

Effects of Acidity in the Isomerization of *n*-Butenes on Mixed Tin-Antimony Oxide Catalysts. A ¹³C NMR Study

J. B. NAGY, J. HARMEL, A. ABOU-KAÏS,¹ M. GUELTON,² AND E. G. DEROUANE³

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

Received February 17, 1983; revised January 6, 1984

The role played by acidic sites in the isomerization of *n*-butenes adsorbed on mixed tin-antimony oxide catalysts is illustrated by the influence of adsorbed acetic acid on the various kinetic constants. However, both acidic and basic sites are found to play a role either in the stabilization or in the transformation of *n*-butenes in the adsorbed phase. A cyclic-type intermediate explains adequately all the experimental results. It can bear either a partial negative charge (most of the studied tin-antimony oxide catalysts belong to this group) or a partial positive charge (for the 30.0, 40.0 at.% Sb catalysts and those modified by acetic acid adsorption) as shown by the relative amounts of *cis*- and *trans*-2-butenes which are formed in the early stages of the 1-butene isomerization reaction. The presence of strong Brønsted acid sites on the 30.0 at.% Sb catalyst is suspected from its higher polymerization activity for *n*-butenes.

INTRODUCTION

It was proposed in a previous paper that dual-site catalysis was occurring in the reaction of butenes on mixed tin-antimony oxide catalysts (1). Adjacent acidic and basic sites were shown to play a definite role both in the isomerization (1) and in the oxidation (2) of *n*-butenes. It was also emphasized that at low temperatures a cyclic complex can characterize the adsorption of *n*-butenes on tin-antimony oxides (1), on a synthetic near-faujasite germanium zeolite (NaGeX) (3, 4) and on NaY and HY zeolites (5). Species resembling such cyclic complexes were proposed as possible intermediates on the isomerization reaction path, leading to the reaction products either

through a concerted or a stepwise proton transfer (1, 3-5).

If the rate determining step in the isomerization does not involve the participation of surface OH groups (Brønsted acid centers) (6), the presence of water depletes the activity. On the contrary, water has a promoting effect on zeolites (7, 8) and MoO₃ catalyst (9), where the dual site acid-base catalysis plays the determining role (9).

We report in this paper on the promotion or the poisoning by acetic acid of mixed tin-antimony oxide catalysts used in the isomerization of *n*-butenes. A promoting effect appears at low coverage while decreasing rates are observed with increasing amounts at higher acetic acid coverage.

EXPERIMENTAL

Mixed tin-antimony oxides were supplied by I.C.I. PLC. 30 and 40 at.% Sb content samples were calcined in air at 873 K for 16 h as previously described (1, 2).

Catalyst (1.5 g) was then degassed at 673 K for 1 h down to a final pressure of $2 \times$

¹ Permanent address: CNRS Libanais et Faculté des Sciences II, Département de Chimie, Université Libanaise, Mansourieh, Lebanon.

² Permanent address: Laboratoire de Catalyse et de Physico-Chimie des Surfaces, Université des Sciences et Techniques de Lille, 59650 Villeneuve d'Ascq, France.

³ To whom correspondence concerning this paper should be sent.

TABLE 1

Adsorption of 1-Butene on 40.0 at.% Sb Sn-Sb Oxide Catalysts in Presence of Various Amounts of Acetic Acid (HAc)

W_{Catalyst} (g)	n_{HAc} (μmol)	θ_{HAc}^a	$P_{\text{B}_1}^b$ (Torr)	$\theta_{\text{B}_1}^{\text{max}c}$
1.46	0	0	555	1.7
1.56	20.7	0.05	538	1.6
1.55	44.7	0.11	548	1.6
1.46	94.1	0.25	550	1.7

^a Computed from the maximum amount of adsorbed acetic acid, $5.2 \mu\text{mol m}^{-2}$ taken from Ref. (11).

^b 1-Butene pressure.

^c Maximum possible surface coverage by 1-butene, assuming that its total amount in the NMR tube is adsorbed on the catalyst. Surface area for a molecule of 1-butene is taken from Ref. (5) (35 \AA^2). See also footnote *a* of Table 2.

10^{-6} Torr in a glass NMR cell. This activation was accompanied by an approximate 2% weight loss.

