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^{13}C NMR Investigation of the Isomerization of 1-Butene on a Synthetic Near-Faujasite Germanium Zeolite

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^{13}C Nuclear magnetic resonance has been used to study the isomerization of 1-butene to the 2-butene isomers, the reaction being conducted at 573 K and below monomolecular coverage. The NMR data enable the reaction kinetics to be determined and the absence of polymerization to be proved. They also enable the equilibrium constants (at 573 K) between the various isomers to be measured. By comparison of the latter with gas-phase data, the relative adsorption constants can be calculated for both the *cis*-2- and *trans*-2-butene isomers. *cis*-2-Butene is found to be more stabilized upon adsorption than *trans*-2-butene. Although the adsorbed butene species observed by NMR are identified as π-complexes with active sites on the surface (probably Na^+ ions), it is proposed that the isomerization reaction occurs at 573 K via a cyclic transition state involving the butene molecule and the simultaneous presence of an acidic and a basic Brønsted site on the surface. That explains the differences in activity and selectivity (toward the formation of *cis*-2-butene) between the NaGeX and the NaHGeX zeolites. The equilibrium constants between the various isomers in the adsorbed state differ from the corresponding gas-phase values because of differences in the adsorption constants of the various isomers.

INTRODUCTION

Although the isomerization of *n*-butenes has been extensively studied over various catalysts (*1*), only very few investigations report the direct observation, by ^{13}C nuclear magnetic resonance (CNMR), of the interconversion between these olefins. Michel *et al.* (*2*) have studied the isomerization of 1-butene on a NaCaY (67% Ca) zeolite while Kriz and Gay (*3*) followed the transformation of 1-butene and *cis*-2-butene on alumina. More recently, we detected the 2-butene products starting from 1-butene after adsorption of the latter on a properly activated HY zeolite (*4*). Unfortunately, because of the simultaneous polymerization side-reaction(s), no quantitative kinetic and thermodynamic (equilibrium ratios) data could be derived.

The kinetics of the isomerization of *n*-butenes have recently been investigated (*5*) over a partially acidified synthetic near-faujasite germanium zeolite, NaHGeX (Na and H indicate that the counterions are, respectively, Na^+ and H^+; Ge indicates that Si is substituted by germanium, and X refers to the crystal structure). The work indicated that polymerization was almost nonexistent on this type of catalyst. In the present study, the pure sodium form,

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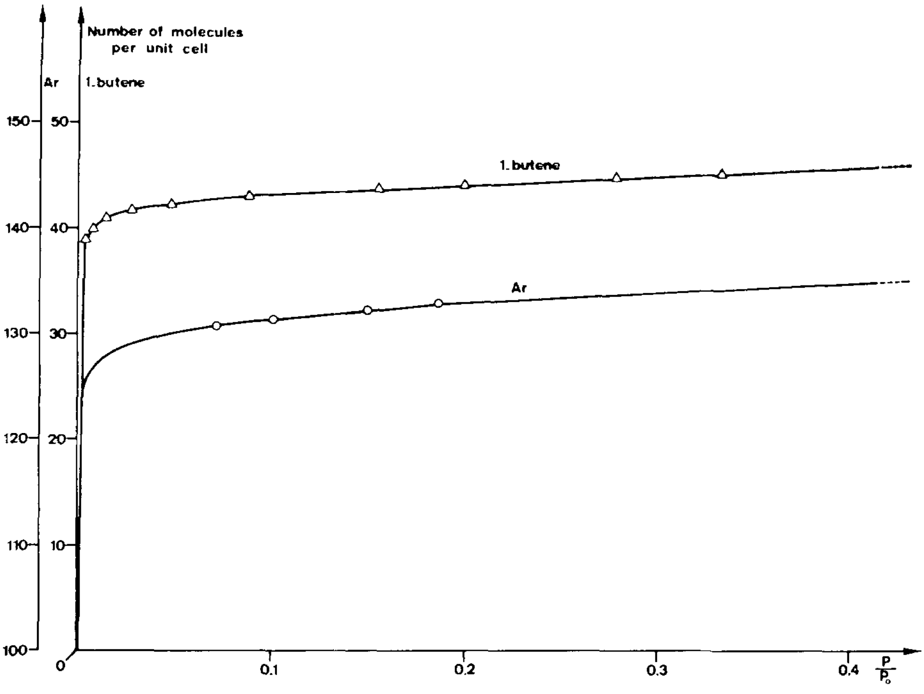


FIG. 1. Adsorption isotherms of 1-butene (△, 291 K) and Argon (○, 77 K) on the NaGeX zeolite activated at 573 K.

