JOURNAL OF CATALYSIS 34, 423–430 (1974)

The Isomerization of *cis*-2-Butene Over Silica–Alumina Catalysts

II. Kinetic Study

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Received July 26, 1973; revised January 15, 1974

cis-2-Butene isomerization has been studied on four silica–aluminas of different aluminum contents. The reaction leads to double-bond migration and *cis–trans* conversion. The deactivation of all catalysts obeys two exponential laws which allow two initial rates to be calculated. One of these is related to Lewis-oxidizing sites, the other one to Brønsted acidic sites. Kinetic studies show that the rate is first order in reactant pressure for one of the catalysts whereas it obeys the Langmuir equation for the other ones. For the latter, activation energies and chemisorption enthalpies have been calculated which allow a mechanism for the isomerization to be proposed. The isomerization proceeds through the same mechanism on both types of active site. A common activated complex is involved in both double-bond and *cis–trans* isomerizations.

INTRODUCTION

As already mentioned (*1*), the catalytic isomerization of *n*-butenes has been extensively studied. On silica–alumina catalysts the reaction takes place under mild conditions and leads only to double-bond and *cis–trans* isomerization. The isomerization can proceed through either a *sec*-butyl carbonium ion (*2*), a concerted mechanism (*3*, *4*) or a butenyl (allylic) carbonium ion (*5*).

In order to correlate the isomerizing activities and the acidic properties of different silica–aluminas, a kinetic study of *cis*-2-butene isomerization has been undertaken. Some initial work carried out by the microcatalytic technique on a catalyst provided by Ketjen Co. showed a rapid deactivation phenomenon with run time (*1*). The activity decreased according to two exponential laws, one of which was correlated qualitatively with Lewis sites and the other with Brønsted sites. The present work is concerned with a further study of this deactivation and with *cis*-2-butene isomerization on silica–aluminas with reduced aluminum contents.

EXPERIMENTAL METHODS

Materials

A silica–alumina catalyst supplied by Ketjen Co. and containing 14 wt% of alumina has been studied. From this starting material designated K-14, three other samples designated K-9.4, K-2.4 and K-0.1 have been prepared by extracting aluminum with aqueous HCl solution as described elsewhere (*6*). This treatment does not leave any chloride ions on the solids (*6*). Alumina contents and surface areas of the four samples are listed in Table 1.

Reactant

cis-2-Butene was provided by Air Liquide and contained less than 0.3% of 1-butene and *trans*-2-butene. This material was dried over magnesium perchlorate.

Catalytic Activity Measurements

Steady-state flow experiments have been performed in a microcatalytic reactor as previously described (*1*). The catalyst was pretreated for 16 hr at 400°C in flowing hydrogen (4 liters hr^{-1}) before the test.

TABLE 1
ALUMINA CONTENTS AND SURFACE AREAS OF THE CATALYSTS

Catalysts	$Al_2O_3/(Al_2O_3 + SiO_3)$ (wt%)	S (m^2g^{-1})[a]
K-14	14	575
K-9.4	9.4	525
K-2.4	2.4	715
K-0.1	0.1	740

[a] Measured by BET method applied to N_2 adsorption after a 15 hr vacuum evacuation at 400°C.

The carrier gas was hydrogen; the reactant pressure varied from 20 to 200 Torr and the total flow rate was 6 liters hr^{-1}. Rates are expressed in moles per second per gram (or mole s^{-1} m^{-2}). The reaction products in the temperature range 65–105°C are 1-butene and *trans*-2-butene.

RESULTS AND DISCUSSION

Deactivation Study

It has already been shown that the deactivation phenomenon on K-14 obeys two independent exponential laws (*1*). The isomerizing activity is described by the relation:

$$A_T = A_L + A_B = a_L e^{-c_L t} + a_B e^{-c_B t}, \quad (1)$$

where A_i	activity (% conversion per g of catalyst)
t	time
a_i	activity (mole $liter^{-1}$ g^{-1}) at zero time
c_i	lifetime of active sites (min^{-1})

From experiments in which the acidic, oxidizing and reducing catalyst sites have been poisoned before determining catalytic activity, it has been possible to assign A_L, a_L and c_L to Lewis-oxidizing sites (L) and A_B, a_B and c_B to Brønsted sites (B) (*1*). Additional uv experiments have shown that the deactivation phenomenon takes place mainly on Lewis acid sites by butene oligomerization. Furthermore the ratio Lewis activity/Brønsted activity depends on the reaction temperature. At room temperature only Lewis sites are operative and at 85°C they are 15 times more active than the Brønsted sites. The question arises as to how the deactivation phenomenon can be analyzed and what are the active sites on the dealuminated materials K-9.4, K-2.4 and K-0.1.

