Kinetics of the Catalytic Monomolecular Interconversion of Three Components

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A Langmuir-type initial rate equation $r_{ij}{}^0 = a_{ij}p_i{}^0/(1 + b_i p_i{}^0)$ ($p_i{}^0$, initial pressure of reactant i; a_{ij} and b_i, constants characteristic of the overall transformation $i \to j$ and of the sorption of reactant i, respectively) is valid, irrespective of the reaction paths involved in the catalytic interconversion of three components. A general correlation between the constants a_{ij} and b_i determined experimentally and the rate (and equilibrium) constants is demonstrated. Arrhenius plots of these constants are used to calculate the energy steps accompanying elementary transformations and an energy scheme of the total conversion cycle is constructed, which supports the conversion scheme initially presumed. The catalytic isomerization of n-butene on H- and Ni-clinoptilolite, silica–alumina, alumina, and zinc oxide is discussed.

INTRODUCTION

For the monomolecular interconversion (isomerization) of three components i, j, and k, the scheme of overall conversions is given in the most general case, in a triangle form (Scheme I). The variation of composition with time is determined by six overall rate constants k_{ij}, k_{ji}, k_{jk}, etc. which can be calculated, e.g., by the method of Wei and Prater (*1*). Accordingly, phenomenological rate equations are established, which do not represent the interaction with the catalyst, thus at constant pressure and temperature:

$$r_i = (k_{ij} + k_{ik})\xi_i - k_{ji}\xi_j - k_{ki}\xi_k \quad (1)$$

where r_i is the conversion rate of component i; ξ_i, ξ_j, ξ_k are mole fractions of the components; k is a rate constant, expressed in units defined by the units of r_i (e.g., mole $g_{catalyst}^{-1}$ s^{-1}); and two letter subscripts refer to the respective transformation. Equation (1) has been widely used to evaluate the kinetics of catalytic n-butene isomerization as suggested by Haag and Pines for the determination of relative rate constants from selectivity

curves (*2*) or by Kalló *et al.* for the determination of absolute values from conversion isotherms (*3*).

Langmuir-type adsorption of n-butene isomers on chromia-alumina has been considered by Amenomiya and Cvetanović, who calculated the adsorption constants and rate constants of the triangle surface reaction from initial conversion rates (*4*). Other interactions with the catalyst may also be assumed, e.g., formation of a common surface intermediate x, as, e.g., a sec-butyl-carbenium ion (*5*). In the latter case no surface reaction takes place, only adsorption and desorption steps being involved, whose rate constants are, however, in an unambiguous though not direct correlation with the phenomenological rate constants in Eq. (1) (*6*). Thus the adsorption rate constant of component i is given by Eq. (2):

$$k_{ix} = k_{ij} + k_{ik} + \frac{k_{ij}k_{ik}}{k_{kj}}. \quad (2)$$

No desorption rate constants, only desorption probabilities can be calculated from the phenomenological rate constants (*6*), e.g., the probability of desorption of x

SCHEME I

SCHEME II (x, y, z are surface intermediates).
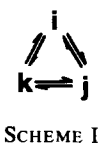
into i is

$$k^*_{xi} \equiv k_{xi}/(k_{xi} + k_{xj} + k_{xk})$$
$$= k_{ji}/k_{jx} = k_{ki}/k_{kx}. \quad (3)$$

This is due to the fact that in Eq. (1) the rate is defined by a first-order kinetic expression (vide infra).

The above problems justify a more comprehensive investigation of the kinetics.

FORMULATION OF THE KINETICS

The overall conversion may take place through different, more or less stable, surface intermediates, whose formation and transformation take place via activated complexes. If the catalytic interconversion is described by different schemes involving different intermediates, in the presence of all three components, the rate equations derived are rather complex even in the simplest case when only a single intermedi-

ate is formed $i \rightleftharpoons x \overset{j}{\underset{k}{\rightleftarrows}}$ (7). Initial rate

equations are clearer, practically more applicable, when only reactant i is present and its conversion to j is considered. A general transformation scheme is then Scheme II, which represents practically all reasonable possibilities for initial conversion (though in some instances more than three surface intermediates might be taken into account, see Scheme VIII below).