NaGeX, has been used, and it will be shown that no polymerization at all occurs on its surface.

The absence of the polymerization side-reaction enables us to reach two objectives. The first is to show that CNMR can be used to provide *quantitative data on catalytic* (surface) *reaction kinetics* using an amount of reagent *below monomolecular coverage* (i.e., in conditions where diffusion effects are likely not to interfere) provided the necessary conditions for such an achievement are met and optimized. The second is to demonstrate that CNMR is a suitable means for the determination of *equilibrium constants in the adsorbed state.* In such conditions, the catalyst does participate in the reaction, and the observed equilibrium constant in the adsorbed state must differ from the corresponding value in the gas phase. Differences between these values, as we shall show, are explained by the nature of the surface complex and the respective values of the adsorption constants for both the reagents and products.

EXPERIMENTAL

The NaGeX zeolite was progressively dehydrated and activated up to 573 K and at a final pressure of $2 \cdot 10^{-6}$ Torr.

The adsorption isotherm of 1-butene was measured at 291 K using a Sartorius electrobalance. Saturation, as seen from Fig. 1, corresponds to about 141 mg of butene/g of zeolite, i.e., about 47 1-butene molecules per unit cell. Assuming that the adsorbed phase and the liquid have the same density in the same conditions, one calculates from the extrapolated density value (*18*) (0.595) a porous volume of 0.237 cm^3 g^{-1}. In this approximation, the effective volume of a 1-butene molecule, is 0.156 nm^3, and its corresponding effective surface is approximately 0.35 nm^2. An Ar adsorption isotherm (data also shown in

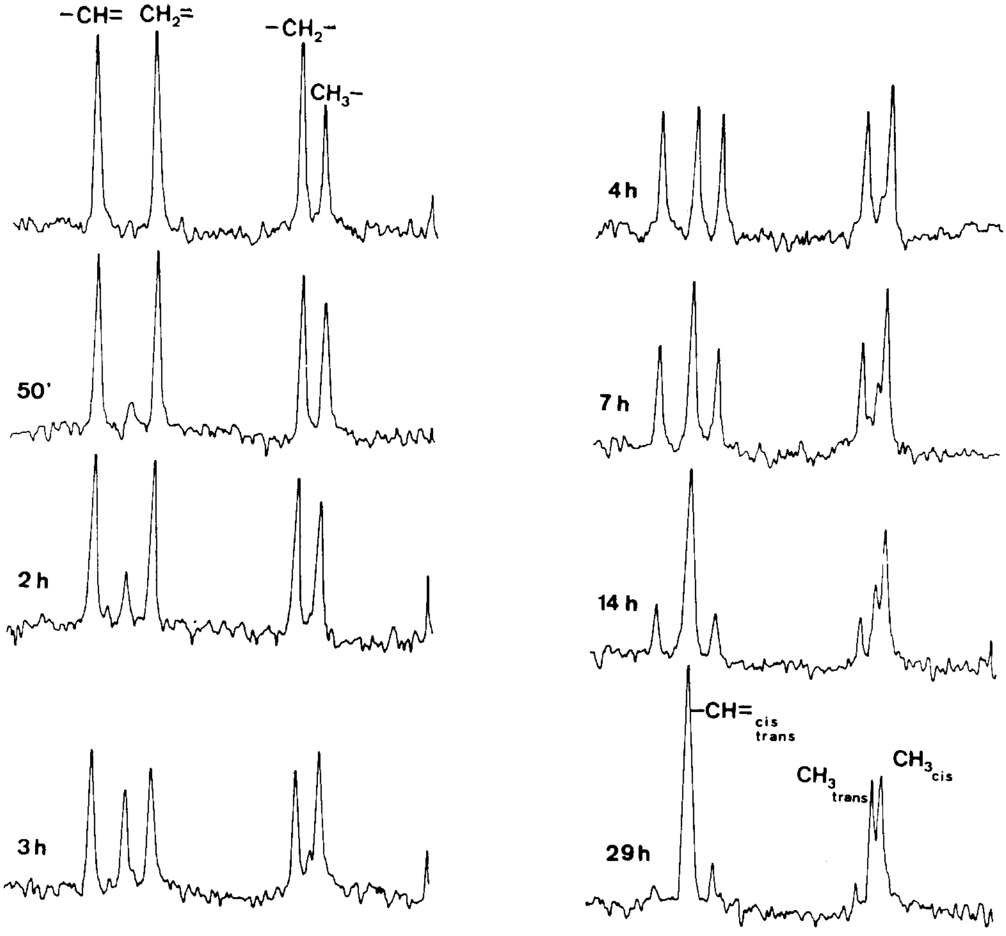


FIG. 2. CNMR spectra observed at various time intervals during the isomerization of 1-butene at 573 K. Spectra are recorded at 293 K.

