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## KINETICS OF *n*-BUTENE ISOMERIZATION STUDIED BY STOPPED-FLOW GAS CHROMATOGRAPHY

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### SUMMARY

The kinetics of isomerization of *n*-butenes on molecular sieve 13X, silica gel and alumina were studied by stopped-flow gas chromatography. The results are explained by assuming a reaction scheme with two kinds of active sites and a common intermediate. Based on this scheme, analytical expressions are derived describing the various rate laws. These are used to calculate rate constants of isomerization on the three catalytic surfaces, at various temperatures. Activation energies and entropies for each kind of active sites and for each reaction have been determined.

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### INTRODUCTION

The catalytic isomerization of *n*-butenes on various surfaces continues to be of interest, particularly on zeolites<sup>1</sup>. Most of these studies, however, involved static experiments and few employed the microcatalytic technique. The theory of the stopped-flow gas chromatographic technique for measuring reaction rates on a surface with many kinds of active sites was recently described by Katsanos<sup>2</sup>. By means of the equations derived, rate constants for surface reactions can be determined accurately, over the whole range of conversions. We have used this method to study the isomerization of *n*-butenes on molecular sieve 13X, silica gel and activated alumina.

### EXPERIMENTAL

#### *Materials*

Molecular sieve 13X, 80–100 mesh (Applied Science Labs., State College, PA, U.S.A.), had the formula  $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot x \text{H}_2\text{O}$ . Silica gel (S x 143; Matheson, Coleman & Bell, East Rutherford, NJ, U.S.A.), 100–120 mesh, had pH  $2.0 \pm 0.3$ , and alumina (BDH, Poole, Great Britain) was acidic, Brockmann grade I, 100–120 mesh.

Chromosorb P, acid washed, 60–80 mesh (Varian Aerograph, Walnut Creek, CA, U.S.A.), ethylene glycol (purum; Eastman, Rochester, NY, U.S.A.) and silver nitrate (pro analysi; E. Merck, Darmstadt, G.F.R.) were used without further purification. *n*-Butenes (Matheson Gas Products) were 99.9% pure. Helium (99.9% pure; AGA Chropei, Athens, Greece) was used as carrier gas after drying it by passage through molecular sieve 4A. Volumetric gas flow-rates were in the range  $0.50\text{--}0.67 \text{ cm}^3 \text{ sec}^{-1}$ .

### Apparatus and procedure

The details of the application of the stopped-flow technique have been published elsewhere<sup>3</sup>. In the present paper, instead of a 500-cm<sup>3</sup> reservoir, a Pye-Unicam Model 792108/1 gas flow controller was used to maintain a constant flow-rate independent of temperature variations.

Two columns were used in series, heated in separate ovens. The first, 1.5–2 × 0.4 cm I.D., contained 0.2 g of catalyst and was activated at 673°K and 1 Torr for 4 h. It was then heated at 373°K, for 24 h, under carrier gas flow. The second column, 170 × 0.4 cm I.D., was an analytical column filled with 40% ethylene glycol–silver nitrate on Chromosorb P. It was maintained at a constant temperature lower than 323°K.

The stopped-flow intervals were 3 min.

### RESULTS AND DISCUSSION

In each experiment involving stopping and restoring the carrier gas flow, three stop-peaks appear in the chromatogram with well defined retention times, as shown in Fig. 1. The first stop-peak corresponds to *trans*-2-butene, whereas the other two (overlapping) peaks are due to 1-butene and *cis*-2-butene. Retention times remained constant during the same kinetic experiment, and the chromatograms had the same appearance for all *n*-butene reactants.

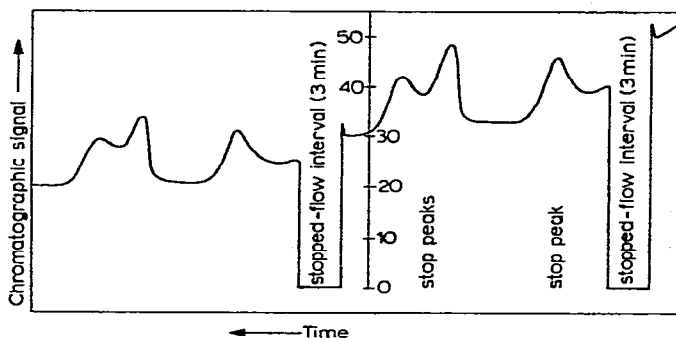


Fig. 1. Part of a typical stopped-flow chromatogram for the isomerization of 1-butene on molecular sieve 13X, at 393.2°K.

