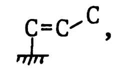
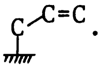
CHEMISTRY LETTERS, pp. 119-122, 1977. Published by the Chemical Society of Japan

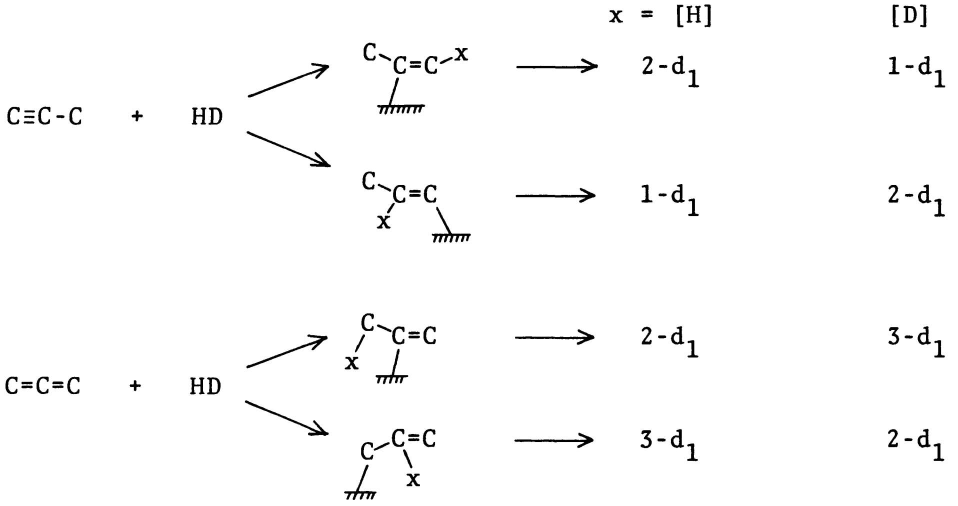
n-PROPENYL AND σ-ALLYL INTERMEDIATES IN THE HYDROGENATION OF METHYLACETYLENE AND ALLENE ON MoS_2

Toshio OKUHARA, Toshihiko KONDO(1), and Ken-ichi TANAKA*
Research Institute for Catalysis, Hokkaido University
Sapporo 060

The hydrogenation of methylacetylene on MoS_2 proceeds through n-propenyl intermediate,  $\mathrm{C{=}C\diagup^{C}}$, however, the hydrogenation of allene occurs through σ-allyl intermediate,  $\mathrm{C\diagup^{C=C}}$. These two intermediates are in marked contrast with the intermediates for the hydrogenation of butadiene and olefins taking place via iso-butenyl and iso-alkyl intermediates on the MoS_2 catalyst.

In the deuteration of methylacetylene and allene over the MoS_2 catalyst, the molecular identity of the deuterium is strictly maintained to give the d_2-propene in a similar manner as the deuteration of butadiene gives d_2-1-butene.(2) The geometrical isomers of the deuterated propene formed by the deuteration of methylacetylene and allene at room temperature are listed in Table 1.

It is known that the deuteration of methylacetylene gives predominantly E-1,2-d_2-propene (90 %), whilst the most abundant d_2-propene in the deuteration of allene is 2,3-d_2-propene (87 %). This result indicates the cis-stereoselective hydrogen addition over the MoS_2 catalyst, and also shows the direct addition of deuterium to allene accompanying little isomerization to methylacetylene. Provided that the hydrogenations occur via the half-hydrogenated intermediates, the conceivable intermediates for the hydrogenation of methylacetylene might be n-propenyl and/or iso-propenyl. In contrast with these, σ-allyl and/or iso-propenyl can be anticipated for the hydrogenation of allene. Accordingly, it is interesting to confirm the preferential intermediate for these two reactions giving the same product propene. For this purpose, the hydrogenation of methylacetylene and allene with HD has been performed, where the orientation in the HD addition will inform us the intermediate of the hydrogenation reaction.[3] That is, the reaction of methylacetylene with HD will give 1-d_1 and 2-d_1-propene and that of allene with HD will give 2-d_1 and 3-d_1-propene, respectively. Providing that the hydrogenation proceeds by the stepwise addition of H or D, conceivable reaction mechanisms are described as follows;



In conformity with the slow hydrogen exchange between D_2 and methylacetylene or allene, the slow step of the hydrogenation reaction may be the first step of hydrogen atom addition forming corresponding half-hydrogenated intermediates as has been confirmed in the hydrogenation of butadiene on the MoS_2 catalyst.[3] According to the above reaction schemes, the geometrical isomers of the d_1-propene should be decided by the first step, because the HD addition maintains its molecular identity to give the d_1-propene selectively.

