

## Isomerization of 1-Butene Adsorbed on Mixed Tin-Antimony Oxide Catalysts. A $^{13}\text{C}$ -NMR Study

JANOS B. NAGY, ANTOINE ABOU-KAÏS,<sup>1</sup> MICHEL GUELTON,<sup>2</sup> JACQUES HARMEL, AND ERIC G. DEROUANE

*Laboratoire de Catalyse, Facultés Universitaires de Namur, 61 rue de Bruxelles, B-5000 Namur, Belgium*

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The adsorption and isomerization of *n*-butenes on tin-antimony oxide catalysts have been studied by  $^{13}\text{C}$ -NMR spectroscopy. From linewidths and intensity variations with temperature, the nature of the adsorbed species was assessed: a cyclic complex describes the low-temperature adsorption (<240 K) and at higher temperature (>240 K) a contact-type complex accounts better for the interaction between the admolecule and the surface. A cyclic complex-like intermediate occurs probably on the reaction path for the double-bond shift and the geometric isomerization of *n*-butenes. By proton abstraction, this complex can give rise to a negatively charged intermediate which accounts for the kinetic observations in the above reactions.

### INTRODUCTION

Although the desorbed reactants or products are generally used to monitor heterogeneous catalytic reactions, a few examples exist where they were studied directly in the adsorbed phase. Recently, uv-visible (1) and ir spectroscopic techniques (1, 2) were used to follow the hydrogenation of benzene on (Pt,M)-Y (M = Na, H, or Ca) zeolite (1) and the isomerization of *n*-butenes on Vycor silica glass (2).

$^{13}\text{C}$ -NMR spectroscopy has the advantage of differentiating between the different carbon atoms and of identifying the specific behavior of the adsorbed molecules. Their kinetic transformations are easily characterized by variations of the parameters of the NMR lines, such as chemical shift, linewidth, relaxation times, or intensity (3, 4). In previous papers we reported on the nature of the interactions between *n*-butenes and the zeolites NaY, HY, and NaGeX

(5, 6). Together with the possible detection of the nature(s) of adsorbed intermediate(s), a major advantage of this spectroscopic analysis is the simultaneous yield of diffusional parameters (energy of activation for diffusion of reactants and products from linewidth variation with temperature) and kinetic parameters (catalytic rate constants).

The purpose of the present paper is to throw some light on the mechanism responsible for the activation of olefins adsorbed on mixed tin-antimony oxide catalysts, in particular for the isomerization of *n*-butenes.

### EXPERIMENTAL

All catalyst samples were supplied by I.C.I. Ltd.: their preparation and properties have been described in the literature (7) (Sb contents are always referred to at.% Sb). They were all precalcined in air at 873 K for 16 h, 1.5 g of catalyst being finally activated at 673 K for 1 h down to a final pressure of  $2 \times 10^{-6}$  Torr in a glass NMR tube. 1-Butene (Prochem, degassed by several freeze-pump-thaw cycles) was then adsorbed at a pressure of about 550 Torr and the sample immediately cooled down to 77 K.

<sup>1</sup> Permanent address: CNRS Libanais et Faculté des Sciences II, Département de Chimie, Université Libanaise, Mansourieh, Liban.

<sup>2</sup> Permanent address: Laboratoire de Catalyse Hétérogène et Homogène. Associé à l'ENSCI, ERA-CNRS 458, Université des Sciences et Techniques de Lille, F-59655 - Villeneuve d'Ascq Cedex, France.

The equilibrium pressure of 1-butene,  $p$  (Torr) at 297 K, the specific area of the catalysts,  $A$  ( $\text{m}^2 \text{g}^{-1}$ ), and the maximum attainable surface coverage,  $\theta_{\text{max}}$  (assuming that the total amount of 1-butene in the NMR tube is adsorbed on the catalyst), are reported in Table 1. In spite of the high  $\theta_{\text{max}}$  values, only adsorbed species are observed at the temperature of measurements (230 K). Because of the rapid cooling, some of the gaseous molecules are condensed on the wall of the NMR tube, the condensed liquid being out of the volume probed by the NMR probe coil. Hence, these molecules are not observed and the effective coverage is certainly below the calculated  $\theta_{\text{max}}$  value.

