

# CARBON-13 NMR STUDY OF *n*-BUTENE ISOMERIZATION IN CaNaY TYPE ZEOLITES

By

D. MICHEL, W. MEILER, H. PFEIFER and H. J. RAUSCHER  
NMR Laboratory of the Department of Physics,  
Karl-Marx-Universität Leipzig, G.D.R.

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Measuring highly resolved carbon-13 nmr spectra, the isomerization of *n*-butenes adsorbed on CaNaY type zeolites has been investigated at temperatures from 300 to 350 K. Relative equilibrium concentrations as determined from nmr line intensities fairly well agree with known data for the thermal equilibrium of *n*-butene isomers in the gas phase. The application of partially <sup>13</sup>C enriched but-1-enes enabled a detailed study of the transformation of the different groups during the double bond isomerization. If but-1-ene <sup>\*</sup>CH<sub>2</sub>=CH—CH<sub>2</sub>—CH<sub>3</sub> (\* denotes the labeling) was used an enrichment of carbon-13 nuclei was only found in the methyl groups of *cis*- and *trans*-but-2-ene molecules. In agreement with this finding the group =<sup>\*</sup>CH— of but-1-ene CH<sub>2</sub>=<sup>\*</sup>CH—CH<sub>2</sub>—CH<sub>3</sub> is transformed to the analogous group of *cis*- and *trans*-but-2-enes. Intermediates were not detected under the present conditions of measurements.

At higher temperature additional resonance lines indicate the occurrence of polymerization reactions.

## 1. Introduction

Some years ago it could be shown that the application of carbon-13 Fourier transform nmr techniques enables the investigation of highly resolved nmr spectra of adsorbed molecules with natural abundance of carbon-13 nuclei [1—3]. In this work a simple conversion (double bond isomerization of *n*-butenes adsorbed in CaNaY zeolites) will be studied to check which statements on a heterogeneous catalytic reaction are possible. The main problem is to correlate the resonance lines occurring during the catalytic process to carbon atoms of molecules or intermediates of the sorbate. For that purpose the use of carbon-13 enriched molecules is of great importance. Thus, after a description of experimental conditions (Chapter 2) spectra are discussed which resulted after conversions of but-1-ene with a carbon-13 enrichment in positions =CH<sub>2</sub> and =CH—, respectively (Chapter 3). Conclusions are summarized in Chapter 4.

## 2. Experimental conditions

Using an HX 90 Fourier transform nmr spectrometer, the <sup>13</sup>C nmr spectra have been measured at 22.63 MHz. The cylindrical sample glass tubes have an external diameter of 10 mm. The capillary containing the lock substance (DMSO-d<sub>6</sub>) is fixed in the axis of the tube so that it is uniformly surrounded by the sorbate. This special kind of sample preparation excludes the investigation of fast reactions.

CaNaY type zeolites (0...88% of Na<sup>+</sup> replaced by Ca<sup>++</sup> ions) were prepared by means of ion exchange starting from a NaY type zeolite (Si/Al=2.6, VEB Chemiekombinat Bitterfeld-Wolfen, G.D.R.).

First of all the zeolites were slowly heated up to 670 K and evacuated during 20 h resulting in a final pressure of about 10<sup>-3</sup> Pa. Then the butenes were adsorbed in vacuo at 77 K. This treatment yields total numbers of zeolitic OH groups as shown in Table I which have been measured by means of proton nmr wide line techniques [4].