The area under the curve for each stop-peak,  $f_s$ , when plotted semilogarithmically as a function of time,  $t$ , at the moment of stopping the carrier gas, yields curves such as those shown in Fig. 2. Empirically, these curves can be described by a function of the form

$$f_s = a_1 \exp(-b_1 t) + a_2 \exp(-b_2 t) \quad (1)$$

where  $a_1$ ,  $a_2$ ,  $b_1$  and  $b_2$  are positive constants depending only on the reaction being studied and the temperature, with  $a_2 > a_1$  and  $b_2 > b_1$ . These four constants can be determined in the usual way by analyzing the curve of radioactivity against time for a mixture of two radioisotopes differing considerably in their decay constants. The method is described in detail elsewhere<sup>4</sup>.

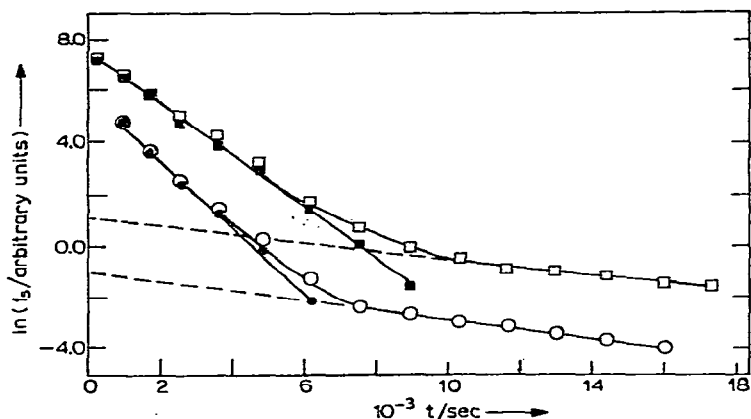
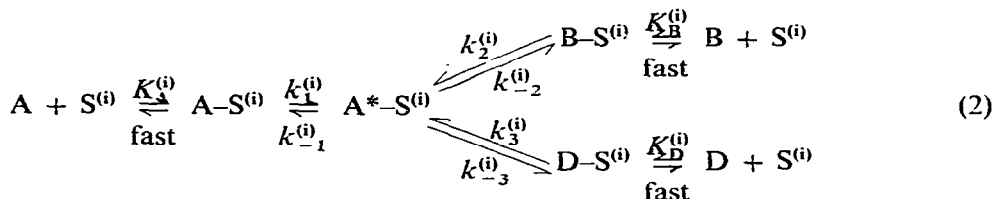


Fig. 2. The area under the stop-peaks plotted semilogarithmically versus time for the isomerization of *cis*-2-butene on silica gel at 468°K, with a volume flow-rate of 0.5 cm<sup>3</sup> sec<sup>-1</sup>. Stop-peaks: □, ■, 1-butene + *cis*-2-butene (left ordinate); ○, ●, *trans*-2-butene (right ordinate). Open symbols are experimental points; filled symbols are points obtained by subtracting from the experimental points the corresponding values calculated from the linear extrapolations represented by the broken lines.

Eqn. 1 can be derived theoretically on the basis of the following mechanism:



Here A, B and D are the three isomeric gaseous *n*-butenes. S<sup>(i)</sup> is the *i*th kind of surface active sites. In the present case it suffices to take *i* = 1 or 2, *i.e.*, only two kinds of sites. A-S<sup>(i)</sup>, B-S<sup>(i)</sup> and D-S<sup>(i)</sup> are adsorbed species of the *n*-butenes with respective (dimensionless) partition coefficients  $K_A^{(i)}$ ,  $K_B^{(i)}$  and  $K_D^{(i)}$ . A\*-S<sup>(i)</sup> is a common surface intermediate for the three butenes, possibly a carbonium ion adsorbed on sites *i*. Finally,  $k_1$ ,  $k_{-1}$ ,  $k_2$ ,  $k_{-2}$ ,  $k_3$  and  $k_{-3}$  are rate constants (sec<sup>-1</sup>) for the surface reactions shown. The above mechanism is in accord with the fact that a common intermediate in the isomerization of butenes has often been postulated<sup>5-12</sup>.