$^{13}\text{C}$ -NMR measurements were performed, as previously described (5, 6), on a Bruker WP-60 Fourier transform spectrometer. At first, the behavior of 1-butene was observed from 180 to 240 K. Then, successive heating cycles to 297 K allowed opportunity for isomerization, the spectra always being recorded at 230 K. After equilibrium in the double-bond shift and the geometric isomerization, the behaviors of *cis*- and *trans*-2-butene have been observed

at temperatures ranging from 180 to 300 K. Temperatures were calibrated using a Chromel-Alumel thermocouple placed inside the NMR tube.

## RESULTS

Typical  $^{13}\text{C}$ -NMR spectra during the 1-butene isomerization in the adsorbed phase on a Sn-Sb-O catalyst containing 87 at. % Sb are illustrated in Fig. 1. The early formation of *cis*-2-butene (the  $\text{CH}_3$  peak of which is overlapping with the  $\text{CH}_3$  peak of 1-butene) is clearly distinguished and the subsequent *cis*-*trans* transformation can also be followed by concentrating on the  $\text{CH}_3$  peak variation (Fig. 2). From the line intensity dependence on time, the double-bond shift kinetic constants,  $k_{1-2}$ , can be easily determined. Because of the partial overlap between the *cis*- and *trans*-2-butene  $\text{CH}_3$  peaks, the *cis*-*trans* isomerization constants,  $k_{c-t}$ , are less accurate.

The  $k_{1-2}$  rate constants together with the *cis*-*trans* isomerization rate constants  $k_{c-t}$  are reported in Table 2. These apparent kinetic constants are strictly first order as evidenced by the good linearity of the logarithmic kinetic plots from which they are derived. The  $k_{1-2}$  constants for the disappearance of 1-butene and the formation of 2-butenes are equal within experimental error, showing clearly that no side reaction such as polymerization takes place simultaneously (except for the different behavior of the 30 at. % Sb-containing catalyst, in which case oligomerization of *n*-butenes was unambiguously identified (8)). The *cis*-*trans* isomerization constants,  $k_{c-t}$ , are always smaller than the corresponding double-bond shift constants,  $k_{1-2}$ . The initial *cis*/*trans* ratio varies with time (Fig. 3) and is generally higher than 2 (see Table 2), exception being made for the catalyst containing 40 at. % Sb where it is equal to 0.55. The equilibrium *cis*/*trans* ratios (0.40–0.75) are also reported in Table 2. They are systematically higher than those corresponding to gas-phase equilibrium (extrapolated value of 0.26 at a temperature of 297 K (9)).

TABLE 1

Adsorption of 1-Butene on Mixed Tin-Antimony Oxides

Catalyst	$p_{\text{B}_1}^a$ (Torr)	$A^b$ ( $\text{m}^2 \cdot \text{g}^{-1}$ )	$\theta_{\text{max}}^c$
$\text{SnO}_2$	550	16	5.3
Sb (at. %)			
5.3	560	36	2.3
10.4	550	47	1.8
19.0	550	67	1.3
30.0	532	51	1.6
40.0	555	50	1.7
75.2	500	43	1.8
87.0	515	60	1.3
$\text{Sb}_2\text{O}_4$	—	44	—

<sup>a</sup> 1-Butene pressure, Torr.

<sup>b</sup> Specific surface area,  $\text{m}^2 \cdot \text{g}^{-1}$ , obtained from the relationship of  $A$  and at. % Sb content (Ref. (7)).

<sup>c</sup> Maximum possible surface coverage by 1-butene.