Table I

Number N<sub>OH</sub> of hydroxyl groups per large cavity ( $\pm 0.4$  OH per large cavity) for different *n* CaNaY type zeolites (*n* denotes the percentage of Na<sup>+</sup> ions replaced by Ca<sup>++</sup>)

<i>n</i>	0	20	40	63	74	88
N <sub>OH</sub>	0.2	0.4	0.5	0.6	0.9	1.0

The sorbates were normal but-1-ene purum (Fluka AG., Buchs-Switzerland), \*CH<sub>2</sub>=CH—CH<sub>2</sub>—CH<sub>3</sub> and CH<sub>2</sub>=\*\*CH—CH<sub>2</sub>—CH<sub>3</sub> with a carbon-13 enrichment of 15% (\*) and 50% (\*\*), respectively. For the preparation of the labelled species at first butanols were synthesized starting from Ba<sup>13</sup>CO<sub>3</sub> (Isotop, Moscow-U.S.S.R.) The dehydration of the respective butanols was carried out in a flow reactor with a  $\gamma$ -alumina catalyst.

### 3. Results and Discussion

#### <sup>13</sup>C-spectra of normal but-1-ene adsorbed on various CaNaY type zeolites

On pure NaY type zeolites a catalytic reaction can be observed in the spectra only when the samples are heated up to 430 K for some hours. If the Ca<sup>++</sup> exchange is increased to about 65%, the carbon-13 nmr spectra of the adsorbed but-1-ene molecules remain only unchanged if the temperature is less than 330 K. The chemical shifts of the various resonance lines with respect to the neat liquids are slightly less than those of butenes adsorbed in NaY type zeolites [1, 2]. For but-1-ene molecules adsorbed on 88 CaNaY (88% of its Na<sup>+</sup> replaced by Ca<sup>++</sup>) the conversion rate at room temperature is so fast that the process cannot be studied by observing the line intensities unless the temperature is lowered. Thus, the present investigations were carried out with (65...70) CaNaY zeolites allowing a convenient measurement at room temperature or higher temperatures. In the interval from 330 to 350 K the intensities of =CH<sub>2</sub> and =CH— resonances of the normal but-1-ene (*cf.* [2]) decreased while an olefinic resonance line occurs with a resonance shift of  $\sigma \approx 1.3$  ppm (upfield with reference to benzene  $\sigma_{C_6H_6} = 0$ ). The dublett splitting of this line in the spectra without proton decoupling indicates the presence of a =CH— group. An assignment of this line to the =CH— groups of *cis*- and *trans*-but-2-ene (which overlap mutually in the beginning of the reaction is not unambiguous since their CH<sub>3</sub>- resonances are difficult to detect. Presumably, the methyl resonance of *cis*-but-2-ene overlaps with the CH<sub>3</sub> group of but-1-ene.

<sup>13</sup>C-spectra of <sup>\*</sup>CH<sub>2</sub>=CH—CH<sub>2</sub>—CH<sub>3</sub> adsorbed on 67 CaNaY type zeolites

In Fig. 1 spectra for a pore filling factor of  $\theta=0.6$  are given which show the intense line of the labelled =CH<sub>2</sub> group besides signals due to the other carbon nuclei of but-1-ene with natural abundance of <sup>13</sup>C nuclei. The weak line at  $\sigma \approx 1.3$  ppm (upfield with reference to benzene) is obviously due to but-2-ene impurities (about 10% *cis*- and 4% *trans*-but-2-ene in this sample). After heating to 330 K a resonance line appears at 118 ppm (initially overlapping with the weak signal of the unenriched methyl group of but-1-ene). Simultaneously, the fairly weak resonance at 1.3 ppm becomes more intense. These peaks unambiguously indicate the presence of *cis*-but-2-ene. The signal at  $\sigma \approx 112$  ppm is characteristic for the formation of *trans*-but-2-ene. This change in the spectra with time (first order reaction, time constant  $t_{1/2} \approx 200$  min at 333 K) demonstrates that the carbon in the terminal group =CH<sub>2</sub> of but-1-ene is converted into methyl groups of *cis*- and *trans*-but-2-ene, respectively. In the equilibrium the *cis/trans* ratio is equal to 1.6 if one takes the carbon-13 nmr peak areas approximately as a measure for the concentration of species. The neglect of possible differences between the Overhauser factors seems to be no source of error because the equilibrium concentrations of but-2-enes (94%) and but-1-ene (6%) at 300 K roughly agree with values obtained by KALLÓ and SCHAY [8] for the thermal equilibrium of butene isomers in the gas phase.