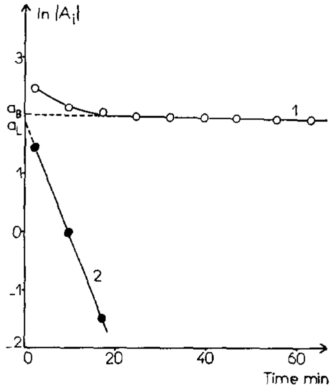


FIG. 1. The ln of the catalytic activity versus run time on K-2.4 at 85°C (1) ln A_T; (2) ln $(A_T - A_B)$.

Figure 1 shows the deactivation of the catalyst as a function of run time. The curve of ln A_T versus run time (A_T is the measured total activity) decreases during the first 20 min and then becomes a straight line (Fig. 1, curve 1). This straight line corresponds to an exponential law which can be written:

$$\ln A_T = \ln A_B = \ln a_B - c_B t. \quad (2)$$

The total activity A_T equals A_B for $t > 20$ min. For $t < 20$ min, plotting ln $(A_T - A_B)$ provides a straight line (Fig. 1, curve 2) according to the equation:

$$\ln(A_T - A_B) = \ln A_L = \ln a_L - c_L t, \quad (3)$$

a_L and a_B are the ordinates for zero time. They correspond to isomerizing activities at the beginning of a run. From these activities a_L and a_B, the initial rates v_L and v_B of product formation can be deduced from the dependence on contact time as described previously (*1*).

In order to investigate the nature of the active sites, the vapor of a reducing reagent (thianthrene), or a base (NH_3), or an oxidizing reagent (trinitrobenzene) have been adsorbed on the catalyst before determining the catalytic activity. In some cases protons have been exchanged by Na^+

TABLE 2
INFLUENCE OF THE NEUTRALIZATION OF ACTIVE SITES ON THE INITIAL RATES

	K-14		K-2.4	
	v_L[a]	v_B[a]	v_L[a]	v_B[a]
Unpoisoned samples	12.8	0.85	4.7	4.7
Neutralization of oxidizing sites with thianthrene (5 hr at 110°C)	0.00	0.83	4.6	4.7
Neutralization of acid sites with NH_3 desorbed at 235°C	0.7	0.00	0.01	0.00
Desorbed at 350°C	6.2	0.74	3.0	2.7
Neutralization of protonic sites 0.28% Na	12.2	0.44	4.7	1.2
Neutralization of reducing sites with trinitrobenzene (¼ hr at 110°C)	0.81	0.52	4.7	4.7

[a] Rates expressed in moles s^{-1} g^{-1} $\times$ 10^6 for a reactant pressure of 30 Torr.

ions before determining the activity. These pretreatments lead to poisoned samples where, respectively, oxidizing centers, acidic sites (Lewis and Brønsted), reducing centers and protons have been neutralized or exchanged. The results are reported in Table 2. Data already published on K-14 (*1*) are also reported in Table 2.

When Lewis and Brønsted acid sites are poisoned (NH_3 adsorption), v_L and v_B decrease on K-2.4 as on K-14. Adsorption of thianthrene on oxidizing sites leaves v_B unchanged on K-14 and K-2.4, but the behavior of v_L is different for the two catalysts. On K-2.4, thianthrene poisoning has no effect. The adsorption of thianthrene on silica–aluminas gives a pink color indicating a charge transfer complex (*7*) which is observed on K-14 and K-2.4. But when butene is introduced and isomerization proceeds, only K-2.4 recovers its original color, i.e., white. So in this case the *cis*-2-butene adsorption is stronger than that of thianthrene occurring on the same sites. This observation can account for the constancy of v_L. The same effect is observed in blocking the reducing sites with trinitrobenzene. The exchange of protons by Na^+ ions decreases v_B and does not affect v_L on K-14 and K-2.4 samples.