In Scheme II the initial rate of formation of j from i is

$$r_{ij}^0 = k_{xj}\theta_x + k_{yj}\theta_y + k_{zj}\theta_z \quad (4)$$

Homogeneity of the active sites is presumed, hence k_{xj}, k_{yj}, $k_{zj} \neq f(\theta)$.

It is convenient to express fractional surface coverages θ_x, θ_y, θ_z as, e.g., in Ref. (1).

Under steady-state conditions, in the initial period where

$$p_i \approx p_i^0; \qquad p_j \approx p_k \approx 0,$$

$$\frac{d\theta_x}{d\tau} = k_{ix}p_i^0\theta_0 + k_{yx}\theta_y + k_{zx}\theta_z$$
$$- (X + k_{xy} + k_{xz})\theta_x = 0 \quad (5)$$

$$\frac{d\theta_y}{d\tau} = k_{iy}p_i^0\theta_0 + k_{xy}\theta_x + k_{zy}\theta_z$$
$$- (Y + k_{yx} + k_{yz})\theta_y = 0 \quad (6)$$

$$\frac{d\theta_z}{d\tau} = k_{iz}p_i^0\theta_0 + k_{xz}\theta_x + k_{yz}\theta_y$$
$$- (Z + k_{zx} + k_{zy})\theta_z = 0 \quad (7)$$

where τ is "contact time"; $\theta_0 = 1 - (\theta_x + \theta_y + \theta_z)$ is the fraction of active sites uncovered; and X, Y, Z are the sums of the respective desorption rate constants of x, y, z: $X \equiv k_{xi} + k_{xj} + k_{xk}$, $Y \equiv k_{yi} + k_{yj} + k_{yk}$, and $Z \equiv k_{zi} + k_{zj} + k_{zk}$. After substitution of θ_0 (see above in parentheses) and rearrangement the determinant of Eqs. (5)–(7) is

$$D = \begin{vmatrix} (X + k_{xy} + k_{xz}) & -(X + k_{xy} + k_{xz} + k_{yx}) & -(X + k_{xy} + k_{xz} + k_{zx}) \\ -k_{xy} & (Y + k_{yx} + k_{yz} + k_{xy}) & (k_{xy} - k_{zy}) \\ -k_{xz} & (k_{xz} - k_{yz}) & (Z + k_{zx} + k_{zy} + k_{xz}) \end{vmatrix} +$$
$$\begin{vmatrix} k_{ix} & -(X + k_{xy} + k_{xz} + k_{yx}) & -(X + k_{xy} + k_{xz} + k_{zx}) \\ k_{iy} & -(Y + k_{yx} + k_{yz} + k_{xy}) & (k_{xy} - k_{zy}) \\ k_{iz} & (k_{xz} - k_{yz}) & (Z + k_{zx} + k_{zy} + k_{xz}) \end{vmatrix} p_i^0 = D_0 + D'p_i^0. \quad (8)$$

The determinants of θ_x, θ_y, θ_z from Eqs. (5)–(7) are

$$D_x = \begin{vmatrix} k_{ix} & -k_{yx} & -k_{zx} \\ k_{iy} & (Y + k_{yx} + k_{yz}) & -k_{zy} \\ k_{iz} & -k_{yz} & (Z + k_{zx} + k_{zy}) \end{vmatrix} p_i^0 = D'_x p_i^0 \qquad (9)$$

$$D_y = \begin{vmatrix} k_{ix} & (X + k_{xy} + k_{xz}) & -k_{zx} \\ k_{iy} & -k_{xy} & -k_{zy} \\ k_{iz} & -k_{xz} & (Z + k_{zx} + k_{zy}) \end{vmatrix} p_i^0 = D'_y p_i^0 \qquad (10)$$

$$D_z = \begin{vmatrix} k_{ix} & (X + k_{xy} + k_{xz}) & -k_{yx} \\ k_{iz} & -k_{xz} & -k_{yz} \\ k_{iy} & -k_{xy} & (Y + k_{yx} + k_{yz}) \end{vmatrix} p_i^0 = D'_z p_i^0. \qquad (11)$$

