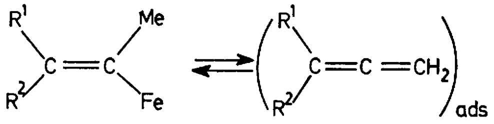
Isomerization of β-Olefins on Iron Films. Evidence for Binuclear Surface Complexes

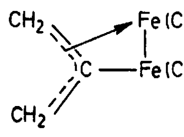
By RAYMONDE TOUROUDE, and FRANÇOIS G. GAULT
(Laboratoire de Catalyse, Université Louis Pasteur, Strasbourg, France)

Summary Characteristic maxima have been observed in the deuterium distribution patterns of the isomers obtained from various *β*-olefins on iron films in the presence of perdeuteriopropene; the results can be interpreted by assuming interconversions between vinyl- and allene-surface complexes.

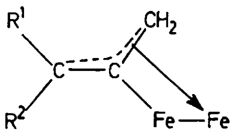
IN the presence of a large excess of C_3D_6, but-1-ene and but-2-enes behave very differently on iron film catalysts.[1] The main reaction of but-1-ene is a very fast exchange, where the deuterium is introduced almost exclusively on the internal vinylic carbon atom; isomerization to but-2-enes is very slow and takes place without deuterium incorporation. On the other hand the exchange of but-2-ene is negligible and its isomerization to but-1-ene is accompanied by the exchange of all the hydrogens of the molecule.



(A) (B)



(C)



(D)

In order to investigate further this latter reaction, the isomerization and exchange of *cis*-pent-2-ene and 2-methyl but-2-ene were studied on iron films. The exchange of the reacting molecules is not important, as already observed in the case of but-2-enes, and isomerization occurs with an incorporation of deuterium leading to characteristic distribution patterns of the deuteriomolecules (Table).

The isomerization of pent-2-ene at −37°C yields deuteriopent-1-enes up to $[^2H_6]$, with a pronounced maximum at $[^2H_5]$. The isomerization of 2-methyl-but-2-ene takes place at 100 °C and the exchange distribution patterns found for the two isomers formed, 2-methyl-but-1-ene (2MB) and 3-methyl-but-1-ene (3MB), are very different. 2MB $[^2H_0]$ and $[^2H_1]$ are the most abundant deuteriospecies, while the distribution of 3MB includes five deuteriomolecules in approximately equal amounts from $[^2H_0]$ to $[^2H_4]$.

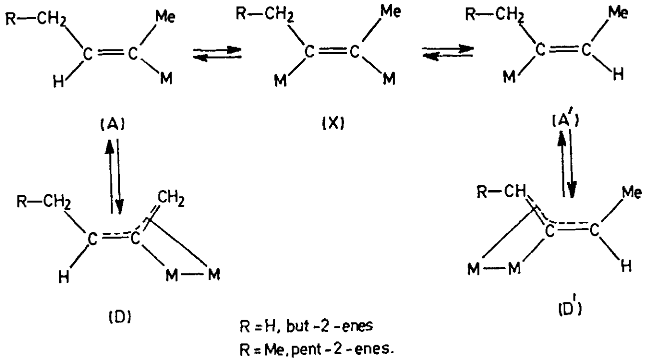
TABLE

Isomerization of *β*- to α-olefins
Deuterium distribution patterns of the isomers

Reacting hydrocarbon	*cis*-butene	*cis*-pentene	2-methyl but-2-ene	
T/°C	−37	−37	100	
C_3D_6/olefin	14	18	21	
Double bond migration/%	1·8	2·0	0·5	2·7
Product	but-1-ene	pent-1-ene	3MB	2MB
$^2H_0$	2·2	1·2	24·1	54·1
$^2H_1$	3·3	1·9	21·8	34·0
$^2H_2$	7·0	4·3	14·5	6·3
$^2H_3$	4·5	8·5	15·2	2·3
$^2H_4$	2·7	25·6	21·4	1·1
$^2H_5$	0·9	45·3	0·9	0·7
$^2H_6$	1·7	9·4	1·2	0·5
$^2H_7$	24·0	1·1	0·9	0·2
$^2H_8$	53·7	0·4		0·2
$^2H_9$		1·4		0·2
$^2H_{10}$		0·8		0·5

The deuterium distribution patterns of the isomers obtained from all three *β*-olefins (but-2-enes, pent-2-ene and 2-methyl but-2-ene) clearly show that the incorporation of extensive amounts of deuterium in the molecule is connected with the possibility of an interconversion between dissociatively adsorbed olefins (**A**) and adsorbed terminal allenes (**B**).

Stable vinyl- and allene-iron complexes have been isolated,[2] the latter ones only as *σ*-vinyl *π*-allylic binuclear species (**C**).[3] It is therefore tempting to describe the adsorbed species (**B**) as binuclear surface complexes (**D**).



While interconversions between (**A**) and (**D**) explain the four exchanged hydrogens in 3-methyl but-1-ene, the maximum at [$^2H_5$] in pent-1-ene necessitates an additional intermediate species (**X**), allowing the exchange of the fifth hydrogen atom on C(3). The interconversions of (**X**) (presumably a di-σ-vinyl complex) with (**A**), (**A'**) and (**D**) fully explain the deuterium pattern of pent-1-enes, provided that the internal σ-vinyl π-allylic species (**D'**) is of minor importance.

On the contrary, in the isomerization of but-2-enes (**D'**) is a terminal adsorbed allene and the interconversions between all five species (**A**), (**D**), (**X**), (**A'**), and (**D'**) account for the complete exchange of the two halves of the molecule.

(*Received*, 12*th August* 1974; *Com.* 1035.)

---

[1] R. Touroude and F. G. Gault, *J. Catalysis*, 1974, **32**, 288, 294; M. Ledoux, F. G. Gault, J. J. Masini, and G. Roussy, preceding communication.

[2] A. N. Nesmeyanov, M. I. Rybinskaya, L. V. Rybin, and V. S. Kaganovich, *J. Organometallic Chem.*, 1973, **47**, 1.

[3] R. Ben-Shoshan and R. Pettit, *Chem. Comm.*, 1968, 247; R. E. Davis, *ibid.*, 248; P. F. Lindley and O. S. Mills, *J. Chem. Soc.* (*A*), 1970, 38.