Thus the poisoning experiments on K-2.4 allow the nature of active sites to be specified qualitatively as on the initial material K-14. The rate v_L is linked to the Lewis acid sites and probably as on K-14 to oxidizing centers, which in dealuminated catalysts are able to adsorb butene stronger than thianthrene. The rate v_B is linked to Brønsted sites. In both cases *cis*-2-butene can displace trinitrobenzene adsorbed on reducing sites. This result implies that, as demonstrated with K-14, these sites play a role in the isomerization.

Kinetic data

i. Rate Dependence with Reactant Pressure

Figures 2a and 3a report the initial rates v_L and v_B versus *cis*-2-butene pressure for 1-butene formation on the four catalysts at 85°C. Figures 2b and 3b refer to *trans*-2-butene formation.

For K-14, the linear relationship between the rate v_L or v_B and reactant pressure (Figs. 2a,b and 3a,b) denotes first order kinetics in the pressure range studied. The behavior of the three dealuminated samples is different. The rates of isomerization obey the Langmuir equation:

$$v = k\frac{bP}{1 + bP}, \qquad (4)$$

where k rate constant (mole s^{-1} g^{-1} or mole s^{-1} m^{-2})
b adsorption equilibrium constant ($Torr^{-1}$)
P *cis*-2-butene pressure (Torr)

Plotting P/v versus P provides a linear form of Eq. (4), (Figs. 2c,d and 3c,d). The

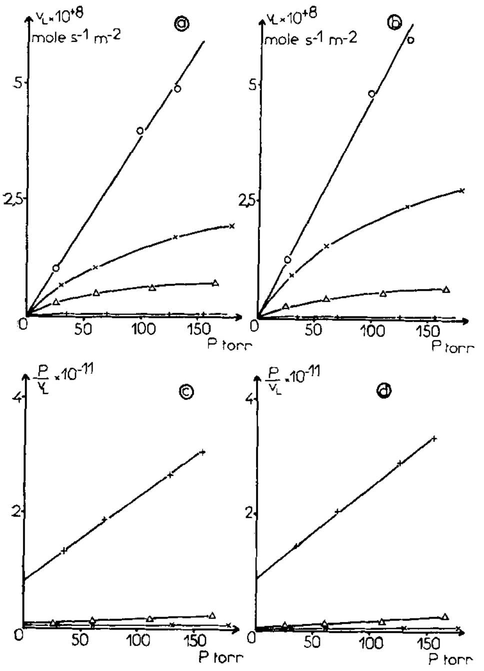


FIG. 2a. v_L variations vs reactant pressure at 85°C for the double-bond shift on the four catalysts; (b) v_L variations vs reactant pressure at 85°C for *cis–trans* conversion on the four catalysts; (c) linear plot of (a); (d) linear plot of (b). (○) K-14, (×) K-9.4, (△) K-2.4, (+) K-0.1.

intercept on the P/v axis and the slope of the straight line allow k and b to be calculated. The validity of Eq. (4) implies that the isomerizing rate is proportional to the coverage θ ($v = k\theta$) so in our catalytic conditions the reaction in the adsorbed state is a slower step than reactant adsorption or product desorption.

Figures 2a,b and 3a,b show identical variations of rates of formation of the two products. This suggests that *cis–trans* and double-bond isomerization are parallel reactions, as already proposed by Hightower and Hall (*2*). Numerical data of kinetic parameters given below will strengthen this view.

In the next two sections data are presented on the variation of aluminum content of the catalysts and reaction temperature, firstly for the isomerization on the Lewis sites and secondly for the isomerization on Brønsted sites.