The theoretical equations are derived using the same assumptions as before<sup>2</sup>, namely that the concentration of active sites is high compared with those of the corresponding adsorbed species, that the isotherms are linear, axial diffusion of the gases in the catalytic bed is negligible, the reacting vapour is introduced as an instantaneous pulse described by a Dirac delta function,  $\delta(t)$ , and finally that equilibration of the reactants and products between the gas and the solid phases is instantaneous.

The same symbols as before<sup>2</sup> are used in the present paper, and the problem is considered separately for two time intervals, *t* and *t*<sub>s</sub>.

*Interval,  $t$ , until stopping of the gas flow*

The concentrations in the gas phase,  $c_A(x, t)$ ,  $c_B(x, t)$  and  $c_D(x, t)$ , and in the adsorbed state,  $q_A^{(i)}(x, t)$ ,  $q_B^{(i)}(x, t)$ ,  $q_D^{(i)}(x, t)$  and  $q_{A^*}^{(i)}(x, t)$ , are determined by the following system of equations.

Mass balance for A and A-S<sup>(i)</sup>:

$$\frac{\partial c_A}{\partial t} + r \sum_i \frac{\partial q_A^{(i)}}{\partial t} = -v \cdot \frac{\partial c_A}{\partial x} - r \sum_i k_1^{(i)} q_A^{(i)} + r \sum_i k_{-1}^{(i)} q_{A^*}^{(i)} \quad (3)$$

(where  $r$  is the volume ratio of solid and gas phases and  $v$  is the linear velocity of carrier gas in interparticle space.)

Here index  $i$  ranges over all active sites participating in the reactions. Since mechanism 2 is symmetrical, the mass balance for B and B-S<sup>(i)</sup> is given by eqn. 3 with subscript B substituted for the subscript A and the rate constants  $k_2^{(i)}$ ,  $k_{-2}^{(i)}$  substituted for  $k_1^{(i)}$ ,  $k_{-1}^{(i)}$ , respectively.  $q_{A^*}^{(i)}$  remains unchanged. Similarly, the mass balance for D and D-S<sup>(i)</sup> is written as in eqn. 3 but with the subscript D instead of A, and  $k_3^{(i)}$ ,  $k_{-3}^{(i)}$  in place of  $k_1^{(i)}$ ,  $k_{-1}^{(i)}$ , respectively.

Rate of change of A\*-S<sup>(i)</sup>:

$$\frac{\partial q_{A^*}^{(i)}}{\partial t} = k_1^{(i)} q_A^{(i)} + k_2^{(i)} q_B^{(i)} + k_3^{(i)} q_D^{(i)} - k^{(i)} q_{A^*}^{(i)} \quad (4)$$

where:

$$k^{(i)} = k_{-1}^{(i)} + k_{-2}^{(i)} + k_{-3}^{(i)} \quad (5)$$

Initial and boundary conditions, with A as reactant:

$$c_A(0, t) = (m/\dot{V}) \delta(t), \quad c_B(0, t) = c_D(0, t) = 0 \quad (6)$$

$$c_A(x, 0) = c_B(x, 0) = c_D(x, 0) = q_{A^*}^{(i)}(x, 0) = 0 \quad (7)$$

where  $m$  is the total mass of A injected and  $\dot{V}$  is the volume flow-rate of carrier gas.

Adsorption isotherms:

$$q_A^{(i)} = K_A^{(i)} c_A, \quad q_B^{(i)} = K_B^{(i)} c_B, \quad q_D^{(i)} = K_D^{(i)} c_D \quad (8)$$

Now, we substitute eqns. 8 into eqns. 3 and 4, remembering that  $rK_A^{(i)}$ ,  $rK_B^{(i)}$  and  $rK_D^{(i)}$  are equal to the partition ratios  $k_A^{(i)}$ ,  $k_B^{(i)}$  and  $k_D^{(i)}$ , respectively, and making the approximation that terms containing  $k_2^{(i)}$  and  $k_3^{(i)}$  are negligible since A is taken as the reactant and most of A\*-S<sup>(i)</sup> is formed from A-S<sup>(i)</sup>. Then, the Laplace transforms with respect to  $t$  of the resulting equations are taken, under the initial conditions 6, and combined to obtain the following equations ( $C_A$ ,  $C_B$  and  $C_D$  are the Laplace transforms of  $c_A$ ,  $c_B$  and  $c_D$  with respect to  $t$ ):