Similar results have been obtained for pore filling factors of  $\theta \approx 0.2$  (Fig. 2). Especially, there were also no additional lines which point to an intermediate state or to further conversions.

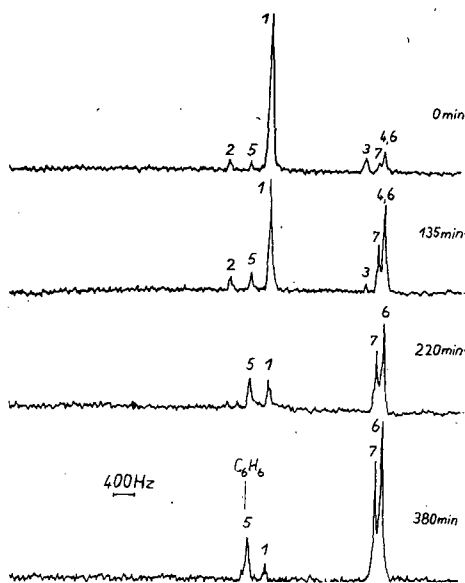


Fig. 1. Carbon-13 nmr spectra of but-1-ene: <sup>\*</sup>CH<sub>2</sub>=CH—CH<sub>2</sub>—CH<sub>3</sub> (\* denotes a 15% enrichment with carbon-13 nuclei), adsorbed on a 67 CaNaY type zeolite with a pore filling factor of  $\theta \approx 0.6$ , during the double bond isomerization: Temperature of measurement 333 K, 4 K scans, pulse interval 0.2 s. Assignment of carbons: but-1-ene: 1 (=CH<sub>2</sub>, enriched), 2,3,4(=CH—, —CH<sub>2</sub>—, —CH<sub>3</sub>, respectively, with natural abundance of nuclei) *cis*-but-2-ene: 5 (=CH—), 6 (—CH<sub>3</sub>, enriched with <sup>13</sup>C after reaction) *trans*-but-2-ene: 5 (=CH—), 7 (—CH<sub>3</sub>, enriched with <sup>13</sup>C after reaction)

<sup>13</sup>C spectra of CH<sub>2</sub>=<sup>\*</sup>CH—CH<sub>2</sub>—CH<sub>3</sub> adsorbed on 67 CaNaY type zeolites

All nmr spectra measured here had a width of 12.5 kHz and were centered near the <sup>13</sup>C nmr resonance of benzene. Since in the low frequency domain no lines appeared, only the right half of these absorption spectra is plotted in Fig. 3.

In this Figure typical spectra are shown for systems with a pore filling factor of  $\theta \approx 0.6$  and a carbon-13 enrichment of 17%. Besides signals of the labelled group

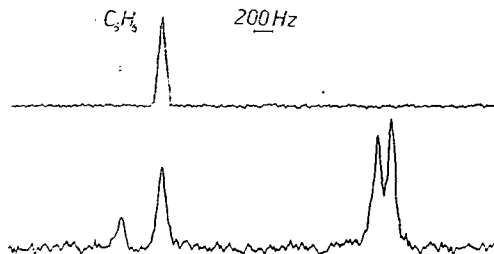


Fig. 2. Carbon-13 nmr spectra of but-1-ene  $^*CH_2=CH-CH_2-CH_3$  (\* denotes a 15% enrichment with carbon-13 nuclei) adsorbed on a 67 CaNaY type zeolite with a pore filling factor of  $\theta \approx 0.2$ : Top spectrum (8 K scans): measurement at room temperature. Bottom spectrum (4 K scans): measurement during the reaction at 333 K.

$=CH-$  of but-1-ene no other peaks could be detected below 310 K which should be attributed to other carbon-13 enriched groups. At 323 K and higher temperatures the group  $=CH-$  of but-1-ene transforms into the group  $=CH-$  of the but-2-enes. The assignment of the new line is based upon its resonance frequency ( $\sigma \approx 1.3$  ppm upfield to benzene) and its doublet structure in spectra without proton decoupling.