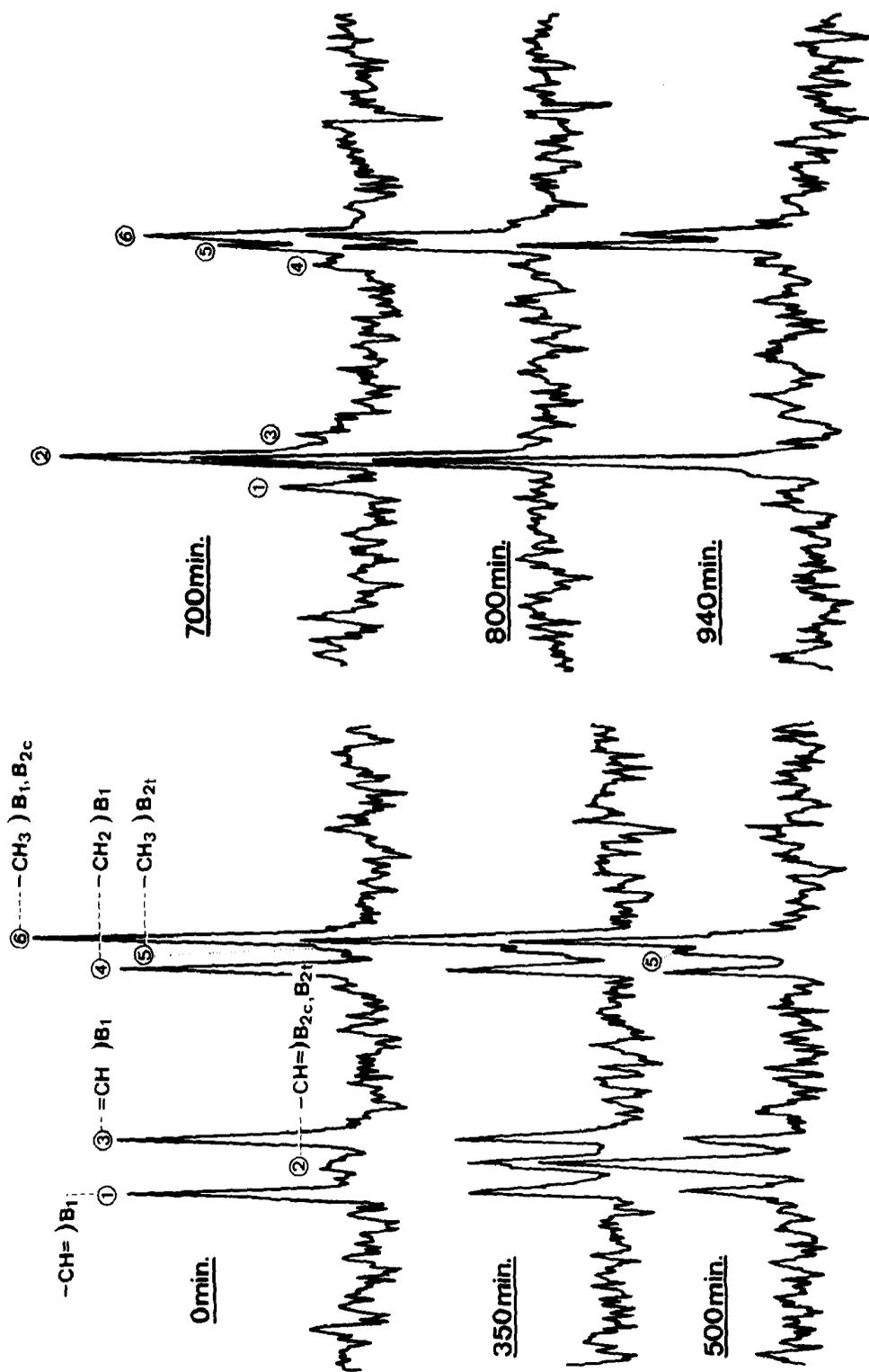


FIG. 1.  $^{13}\text{C}$ -NMR spectra at various time intervals during the isomerization of 1-butene ( $B_1$ ) giving *cis*- ( $B_{2c}$ ) and *trans*-2-butene ( $B_{2t}$ ) at 297 K on mixed tin-antimony oxide (87.0 at.% Sb). Spectra are recorded at 230 K.