$$\frac{dC_A}{dx} + \frac{\Omega_A}{v} \cdot C_A = 0 \quad (9)$$

$$\frac{dC_B}{dx} + \frac{\Omega_B}{v} \cdot C_B = \frac{\Phi_B}{v} \cdot C_A \quad (10)$$

$$\frac{dC_D}{dx} + \frac{\Omega_D}{v} \cdot C_D = \frac{\Phi_D}{v} \cdot C_A \quad (11)$$

where:

$$\Omega_A = \left(1 + \sum_i k_A^{(i)}\right) p + \sum_i k_1^{(i)} k_A^{(i)} - \sum_i \frac{k_1^{(i)} k_{-1}^{(i)} k_A^{(i)}}{p + k^{(i)}} \quad (12)$$

$$\Omega_B = \left(1 + \sum_i k_B^{(i)}\right) p \quad (13)$$

$$\Omega_D = \left(1 + \sum_i k_D^{(i)}\right) p \quad (14)$$

$$\Phi_B = \sum_i \frac{k_1^{(i)} k_{-2}^{(i)} k_A^{(i)}}{p + k^{(i)}} \quad (15)$$

$$\Phi_D = \sum_i \frac{k_1^{(i)} k_{-3}^{(i)} k_A^{(i)}}{p + k^{(i)}} \quad (16)$$

( $p$  is the transform parameter with respect to  $t$ .)

The solutions of eqns. 9 and 10 with respect to  $x$ , subject to conditions 6, are:

$$C_A = \frac{m}{V} \cdot \exp\left(-\frac{\Omega_A x}{v}\right) \quad (17)$$

$$C_B = \frac{m}{V} \cdot \Phi_B \cdot \frac{\exp(-\Omega_B x/v) - \exp(-\Omega_A x/v)}{\Omega_A - \Omega_B} \quad (18)$$

The solution of eqn. 11 is similar to 18 with  $\Omega_D$  and  $\Phi_D$  in place of  $\Omega_B$  and  $\Phi_B$ , respectively.

*Stopped-flow interval,  $t_s$*

Had the carrier gas flow not been interrupted, the interval  $t_s$  would be a continuation of the previous interval  $t$  and the concentration  $c_A$  would again be governed by eqn. 3, with the isotherm 8 substituted for  $q_A^{(i)}$ :

$$\left(1 + \sum_i k_A^{(i)}\right) \cdot \frac{\partial c_A}{\partial t_s} = -v \cdot \frac{\partial c_A}{\partial x} - \sum_i k_1^{(i)} k_A^{(i)} c_A + r \sum_i k_{-1}^{(i)} q_A^{(i)} \quad (19)$$

If, however, the flow of the carrier gas has been stopped ( $v = 0$ ), this equation becomes:

$$(1 + \sum_i k_A^{(i)}) \cdot \frac{\partial c_A'}{\partial t_s} = - \sum_i k_1^{(i)} k_A^{(i)} c_A' + r \sum_i k_{-1}^{(i)} q_A^{(i)} \quad (20)$$

where  $c_A'$  and  $q_A^{(i)}$  are the concentrations when  $v = 0$ .

Subtracting eqn. 19 from 20, assuming that  $q_A^{(i)}$  and  $q_A^{(i)*}$  are approximately equal since  $t_s$  is small, and taking the Laplace transform with respect to  $t$  of the resulting equation, we obtain

$$(1 + \sum_i k_A^{(i)}) \cdot \frac{\partial (\Delta C_A)}{\partial t_s} = v \cdot \frac{\partial C_A}{\partial x} - \sum_i k^{(i)} k_A^{(i)} (\Delta C_A) \quad (21)$$

where  $\Delta C_A = C_A' - C_A$  is the Laplace transform of the enrichment of the gas phase in  $C_A$  during the stopped-flow interval.

Now, the term  $v (\partial C_A / \partial x)$  in eqn. 21 can be estimated from eqn. 17 by differentiation with respect to  $x$ . If this result is substituted in 21 and the resulting equation is integrated with respect to  $t_s$ , noting that  $\Delta C_A = 0$  at  $t_s = 0$ , we obtain

$$\Delta C_A = - \frac{m}{V} \cdot Y \Omega_A \exp\left(-\frac{\Omega_A x}{v}\right) \quad (22)$$

where

$$Y = \frac{1 - \exp\left(-\sum_i k_1^{(i)} g^{(i)} t_s\right)}{\sum_i k_1^{(i)} k_A^{(i)}} \quad (23)$$

and

$$g^{(i)} = \frac{k_A^{(i)}}{1 + \sum_i k_A^{(i)}} \quad (24)$$

is the fraction of A adsorbed on the  $i$ th kind of active sites.