Fig. 1) leads to a porous volume of about 0.20 $cm^3 g^{-1}$, in good agreement with the above value for 1-butene adsorption and previous data (*6*).

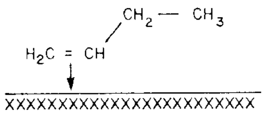
For the NMR measurements, 1-butene was directly adsorbed in the NMR cell at 291 K so as to fill about 80% of the porous volume as measured previously. This will be referred to as a coverage, θ, equal to 0.8. It corresponds to about 37 1-butene molecules per unit cell. The kinetic data were obtained for the reaction conducted at 573 K, by recording spectra at variable time intervals after quenching the reaction by rapidly cooling the NMR cell to room temperature. Quenching at room temperature was checked to be very effective as the CNMR spectrum did not change when a sample was left for 1 month at 298 K. CNMR spectra were obtained using a Bruker WP-60 spectrometer equipped with an external D_2O lock stabilization of the magnetic field. The spectra were calibrated via the carrier spectrometer frequency (*4*). The standard error on chemical shifts is ±0.2 ppm. Each spectrum consists of an accumulation of 2000 scans using a 3-μsec pulse length under broad-band proton decoupling. The gated sequence 4 s–1 s–0.1 s was used to record the nuclear Overhauser effect (NOE)-suppressed decoupled spectra in order to obtain quantitative values for the relative intensities.

RESULTS AND DISCUSSION

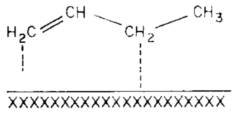
The Chemical Shifts of Adsorbed Butenes

Figure 2 shows the progressive transformation of the CNMR spectrum of 1-butene after variable time intervals at 573 K. The chemical shifts, in parts per million from TMS (tetramethylsilane), of the carbons from the $-CH_3$, $-CH_2-$, $CH_2=$, and $-CH=$ groups are, respectively, 12.7 (−0.2), 26.9 (0), 112.5 (−0.5), and 146.6 (+6.4), the values in parentheses giving the change in chemical shift relative to the liquid state (*4*). For the *cis*- and *trans*-2-butenes, the chemical shifts are: CH_3- (*cis*), 12.3 (+1.7); CH_3- (*trans*), 17.7 (+0.7); $-CH=$ (*cis* and *trans*), 127.8 (+4.5 and +13.2).

The above values and the spectra shown in Fig. 2, i.e., the chemical shift values and the relative peak intensities, are characteristic of a π-type adsorbed complex formed between the *n*-butenes and the surface (*4*, *7*) as illustrated for 1-butene (A). It is worth remembering, however, that a cyclic type adsorbed complex (B) can be observed on the HY zeolite (*4*) and also on the present NaGeX zeolite below 240 K (*7*).



(A)



(B)

One can still raise the question of whether or not the observed chemical shifts really reflect the intimate nature of the adsorbed species. The answer can be found in the adsorption data.

Indeed, it was found that saturation of the zeolite by 1-butene corresponded to about 47 molecules per unit cell or about five or six 1-butene molecules for each supercage (there are eight supercages per unit cell). As in the NMR experiments, only 80% of the 1-butene saturation amount is actually adsorbed (see experimental); one deals with about 37 butene molecules per unit cell or an avarage of 4.5 molecules per supercage. If one now considers that in such nonacidified zerolites mainly sodium cations will act as potential adsorption sites (*16*), there being a maximun of four S_{II} sites per supercage, 32 butene molecules can be expected to be rather strongly adsorbed on the surface, the others being weakly adsorbed or in the inner part of the supercage cavity. Hence, for the NMR experiments, one can consider that about 90% of the butene molecules actually do directly interact with the surface of the zeolite. NMR spectra can then be considered as representative of the adsorbed phase in the present study. [This is often not the case for other literature data, and it points out the need for quoting exact coverage or adsorption condition parameters; see, for example, discussions in ref. (*28*).] For higher surface coverage, and assuming rapid exchange between the "wall-adsorbed" and the "inner-adsorbed" molecules in the supercages, the observed chemical shifts should approach those observed in the liquid state. That seems effectively to be the case (*2*, *17*) although chemical shift variations with surface coverage are rather small for θ values near unity.

