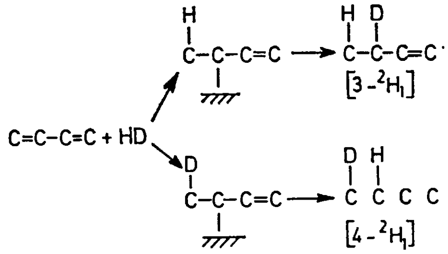
Orientation in the Addition of HD to Butadiene on MoS_2

By TOSHIO OKUHARA and KEN-ICHI TANAKA*
(*Research Institute for Catalysis, Hokkaido University, Sapporo, Japan*)

Summary Hydrogenation of butadiene with HD over MoS_2 gives two geometrical isomers, $[3\text{-}^2H_1]$but-1-ene and $[4\text{-}^2H_1]$but-1-ene; the ratio of the two isomers agrees strictly with the isotope effect for the overall reaction rates with H_2 and D_2.

IN the hydrogenation of butadiene over MoS_2, the molecular identity of hydrogen is strictly maintained to give $[^2H_2]$but-1-ene in the reaction with D_2.[1] In the reaction with HD on MoS_2, two geometrical isomers are formed: $[3\text{-}^2H_1]$- and $[4\text{-}^2H_1]$-but-1-ene. The presence of an isobutenyl intermediate in the isotopic exchange between butadiene and D_2 over MoS_2 has been confirmed by microwave spectroscopy.[2] If the intermediate in the hydrogenation of butadiene is also of isobutenyl rather than n-butenyl form, the reaction of butadiene with HD can be described as in the Scheme. The selectivity to give either of the two geometrical isomers is decided by the first step of H or D addition, because the remaining half of the HD molecule will react successively to maintain its molecular identity. If the mechanism in the Scheme is correct, the ratio of $[3\text{-}^2H_1]$- to $[4\text{-}^2H_1]$-butene in the product, determined by the orientation of HD addition, should agree with the isotope effects for the overall reaction rates with H_2 and D_2.



SCHEME

The hydrogenation of butadiene was carried out with a previously equilibrated isotopic mixture of hydrogen with a ratio of H_2:D_2:HD of 26·8:26·5:46·6; the nearly equal amounts of H_2 and D_2 should minimize errors. The results for the reaction of 18 mmHg of butadiene with 35 mmHg of the hydrogen isotopic mixture are shown in the Figure.

As the conversion increases, [$^2H_1$]butadiene gradually accumulates, so corrections for its presence must be taken into account at higher conversions. Corrections were made for the amount of [4-$^2H_1$]but-1-ene, which could be formed by the reaction of [$^2H_1$]butadiene with H_2, and the amount of [$^2H_2$]but-1-ene, by its reaction with HD. The deuterium atom in [$^2H_1$]butadiene has been shown to be located entirely on the terminal carbon atoms.[2]

The results provide good agreement of the ratio of [3-$^2H_1$]- to [4-$^2H_1$]-but-1-ene with the ratio of [$^2H_0$] to [$^2H_2$] (Figure), the [$^2H_0$]-, [$^2H_1$]-, and [$^2H_2$]-but-1-enes arising respectively by simultaneous hydrogenation with H_2, HD, and D_2. Such agreement with the observed isotope effect suggests that the hydrogenation is stepwise, the slow step being addition of the first 'hydrogen' to the diene to give adsorbed isobutenyl. If the reaction had proceeded *via* the n-butenyl species, the ratio of [3-$^2H_1$]- to [4-$^2H_1$]-but-1-enes should have been 1/1·4, rather than 1·4, the observed isotope effect on hydrogentation rate.

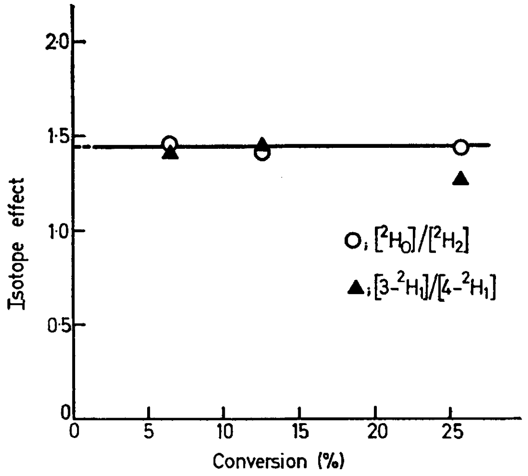


FIGURE. Orientation in the addition of HD to butadiene and the isotope effects for addition of H_2 and D_2 at room temperature

We thank Drs. T. Kondo and S. Saito, Sagami Chemical Research Center, for the microwave spectroscopic analysis.

(*Received, 3rd December* 1975; *Com.* 1346.)

---

[1] T. Okuhara, K. Tanaka, and K. Miyahara, *J.C.S. Chem. Comm.*, 1976, 42.

[2] T. Okuhara, T. Kondo, and K. Tanaka, *J. Phys. Chem.*, submitted for publication.