The adsorption of acetic acid (Merck, suprapure) dried on P_2O_5 and degassed by three freeze-pump-thaw cycles was performed on the 40 at.% Sb sample at 296 K; dosage was determined volumetrically prior to adsorption knowing the vapor pressure at this temperature (13.8 Torr (10)). From the concentration of basic sites corresponding to a maximum of $5.2 \mu\text{mol m}^{-2}$ of adsorbed acetic acid (11), the surface coverage in acetic acid θ_{HAc} (Table 1), could be calculated.

1-Butene (Prochem, degassed by several freeze-pump-thaw cycles) was adsorbed on the sample at a pressure of about 550 Torr; the sample was immediately cooled to 77 K and was maintained at this temperature.

The ^{13}C NMR measurements were performed as previously described (3, 5) on a Bruker WP-60 Fourier transform spectrometer. The kinetic measurements were obtained from successive heating cycles at 297 K, the NMR spectra being always recorded at 230 K. ^{13}C NMR spectra of the oligomerized products were taken on a

JEOL FX 90 Q spectrometer while EPR spectra were recorded on a Bruker BER-420 spectrometer operating in the X band (9.5 GHz).

Mass spectra were obtained with a AEI MS 30 spectrometer. Vapor-phase chromatographic separations were carried out on a Perkin-Elmer Sigma 3 Gas chromatograph using either a capillary SE 30 or a Poropak column.

RESULTS AND DISCUSSION

I. The Effect of Adsorbed Acetic Acid on the 40 at.% Sb Catalyst

The importance of the basic sites in the positional and geometric isomerization of *n*-butenes was already emphasized in a previous paper (1). Progressive poisoning of the catalysts by acetic acid was investigated to ascertain the close although not perfect parallelism between the catalytic activity and the concentration of basic sites.

The variation of the ^{13}C NMR line intensities of the adsorbed *n*-butenes as a function of reaction time leads to two slightly different kinetic behaviors. The first one is illustrated by the reaction of *n*-butenes on the 40 at.% Sb sample (Fig. 1): the *cis/trans* ratio remains always smaller than unity. The second behavior is shown by Fig. 2 for a sample 40 at.% Sb poisoned by acetic acid ($\theta_{\text{HAc}} = 0.05$): the *cis/trans* ratio is here higher than unity at short reaction time. Note, however, that the initial *cis/trans* ratios are never higher than 1.5 on the different samples (Table 2).

Good linear logarithmic plots give evidence for the first-order nature of the kinetic processes, both for the positional (Fig. 3) and the geometric (Fig. 4) isomerization (as illustrated for the sample 40 at.% Sb, $\theta_{\text{HAc}} = 0.05$). Equilibrium *cis/trans* ratios, higher than the corresponding gas-phase value of 0.26 (12) at 297 K, as well as the greater energies of activation for diffusion of *cis*-2-butene, indicate stronger interaction with the surface for *cis*-2-butene as

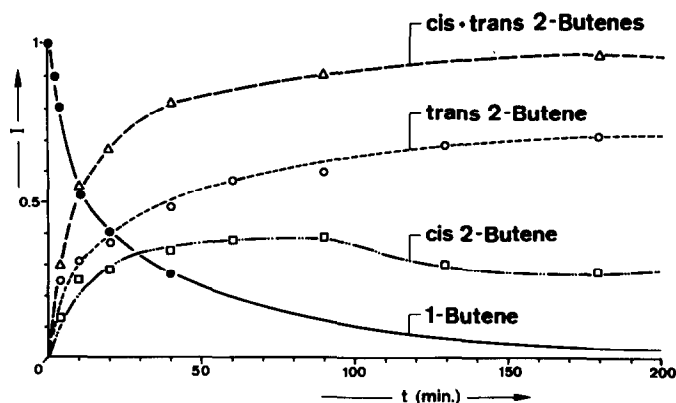


FIG. 1. Concentration change during the isomerization of 1-butene on mixed tin-antimony oxide (40.0 at.% Sb) as obtained from the ^{13}C NMR signal intensities at 297 K.