To obtain the Laplace transform of the area under the stop-peak curve, eqn. 22 is integrated with respect to  $x$  between the limits 0 and  $l$ , i.e., over the entire catalytic column:

$$\mathcal{L}_t f_{s,A} = \int_0^l a \Delta C_A dx = mY [\exp(-\Omega_A t_M) - 1] \quad (25)$$

where  $t_M = l/v$  is the dead volume of the column. The stop-peak area,  $f_{s,A}$ , as a function of the time  $t$  is now obtained by taking the inverse Laplace transform with respect to the parameter  $p$  of eqn. 25, with the approximation that, when  $\Omega_A$  from

eqn. 12 is substituted into eqn. 25, the factor  $\exp\left(\sum_i \frac{k_1^{(i)} k_{-1}^{(i)} k_A^{(i)}}{p + k^{(i)}} \cdot t_M\right)$  is replaced by the

first two terms in its MacLaurin expansion. This is justified because  $t_M$  is very small. The result is

$$f_{s,A}/mY = \exp \left( - \sum_i k_1^{(i)} k_A^{(i)} t_M \right) \{ \delta(t - t_{R,A}) + u(t - t_{R,A}) \cdot \sum_i k_1^{(i)} k_{-1}^{(i)} k_A^{(i)} t_M \cdot \exp [ - k^{(i)} (t - t_{R,A}) ] \} - \delta(t) \quad (26)$$

where  $t_{R,A} = (1 + \sum_i k_A^{(i)}) t_M$  is the retention time of A on the catalytic column, and  $u(t - t_{R,A})$  is the Heaviside unit step function. For stop-times  $t > t_{R,A}$  this equation simplifies to:

$$f_{s,A} = mY \exp \left( - \sum_i k_1^{(i)} k_A^{(i)} t_M \right) \cdot \sum_i k_1^{(i)} k_{-1}^{(i)} k_A^{(i)} t_M \cdot \exp [ - k^{(i)} (t - t_{R,A}) ] \quad (27)$$

$Y$  is given by eqn. 23 and is a constant at constant temperature and constant  $t_s$ .

An analogous procedure for B, through eqns. 19–25, leads to:

$$\mathcal{L}_t f_{s,B} = \frac{mt_s \Phi_B}{1 + \sum_i k_B^{(i)}} \cdot \frac{\exp(-\Omega_B t_M) - \exp(-\Omega_A t_M)}{\Omega_A - \Omega_B} \quad (28)$$

TABLE I

RATE CONSTANTS FOR THE ISOMERIZATION OF *n*-BUTENES ON MOLECULAR SIEVE 13X AT VARIOUS TEMPERATURES

All errors given in this and the following tables are "standard errors".

Reactant	T (°K)	$10^4 k^{(1)} (\text{sec}^{-1})$ from		$10^3 k^{(2)} (\text{sec}^{-1})$ from	
		<i>trans</i> -2-Butene	Other two isomers	<i>trans</i> -2-Butene	Other two isomers
1-Butene	408.2	1.75 ± 0.02	1.66 ± 0.04	0.48 ± 0.04	0.50 ± 0.08
	413.2	2.1 ± 0.1	2.05 ± 0.09	0.59 ± 0.08	0.58 ± 0.02
	421.2	2.6 ± 0.2	2.5 ± 0.1	0.80 ± 0.06	0.81 ± 0.06
	437.2	4.2 ± 0.4	3.6 ± 0.2	1.6 ± 0.1	1.61 ± 0.09
	453.2	7.2 ± 0.4	6.8 ± 0.8	3.0 ± 0.8	2.9 ± 0.4
<i>cis</i> -2-Butene	410.2	2.16 ± 0.08	2.03 ± 0.06	—	—
	414.3	2.6 ± 0.2	2.7 ± 0.1	—	—
	419.2	3.4 ± 0.2	3.5 ± 0.2	1.05 ± 0.08	1.04 ± 0.08
	422.2	3.7 ± 0.2	4.2 ± 0.2	1.2 ± 0.1	1.17 ± 0.09
	428.2	4.7 ± 0.9	4.8 ± 0.6	1.51 ± 0.08	1.42 ± 0.06
	441.2	6.3 ± 0.6	6.2 ± 0.6	2.3 ± 0.4	2.3 ± 0.4
<i>trans</i> -2-Butene	413.2	2.3 ± 0.2	2.3 ± 0.4	—	0.83 ± 0.04
	418.3	2.67 ± 0.08	2.5 ± 0.2	0.88 ± 0.08	—
	423.1	3.6 ± 0.4	3.20 ± 0.06	1.1 ± 0.1	1.13 ± 0.09
	428.0	4.10 ± 0.08	4.01 ± 0.06	1.24 ± 0.09	1.5 ± 0.4
	433.2	4.76 ± 0.09	4.5 ± 0.4	1.6 ± 0.2	1.75 ± 0.02
	443.1	5.97 ± 0.06	5.8 ± 0.2	—	—

