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Study of the Isomerization of *n*-Butenes on Alumina Impregnated with Na_2CO_3 Using Gas Chromatographic Technique*

S. OGASAWARA† AND R. J. CVETANOVIĆ

From the Division of Applied Chemistry, National Research Council, Ottawa, Canada

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Isomerization of *n*-butenes has been studied on Al_2O_3 impregnated with 5 wt % Na_2CO_3 using the gas chromatographic technique. The adsorption equilibrium constants, the rates and the activation energies of the isomerization reactions have been determined simultaneously. The isomerization reactions are of first order in the reactant olefins. Their mechanism is discussed in the light of the obtained results.

INTRODUCTION

Catalytic isomerization of *n*-butenes is potentially of considerable fundamental interest. The process is relatively simple and its study could be of significance for the understanding of the catalytic behavior of olefins in general.

An interesting feature of the catalytic isomerization of *n*-butenes is the preferential formation of the thermodynamically *less* stable isomers in the initial stages of the process. This "stereoselectivity" has been recently investigated by Haag and Pines (*1, 2, 3*) Lucchesi *et al.* (*4*), Foster and Cvetanović (*5, 6*), and Brouwer (*7*). Not infrequently in these reactions the double bond migration occurs more readily than the *cis–trans* isomerization. The relative extent of the two isomerization processes is strongly dependent on the type of catalyst used and may also be varied by altering the surface properties of the catalyst. The stereospecificity observed with alkaline catalysts has been discussed in terms of the usually postulated carbanion mechanism (*1, 2*) while the carbonium ion mechanism has been considered in the case of acidic catalysts (*3*). Significant distinctions between typical acidic and basic catalysts have been found (*6*); the ease of *cis–trans* isomerization has been ascribed to the readily occurring free rotation in the intermediate carbonium ions while the double bond migration has been considered from the point of view of a dissociative mechanism (with formation of chemisorbed carbanions or radicals) or alternatively the concerted ("hydrogen switch") mechanism. A study of butene isomerization on several solid acids has led to the suggestion that on these catalysts *cis–trans* isomerization results from carbonium ion formation while double bond migration occurs by the hydrogen switch mechanism (*7*).

In the present work the gas chromatographic technique was used to obtain simultaneously the adsorption equilibrium constants and the rates of butene isomerization reactions. The reaction order and the activation energies have been determined and the reaction mechanism is discussed. Alumina impregnated with 5 wt % Na_2CO_3 served as the catalyst. The impregnated alumina was chosen because of its relatively low activity, which permitted work at low conversions, and because it exhibited a direct proportionality of the adsorbed amounts of the olefins to their partial pressures in the vapor phase, as discussed elsewhere (*8*).

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† N.R.C. Postdoctorate Fellow 1960–62.

EXPERIMENTAL

The experimental arrangement consisted of a conventional gas chromatographic apparatus with a packed column of the catalyst and a thermal conductivity detector (a Gow-Mac thermal conductivity cell). The experiments were carried out at pressures lower than atmospheric. The general outline of the apparatus is shown in Fig. 1.

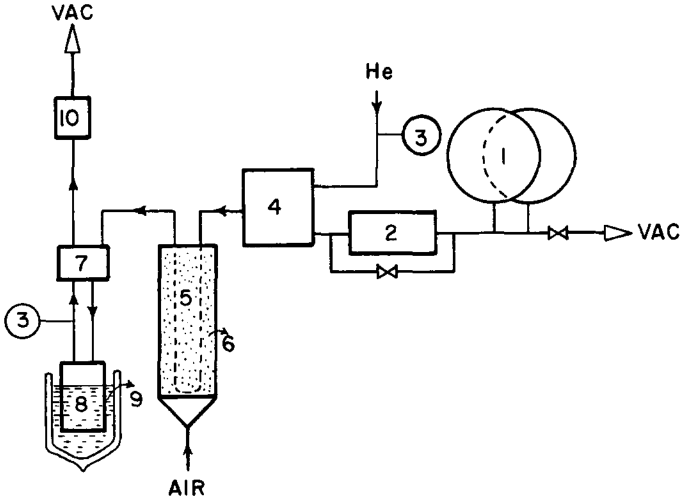


FIG. 1. Schematic diagram of the apparatus. 1. Storage bulb. 2. Sample measuring device. 3. Manometer. 4. Sample injection device. 5. Column. 6. Fluidized bed. 7. Detector. 8. Sample collecting tube. 9. Liquid nitrogen. 10. Pressure regulator.