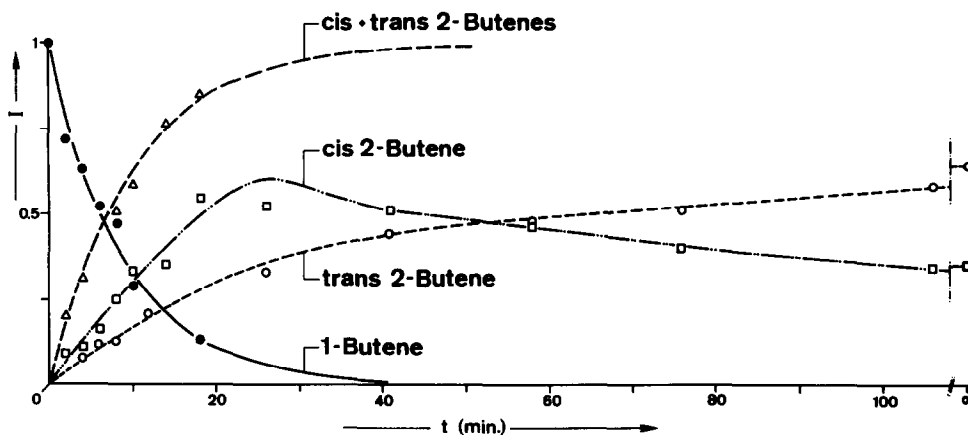


FIG. 2. Isomerization of 1-butene adsorbed on a mixed tin-antimony oxide (40.0 at.% Sb) modified by acetic acid adsorption ($\theta_{\text{HAc}} = 0.05$) at 297 K.

TABLE 2

Kinetic Constants at 297 K and Energies of Activation for Diffusion (E^d)^a of 1- and 2-Butenes on 40.0 at.% Sb Sn-Sb-O Catalysts Modified by Acetic Acid Adsorption

θ_{HAc}	$k_{1-2} \times 10^{5b}$ ($\text{min}^{-1} \text{m}^{-2}$)	$k_{c-t} \times 10^{5b}$ ($\text{min}^{-1} \text{m}^{-2}$)	$\left(\frac{\text{cis}}{\text{trans}}\right)_{\text{initial}}$	$\left(\frac{\text{cis}}{\text{trans}}\right)_{\text{equilibrium}}^c$	$E_{\text{B}1}^d$	$E_{\text{B}2c}^d$	$E_{\text{B}2t}^d$	Ref.
0	63	9	0.55	0.39	1.7	1.6	1.4	(1)
0.05	133	24	1.5	0.58	1.8	2.0	1.8	This work
0.11	53	1.2	1.0	0.44	1.4	1.8	1.5	This work
0.25	0.33	Very small	1.5	0.82	0.9	0.8	0.6	This work

^a Energies of activation for diffusion determined from the ^{13}C NMR linewidth variation with temperature (1). Only relative values need to be taken into account.

^b The specific area of 40.0 at.% Sb catalysts of $50 \text{ m}^2 \text{ g}^{-1}$ was taken from Ref. (2); k_{1-2} , positional, and k_{c-t} , geometric, isomerization constants.

^c The gas phase *cis/trans* equilibrium ratio is equal to 0.26 (calculated from data of Ref. (12)) at 297 K.

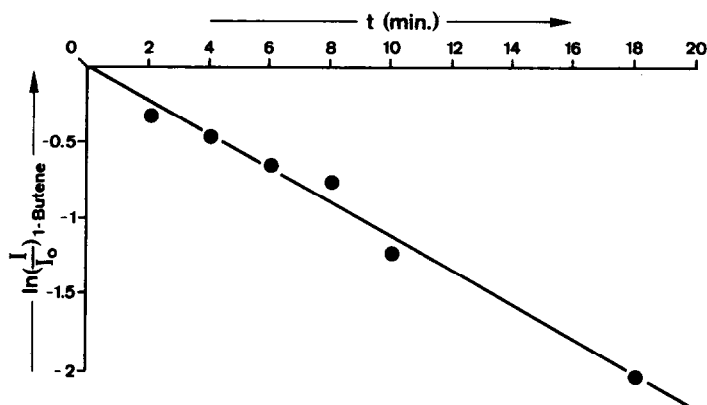


FIG. 3. First-order plot of 1-butene isomerization on the 40.0 at.% Sb catalyst modified by acetic acid ($\theta_{\text{HAc}} = 0.05$) at 297 K.

compared to the *trans*-isomer (1, 3). The energies of activation for diffusion were computed from the ^{13}C NMR linewidth variation with temperature as previously described (1). Only their relative values have to be taken into account.