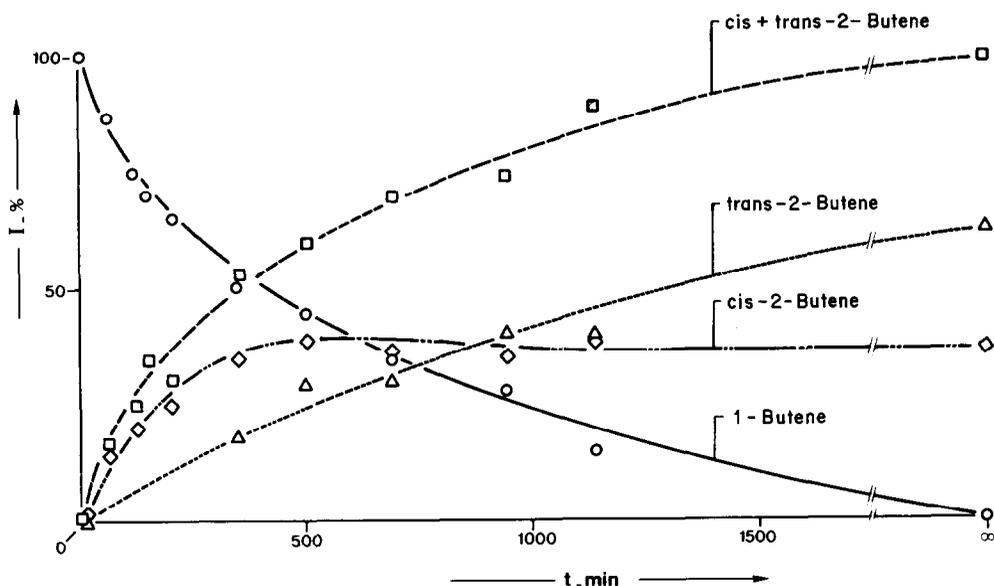


FIG. 2. Conversion of 1-butene on mixed tin-antimony oxide (87.0 at.% Sb), as obtained from the NMR signal intensities.

The relative stability of the adsorbed species is indicated by the activation energy for diffusion of the reactants and products determined from the variation of the  $^{13}\text{C}$ -NMR linewidths with temperature (see Table 3).

## DISCUSSION

We shall focus our attention on various points which are relevant to the understanding of the catalytic behavior of such materials, namely, the nature of the adsorbed species and that of the activated complex and the active sites.

### *The Nature of the Adsorbed Species*

The intensity variations of the  $^{13}\text{C}$ -NMR lines as functions of temperature can throw some light on the nature of the adsorbed species because they depend intimately on the longitudinal ( $T_1$ ) and transverse ( $T_2$ ) relaxation times (10). At low temperatures (163 K), three carbons (1, 2, and 3) of 1-butene give similar NMR intensities, smaller however than those of the more mobile methyl group (Fig. 4). This observation has been assigned previously (6) to a cyclic complex in which two different but adjacent sites are necessary to adsorb the molecule: the  $\pi$ -electrons on  $\text{C}_1$  interact with a Brønsted or Lewis acid site while a hydrogen on the  $\text{C}_3$  carbon forms a hydro-

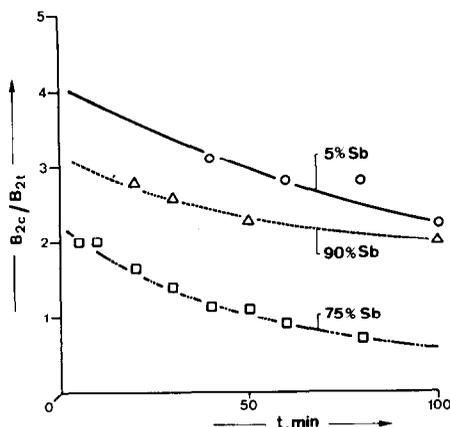


FIG. 3. Time dependence of the *cis/trans* ratio during the isomerization of 1-butene at 297 K on various tin-antimony oxide catalysts.

TABLE 2

Surface Basicity ( $\theta_B$ ) and Positional ( $k_{1-2}$ ) and Geometric ( $k_{c-t}$ ) Isomerization of 1- and 2-Butenes at 297 K Adsorbed on Sn-Sb-O Catalysts

Catalyst	$\theta_B^a$	$k_{1-2} \times 10^5$ ( $\text{min}^{-1} \cdot \text{m}^{-2}$ )	$k_{c-t} \times 10^5$ ( $\text{min}^{-1} \cdot \text{m}^{-2}$ )	$[\text{cis}/\text{trans}]_{\text{equilibrium}}^b$	$[\text{cis}/\text{trans}]_{\text{initial}}$
SnO <sub>2</sub>	0.66	0	0	—	—
Sb (at.%)					
5.3	0.36	23	4.7	0.67	4.5
10.4	0.41	1.1	0.13	0.53	>2
19.0	0.50	6.7	2.1	0.57	>3
30.0	0.77	$\geq 150^c$	22	—	—
40.0	0.89	63	9	0.67	0.55
75.2	0.79	27	6.2	0.40	2.5
87.0	0.62	2.7	2.0	0.76	3
Sb <sub>2</sub> O <sub>4</sub>	0.45	0	0	—	—

<sup>a</sup> Obtained from the amount of adsorbed acetic acid and standardized to unity for the value of the 55.0 at. % Sb catalyst (Ref. (7)).