Since  $t_M$  is very small, the exponential functions can again be approximated by the first two terms of their MacLaurin expansions, with the result:

$$\mathcal{L}^{-1} f_{s,B} = \frac{mt_s \Phi_B}{1 + \sum_i k_B^{(i)}} \cdot t_M \quad (29)$$

By taking the inverse Laplace transform with respect to  $p$  of this equation, we obtain the area under the stop-peak of B:

$$f_{s,B} = \frac{mt_s t_M}{1 + \sum_i k_B^{(i)}} \cdot \sum_i k_1^{(i)} k_{-2}^{(i)} k_A^{(i)} \exp(-k^{(i)} t) \quad (30)$$

A similar equation can be derived for  $f_{s,D}$ .

The theoretical eqns. 27 and 30 coincide with the empirical eqn. 1 if  $i = 1$  and 2, *i.e.*, only two kinds of active sites. This is in agreement with results reported for alumina<sup>13,14</sup>. Thus, the proposed mechanism 2 is consistent with the experimental findings. The analysis of the latter by means of eqns. 27 and 30 permits the calculation of  $k^{(1)}$ , which is identified with  $b_1$  of eqn. 1, and of  $k^{(2)}$ , which is identified with  $b_2$ . This was done for each butene reactant, and the results are collected in Tables I–III for the three catalytic surfaces studied. As predicted by the theoretical equations, the values for the rate constants calculated from the stop-peaks of the reactants and of the products are the same, within experimental error.

TABLE II

RATE CONSTANTS FOR THE ISOMERIZATION OF *n*-BUTENES ON SILICA GEL AT VARIOUS TEMPERATURES

Reactant	T (°K)	$10^4 k^{(1)}$ (sec <sup>-1</sup> ) from		$10^3 k^{(2)}$ (sec <sup>-1</sup> ) from	
		<i>trans</i> -2-Butene	Other two isomers	<i>trans</i> -2-Butene	Other two isomers
1-Butene	415.2	1.5 ± 0.8	1.6 ± 0.2	0.83 ± 0.09	0.8 ± 0.1
	433.2	1.9 ± 0.4	2.0 ± 0.2	1.1 ± 0.1	1.1 ± 0.1
	446.2	3.1 ± 0.4	3.5 ± 0.4	1.21 ± 0.08	1.2 ± 0.1
	466.2	4.0 ± 0.8	4.1 ± 0.8	1.5 ± 0.2	1.4 ± 0.4
	490.2	6.7 ± 0.6	6.8 ± 0.9	—	—
	506.2	9.5 ± 0.9	9.5 ± 0.9	—	—
	523.2	11.0 ± 0.9	10.9 ± 0.9	—	—
<i>cis</i> -2-Butene	453.2	1.13 ± 0.08	1.2 ± 0.4	—	—
	468.2	1.7 ± 0.2	1.6 ± 0.4	0.73 ± 0.08	0.69 ± 0.08
	498.2	2.9 ± 0.9	3.2 ± 0.2	0.86 ± 0.09	0.87 ± 0.07
	511.2	3.2 ± 0.6	3.5 ± 0.9	1.10 ± 0.08	1.05 ± 0.09
	538.1	5.1 ± 0.8	5.3 ± 0.2	1.26 ± 0.04	1.20 ± 0.04