The dependence of the kinetic constants on the acetic acid surface coverage is shown in Fig. 5. For $\theta_{\text{HAc}} = 0.05$, the rate of positional isomerization (k_{1-2}) is approximately doubled over the value observed for $\theta_{\text{HAc}} = 0.00$, while an increase by a factor of 2.6 is shown in the geometric isomerization (k_{c-t}). Further addition of adsorbed acetic acid results in a lowering of the reaction rate ($\theta_{\text{HAc}} = 0.11$) to reach finally at $\theta_{\text{HAc}} = 0.25$ a reduction of about an order of magnitude for the positional isomerization, while

the geometric isomerization is totally inhibited within experimental errors.

The presence of a maximum in the kinetic constant vs θ_{HAc} curves shows the additional role of the acidic sites of the catalyst. At $\theta_{\text{HAc}} = 0$, the proton transfer from the surface to the reactants occurs probably quite fast, leading to a low *cis/trans* ratio (0.55) on this 40 at.% Sb catalyst. At low θ_{HAc} , the higher concentration of Brønsted acid centers resulting from the dissociation of acetic acid increases the number of neighboring acid-base pairs; hence the isomerization rate increases. A further increase in θ_{HAc} , however, will destroy adjacent acid-base pairs by poisoning basic sites and it leads to decreasing isomerization rates. As the maximum in the kinetic

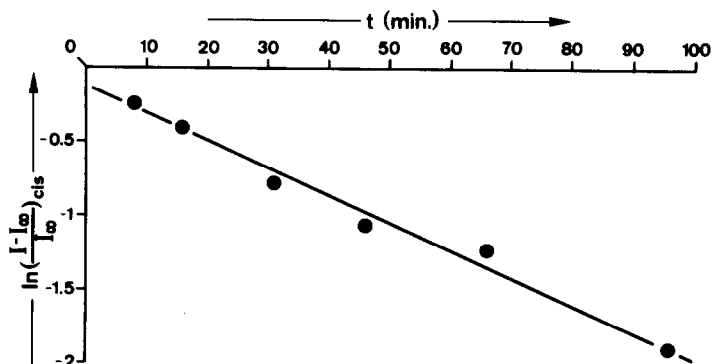


FIG. 4. Kinetic plot of the *cis-trans* isomerization of *cis*-2-butene on the 40.0 at.% Sb catalyst modified by acetic acid ($\theta_{\text{HAc}} = 0.05$) at 297 K.

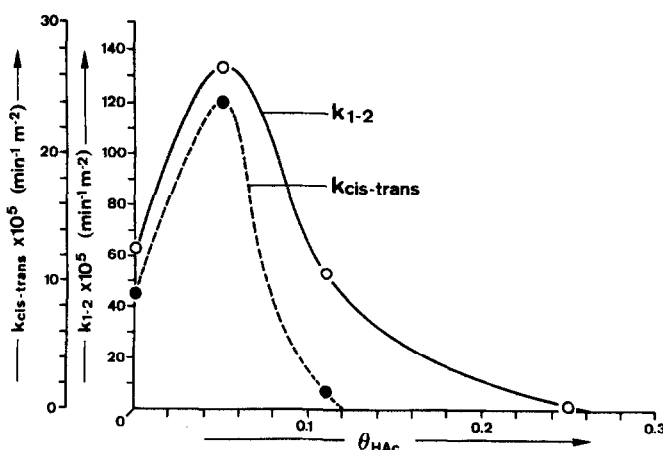


FIG. 5. Variation of the isomerization constants k_{1-2} (○) of 1-butene and the geometric isomerization constants $k_{\text{cis-trans}}$ (●) of *cis*-2-butene as functions of the surface coverage θ_{HAc} of acetic acid on the 40 at.% Sb catalyst.

constants occurs at a rather low θ_{HAc} , neighboring positions of the acid-base centers are probably required at the active site, matching closely the configuration of the transition state as it was previously proposed (1, 3). The cyclic-type adsorbed species (1, 3, 4) fits quite well a reaction scheme where the 1 and 3 carbon atoms of the *n*-butenes interact with the surface and are in a favorable configuration for proton transfers.

In a previous paper, the role of basic active sites was emphasized and a negatively charged transition state adequately explained the kinetic results. The present work shows that the Brønsted acid sites can change the reaction mechanism from a carbanion type to a positively charged intermediate depending on the relative importance of proton abstraction or protonation of the butene molecule. A cyclic-type intermediate on the reaction path can easily explain both the rate determining proton abstraction (resulting in a carbanion intermediate) or protonation (giving a carbenium ion intermediate) followed by the allylic proton abstraction.