The preparation and pretreatment of the catalyst have been described in another publication (*8*). The experimental conditions used are summarized in Table 1.

TABLE 1

EXPERIMENTAL CONDITIONS

Catalyst	Al_2O_3[a] + 5 wt % Na_2CO_3
Column length	240 cm
Catalyst weight and volume	35.4 g, 40 cc
Carrier gas	He
Flow rate	Ca. 10 cc/min (at 25°C, 1 atm)
Temperature	100–170°C
Sample size	1–10 μmole
Sample gases	Butene-1, *trans*-butene-2, *cis*-butene-2[b]
Pressure ratio (inlet/outlet)	5.3–5.8

[a] Alcoa (F-20), 80–200 mesh.

[b] Phillips research grade.

A known amount of sample was injected into the column as a pulse and the effluent gas from the column was collected in a liquid nitrogen trap for further analysis. For the gas chromatographic analysis of the products, dimethyl sulfolane on alumina and propylene carbonate on Celite columns were used alternatively.

RESULTS

The irreversible adsorption in the system used was found to be relatively quite small and has been ignored. The chromatographic peaks were nearly symmetrical, indicating a direct proportionality between the adsorbed amounts of the reactants on the catalyst surface and their vapor pressures in the gas phase. The adsorption equilibrium constants (K) can be calculated in this case (*8, 9*) from the following equation

$$V_R^0/W = KRT \qquad (1)$$

where V_R^0 is the corrected retention volume, W is the total weight of the catalyst, R is the gas constant, and T the absolute temperature.

The use of Eq. (1) to determine the heats of adsorption has been outlined in the earlier communication (*8*). For present purposes, the adsorption constants have been calculated directly from the same data and their values for *cis*-butene, *trans*-butene, and butene-1 at different temperatures are shown in Fig. 2. The adsorption constants of the three isomers are seen to be practically the same at the same temperatures.

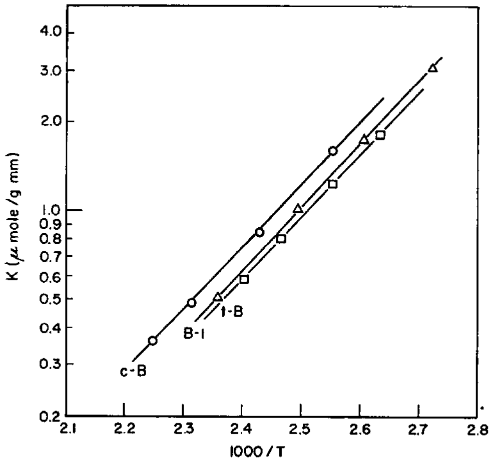


FIG. 2. The dependence of the adsorption equilibrium constants on temperature (c-B = *cis*-butene-2; B-1 = butene-1; t-B = *trans*-butene-2).

As pointed out in the introduction, it was possible with the treated alumina catalyst used to restrict the isomerization reactions to very low conversions. As an example, in Table 2 the percentage conversions at 119° and 150°C are compared with the corresponding equilibrium compositions.

TABLE 2

COMPARISON OF THE PERCENTAGE CONVERSIONS AT 119° AND 150°C WITH THE CORRESPONDING EQUILIBRIUM VALUES

Reaction	Per cent conversions and equilibrium compositions At 119°C	At 150°C
B-1 ↗ c-B[a]	1.64	2.30
B-1 ↘ t-B[a]	0.73	1.24
c-B → t-B[b]	4.0	6.0
t-B → c-B[b]	1.95	3.1
(B-1)$_e$[c]	5.4	6.7
(t-B)$_e$[c]	65.1	62.3
(c-B)$_e$[c]	29.5	31.0
c-B/t-B(observed)	2.24	1.86
(c-B)$_e$/(t-B)$_e$	0.454	0.487

[a] c-B = *cis*-butene; t-B = *trans*-butene; B-1 = butene 1.

[b] Butene-1 formed from *cis*- and *trans*-butene was too small to measure.

[c] Equilibrium composition calculated from the data in ref. (*10*).

The ratios of the two butene-2 isomers formed from butene-1 are compared with the corresponding equilibrium ratios at 119° and 150°C in the last two rows in Table 2. It is evident that in this case as well (*1–7*) *cis*-butene is much more readily formed from butene-1 than the thermodynamically more stable *trans*-butene.