<sup>b</sup>  $[\text{cis}/\text{trans}]_{\text{gas phase}} = 0.26$ .

<sup>c</sup> Estimated value from the  $\ln k_{1-2}$  vs  $\ln k_{c-t}$  relationship.

gen bond with an adjacent basic site. At higher temperature (260 K), the intensities of the NMR lines of the four carbons become comparable due to the nearly similar mobility of the carbon atoms. As the NMR chemical shifts are close to those observed in the liquid phase, only a contact-type (nonspecific) interaction must occur between the adsorbed molecule and the sur-

face. A specific interaction would indeed lead to distinct chemical shifts for the different carbon atoms (6). The temperature at which the mobile contact complex appears follows roughly the reactivity of 1-butene. It is slightly less than 200 K for pure SnO<sub>2</sub> (poor catalyst) and higher than 240 K for catalysts with 30 and 40 at. % Sb.

The energy of activation for diffusion of 1- and *trans*-2-butenes (Table 3), as evaluated for temperature ranges where the cyclic complex is preponderant, varies along with the basicity of these catalysts as globally evaluated by the amount of adsorbed acetic acid (7) ( $\theta_B$ ), or with their isomerization activity ( $k_{1-2}$  and  $k_{c-t}$ , see Table 2). It seems therefore that the adsorbed cyclic complex is probably related to an intermediate along the reaction path.

It is most interesting to note that the equilibrium *cis/trans* ratios are significantly higher (0.40–0.75) than the thermodynamic *cis/trans* ratio (0.26) in the gas phase. The equilibrium constants in the adsorbed phase must of course contain implicitly the ratio of the adsorption coefficients of *cis*- and *trans*-2-butenes (6, 11). On most cata-

TABLE 3

Energy of Activation for Diffusion ( $\text{kcal} \cdot \text{mol}^{-1}$ ) of 1-Butene ( $E_{B_1}^d$ ), *cis*-2-Butene ( $E_{B_c}^d$ ), and *trans*-2-Butene ( $E_{B_t}^d$ )

Catalyst	$\theta_B^a$	$E_{B_1}^d$	$E_{B_c}^d$	$E_{B_t}^d$
SnO <sub>2</sub>	0.66	1.2	—	—
Sb (at.%)				
5.3	0.36	1.0	1.6	1.4
10.4	0.41	0.4	1.2	0.6
19.0	0.50	1.0	1.4	1.0
30.0	0.77	1.5	2.2	2.0
40.0	0.89	1.7	1.6	1.4
75.2	0.79	0.9	1.6	1.2
87.0	0.62	0.9	1.4	0.9
Sb <sub>2</sub> O <sub>4</sub>	0.45	—	—	—

<sup>a</sup> Relative basicity of the catalyst (see Table 2).