Using Cramer's rule, the coverages can be calculated from Eqs. (8)–(11). By substitution of these into Eq. (4), the initial rate of conversion $i \to j$ according to Scheme II is expressed with the rate constants and the pressure of reactant i as follows:

$$r_{ij}^0 = \frac{k_{xj} \dfrac{D'_x}{D_0} p_i^0 + k_{yj} \dfrac{D'_y}{D_0} p_i^0 + k_{zj} \dfrac{D'_z}{D_0} p_i^0}{1 + \dfrac{D'}{D_0} p_i^0}. \qquad (12)$$

(After appropriate substitutions and rearrangements Eq. (311) in Ref. (*1*) can be written in the form of Eq. (12); the latter corresponds, however, to a transformation, which involves parallel formation of surface intermediates and expresses the initial rate in a cyclic conversion scheme.) Equation (12) is formally

$$r_{ij}^0 = a_{ij} p_i^0 / (1 + b_i p_i^0) \qquad (13)$$

however, coefficients a_{ij} and b_i, being combinations of the different rate constants, are too complicated for a general discussion. In
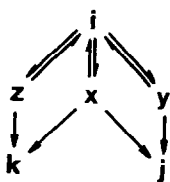
Scheme III

order to obtain simpler rate equations, we considered certain special cases. Thus, for one group of conceivable simpler schemes we may set $k_{yk} = k_{zj} = 0$ and $k_{yz} = k_{zy} = 0$.

(a) If there are no surface reactions (Scheme III), $k_{xy} = k_{yx} = k_{xz} = k_{zx} = 0$, then Eqs. (8)–(11), simplified accordingly, are to be substituted into Eq. (12). The determinants yield

$$r_{ij}^0 = \frac{\left(k_{xj} \dfrac{k_{ix}}{X} + k_{yj} \dfrac{k_{iy}}{Y}\right) p_i^0}{1 + \left(\dfrac{k_{ix}}{X} + \dfrac{k_{iy}}{Y} + \dfrac{k_{iz}}{Y}\right) p_i^0}$$

$$= \frac{[(a_{ij})_x + (a_{ij})_y] p_i^0}{1 + [(b_i)_x + (b_i)_y + (b_i)_z] p_i^0}. \qquad (14)$$

(b) If the conversion of i proceeds only through its single adsorbed species x, i.e.,

$$k_{iy} p_i^0 = k_{iz} p_i^0 = k_{yi} = k_{zi} = 0 \qquad (15)$$

then Scheme II reduces to Scheme IV.

(ba) If the surface reactions are in equilibrium in Scheme IV, then

$$k_{xy}, k_{yx}, k_{xz}, k_{zx}$$
$$\gg k_{ix} p_i^0, k_{xi}, k_{xj}, k_{xk}, k_{yj}, k_{yk}. \qquad (16)$$

Some terms are zero in Eqs. (8)–(11) because of criteria (15) and others can be neglected as a consequence of (16). By making corresponding substitutions, one obtains

$$r_{ij}^0 = \frac{(k_{xj} + K_{xy}k_{yj})\dfrac{k_{ix}}{k_{xi} + k_{xj} + k_{xk} + K_{xy}k_{yj} + K_{xz}k_{zk}}p_i^0}{1 + \dfrac{k_{ix}(1 + K_{xy} + K_{xz})}{k_{xi} + k_{xj} + k_{xk} + K_{xy}k_{yj} + K_{xz}k_{zk}}p_i^0}$$

$$= \frac{(k_{ij})_x(k_i)_x p_i^0}{1 + (b_i)_x p_i^0} = \frac{(a_{ij})_x p_i^0}{1 + (b_i)_x p_i^0} \tag{17}$$

where $(k_{ij})_x = k_{xj} + K_{xy}k_{yj}$ (K is an equilibrium constant, e.g., $K_{xy} = k_{xy}/k_{yx}$). Equation (17) gives the rate of conversion proceeding simultaneously via $i \rightarrow x \rightarrow j$ (reflected by k_{xj} in $(k_{ij})_x$) and $i \rightarrow x \rightleftharpoons y \rightarrow j$ (reflected by $K_{xy}k_{yj}$ in $(k_{ij})_x$).