In view of the low conversions it was justifiable to calculate the initial reaction rates by dividing the amounts of the products formed by the retention times. The reaction was found to be of first order in the reactant olefin, as seen from Table 3, where the percentage conversion of butene-1 to butene-2 ($Q_{1\to2}$) divided by the retention time (τ) is seen to be independent of a tenfold variation in sample size.

TABLE 3

FIRST ORDER DEPENDENCE OF THE INITIAL REACTION RATES ON THE SAMPLE SIZE IN THE ISOMERIZATION OF BUTENE-1 TO BUTENE-2

Sample size (μmole)	1.2	5.4	13.0
$Q_{1\to2}/\tau$	1.3	1.4	1.2

The initial rates of the observed isomerization reactions are plotted in Fig. 3 as a

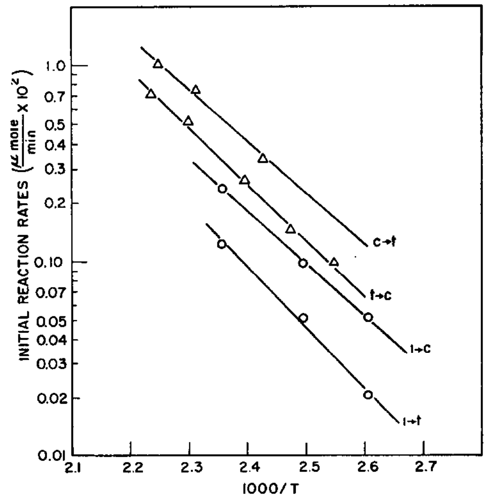


FIG. 3. The dependence of the initial reaction rates on temperature (c,t,1, stand respectively for *cis*-butene-2, *trans*-butene-2, and butene-1).

function of $1/T$. The apparent activation energies (E_{app}) obtained from these plots are given in Table 4 together with the corresponding heats of adsorption ($-\Delta H_{\mathrm{ads}}$) (*8*).

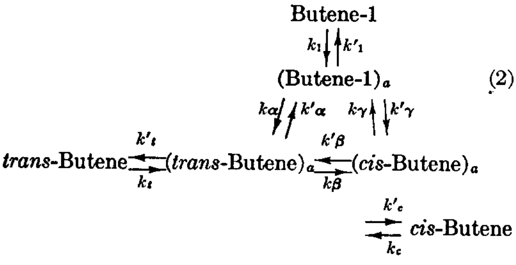
TABLE 4
Apparent Activation Energies (E_{app}) and Heats of Adsorption ($-\Delta H_{\mathrm{ads}}$)

Reaction		E_{app}(kcal/mole)	$-\Delta H_{\mathrm{ads}}$(kcal/mole)
B-1	↗ *c*-B	12.3	9.2
	↘ *t*-B	14.3	
c-B	↗ B-1	—	9.0
	↘ *t*-B	12.7	
t-B	↗ *c*-B	13.5	9.0
	↘ B-1	—	

The activation energy of the isomerization of butene-1 to *cis*-butene (12.3 kcal) is very much the same as found by Brouwer for the same reaction on dry self-poisoned alumina (12.5 ± 0.4 kcal). The difference between the activation energy of the reaction *cis*-butene → *trans*-butene and of its reverse reaction, *trans*-butene → *cis*-butene, should equal the heat of the reaction. The value of 0.8 kcal/mole thus obtained compares well with the corresponding literature (*10*) value of one kcal/mole. It was not possible to measure similarly the initial rates and determine the activation energies of isomerization of *cis*- and *trans*-butene to butene-1 because of the very small amounts of butene-1 formed in these reactions.

Discussion

The results of the present study may first be discussed on the basis of the following formal reaction scheme.



(2)

where the subscript *a* indicates the (physically) adsorbed molecules.

The surface isomerization reactions (α, α', β, β', γ, γ') are unspecified in detail and may include interaction of the (physically adsorbed or gas phase) olefin molecules with the catalytic active sites to form carbonium ions, carbanions, or to undergo isomerization by the concerted hydrogen switch mechanism. A similar formal reaction scheme has been used by Haag and Pines (*2, 3*) to evaluate the relative rates of the six isomerization reactions. Reaction scheme (2), as written, includes the adsorption equilibria as well and the values of the ratios of the adsorption equilibrium constants affect the calculated values of the relative rates of isomerization. However, since the adsorption equilibrium constants of the three *n*-butenes are found to be very similar, the rates of isomerization are not significantly affected; from the point of view of the determination of relative rates of isomerization it is therefore to a good approximation immaterial in this case whether it is assumed that the physically adsorbed or the gas phase molecules enter into the surface isomerization reactions (α, α', etc.).