Accordingly, if the reaction would proceed via the iso-propenyl intermediate, the 2-d_1-propene prevails over the 1-d_1-propene or the 3-d_1-propene by the isotope effect in the intermediate formation.

On the contrary, if the intermediates are the n-propenyl or the σ-allyl species, 1-d_1-propene > 2-d_1-propene for methylacetylene and 3-d_1-propene > 2-d_1-propene for allene are expected. As the reaction with HD proceeds, H_2 and D_2 are formed by the equilibrium reaction, which results in the formation of d_0-propene and

Table 1. Geometrical Isomers formed in the Reaction of Allene and Methylacetylene with HD or D_2 at room temperature.

reaction	conv. (%)	deuterium distribution in propene (%).				structural distribution of deuterium (%).			isotope effect	
		d_0	d_1	d_2	d_3		d_2			
$C\equiv C-C + D_2$	2.0					E-1,2	Z-1,2	1,1-		
		-	3.7	92.7	3.6	90.0	10.0	-		
							d_1		d_0**	1-d_1
$C\equiv C-C + HD$	2.3					2-	E-1	Z-1	d_2	2-d_1
		21.8	62.7	15.5	-	42.9	50.0	6.9	1.28	1.33
							d_2			
$C=C=C + D_2$	5.0					2,3-	E-1,2	Z-1,2		
		-	2.4	89.7	9.7	87.0	11.6	1.4		
							d_1		d_0**	3-d_1
$C=C=C + HD$*	5.8					3-	2-	1-	d_2	2-d_1
		23.7	52.9	22.4	-	52.4	45.0	2.6	1.16	1.16

* The simultaneously occuring isomerization gave 2.2 % of methylacetylene being composed by 84.1 % of d_0- and 15.9 % of d_1-species.

** Corrected value.

d_2-propene. The isotope effect for the reaction with H_2 and D_2 was estimated by correcting the value of d_0-propene/d_2-propene with the ratio of H_2/D_2 because the reaction is the first order in hydrogen pressure. As shown in Table 1, the reaction of methylacetylene with HD gives 1-d_1- and 2-d_1-propene in the ratio of 1.33. In the hydrogenation of allene, methylacetylene was formed by the isomerization reaction, then, the participation of the methylacetylene in the hydrogenation of allene was estimated by using this characteristic ratio for methylacetylene. By making the correction of methylacetylene contribution, the ratio of 3-d_1-/2-d_1-propene for the allene hydrogenation became 1.16.

It should be mentioned that the over-all isotope effect for the reactions with H_2

and D_2 are in fair agreement with the ratio of the geometrical isomers formed by the reaction with HD for allene as well as for methylacetylene.

If the hydrogenation would proceed through the two intermediates in comparable weight, the over-all isotope effect d_0/d_2-propene should be larger than the ratio of 1-d_1-/2-d_1-propene or 3-d_1-/2-d_1-propene.

Accordingly, the hydrogenation of methylacetylene and allene should occur via one predominant intermediate, the n-propenyl for methylacetylene and the σ-allyl for allene. Furthermore, the fact that the ratio of 1-d_1-/2-d_1-propene for the methylacetylene is different from that of 3-d_1-/2-d_1-propene for allene may suggest distinctive intermediates for the two reactions, that is, the iso-propenyl intermediate being common to the both reactions might be ruled out.

This finding is in contrast to the hydrogenation of butadiene and/or α-olefins on the MoS_2 catalyst in which the iso-butenyl and the iso-alkyl intermediates are prevailing.$^{4)}$

Such differences of the intermediates are explainable by the steric hindrance of the intermediates, that is, the iso-propenyl species might have larger steric strain than the n-form intermediates such as n-propenyl and σ-allyl species because the carbon atom held to the active site are bound with a methyl and a double bonded methylene.

References;

1) Sagami Chemical Research Center, Nishi-Ohnuma, Sagamihara, Kanagawa 229.

2) T. Okuhara, K. Tanaka, and K. Miyahara, J. Chem. Soc., Chem. Comm. 42 (1976); T. Okuhara, T. Kondo, and K. Tanaka, Chem. Lett., 717 (1976).

3) T. Okuhara and K. Tanaka, J. Chem. Soc., Chem. Comm., 199 (1976).

4) T. Okuhara, K. Kondo, and K. Tanaka, submitted for publication.

(Received November 17, 1976)