Indeed, similar changes in reaction mechanism were already observed, where both acidic and basic sites could play a defi-

nite role in the reaction (3, 8, 13). This mechanism has been referred to as the "hydrogen switch" (14). The isomerization rate of 1-butene on alumina goes also through a maximum as a function of the surface hydroxyl concentration (8). The isomerization of 1-butene proceeds through a carbanion-like transition state on the basic NaGeX zeolite (3), while a carbenium ion intermediate explains the results for the more acidic NaHGeX (20% protonated) zeolite (13).

A smaller initial *cis/trans* ratio indicates a greater role of protonation in the kinetic steps (Table 2). Therefore, the relatively higher *cis/trans* ratio on the more protonated samples (1–1.5 if $\theta_{\text{HAc}} = 0.05$ –0.25) in comparison with that of the "unpoisoned" one (0.55 if $\theta_{\text{HAc}} = 0$) is surprising and this discrepancy is not explained at present.

The parallelism between the energy of activation for diffusion of the reactant measured by ^{13}C NMR (1) and its reactivity is clearly seen from Table 1. Energies of activation for diffusion present also a maximum at $\theta_{\text{HAc}} = 0.05$.

An interesting comparison comes from the relationship of k_{1-2} obtained on different Sb content catalysts (1) with the product of

TABLE 3

Relationship between the Kinetic Constants of the Positional Isomerization of 1-Butene (k_{1-2} at 297 K) Adsorbed on Sn-Sb-O Catalysts and the Product of the Bulk Acid-Base Concentration ($\theta_A \cdot \theta_B$)

Support	k_{1-2}^a ($\text{min}^{-1} \text{m}^{-2}$)	θ_A^b	θ_B^c	$\theta_A \cdot \theta_B$
SnO ₂	0	1	0.66	0.66
5.3%	23	0.54	0.36	0.19
10.4%	1.1	0.40	0.41	0.16
19.0%	6.7	0.25	0.50	0.12
30.0%	≥ 150	0.21	0.77	0.16
40.0%	63	0.19	0.89	0.17
75.2%	27	0.13	0.79	0.10
87.0%	2.7	0.02	0.62	0.01
Sb ₂ O ₄	0	0	0.45	0

^a From Ref. (1).

^b Standardized at the value of the SnO₂ catalyst (Ref. (11)).

^c Standardized at the value of 55.0 at.% Sb catalyst (Ref. (11)).

the acidic (θ_A) and basic (θ_B) sites concentration following the kinetic equation $R_{1-2} = k_{1-2}[1B]\theta_A\theta_B$. These latter values are taken from Ref. (11) and the acidity measured by micromoles per square meter of adsorbed pyridine is arbitrarily normalized to 1 on its highest value for SnO₂, while the basicity obtained from acetic acid adsorption (in $\mu\text{mol m}^{-2}$) is normalized to 1 for its maximum value corresponding to the 55.0 at.% Sb catalyst (Table 3).

Figure 6 shows three different behaviors

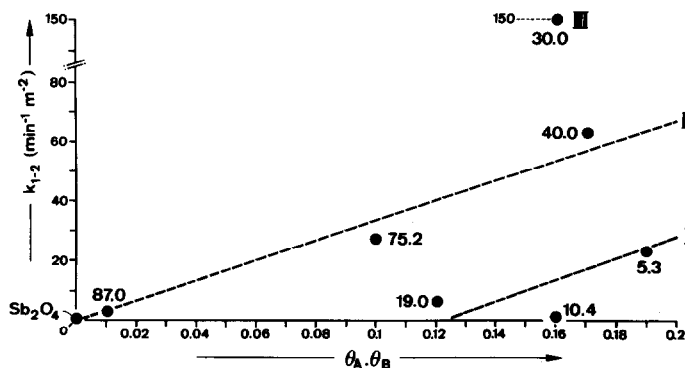


FIG. 6. Correlation of the positional isomerization constants k_{1-2} of 1-butene with the product of acid-base properties of various mixed tin-antimony oxide catalysts (at.% Sb is indicated).

for the 5–20, the 40–100, and the 30 at.% Sb catalysts. In the intermediate region of 40–100 at.% Sb a certain parallelism is detected (Region II); more scatter is observed for the low Sb content catalysts (Region I). The 30 at.% Sb catalyst behaves quite differently in that oligomerization is also observed. Regions I and II can be tentatively linked to the drastic changes in basicity in Region I and a quite monotonous change in Region II (11). Although knowledge of the bulk acid-base properties sheds some light on the isomerization activity, it must be emphasized that not only the concentration but also the strength of the acid-base sites should be considered. Indeed, pure SnO₂ is inactive for isomerization in similar catalytic conditions, although it has the highest $\theta_A \cdot \theta_B$ product value (Table 3).