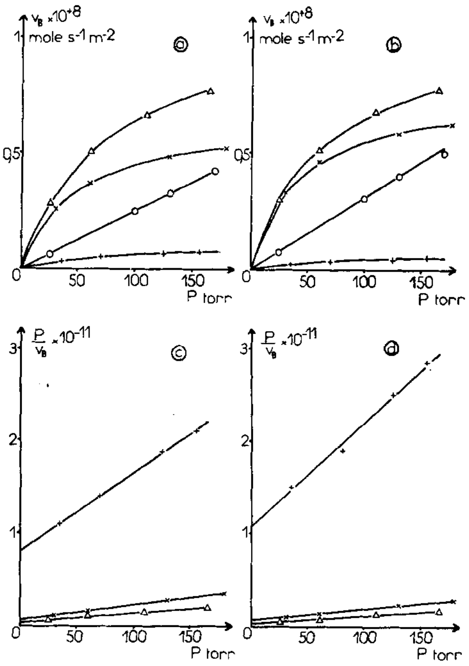


FIG. 3a. v_B variations vs reactant pressure at 85°C for the double-bond shift on the four catalysts; (b) v_B variations vs reactant pressure at 85°C for *cis–trans* conversion on the four catalysts; (c) linear plot of (a); (d) linear plot of (b). (○) K-14, (×) K-9.4, (△) K-2.4, (+) K-0.1.

ii. Isomerization on Lewis Acid Sites

Kinetic parameters k and b are not available separately on K-14 because the sample obeys first order kinetics. Table 3 reports k and b values at 85°C on dealuminated catalysts for the double-bond and *cis–trans* isomerizations.

Aluminum removal causes a decrease in k_1 (1-butene formation) and in k_t (*trans*-2-butene formation), so the number of active sites has decreased. The same pattern is available considering the number of Lewis acid sites vs aluminum content from K-14 to K-0.1 (*8*). The parallel decrease in Lewis acidity from K-14 to K-0.1 and in the number of Lewis active sites from K-9.4 to K-0.1 leads us to the reasonable assumption that on K-14 there is a greater number of isomerizing sites of Lewis type than on dealuminated catalysts. The upper position of the K-14 curves in Fig.

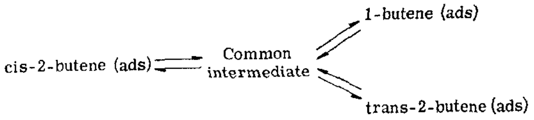
TABLE 3

k AND *b* VALUES AT 85°C ON DEALUMINATED CATALYSTS FOR REACTION ON LEWIS SITES

		cis-2-Butene → 1-butene		*cis*-2-Butene → *trans*-2-butene	
Catalysts	k_1/k_t	$k_1 \times 10^9$ (mole s^{-1} m^{-2})	$b_1 \times 10^3$ ($Torr^{-1}$)	$k_t \times 10^9$ (mole s^{-1} m^{-2})	$b_t \times 10^3$ ($Torr^{-1}$)
K-9.4	0.7	33	8	47	8
K-2.4	1.1	9.7	18	9	18
K-0.1	1.1	0.7	17	0.6	17

2a,b is consistent with the above arguments.

The *b* values for double-bond and *cis–trans* isomerization are equal. A ratio k_1/k_t close to unity and constant over a run has been found. These results strongly suggest that the two reactions take place on the same kind of sites through a common intermediate according to the scheme proposed by Hightower and Hall (*2*):



(5)

Therefore the total rate for irreversible product formation (1-butene + *trans*-2-butene) will be at low conversion:

$$v_L = (k_1 + k_t)\frac{bP}{1 + bP}. \tag{6}$$

The rate v_L does not always increase with temperature but exhibits a maximum value near 85°C as reported in Table 4 for K-14 and K-2.4. This result is well understood considering previous results on the deactivation phenomenon on K-14 and K-2.4 (*1*, *9*) and on other silica–aluminas (*2*, *10–12*). The isomerization of *cis*-2-butene on what we have called "Lewis sites," for clarity, in fact does not take place directly on these sites. A first step consists of *cis*-2-butene oligomerization on Lewis sites in the very first minutes of a run. The oligomers are strongly chemisorbed and have some hydrogen atoms with acidic properties induced by the catalyst; then they can act as Brønsted sites when a *cis*-2-butene molecule of the gas phase collides with the surface. Polymerization, or better oligomerization of butene exhibits a maximum activity with increasing temperature (*9*). Then logically isomerization must follow the same temperature pattern which explains the data reported in Table 4.