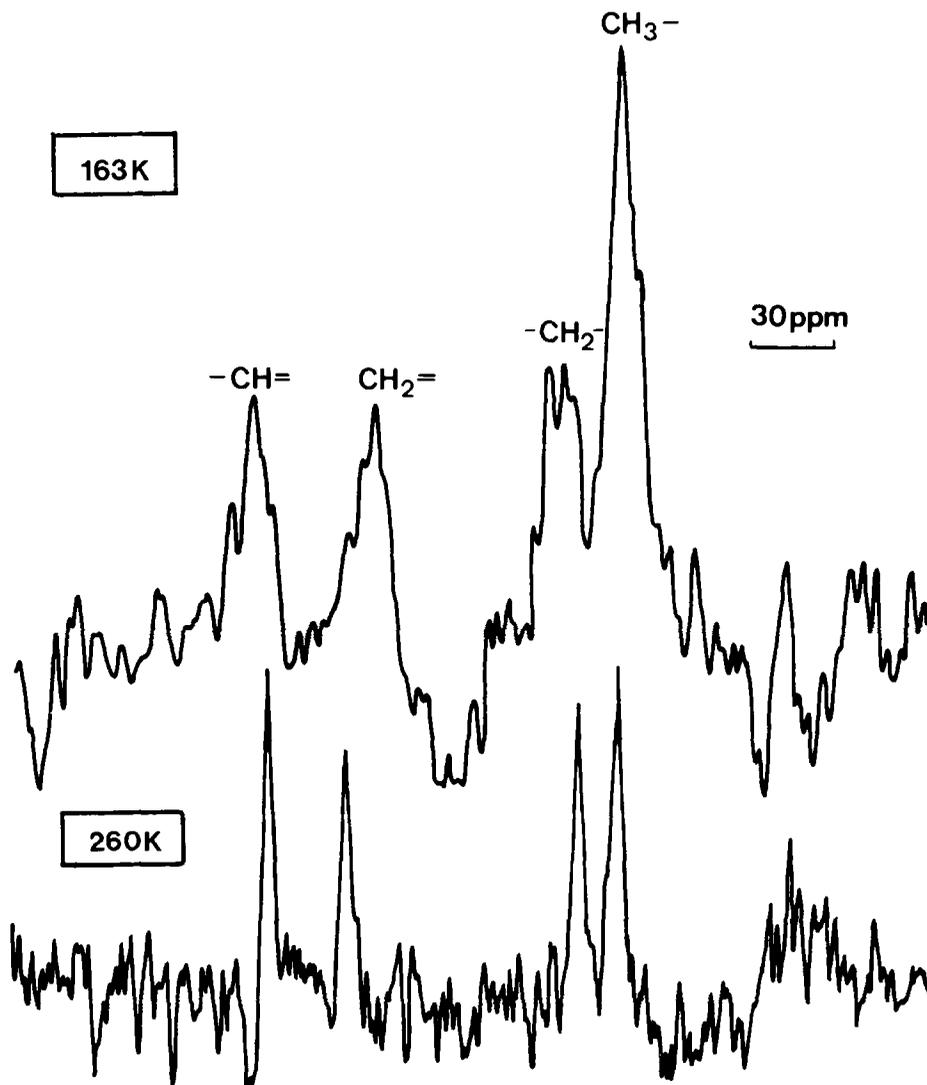


FIG. 4.  $^{13}\text{C}$ -NMR spectra of 1-butene adsorbed on a mixed tin-antimony oxide (5.3 at.% Sb) at 163 and 260 K.

lysts the *cis* isomer is somewhat more strongly adsorbed than the *trans* isomer (6), the difference in the apparent heats of adsorption being roughly  $0.5 \text{ kcal} \cdot \text{mol}^{-1}$  (12).

*The Nature of the Transition State and of the Surface Active Sites in the Double-Bond Shift of 1-Butene*

The initial *cis/trans* ratios are always higher than 2, only with one exception for the 40 at.% Sb catalyst (Table 2). These

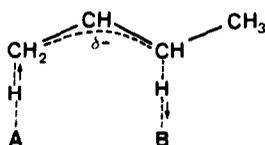
ratios also exceed the corresponding thermodynamic ratios, showing clearly the kinetic control of the product formation in the early stage of the reaction (Table 2, Fig. 2). They usually decrease with time to a final value where the more stable *trans* compound becomes preponderant (thermodynamic control).

The rather high initial *cis/trans* ratio is characteristic of an anionic transition state (6, 13-15). Indeed, the *cis*- $\pi$ -allyl anion is more stable than its *trans* conformation,

due either to a more favorable direct interaction in the *cis* form between the C<sub>1</sub> atom and the corresponding hydrogen atom on C<sub>4</sub> (16) or to a smaller destabilization because of less delocalization in the  $\pi$ -electron system of the *cis* with respect to the *trans* form (17).

The variation of the double-bond shift rate constants,  $k_{1-2}$ , with the surface basicity of the various catalysts also supports the proposal of an anionic-type transition state (Table 2).

From the close relationship between the catalytic activity and the presence of a cyclic-type adsorbed species on the one hand, and the anionic transition state on the other, it is tempting to postulate a cyclic transition state in which the simultaneous but asynchronous movement of protons can induce an anionic character (6, 14).