The Isomerization of 1-Butene

At 573 K, first-order kinetics are strictly obeyed for the disappearance of 1-butene and the formation of the 2-butenes (*cis*

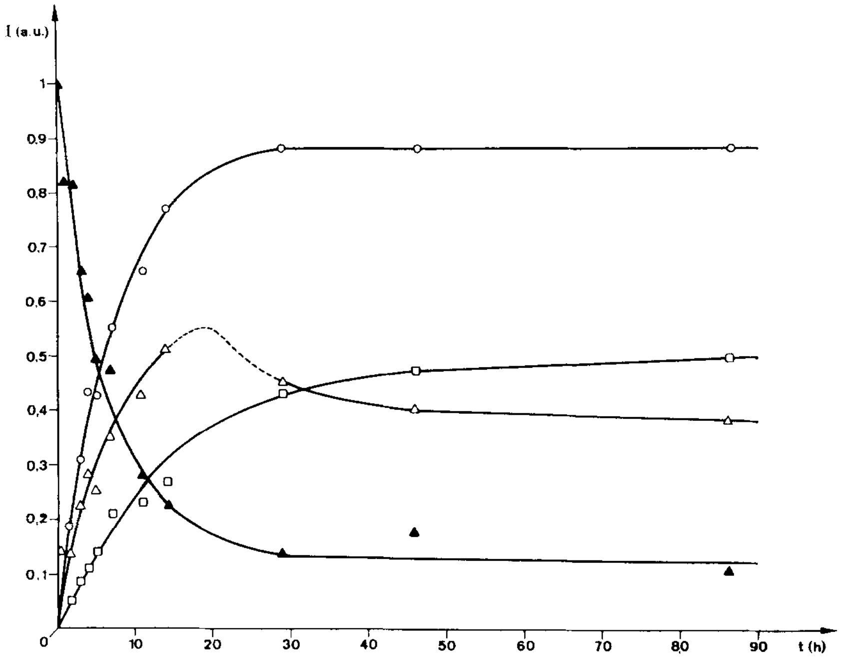


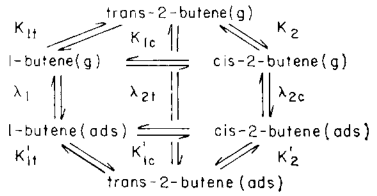
FIG. 3. Kinetics of 1-butene isomerization at 573 K as obtained from the NMR signal intensities: ▲, 1-butene; △, *cis*-2-butene; □, *trans*-2-butene; and ○, *cis*-2- and *trans*-2-butenes.

plus *trans*) as evidenced by logarithmic plots of the intensity variations (vs time) shown in Fig. 3. The apparent rate constants, k_{app}, for the disappearance of 1-butene and the formation of the 2-butenes are exactly equal within the experimental error (0.140 ± 0.001 hr^{-1}), proving unambiguously that no polymerization takes place under our experimental conditions.

From the kinetic data reported in Fig. 3, it is also clear that *cis*-2-butene is formed preferentially in the early stage of the reaction and that the geometric *cis–trans* isomerization is slower than the double-bond shift.

From the NMR data, the equilibrium ratios (i.e., the equilibrium constants) between the various isomers adsorbed on the zeolite have been calculated. They are compared in Table 1 with the corresponding values in the gas phase at 573 K (*8*, *9*). Considering the estimated 5% error on the NMR intensities, the observed difference between the equilibrium constants in the adsorbed state and in the gas phase appears to be very significant.

This discrepancy can be explained by considering the following scheme which combines all possibilities for the isomerization of the *n*-butenes:



where (g) and (ads), respectively, indicate gaseous and adsorbed species, with K_i and K'_i being equilibrium constants and λ_i the adsorption constant.

From the 1-butene adsorption isotherm (Fig. 1), correcting for the difference in temperature and assuming a Langmuir isotherm, one can derive the absolute value of the adsorption constant of 1-butene on

TABLE 1

Equilibrium Constants at 573 K for the Various *n*-Butene Isomers Adsorbed and in the Gas Phase

K_2 or K'_2[a]	K_{1c} or K'_{1c}[b]	K_{1t} or K'_{1t}[c]	Reference
1.3	3.1	4.0	Adsorbed, this work
1.60	1.54	2.46	Gas phase (*9*)
1.48	1.92	2.85	Gas phase (*8*)

[a] K_i and K'_i are corresponding values in the gas phase and the adsorbed state. K_2 = (*trans*-2-butene)/(*cis*-2-butene).

