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INTRAMOLECULAR HYDROGEN EXCHANGE IN 2,3-DIMETHYLBUTANE CATALYSED BY NICKEL

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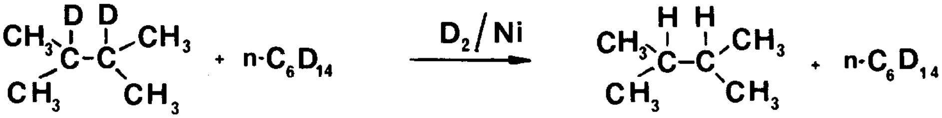
SUMMARY: A cross experiment with a specifically labeled hydrocarbon reveals that intramolecular hydrogen exchange is an important process for saturated hydrocarbons chemisorbed on a nickel catalyst.

Attack of unactivated C-H bonds represents the initial step of most important technical processes such as petroleum refining and functionalization of saturated hydrocarbons. Despite this importance little is known about the exact mechanism of C-H bond activation by heterogeneous catalysts. H/D exchange experiments have already been applied successfully to the investigation of some mechanistic aspects.[1] In this paper we present the first evidence for intramolecular hydrogen exchange in saturated hydrocarbons catalysed by nickel on silica.

All experiments have been conducted with a gas phase flow apparatus as described previously.[2] The substrate was vaporized in a stream of deuterium at atmospheric pressure and passed through the horizontal catalyst bed containing the nickel on silica catalyst.[3] The products were collected in a cold trap and separated by preparative GC. The experimental results are summarized in the table. The catalyst has been cleaned with deuterium at 400°C prior to each experiment.

A 1:1 mixture of specifically deuterated 2,3-dimethylbutane (1a) and perdeuterated n-hexane (2a) was passed over the nickel catalyst at 160°C (exp. 1). After separation product 2 showed no significant change (slight decrease of the deuterium content from 98% to 97%) whereas 1 had suffered considerable deuteration (increase of the deuterium content from 14 to 84%). Most important however is the observation that the deuterium content at the tertiary position had actually decreased (from 94% to 90%) indicating significant hydrogen transfer from the only hydrogen source in the system, the terminal methyl groups in 1. The fact that we observed absolute decrease of the deuterium content at the tertiary position despite a complete conversion of 1a to higher deuterated 1 (MS data) is especially remarkable and demonstrates the dominance of intramolecular hydrogen scrambling:



(14% D) (98% D) (84% D) (97% D)

1a 2a 1 2

Structure dependent selectivity could be excluded with experiment 2, where both undeuterated hydrocarbons 1b and 2b were unselectively deuterated when passed together over the catalyst. The difference in total deuteration (58% in 1 and 64% in 2) may be due to differences in chemiesorption or vapor pressure.

A large isotope effect inhibiting the hydrogenation of 2a in experiment 1 could be excluded by experiment 3 where 2a was easily hydrogenated with hydrogen as carrier gas at 160°C. Comparison of the total exchange achieved in 2 in experiments 2 and 3 points to a rather small isotope effect in agreement with a value of 1.8 determined for nickel films at 168°C by Flanagan and Rabinovitch.[4]

When we repeated experiment 1 at higher temperatures (180°C, experiment 4) substantial hydrogen transfer to 2a was observed. This indicates now large increase of the equilibration of the hydrogen and deuterium isotopes present at the surface (multiple inter molecular exchange), but the dominance of the intra versus the inter molecular exchange can still be recognized (see table). Experiment 5 shows no hydrogen scrambling at a temperature where no exchange occurs.

Table: Isotopic exchange experiments in the gas phase with a nickel on silica catalyst

Exp. Nr.	substrate	carrier gas	Deuterium in the substrate			reaction temp.	Deuterium in the product		
			total	CH_3	CH (atom%)		total	CH_3	CH (atom%)
1	1a	D_2	14%	2%	94%	160°C	84%	83%	90%
	2a		98%				97%		
2	1b	"	0%	0%	0%	160°C	58%	58%	58%
	2b		0%				64%		
3	2a	H_2	98%			160°C	59%		
4	1a	D_2	14%	2%	94%	180°C	81%	81%	84%
	2a		98%				85%		
5	1a	D_2	14%	2%	94%	80°C	no reaction		

reaction conditions: flow rate 20 ml/min, D_2/substrate ratio 15:1. The total deuterium content was determined by mass spectroscopy; the deuterium distribution by integration of the proton magnetic resonance spectrum.

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References

1. for reviews see: Burwell, R.L. Accounts Chem. Res., 1969, 2, 289; Catal. Rev. 1972, 7, 25; Kemball, C. Advan. Catal. 1959, IX, 223; Ozaki, A. 'Isotopic Studies of Heterogeneous Catalysis' Academic Press, New York, 1977.
2. Grubmüller, P.; Maier, W.F.; Schleyer, P.v.R.; McKervey, M.A.; Rooney, J.J. Chem. Ber. 1980 113, 1989.
3. Catalyst preparation: 5g $Ni(NO_3)_2 \cdot 6H_2O$, dissolved in 10 ml water, was stirred with 5g silica and the water was evaporated on a rotatory evaporator. The resulting solid was dried at 125°C and ground finely. 500mg of this material was packed between glass wool plugs in the center of the reactor tube (ϕ 8mm) and reduced in a slow stream of hydrogen at atmospheric pressure.
4. Flanagan, T.B.; Rabinovitch, B.S. J. Phys. Chem. 1956, 60, 724.

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