TABLE 4

DEPENDENCE OF v_L WITH REACTION TEMPERATURE FOR K-14 AND K-2.4

Reaction temp (°C)	$v_L \times 10^8$ (mole s^{-1} m^{-2})	
	K-14[a]	K-2.4[b]
28	1.1	
65		0.23
85	10	0.65
100		0.10
105	1.3	

[a] Reactant pressure, 120 Torr.

[b] Reactant pressure, 30 Torr.

iii. Isomerization on Brønsted Sites

Activation energy and chemisorption enthalpy. Tables 5 and 6 report *b* and *k* values on dealuminated catalysts for double-bond shift (Table 5) and for *cis–trans* conversion (Table 6) at reaction temperatures between 65 and 105°C. The Arrhenius law is followed and in this case activation energies and chemisorption enthalpies have been determined for each catalyst.

At 85°C the kinetic parameters *k* and *b* are available for the three samples and can be compared. Both for double-bond shift and *cis–trans* conversion, the removal of aluminum between K-9.4 and K.2.4 slightly increases k_1 and k_t, and decreases them between K-2.4 and K-0.1. The *b* values decrease monotonously with the removal

TABLE 5

k, b, E, AND ΔH VALUES FOR *cis*-2-BUTENE → 1-BUTENE ON DEALUMINATED SAMPLES FOR SEVERAL REACTION TEMPERATURES ON BRØNSTED SITES

Reaction temp (°C)	$k_1 \times 10^8$ (mole s^{-1} m^{-2})			$b_1 \times 10^3$ (Torr^{-1})		
	K-9.4	K-2.4	K-0.1	K-9.4	K-2.4	K-0.1
65	0.12	0.17		85	57	
75	0.27	0.36		43	27	
85	0.65	1.1	0.12	22	14	10
95			0.31			8.3
105			1.2			6.4
E (kcal mole^{-1} ± 1)	20	21	30			
$-\Delta H$ (kcal mole^{-1} ± 2)				16	17	7

of aluminum. Compared with the two other dealuminated samples, K-0.1 gives a low chemisorption enthalpy (-7 kcal mole^{-1}) which indicates a weak interaction butene–surface, while its high activation energy (30 kcal mole^{-1}) shows a large energy step between adsorbed phase and activated complex. Consequently it may be suggested that butene adsorbed on K-0.1 is closer to the gas phase configuration than on K-9.4 and K-2.4 samples. Therefore in that particular case there is probably a change in entropy between the adsorbed state and the activated complex, i.e., $\Delta S^\ddagger$ does not equal zero.

For each catalyst the same values of ΔH and E are obtained for the two reactions (double-bond and *cis–trans* isomerizations). So the adsorption step takes place on the same kind of site (same ΔH) and the barrier height between chemisorbed reactant and activated complex are the same (same E). Thus the two reaction paths involve the same activated complex. These results corroborate the mechanism Eq. (5) already described for the isomerization on Lewis acid sites.

Selectivity. The aluminum content modifies also the ratio k_1/k_t which represents the selectivity (S) of the reaction (Table 7). The S value for thermodynamic equilibrium at 85°C is 0.1 (*13*). This is quite different from the experimental values (~1). Table 7 shows that the selectivity increases slightly from K-14 to K-2.4 and more from K-2.4 to K-0.1.

Nature of the activated complex. Two main reaction paths have been proposed in previous papers. Starting from *cis*-2-butene as reactant, the double-bond shift and *cis–trans* conversion are consecutive reactions according to Eq. (7) described by Turke-

TABLE 6

k, b, E, AND ΔH VALUES FOR *cis*-2-BUTENE → *trans*-2-BUTENE ON DEALUMINATED SAMPLES FOR SEVERAL REACTION TEMPERATURES ON BRØNSTED SITES