[b] K_{1c} = (*cis*-2-butene)/(1-butene).

[c] K_{1t} = (*trans*-2-butene)/(1-butene).

the NaGeX zeolite at 573 K, i.e., $\lambda_1 = 5\cdot 10^{-2}$ Torr^{-1}. The adsorption constants of the *cis*- and *trans*-2-butene isomers can also be estimated, relative to λ_1, by considering the former equilibria and the data reported in Table 1. Indeed, it is seen that:

$$\frac{K'_{1,\mathrm{c\ or\ t}}}{K_{1,\mathrm{c\ or\ t}}} = \frac{\lambda_{2,\mathrm{c\ or\ t}}}{\lambda_1}$$

The relative adsorption constants for the *n*-butenes on NaGeX, calculated in this manner, are reported in Table 2 where they are also compared with experimental values measured on NiO at 533 K [from competitive oxidation data, ref. (*10*)] and to the relative stabilization energies of the π-complexes of the *n*-butenes with bromine in solution in Freon 112 (*20*). The respective ionization energies of the *n*-butenes have also been indicated in Table 2.

The very same trend exists between the relative adsorption constants for the *n*-butenes adsorbed on NiO and on the NaGeX zeolite. In addition, the data for both systems follow the variations of the ionization energies for the *n*-butenes as well as of the relative stabilization energies when the *n*-butenes make π-complexes with Br_2. (It is useful to remember at this point that the smaller the stabilization energy Γ_i, the stronger is the bonding in the charge transfer complex (*22*) because of increased resonance between purely covalent and purely ionic extreme forms.) Hence, a self-consistent picture can be proposed for all three systems: The lower the ionization energy of the donor molecule, the lower is the relative stabilization energy of the charge transfer complex, and hence the higher is its stability, the latter being reflected in the relative adsorption constant due to charge transfer between the adsorbate and an active surface site.

The former analysis of our own and of other experimental data leads to two important conclusions. First, it brings further support to the identification of the *n*-butenes as π-complexes with the surface of the NaGeX zeolite. Second, the observed parallelism between the variations of λ_i/λ_1 (for NaGeX and NiO) and Γ_i (for Br_2 as acceptor) could possibly indicate that backbonding from the Ni^{2+}d orbitals plays no role in the formation of the butene to surface bond on NiO, as d orbitals cannot participate in the bonding in the two other systems. From the values of the relative adsorption constants, λ_i/λ_1, one can also estimate that, at 573 K and on NaGeX, *cis*-2-butene is more stabilized than *trans*-2-butene upon adsorption.

The higher adsorption constant of *cis*-2-butene (hence, the higher stability of the complex) as compared to *trans*-2-butene, although not observed in NiO or by complexation with Br_2, is not unique. Indeed such a possibility was already pointed out following olefin isomerization studies on alumina (*25*). Quantum theoretical calculations by Chuvylkin *et al.* (*14*, *27*) in the CNDO-2 approximation show no correlation between the calculated charge density of the π-bond and the relative adsorption constants. The same is true if more reliable and sophisticated calculations are undertaken, for example, using an *ab-initio* STO-3G approach (*26*). Hence, the difference in the adsorption constants should probably not be assigned to differ-

TABLE 2

Relative Adsorption Constants of Butenes on NaGeX and NiO and Relative Stabilization Energies of the Charge-Transfer Complexes between *n*-Butenes and Br_2[a]

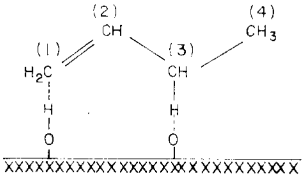
Electron donor	Ionization energy (eV) (*21*)	λ_i/λ_1(NaGeX) (573 K)	λ_i/λ_1(NiO) (533 K) (*10*)	Γ_{rel} (*20*)
1-Butene	9.73	1	1	1
cis-2-Butene	9.31	2	1.45	0.63
trans-2-Butene	9.28	1.64	1.46	0.61

[a] See text for definition and evaluation of λ_i/λ_1. $\Gamma_{rel} = (\Gamma_i - \Gamma_{TME})/(\Gamma_{1\text{-butene}} - \Gamma_{TME})$; relative stabilization energy for the charge-transfer complex. Tetramethylethylene (TME) is used as reference. Γ_i is the energy difference (in kilocalories per mole) between the ionic form and the nonbonding state as obtained from the charge-transfer absorption band for the complexes with bromine (*22–24*).

ences in electronic structure but rather to steric or entropy effects.