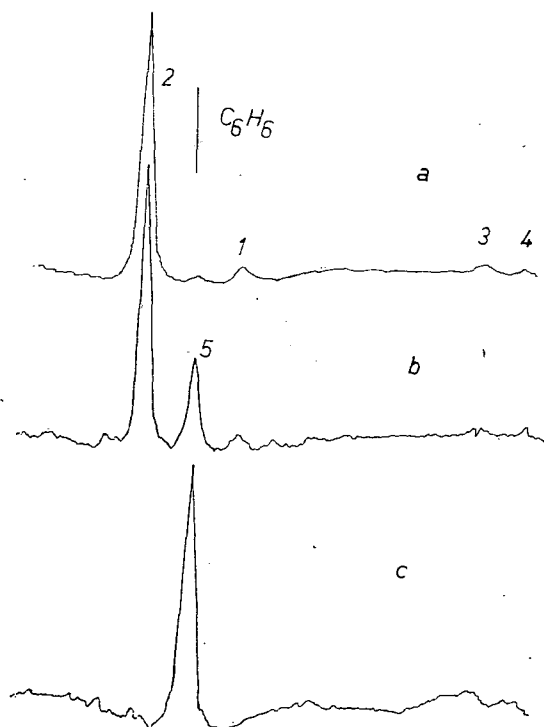


Fig. 3. Carbon-13 nmr spectra of but-1-ene  $CH_2=^*CH-CH_2-CH_3$  (\* denotes a 17% enrichment with carbon-13 nuclei), adsorbed on 67 CaNaY type zeolites with a pore filling factor of  $\theta \approx 0.6$ , during the double bond isomerization. Measurements a) at 300 K before reaction (16 K scans), b) at 350 K during the reaction (8 K scans), c) at 300 K after reaction (8 K scans). Pulse interval 0.16 s.

Assignment of carbons:  
 but-1-ene: 2 ( $=CH-$ , enriched), 1,3,4 ( $=CH_2$ ,  $-CH_2-$ ,  $-CH_3$ , with natural abundance, respectively)  
 but-2-enes: 5 ( $=CH-$ , enriched after reaction).

In agreement with the former spectra (where the methyl resonances of but-2-enes were observed when starting with the  $^*CH_2=$  labelled but-1-ene) this signal can be attributed unambiguously to but-2-enes. It was possible to obtain results also for very low pore filling factors ( $\theta=0.07$ ) in the case of but-1-ene enriched with 50%  $^{13}C$  nuclei in the position  $=CH-$  (Fig. 4). Similarly, a transformation of this group of but-1-ene into the respective group of but-2-ene molecules was found as a consequence of double bond isomerization. The absence of further signals again is typical for the experiments so far. However, as will be discussed in more detail elsewhere [5], much more involved spectra are obtained after heating the samples to temperatures above 360 K. This is due to polymerization reactions where the presence of numerous overlapping lines leads to fairly broad resonances even in the case of high carbon-13 enrichments. This line broadening is probably the reason for the (apparent) single line spectrum mentioned in [2].

#### 4. Conclusions

i) The application of carbon-13 Fourier transform nmr technique enables the observation and investigation of highly resolved nmr spectra of adsorbed molecules. As could be shown in this work the nmr method is a powerful tool for studying heterogeneous catalytic reactions *in situ*.

ii) The use of molecules enriched with carbon-13 nuclei in defined positions, not only facilitates the assignment of the lines and the measurement of signal for very low pore filling factors, but also enables the investigation of the change of the bond of the respective carbons during the catalytic reaction. Hence, new insights into elementary steps of catalytic processes become possible.

iii) As an example, the *n*-butene isomerization has been investigated at room temperature and higher temperatures using CaNaY type zeolites where 67% of  $Na^+$  ions were replaced by  $Ca^{++}$ . This catalytic process has been chosen not only because of the great number of kinetic and spectroscopic work already done [6–10], but also because of the lack of further reactions in the case if the measurements are restricted to a certain temperature interval (300 to 350 K). At temperatures above 350 K polymerization reactions occur which can be inferred from the overlap of numerous lines in that region of  $^{13}C$  resonances where in general signals of aliphatic  $CH_n$  ( $n=0, \dots, 3$ ) groups appear.