Reaction temp (°C)	$k_t \times 10^8$ (mole s^{-1} m^{-2})			$b_t \times 10^3$ (Torr^{-1})		
	K-9.4	K-2.4	K-0.1	K-9.4	K-2.4	K-0.1
65	0.15	0.17		85	57	
75	0.34	0.38		45	28	
85	0.76	1.1	0.09	26	15	9.9
95			0.23			8.3
105			1.04			6.0
E (kcal mole^{-1} ± 1)	19	21	30			
$-\Delta H$ (kcal mole^{-1} ± 2)				15	16	7

TABLE 7
SELECTIVITY VALUES S ON BRØNSTED SITES AT 85°C

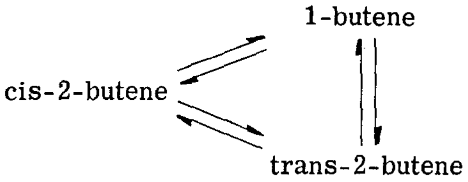
	K-14[a]	K-9.4	K-2.4	K-0.1
$S = k_1/k_t$	0.80	0.85	0.93	1.4

[a] On K-14 the selectivity has been calculated from the ratio v_1/v_t, k_1 and k_t being not separately available because first order kinetics are obeyed in this case.

vich and Smith (*4*) and Leftin and Hermana (*5*):

$$cis\text{-2-butene} \rightleftharpoons \text{1-butene} \rightleftharpoons trans\text{-2-butene}. \quad (7)$$

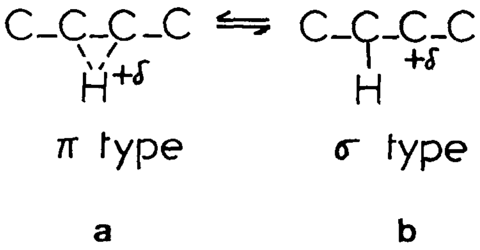
Equation (8) describes the double-bond and *cis–trans* isomerizations as parallel reactions involving the same activated complex as Eq. (5). It may be written as follows:



(8)

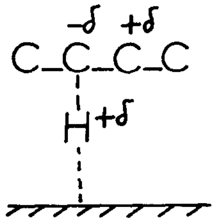
This reaction has been extensively discussed by Hightower and Hall (*2*).

As pointed out in this paper the experimental data fit best to Eq. (8). The question raised now is to specify the nature of the activated complex. Hightower and Hall (*2*) have described a *sec*-butyl carbonium ion as the intermediate complex which can explain their selectivities ($0.5 < S < 1.1$). Theoretically, taking into account C–H bond energies in CH_3 or CH_2 groups and using statistical arguments, the selectivity is equal to 0.75 (*2*). The good agreement between this theoretical value and those observed on K-14, K-9.4 and K-2.4 (Table 7) leads us to assume reasonably that a *sec*-butyl carbonium ion is the activated complex. On K-0.1, S (1.4) differs to some extent from 0.75. This catalyst has weaker acid sites compared to the three other silica–aluminas (*6*) and the high S value might then be explained as follows. The Brønsted sites on silica–alumina may be depicted as hydrogen atoms which are more or less acidic. A more acidic hydrogen atom bears a positive charge $+\delta$ which is greater than that of a less acidic one. According to this picture the adsorption and reaction steps may be visualized as follows. The adsorption of *cis*-2-butene takes place by interaction of the double bond and of a hydrogen atom bearing a positive charge $+\delta$. The interaction may be of π or σ type [Eq. (9)]:



(9)

In the first case (a) the $H^{+\delta}$ empty s orbital combines with the full π orbital of the double bond. In the second case (b) it combines with an sp^3 full orbital of the negative end in the polarized double bond and a carbonium ion is formed. In fact π and σ types are in equilibrium. If the proton bears a positive charge +1, a π complex will form readily and give the σ complex which already holds the *sec*-butyl carbonium ion configuration. If the active site is a hydrogen atom bearing a positive charge smaller than unity, the $H^{+\delta}$ s orbital is not quite empty. The interaction with the double bond will be less than in the case H^+ double bond, providing a lower chemisorption enthalpy (as experimentally found in Tables 5 and 6). The σ type complex has to be formed and can be represented as:



(10)