On the basis of proton NMR relaxation time measurements for *n*-butenes adsorbed on NaX and NaY zeolites (the surface coverage spanning the range 0.5 to 0.8), Kärger and Michel (*19*) also concluded that there was a stronger interaction of *cis*-2-butene with Na^+ ions than for the *trans*-2- and 1-butenes. It is very well known that NMR relaxation data closely reflect the state of motion of surface species, this being sensitive to both bonding to the surface and steric effects. Possibilities for the latter are steric hindrance to diffusion through the windows linking the supercages (*19*), and also, in our view, the fact that a U-shaped molecule like *cis*-2-butene would fit more easily on the wall of a spherical supercage than a linear molecule such as *trans*-2-butene.

The first-order kinetic rate constant (0.14 hr^{-1}) that we measure at 573 K on the NaGeX zeolite is five times lower than the value reported on the NaHGeX (20% protonated) zeolite (*5*). A second difference between the kinetic behavior on the protonated and unprotonated materials can be found in the initial rates of formation of the *cis*-2- and *trans*-2-isomers from 1-butene. Indeed, the geometric isomerization is also slower on the NaGeX zeolite and the initial *cis*-2/*trans*-2-butene ratio is found by NMR to be equal to 3.7 (see Fig. 3). The latter is equal to k_{1c}/k_{1t}, with k_{1c} and k_{1t} being the first-order rate constants for the isomerization of 1-butene to *cis*-2-butene and trans-2-butene, respectively (*11*). This value is much larger than the one reported on the NaHGeX zeolite (*5*) (k_{1c}/k_{1t} = 0.76), but it compares very well to the *cis*-2/trans-2-butene ratio of 4.4 observed on more basic catalysts like alumina activated at 973 K (*11*). The high *cis*-2- to *trans*-2-butene ratio suggests a carbanion-type mechanism, where the *cis*-isomer is more stabilized than the trans-isomer (*1b*, *12–14*). Our results could then be interpreted, as proposed previously for basic catalysts (*1b*, *12*), by the existence of a cyclic-type transition complex:



in which the cyclic tranfer of protons must be asynchronous in order to allow the formation of a carbanion-like transition state. The breaking of the C3–H bond must precede the formation of the C1-H bond.

It is interesting to note that such a cyclic adsorbed transition complex has been observed below 240 K on the zeolite (7). The fact that it is not observed above that temperature by NMR does not mean that it is not present: Either its concentration is too low (it should be in equilibrium with the π-complex) and/or its lifetime is smaller than 10^{-8} s (NMR will not detect species with lifetime shorter than the Larmor period), decreasing lifetime and concentration eventually meaning increasing reactivity possibily leading to isomerization.

Our proposed mechanism further requires the simultaneous presence of an acidic and of a basic Brønsted site as also suggested previously (*15*). Obviously, if the surface acidity is increased (for instance, by exchanging Na^+ by protons in NaGeX), the protonation of the starting 1-butene (i.e., for formation of the C1–H bond) is easier and that results, as observed experimentally (*5*), in a carbonium-type transition state leading to a *cis*-2- to *trans*-2-butene ratio close to unity.

No data, at present, enable us to propose a mechanism for the geometric isomerization of the 2-butenes.

CONCLUSIONS

The present CNMR study shows clearly some distinct features concerning the isomerization of 1-butene on an NaGeX zeolite.

First, the complete absence of polymerization is established. Second, this material is found to increase the selectivity toward the formation of *cis*-2-butene, most probably via a cyclic carbanion-like transition state where a concerted but asynchronous proton transfer occurs between the adsorbate and the surface. Third, 1-butene and *cis*-2- and *trans*-2-butenes are adsorbed on NaGeX, at room temperature, as π-complexes, as evidenced by the parallelism which exists between their adsorption equilibrium constants and some parameters characteristic of charge transfer complexes. The adsorption constants are different for the various isomers, and therefore the equilibrium constants for the 1-butene to 2-butenes isomerization in the adsorbed state differ from the gas-phase values.

In more general terms, the present investigation also proves that CNMR can indeed be considered as a useful means for the study of catalytic reactions and the identification of surface processes and intermediates, provided that care is taken to assess the validity of the experimental parameters, i.e., the full significance of the chemical shifts and peak intensities.

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