Change from a σ-Alkyl Intermediate to a Carbonium Ion Intermediate in Reactions of Olefins on a Molybdenum Sulphide Catalyst

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Summary The double bond migration of 2-methylbut-1-ene on MoS_2 occurs predominantly by a carbonium ion mechanism, while isomerization and hydrogen exchange of other olefins proceed through σ-alkyl intermediates.

THE isomerization of 2-methylbut-1-ene was performed simultaneously with other reactions such as the isomerization of *cis*-but-2-ene or the hydrogen exchange reaction of C_2H_4–C_2D_4 or C_3H_6–C_3D_6, which are known to occur by an associative mechanism.[1] MoS_2 from the same batch used in the previous experiments[2] was evacuated at 450 °C for several hours, and employed as the catalyst at room temperature.

When a mixture of 2-methylbut-1-ene and *cis*-but-2-ene, at a pressure of 17 and 24 Torr, respectively, was in contact with the MoS_2 surface, 2-methylbut-1-ene isomerized to 2-methylbut-2-ene, but *cis*-but-2-ene only isomerised partially. With the addition of hydrogen, however, the isomerization of *cis*-but-2-ene was markedly accelerated, but it had little influence on the isomerization of 2-methyl but-1-ene. Other reactions, such as the intermolecular hydrogen exchange of propene and ethylene, which proceed through the half-hydrogenated intermediates, showed a similar trend.

TABLE 1. Microwave spectroscopic analysis of [$^2H_1$]isobutene formed by the exchange between [$^2H_0$]- and [$^2H_8$]-isobutene at room temperature

% [$^2H_1$]Isobutene formed	Ratio of [1-$^2H_1$] to [3-$^2H_1$] isobutene
7·4	80:20
13·8	66:34
Equilibrated	25:75

If the isomerization of 2-methylbut-1-ene on MoS_2 is attributed to a dissociative mechanism, as is the case with the isomerization of but-1-ene on ZnO,[3] 3-methyl but-1-ene might also be expected to isomerise by the same mechanism.[4] This was not the case, as 3-methylbut-1-ene did not isomerise either in the presence or absence of hydrogen, while hydrogenation occurred readily. With the addition of 2-methylbut-1-ene in the presence of 3-methylbut-1-ene, however, 2-methylbut-2-ene was formed.

In our previous work,[5] half-hydrogenated intermediates such as isopropyl or isobutyl intermediates formed on MoS_2 were found to have restricted rotation around the co-ordination bond resulting in slow migration of the double-bond. The slow isomerization of 3-methylbut-1-ene in the presence of hydrogen might be attributed to this restricted rotation in the half-hydrogenated species.

The specific behaviour of 2-methylbut-1-ene on the MoS_2 catalyst seems to be attributable to the formation of a tertiary carbonium ion. If this is the case, an interesting question arises as to whether isobutene also leads to a carbonium ion on MoS_2. The hydrogen exchange reaction between [$^2H_0$]- and [$^2H_8$]-isobutene was rather slow in the absence of hydrogen and was markedly accelerated by hydrogen addition at room temperature. Microwave spectroscopic analyses of [$^2H_1$]isobutene formed are listed in Table 1, which indicates preferential exchange of the vinylic hydrogens as in the hydrogen exchange of propene

TABLE 2. Intermediates of the hydrogen exchange reaction on MoS_2 as compared with the reaction on bismuth phosphate

	MoS_2	Bismuth phosphate[a]
Propene	σ-Alkyl	σ-Allyl
But-1-ene	"	"
3-Methylbut-1-ene	"	"
Isobutene	"	Carbonium ion
2-Methylbut-2-ene	—	"
2-Methylbut-1-ene	Carbonium ion	"

[a] P:Bi, 1:1, see ref. 6.

and/or but-1-ene on MoS_2. The characteristic property of isobutene on MoS_2 may be caused by the restricted rotation around the co-ordination bond.

These findings reveal that 2-methylbut-1-ene may accept a proton from the MoS_2 surface, probably from the sulphide ion, to form a tertiary carbonium ion, but the proton-donating ability of the MoS_2 surface may not be sufficient to form a carbonium ion by donating a proton to isobutene and/or 3-methylbut-1-ene. The hydrogen exchange reaction of olefins other than 2-methyl but-1-ene accordingly, occurs predominantly *via* σ-alkyl intermediates, and the restricted rotation of these half-hydrogenated species results in a slow migration of the double bond.

To the best of our knowledge, only one other case has been reported where there is this change in the reaction mechanism, namely, with bismuth phosphate, as catalyst;[6] see Table 2.

The active sites for formation of the half-hydrogenated intermediates may be located on the side of a layer of MoS_2 crystallite,[5] but the carbonium ion may be formed on the sulphide ion layer. This supposition has been verified recently in our laboratory by using an MoS_2 single crystal.

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