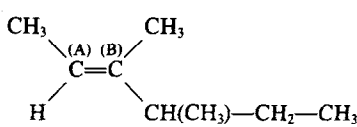
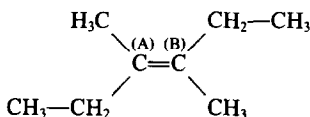
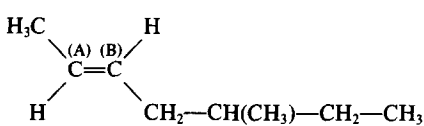
The effects of adsorbed acetic acid on the reaction rates of isomerization are consistent with the role of dual acid-base sites and the formation of a cyclic intermediate. However, the nature of the active sites is not known at present and only a qualitative picture can be obtained from this study. In addition it would be interesting to probe by independent measurements the change in acid-base properties due to acetic acid adsorption.

II. Oligomerization of 1-Butene on the 30 at.% Sb Catalyst

The activity of the 30 at.% Sb catalyst for

TABLE 4

¹³C NMR and Chromatographic Data of the Dimerization Products of *n*-Butenes on the 30 at.% Sb Catalyst

Product ^a	$\delta_{\text{calc.}}^b$ (ppm)		$\delta_{\text{meas.}}$ (ppm)		Yield (%)
	A	B	A	B	
I 	118.1 (119.4) ^c	142.4 (139.85) ^c	118.1	140.2	79
II 	131.3	131.3	130.9	130.9	17
III 	128.2	130.2	126.2	130.9	4

^a The *Z* and *E* isomers.^b Value $\delta_{\text{CH}_2=\text{CH}_2} = 123.3$ ppm (17); only the δ values of the *E* isomers are reported, the *Z* isomers having a greater shift of ca. 1.0 ppm (except for **III**).^c Ref. (18).

the isomerization of 1-butene is quite high in comparison with the other catalyst samples. The kinetic constant k_{1-2} ($>150 \text{ min}^{-1} \text{ m}^{-2}$) must be estimated from the $k_{1-2} - k_{c-t}$ relationship (1).

Following a fast isomerization into *cis*- and *trans*-2-butenes, oligomerization occurs at 297 K with a kinetic constant of $3 \times 10^{-5} \text{ min}^{-1} \text{ mol}^{-1} \text{ m}^{-2}$ as determined from a second-order kinetic plot.

The ¹³C NMR spectra of the adsorbed molecules reveal lines at 11.7, 17.3, 27.2, 35.4, and 44.1 ppm in the paraffinic region and 118.1, 126.2, 130.9, and 140.2 ppm in the olefinic region. The lines at 11.7, 17.3, and 126.2 ppm characterize the unconverted *cis*- and *trans*-2-butenes. After desorption of the more volatile products, two broad lines are observed near 130 and 10 ppm which correspond to more strongly adsorbed oligomers. An EPR signal is observed on the same sample at $g = 2.0020$ (the linewidth $\Delta H = 13.7$ G) possibly arising from organic radical (15) species.

Mass spectrometric measurements of the desorbed products indicate the presence of species with a molecular weight of 112, possibly the dimer C_8H_{16} . Chromatographic analysis reveals the presence of six different products, the retention times of which are smaller than those of the corresponding linear octenes.

Table 4 summarizes the results, including the most probable branched dimers with their calculated (from additivity relationships (16)) and observed ¹³C NMR chemical shifts. The percentage yield of each isomer is obtained from chromatographic data. The attribution of the chromatographic peaks was made on the following reasoning. The 3,4-dimethyl-2-hexene (**I**) and 3,4-dimethyl-3-hexene (**II**) isomers are formed directly from two 2-butene molecules and are thus the most probable ones. Moreover, the NMR line intensities of product (**I**) are more intense and therefore (**I**) should also be the major product in the chromatographic analysis (79%). Product (**III**), the 5-

methyl-2-heptene, is formed from a 1-butene and a 2-butene molecule. It is then the less probable compound observed in the smallest amount (4%). The identification of the chromatographic peak of product (II) is thus obvious, yielding 17%. It should be emphasized that there is a very good agreement between the calculated and observed NMR shifts.