To calculate the relative rate constants of the surface isomerization reactions in the present work, the following relationships were employed

$$\frac{k'\alpha}{k\alpha} = \frac{K_1}{K_t}\,\frac{(\text{B-1})_{\mathrm{e}}}{(t\text{-B})_{\mathrm{e}}}; \qquad \frac{k'\beta}{k\beta} = \frac{K_t}{K_c}\,\frac{(t\text{-B})_{\mathrm{e}}}{(c\text{-B})_{\mathrm{e}}}; \qquad \frac{k'\gamma}{k\gamma} = \frac{K_c(c\text{-B})_{\mathrm{e}}}{K_1(\text{B-1})_{\mathrm{e}}} \tag{3}$$

$$\frac{[d(c\text{-B})/dt]_0{}^{1\to \mathrm{c}}}{[d(c\text{-B})/dt]_0{}^{t\to \mathrm{c}}} = \frac{k'\gamma}{k'\beta}\,\frac{K_1}{K_t}\,\frac{(\text{B-1})_0}{(t\text{-B})_0} \tag{4}$$

$$\frac{[d(t\text{-B})/dt]_0{}^{\mathrm{c}\to \mathrm{t}}}{[d(t\text{-B})/dt]_0{}^{1\to \mathrm{t}}} = \frac{k'\beta}{k'\alpha}\,\frac{K_c}{K_1}\,\frac{(c\text{-B})_0}{(\text{B-1})_0} \tag{5}$$

where the superscripts $1 \to c$, etc., indicate the isomerization of butene-1 to *cis*-butene, etc., and subscript $_0$ indicates the measured initial rates and the corresponding concentrations of the olefin reactants.

The relative rates obtained in this manner at 119° and 150°C, taking arbitrarily $k'\alpha = 1$, are given in Table 5.

The slowest of the six isomerization reactions on the catalyst used is the double bond migration in the *trans*-butene followed by the same process in the *cis*-butene. Both in the case of *cis*- and *trans*-butene the geometric isomerization is much more rapid than the double bond shift ($k\beta \gg k'\alpha$, $k'\beta \gg k\gamma$). At the same time, in the case of butene-1 the double bond shift occurs quite readily, but the formation of the less stable *cis*-butene then predominates.

TABLE 5
The Relative Rate Constants

	$k\alpha$	$k'\alpha$	$k\beta$	$k'\beta$	$k\gamma$	$k'\gamma$
119°C	11.1	1	25.0	42.6	2.8	18.0
150°C	8.8	1	18.6	29.8	2.3	12.5

The adsorption processes indicated in the reaction scheme (2) are those responsible for finite retention times observed in the present work and are most probably physical in character (including here also such potential interactions as hydrogen bonding or π-complex formation). They are unlikely to be connected with the rate-determining steps in the isomerization reactions. The existence of finite retention times would itself rule out the adsorption as rate controlling, and if the desorption were rate controlling, it would be expected that

$$r_1 = \frac{[d(c\text{-B})/dt]_0^{1\to c}}{[d(c\text{-B})/dt]_0^{t\to c}} = \frac{(t\text{-B})_e}{(\text{B-1})_e}\,\frac{(\text{B-1})_0}{(t\text{-B})_0} \qquad (6)$$

and

$$r_2 = \frac{[d(t\text{-B})/dt]_0^{c\to t}}{[d(t\text{-B})/dt]_0^{1\to t}} = \frac{(\text{B-1})_e}{(c\text{-B})_e}\,\frac{(c\text{-B})_0}{(\text{B-1})_0} \qquad (7)$$

That these relationships are not obeyed is evident from Table 6, in which the ratios of the initial rates are compared with the corresponding isomer ratios at equilibrium [the initial concentrations of the olefins were the same so that $(\text{B-1})_0/(t\text{-B})_0 = (c\text{-B})_0/(\text{B-1})_0 = 1$].