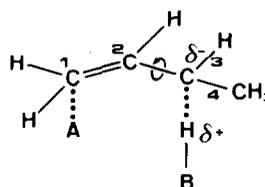
This model requires an acid (A)–base (B) pair at adjacent positions and it explains quite well the qualitative although not quantitative agreement between the basi-

city and the catalytic dependences on Sb content.

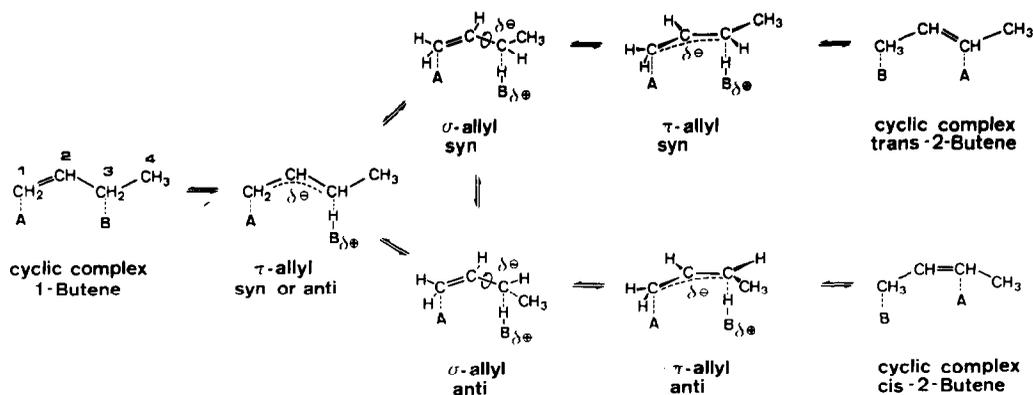
The observed cyclic complex is therefore a potential intermediate in the reaction because the molecule has already adopted a configuration which may be necessary to form the transition state (entropy activation).

#### The *cis*–*trans* Geometric Isomerization

The variation with surface basicity of the activity for *cis*–*trans* isomerization parallels approximately that of the double-bond shift rate constant,  $k_{1-2}$ . However, the most probable intermediate, which accounts for the easy *cis*–*trans* isomerization is a  $\sigma$ -allyl-type complex formed between C<sub>3</sub> of the carbanion and an acidic site of the catalyst (16):



A complete reaction scheme for both the double-bond shift and the geometric isomerizations in the adsorbed phase is then described as follows:



It is a “star”-type kinetic scheme as was also proposed for other basic catalysts (13, 18). The adjacent acidic (A) and

(B) sites are able to stabilize either the  $\pi$ -allyl anionic-type intermediate or the *syn*- and *anti*- $\sigma$ -allyl anionic intermediates.

Note that the acidic site A and the basic site B are only indicative because different types of acid–base pairs may definitely be present on these catalysts (19). For the 2-butenes the A and B sites have been inverted in order to account for the more stable adsorbed species.

#### CONCLUSIONS

$^{13}\text{C}$ -NMR spectroscopy gives valuable information on the configuration of adsorbed molecules and enables one to obtain quantitative data on the rates of their transformation. The nature of the adsorbed species at different temperatures together with their energy of activation for diffusion can be determined from the variation of line intensities and linewidths with temperature. On antimony–tin oxide catalysts, a cyclic-type complex is the main adsorbed species at low temperature (<240 K) while at higher temperature (>240 K) we propose that a contact-type complex characterizes the interaction between the surface and the ad-molecule. From a kinetic study of the isomerization, the nature of the transition states and of the active sites has been inferred. The cyclic complex, the geometry of which conforms well to a likely concerted proton transfer, leads in a rate-determining step to  $\pi$ -allyl and  $\sigma$ -allyl negatively charged intermediates which are the same in both the double-bond shift and the geometric isomerizations. The high initial *cis/trans* ratios and the variation of activities with surface basicity are unambiguous evidence in favor of a negatively charged intermediate. Finally, the equilibrium *cis/trans* ratios differ from those in the gaseous state, showing clearly the preferential adsorption of *cis*-2-butene relative to *trans*-2-butene.

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