TABLE III  
RATE CONSTANTS FOR THE ISOMERIZATION OF n-BUTENES ON ALUMINA AT VARIOUS TEMPERATURES

Reactant	T (°K)	10 <sup>4</sup> k <sup>(1)</sup> (sec <sup>-1</sup> ) from		10 <sup>3</sup> k <sup>(2)</sup> (sec <sup>-1</sup> ) from	
		<i>trans</i> -2-Butene	Other two isomers	<i>trans</i> -2-Butene	Other two isomers
1-Butene	498.2	2.3 ± 0.6	2.3 ± 0.6	0.9 ± 0.2	0.87 ± 0.04
	510.2	3.2 ± 0.9	3.3 ± 0.8	1.0 ± 0.2	1.0 ± 0.1
	519.2	4.0 ± 0.9	3.9 ± 0.8	1.21 ± 0.04	1.19 ± 0.06
	538.2	6.3 ± 0.9	6.36 ± 0.09	1.34 ± 0.06	1.27 ± 0.08
<i>cis</i> -2-Butene	493.2	1.72 ± 0.09	1.7 ± 0.2	1.0 ± 0.1	0.8 ± 0.1
	506.2	2.3 ± 0.8	2.3 ± 0.2	1.11 ± 0.06	0.9 ± 0.2
	519.2	3.1 ± 0.9	3.2 ± 0.4	1.22 ± 0.08	1.04 ± 0.06
	528.2	3.8 ± 0.4	3.8 ± 0.9	1.31 ± 0.06	1.1 ± 0.2

TABLE IV  
ACTIVATION ENERGIES AND ENTROPIES FOR THE ISOMERIZATION OF BUTENES ON THREE DIFFERENT CATALYTIC SURFACES

Reactant	Product	E <sub>a</sub> (kJ mol <sup>-1</sup> )		-ΔS‡ (J °K <sup>-1</sup> mol <sup>-1</sup> )	
		Sites 1	Sites 2	Sites 1	Sites 2
<i>On molecular sieve 13X</i>					
1-Butene	<i>trans</i> -2-Butene	63 ± 1	48 ± 2	166 ± 2	212 ± 4
1-Butene	1-Butene + <i>cis</i> -2-butene	62 ± 1	46 ± 4	167 ± 2	217 ± 8
<i>cis</i> -2-Butene	<i>trans</i> -2-Butene	54 ± 2	52 ± 4	183 ± 4	200 ± 10
<i>cis</i> -2-Butene	1-Butene + <i>cis</i> -2-butene	54 ± 1	51 ± 6	185 ± 3	200 ± 20
<i>trans</i> -2-Butene	<i>trans</i> -2-Butene	59 ± 5	50 ± 4	175 ± 8	205 ± 8
<i>trans</i> -2-Butene	1-Butene + <i>cis</i> -2-butene	57 ± 5	50 ± 3	180 ± 10	206 ± 8
<i>On silica gel</i>					
1-Butene	<i>trans</i> -2-Butene	18 ± 1	35 ± 2	271 ± 3	246 ± 3
1-Butene	1-Butene + <i>cis</i> -2-butene	17 ± 3	33 ± 2	274 ± 6	249 ± 4
<i>cis</i> -2-Butene	<i>trans</i> -2-Butene	17 ± 3	35 ± 2	280 ± 6	256 ± 3
<i>cis</i> -2-Butene	1-Butene + <i>cis</i> -2-butene	17 ± 2	36 ± 2	280 ± 3	253 ± 3
<i>On alumina</i>					
1-Butene	<i>trans</i> -2-Butene	23 ± 4	56.0 ± 0.5	269 ± 7	215 ± 1
1-Butene	1-Butene + <i>cis</i> -2-butene	22 ± 5	56 ± 2	272 ± 8	215 ± 5
<i>cis</i> -2-Butene	<i>trans</i> -2-Butene	18 ± 6	49 ± 1	280 ± 10	230 ± 2
<i>cis</i> -2-Butene	1-Butene + <i>cis</i> -2-butene	20 ± 1	50 ± 1	276 ± 2	228 ± 3

From the variation of the rate constants with temperature, activation energies and entropies for both kinds of active sites have been calculated, by means of conventional Arrhenius plots. The results are given in Table IV and support the hypothesis of a common intermediate. The activation energies on sites 2 of the molecular sieve 13X are close to those reported in the literature<sup>15</sup> for zeolite NaY ( $44.4 \pm 0.8$  kJ mol<sup>-1</sup>).

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