TABLE 6
Comparison of the Ratios of the Initial Rates with the Corresponding Ratios of the Isomers at Equilibrium

Ratios in Eqs. (6, 7)	119°C	150°C
r_1	0.78	0.71
$(t\text{-B})_e/(\text{B-1})_e$	12.1	9.3
r_2	5.2	4.4
$(\text{B-1})_e/(c\text{-B})_e$	0.18	0.31

The experimental results show that the rates of isomerization are proportional to the amounts of olefins passed through the column (i.e. to the sample size) and therefore both to the concentration of the reactant olefins in the gas phase and to the amount adsorbed on the catalyst. The reaction itself involves an activation energy and entails either chemisorption of the olefins on the catalyst surface or a concerted mechanism without chemisorption (the "hydrogen switch" mechanism). In what way the observed activation energies (E_{app}) are related to the activation energies of the rate-determining steps of the isomerization reactions depends on whether reactant molecules from the gas phase or from the physically adsorbed layer, or both, interact with the active sites of the catalyst. Writing, respectively, N_a and N_g for the concentration of the adsorbed and the gas phase molecules of the reactant olefin ($N_a + N_g = N$), and N_s for the concentration of the active sites, the rate of isomerization (R_i) is

$$R_i = k_a \,.\, N_a \,.\, N_s \qquad (8)$$

or

$$R_i = k_g \,.\, N_g \,.\, N_s \qquad (9)$$

with (8) holding if only physically adsorbed molecules and (9) if only gaseous olefin molecules interact with the active sites. If it can be assumed that N_s is temperature independent, then the temperature dependence of N_a and N_g has to be taken into account in determining E_a and E_g from the initial rates per unit sample size. In view of the relationships discussed previously (*8*)

$$N_a/N = V_R^\circ/(V_R^\circ + V_g)$$

and

$$N_g/N = V_g/(V_R^\circ + V_g)$$

where V_g is the void volume of the column. (Neglecting the pressure drop correction, therefore, $N_a/N \approx (t_R - t_0)/t_R$ and $N_g/N \approx t_0/t_R$, t_R and t_0 being the total retention time and the dead time, respectively.) Therefore,

$$k_a = R_i(1 + V_g/V_R^\circ)/N \times N_s$$

and

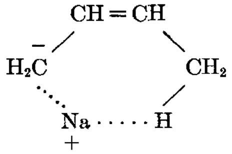
$$k_g = R_i(1 + V_R^\circ/V_g)/N \times N_s$$

As a result, when $V_R^0/V_g >> 1$, as in present experiments, E_{app} is approximately equal either to E_a or to $[E_g + (-\Delta H_{ads})]$, depending on whether the physically adsorbed or the gaseous molecules interact directly with the active sites of the catalyst. If both reactions occur simultaneously, E_{app} represents a composite value of E_a and E_g which depends on their relative importance. Since $V_R^0/V_g >> 1$ in the studied reactions, $N_a >> N_g$, i.e. at any time most of the olefin molecules are adsorbed on the surface of the catalyst. It could be assumed that in this case it is the physically adsorbed molecules which principally enter into the isomerization reactions so that the activation energies of the rate-determining steps of these surface reactions would then be equal to the E_{app} values given in Table 4 to a good approximation. Otherwise the activation energies of the slow steps in these isomerization reactions would have unusually low values.

The identification of the rate-determining steps depends on a detailed knowledge of the reaction mechanisms. These are unfortunately still uncertain. The rate of the surface reaction may be controlled by adsorption into the chemisorbed layer, rearrangement of the chemisorbed molecules, or their desorption. It is unlikely, at least in some cases, that desorption is rate controlling since the desorbed isomers are not equilibrated (*7*). Inasmuch as the hydrogen switch mechanism is indeed involved in some olefin isomerization reactions, the ambiguity disappears and the rate-determining step is then the concerted reaction of the (physically adsorbed or gaseous) olefin molecules with a pair of suitably spaced proton (or hydride ion, or hydrogen atom) accepting and donating sites.

The nature and the mechanism of the interaction of olefins with catalytic substances have been the subject of considerable attention and discussion. Formation of chemisorbed carbonium ions, carbanions, and radicals (produced associatively or dissociatively) is generally considered in connection with the acidic, basic, and electroneutral ("electronic") catalytic materials, respectively. The stereoselectivity in the olefin isomerization has been only recently investigated in some detail and it presents an additional experimental fact for which the considered mechanisms have to account. It may, of course, be hoped that its understanding may also help in discriminating between the alternative mechanistic possibilities, although at present this matter can still be discussed only speculatively.