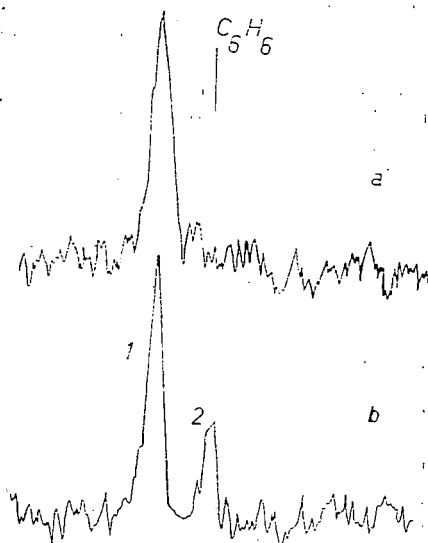
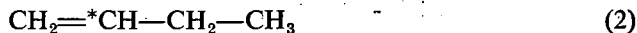


Fig. 4. Carbon-13 nmr spectra of but-1-ene  $CH_2=^*CH-CH_2-CH_3$  (\* denotes a 50% enrichment with carbon-13 nuclei), adsorbed on 67 CaNaY type zeolites with a pore filling factor of  $\theta \approx 0.07$ . Measurements (16 K scans) a) at 300 K before reaction, b) at 340 K during reaction. Pulse interval 0.16 s. Assignment of carbons: 1 and 2 ( $=CH-$  groups of but-1-ene and but-2-enes, respectively). Carbons with natural abundance of  $^{13}C$  nuclei were not detected.

The interpretation of data is based on conversions of but-1-enes which were partially enriched with carbon-13, viz.



and



where \* denotes the carbon-13 labelling which amounts to 15 and 50%, respectively.

iv) Within the limits of experimental error the labelled nuclei were found only in the  $-CH_3$  groups and  $-CH=$  groups of *cis*- and *trans*-but-2-ene if the reaction started with but-1-ene molecules of type (1) and (2), respectively. Hence, a cyclic intermediate structure with four identical carbons can be excluded which, when participating in the conversion, should lead to a random distribution of carbons in the but-2-ene molecules formed.

v) In agreement with conclusions of WEEKS and BOLTON [9], the double bond isomerization of *n*-butenes is a pure intramolecular reaction.

#### References

- [1] Michel, D.: Surf. Sci. **42**, 453 (1974).
- [2] Michel, D., W. Meiler, H. Pfeifer: J. molec. Catalysis **1**, 85 (1975/76).
- [3] Kriz, J. F., I. D. Gay: J. Phys. Chem. **80**, 2951 (1976).
- [4] Meister, P.: Diplomarbeit, Sektion Physik der Karl-Marx-Universität, Leipzig 1975.
- [5] Michel, D., et al.: to be submitted to J. molec. Catalysis.
- [6] Jutand, A., H. Vivien, J. Conard: Surf. Sci. **32**, 258 (1972).
- [7] Fraissard, J., S. Bielikoff, B. Imelik: C. R. Acad. Sc. Paris **271**, 897 (1970).
- [8] Kalló, D., G. Schay: Acta Chim. Acad. Sci. Hung. **39**, 183 (1963).
- [9] Weeks, Th. J. jr., A. P. Bolton: Chem. Soc. Faraday Trans. I **70**, 1676 (1974).
- [10] Baranski, A., S. Ceckiewicz, J. Galuszka: Bull. Acad. Pol. Sci., Ser. Chim. **24**, 645 (1976).