This system is less ionic than the *sec*-butyl carbonium ion. To obtain the activated configuration (supposed to be that of the *sec*-butyl carbonium ion) the energy provided to the system must be greater than in the case of H^+ as the active site. The

TABLE 8
Variations of Selectivity with Reaction Temperature on Dealuminated Catalysts

Reaction temp (°C)	Selectivity S		
	K-9.4	K-2.4	K-0.1
65	0.83	1.0	
75	0.90	0.96	
85	0.85	0.93	1.4
95			1.3
105			1.1

transformation of scheme (10) into Eq. (9b) might require an intermediate step corresponding to the concerted mechanism proposed by Brouwer (*3*) and Turkevich and Smith (*4*) which promotes 1-butene formation. This intermediate step is not favored by a reaction temperature increase which promotes the surface–$H^{+\delta}$ bond rupture. Then the ratio k_1/k_t will decrease when the reaction temperature is raised on catalysts involving such a concerted mechanism. Table 8 reports S values for K-9.4, K-2.4 and K-0.1 at different temperatures. On K-9.4, S does not change with temperature. In this case it can be said that the intermediate complex is the *sec*-butyl carbonium ion, the activated complex being the carbonium ion in the excited state. From K-2.4 to K-0.1, the S decrease is more important as the aluminum is extracted. The concerted mechanism would become more and more important though the *sec*-butyl carbonium ion must not be neglected.

Conclusion

Dealuminated catalysts exhibit an activity decrease with run time which obey exponential laws. Determination of kinetic parameters with the help of the Langmuir equation gives information on (i) the nature of the activated complex and (ii) the kinetic orders vs reactant pressure, thereby allowing the catalyst activities to be compared.

i. The double-bond and *cis-trans* isomerizations are parallel reactions taking place on the same kind of active site (Lewis or Brønsted acid sites). The nature of the activated complex may vary according to the acidity strength of the samples studied. Besides the classical *sec*-butyl carbonium ion described by Hightower and Hall (*2*), a concerted mechanism proposed by Brouwer (*3*) and Turkevich and Smith (*4*) may be involved on weak acid catalysts promoting 1-butene formation.

ii. The kinetic order with respect to reactant pressure is unity on K-14 and varies from unity to zero on dealuminated materials as reactant pressure is raised. Comparison of the different catalyst activities should also be made in conditions of first order kinetics (low reactant pressure). These activities could then be quantitatively compared with the other chemical properties of the solids. An attempt to make quantitative correlations for different aluminum contents will be described in another paper.

References

1. Ballivet, D., Barthomeuf, D., and Trambouze, Y., *J. Catal.* **26**, 34 (1972).

2. Hightower, J. W., and Hall, W. K., *J. Phys. Chem.* **71**, 1014 (1967).

3. Brouwer, D. M., *J. Catal.* **1**, 22 (1962).

4. Turkevich, J., and Smith, R. K., *J. Phys. Chem.* **16**, 466 (1948).

5. Leftin, H. P., and Hermana, E., *Proc. Int. Congr. Catal. 3rd, 1964* **2**, 1064 (1965).

6. Barthomeuf, D., Ballivet, D., Devaux, R., and Trambouze, Y., *Bull. Soc. Chim. Fr.* **5**, 1495 (1967).

7. Naccache, C., unpublished data.

8. Ballivet, D., Barthomeuf, D., and Pichat, P., *J. Chem. Soc. Faraday Trans. I* **68**, 1712 (1972).

9. Ballivet, D., Basset, J., Barthomeuf, D., Mathieu, M. V., Trambouze, Y., and Prettre, M., *in* "Reaction Transition States," p. 37. Gordon and Breach, New York, 1973.

10. Ozaki, A., and Kimura, K., *J. Catal.* **3**, 395 (1964).

11. Clark, A., and Finch, J. N., *Proc. Int. Congr. Catal. 4th*, pap. No. 75 (1968).

12. Webb, A. N., *Actes Congr. Int. Catal. 2nd, 1960* **2**, 1289 (1961).

13. Kilpatrick, J. E., Prosen, E. J., Pitzer, K. S., and Rossini, F. E., *J. Res. Nat. Bur. Stand.* **36**, 559 (1946).