Preferential formation of *cis*-butene-2 rather than the thermodynamically more stable *trans*-butene isomer in the isomerization of butene-1 on alkaline catalysts was postulated by Pines and Haag to be due to the participation in the transition state of a cyclic structure. In the case of sodium anthracene or sodium alumina this would have the form



Cvetanović and Foster (*5*) suggested that a geometric factor was likely to be of importance. In scanning a number of catalytic materials they found (*6*) that typical alkaline catalysts selectively favored double bond migration (with preferential formation of *cis*-butene-2 from butene-1) while typical acidic catalysts favored *cis–trans* isomerization. Some metals also favored double bond migration (although apparently with much less pronounced preference for *cis*-butene formation from butene-1). In agreement with the views of Haag and Pines (*1, 2, 3*) the differences in the behavior were thought to be primarily associated with the predominance of carbonium ion formation with acidic catalysts and of carbanions with alkaline catalysts. Carbonium ions were regarded as permitting free rotation around the original olefinic double bond and thus inducing preferential *cis–trans* isomerization, with double bond migration becoming important only at higher temperatures. Carbanions were regarded as leading preferentially to double bond migration. However, Foster and Cvetanović (*6*) found also considerable differences in selectivity from catalyst to catalyst and even of the same catalyst when subjected to surface treatment [such as potash impregnation (*5*) or acid washing (*6*)]. This was thought to be perhaps due to a duality of character of the catalysts, either as an inherent property or due to gross inhomogeneities. The concerted hydrogen switch mechanism or a (nonconcerted) dissociative mechanism were considered responsible for double bond migration on metals, with the associative mechanism being responsible for *cis-trans* isomerization in this case. These views were necessarily speculative and their tentative character was underlined.

More recently, Brouwer (*7*) studied several solid acidic catalysts and stressed strongly the duality of the function of the catalyst surface in contrast to the single mechanism involving carbonium ions and π-complexes considered by Haag and Pines (*3*). Brouwer observed pronounced differences in the selectivity of γ-alumina depending on whether it was used dry or "wet." In comparing the isomerization of *n*-butenes, *n*-pentenes, and *n*-hexenes, he concluded that *cis–trans* isomerization occurred by the carbonium ion mechanism, as is usually accepted, but postulated that the double bond shift occurred largely by the concerted hydrogen switch mechanism. The preferential formation of *cis*-butene in the double bond isomerization of butene-1 was visualized as being due to the geometric requirement of the olefin accommodation on the catalyst surface in the course of the concerted reaction. This steric factor was regarded as capable of explaining also the seemingly anomalous *cis/trans* ratio of the 2-hexenes formed from *cis*-hexene-3.

There is evidently some divergence of views regarding the detailed mechanisms to be invoked to explain the stereoselectivity in olefin isomerization. However, in view of the findings that the selectivity of some catalysts can be varied by simple surface treatment and that in general it varies from catalyst to catalyst, it would seem likely that two simultaneous mechanisms are involved. The carbonium ion mechanism is generally accepted as inducing predominant geometric isomerization. An equivalent mechanism, involving chemisorbed radicals resulting from associative chemisorption, could perhaps occur on some nonacidic catalysts, such as metals. The process mainly responsible for double bond migration on the other hand can be identified either with dissociative chemisorption to form allylic ions or radicals or, alternatively, with the concerted hydrogen switch mechanism. The kinetic consequences of these two alternative mechanisms are very similar and are therefore difficult to differentiate experimentally, especially if in the former the adsorption into the chemisorbed layer is the slow step. The results of the present study show that the activation energies of the surface reactions responsible for the *cis–trans* isomerization and for the double bond migration are very similar, suggesting similar energy barriers in the two processes. Unfortunately, meaningful comparisons of the entropies of activation cannot be made in the absence of a knowledge of the concentrations of the active sites responsible for the two isomerization reactions. Assuming that these are similar in magnitude the entropies of activation of the two processes are also similar. If the *cis–trans* isomerization on the catalyst used in this work involves proton donation to the olefin to form carbonium ions,* then it would be expected that in a concerted proton donation and proton acceptance by the catalyst, as visualized (*7*) in the double bond migration by the "hydrogen switch" mechanism, the activation

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* Although the catalyst used in this work was impregnated with 5% Na_2CO_3 to reduce its activity, complete suppression of acid sites cannot be assumed. There is both the possibility of incomplete neutralization and of formation of new acid sites during catalyst treatment *after* the impregnation.

energy would have to be appreciably smaller. This is not the case, as evident from the data in Table 4. The present results seem therefore to favor the assumption of a chemisorption process in the double bond migration on the catalyst used rather than the concerted "hydrogen switch" mechanism. However, it is felt that more extensive experimental information is required before a choice can be made with certainty between these alternatives.

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