Exchange and Vinylic Adsorption of α-Olefins on Iron and Nickel Films

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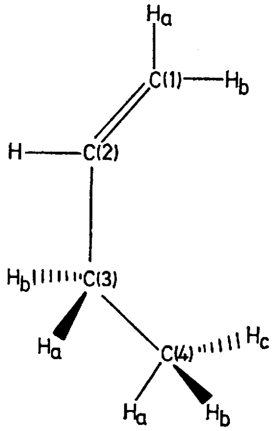
Summary The exchange of but-1-ene on iron and nickel films proceeds by dissociative adsorption on the vinylic carbon atoms; the most reactive hydrogen atom in this reaction is that bound to C(2).

MOST of the results dealing with isomerization and exchange of olefins, during the past twenty years, have been interpreted in terms of interconversions between π-olefinic and σ-alkyl adsorbed species (Horiuti–Polanyi mechanism.[1]) However, a recent study of the exchange of α-olefins on iron films in the presence of C_3D_6, strongly suggests that the adsorption of these molecules is dissociative rather than associative and involves the rupture of vinylic carbon hydrogen bonds.[2] Since only indirect proofs have so far been provided, based mainly on the number of exchangeable hydrogen atoms, we have now precisely located the deuterium atoms in the exchanged molecules by microwave analysis, in order to confirm the adsorption mechanism.

The rotational spectrum of butenes was measured with a 50 kHz square-wave Stark modulator microwave spectrometer. The measurements were made at dry ice temperature using a 5 m absorption cell and a zero based square-wave field amplitude of 1000 V cm^{-1}. The composition of the deuteriobutenes was determined, within ± 5%, by measuring the intensities of the rotational $3_{13} \rightarrow 2_{12}$ transition for the skew form[3] and checked by using the $3_{12} \rightarrow 2_{11}$ lines of the spectrum for the same conformation.

The fine and hyperfine distributions of the deuteriobut-1-enes on iron films, obtained by mass spectrometry and microwave spectroscopy respectively, are given in the first two rows of the Table. The reactions were effected with a very high $C_3D_6:C_4H_8$ ratio (*ca.* 17) to avoid any isotopic dilution. Analysis of the [$^2H_1$] species shows that the vinylic hydrogen on C(2) is much more reactive than any other hydrogen. In run 1, where the conversion in deuteriobut-1-enes is very high, the [$^2H_2$] species may be considered as obtained mainly by readsorption of the [$^2H_1$] molecules; their analysis shows that the two other exchangeable hydrogens are also vinylic, the *trans* H_a on C(1) being twice as reactive as the *cis* H_b.



The exchange and isomerization of but-1-ene was studied on nickel films in the presence of C_3D_6. The fine and hyperfine distributions of the monodeuteriated species are reported in the third row of the Table. Although the same order is found for the reactivities of the three vinylic hydrogen atoms, the difference between them is not as large on nickel as on iron. An exchange experiment was also performed on nickel film in the presence of deuterium. The results are substantially the same as in the presence of C_3D_6; more than 80% of the deuterium in [$^2H_1$]-but-1-ene is located on C(2).

We thus conclude that the only reactive hydrogens in exchange of but-1-ene on iron and nickel are the vinylic hydrogens, with the following order of reactivity:

$$\text{H-2} >> \text{H-1a} > \text{H-1b}$$

TABLE

Distribution of deuteriobut-1-enes and deuteriopropenes formed on iron and nickel catalysts.

Catalyst	Fe	Fe	Ni	Ni	Ni	
Run	1	2	3	ref. 5	ref. 5	
T/°C	−37	−37	0	17	20	
Isomerization	4·9	1·0	12·7			
$^2H_0$	16·4	83	46·8	58·4	57·5	$^2H_0$
$^2H_1$	59·1	17	37·1	33·3	25·0	$^2H_1$
$^2H_2$	18·7	<1	9·9	7·3	10·8	$^2H_2$
$^2H_3$	5·1	—	3·3	1·0	4·8	$^2H_3$
$^2H_4$	0·7	—	1·4			
1a-[$^2H_1$]	0	0	10	9·5	11·4	*trans*-CHD=CH–Me
1b-[$^2H_1$]	0	0	4	9·9	11·7	*cis*-CHD=CH–Me
2-[$^2H_1$]	100	100	86	58·1	40·7	CH_2=CD–Me
3-[$^2H_1$]	0	0	0	22·2	36·2	CH_2=CH–CH_2D
4-[$^2H_1$]	0	0	0			
1a-2[$^2H_2$]	66	—	>80			
1b-2[$^2H_2$]	34	—	<20			
other [$^2H_2$]	0	—	0			

This demonstrates unambiguously, for the first time, the validity of the dissociative mechanism proposed by Farkas and Farkas for the exchange of olefins.[4]

Although the presented results deal with but-1-ene and not propene, vinylic exchange could also be an important factor in the exchange of propene with deuterium on nickel, as studied by Hirota and his co-workers.[5] The differences between the hyperfine distributions of but-1-enes and of propenes, reported in the 4th and 5th rows of the Table, especially the presence of large amounts of 3-[$^2H_1$]propene, could be explained if exchanged and isomerized propenes, which cannot be distinguished in the reaction products, were formed by two independent mechanisms.

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