism based upon one-step exchange would not be appropriate.<sup>8)</sup>

The present authors have shown the necessity for the consideration of the isotope effect in the ethyl radical when *trans*- $C_2D_2H_2$  is exposed to a catalyst.<sup>2),6),8)</sup> MIYAHARA observes good agreement in his analysis for the equilibration of  $C_2D_4$ - $C_2H_4$  mixtures but rather poor agreement for the relative *cis*- $C_2D_2H_2$  percentage in the equilibration of pure *trans*- $C_2D_2H_2$ . In fact his values for *cis*- $C_2D_2H_2$  correspond to the prediction if the isotope effect were to be neglected (dotted line, Figure I, reference 2) and not to the observed values. It is difficult to see how MIYAHARA's scheme can account for the large variation with temperature of the initial ratios of (*cis*- $C_2D_2H_2$ )/( $C_2DH_3$  plus  $C_2D_3H$ ), e. g., the ratio is 8.00 at  $-78^\circ C$  and 1.28 at  $148^\circ C$ .<sup>6)</sup> This large variation is readily interpreted in terms of an isotope effect, and an ARRHENIUS plot of experimental values of  $\log(C-H/C-D)$  gives an activation energy of 1.5 kcal/mole in reasonable agreement with the expected value for the zero point energy difference of the C-H and C-D bonds.

The uniqueness of the *trans*- $C_2D_2H_2$  equilibration as compared to the  $C_2D_4$ - $C_2H_4$  equilibration is emphasized by the fact that for the latter any rate equations based upon one-step exchange (not necessarily *via* the ethyl radical intermediate) will give, upon solution, excellent agreement with experiment over the entire range of reaction. Stoichiometry requirements mask the isotope effect in the  $C_2H_4$ - $C_2D_4$  system.

**References**

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