As the formation of these oligomers necessitates strong Brønsted acid sites, this observation explains the high isomerization activity of the 30 at.% Sb-containing catalyst. The protonation of the reactant should also occur prior to the allylic proton abstraction resulting in an intermediate carbenium ion formation.

CONCLUSIONS

The importance of both acidic and basic sites in the isomerization of *n*-butenes over Sn–Sb oxide catalysts is shown by the effect of adsorbed acetic acid. The results are best explained by the formation of a cyclic intermediate which requires adjacent acid–basic sites for its stabilization as well as its further conversion to isomers. On most of the catalysts the proton abstraction occurs prior to the proton transfer (1). However, on the 30.0, 40.0 at.% Sb catalysts, and on those treated by acetic acid, the two processes can either be simultaneous (hydrogen switch mechanism (14)) or the proton transfer can precede the proton abstraction (carbenium ion mechanism). The oligomerization reaction occurring on the 30 at.% Sb catalyst strengthens the hypothesis of a carbenium ion intermediate in the isomerization reaction on this particular catalyst.

ACKNOWLEDGMENTS

The authors are very grateful to Dr. J. C. McAteer and to I.C.I. PLC (Central Research Laboratory, Run-

corn, U.K.) for their kind supply of the catalyst oxides. Mr. A. Burlet and Dr. A. M. Léonard-Coppens are acknowledged for the additional ¹³C NMR measurements and the mass spectral analysis.

REFERENCES

1. B. Nagy, J., Abou-Kaïs, A., Guelton, M., Harmel, J., and Derouane, E. G., *J. Catal.* **73**, 1 (1982).
2. McAteer, J. C., *J. Chem. Soc., Faraday Trans. I* **75**, 2768 (1979).
3. B. Nagy, J., Guelton, M., and Derouane, E. G., *J. Catal.* **55**, 43 (1978).
4. Derouane, E. G., and B. Nagy, J., "ACS Symposium Services, Symposium on Catalytic Materials, San Francisco, June 13–15, 1983," in press.
5. B. Nagy, J., Gigot, M., Gourgue, A., and Derouane, E. G., *J. Mol. Catal.* **2**, 265 (1977).
6. Hattori, H., Yoshii, N., and Tanabe, K., in "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972," p. 233, North-Holland/American Elsevier, Amsterdam/New York, 1973.
7. Germain, J. E., "Catalytic Conversion of Hydrocarbons." Academic Press, New York, 1969.
8. Gerberich, H. R., and Hall, W. K., *J. Catal.* **5**, 99 (1966).
9. Halász, I., and Gáti, Gy., *React. Kinet. Catal. Lett.* **12**, 411 (1979).
10. Handbook of Chemistry and Physics (R. C. Weast, Ed.), 51st ed., p. D147. Chem. Rubber Pub. Co., Cleveland, 1970–71.
11. McAteer, J. C., *J. Chem. Soc., Faraday Trans. I* **75**, 2762 (1979).
12. Egger, K. W., Golden, D. M., and Benson, S. W., *J. Amer. Chem. Soc.* **86**, 5420 (1964).
13. Poncelet, G., Dubru, M. L., and Jacobs, P. A., in "Molecular Sieves II" (Katzner, J. R., Ed.), American Chemical Society, Symposium Series N°40, p. 606. Amer. Chem. Soc., Washington, D.C., 1977.
14. Turkevich, J., and Smith, R. K., *J. Phys. Chem.* **16**, 466 (1948).
15. Wertz, J. E., and Bolton, J. R., "Electron Spin Resonance." McGraw–Hill, New York, 1972.
16. Dorman, D. E., Jautelat, M., and Roberts, J. D., *J. Org. Chem.* **36**, 2757 (1971).
17. Levy, G. C., and Nelson, G. L., "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley–Interscience, New York, 1972.
18. de Haan, J. W., and Van de Ven, L. J. M., *Org. Magn. Reson.* **5**, 147 (1973).