(bb) If the surface reactions are rate determining, then

$$k_{ix}p_i^0, k_{xi}, k_{yj}, k_{zk}$$
$$\gg k_{xy}, k_{yx}, k_{xz}, k_{zx} \tag{18}$$

and the fast transformation $i \rightarrow x \rightarrow j$ and $i \rightarrow x \rightarrow k$ should obviously be excluded in Scheme IV:

$$k_{xj} = k_{xk} = 0. \tag{19}$$

With criteria (15), (18), and (19) the rate of conversion via $i \rightleftharpoons x \rightarrow y \rightarrow j$ is

$$r_{ij}^0 = \frac{k_{xy}K_{ix}p_i^0}{1 + K_{ix}p_i^0}$$
$$= \frac{(k_{ij})_x(k_i)_x p_i^0}{1 + (b_i)_x p_i^0} = \frac{(a_{ij})_x p_i^0}{1 + (b_i)_x p_i^0} \tag{20}$$

which is a well-known equation in Langmuir–Hinshelwood kinetics.

From rate expressions (13), (14), (17), (20) (and, in fact, for any conceivable scheme based on uniform catalyst activity) it may be concluded (see Scheme II for adequate constants) that

(i) The initial rate of conversion of any component (i) into either of the other components (j) can be given in the form of a Langmuir-type equation irrespective of the scheme of transformation

$$r_{ij}^0 = \frac{a_{ij}p_i^0}{1 + b_i p_i^0}. \tag{21}$$

(ii) The quotient $a_{ij}/a_{ji} = K_{ij}$ (K_{ij} is the equilibrium constant of conversion $i \rightleftharpoons j$); this resembles the traditional dynamic definition of the equilibrium constant K as the ratio of rate constants for the forward and reverse elementary reactions (8), which is the consequence of the Principle of Detailed Balances as found by Wei and Prater (1), too.

(iii) The ratio of parallel conversions, i.e., the selectivity from Eq. (21)
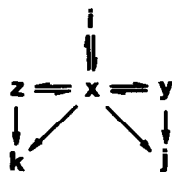
$$S = \frac{a_{ij}}{a_{ik}} \tag{22}$$

is independent of the pressure.

The following conclusions are valid if either the sorption steps or the surface reaction(s) are rate-determining:
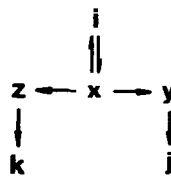
(iv) a_{ij} in Eq. (21) consists of as many terms as the number of surface intermediates simultaneously involved in the conversion of i to j

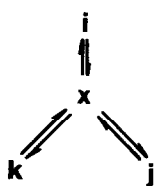$$a_{ij} = (a_{ij})_x + (a_{ij})_y + \ldots . \tag{23}$$
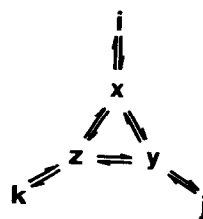
(v) Any term on the right-hand side of

SCHEME IV

SCHEME V

SCHEME VI

SCHEME VII

Eq. (23) is a product of two constants

$$(a_{ij})_x = (k_{ij})_x(k_i)_x \qquad (24)$$

where

$(k_{ij})_x = k_{xj}$ if j is formed via path $i \to x$ $\to j$. If it is formed via path i $\to x \to y \to j$, then

$(k_{ij})_x = k_{xy}$ if surface reaction $x \to y$ is rate-determining

$(k_{ij})_x = K_{xy}k_{yj}$ if surface reaction $x \rightleftharpoons y$ is at equilibrium;

$$(k_i)_x = k_{ix}/(k_{xi} + k_{xj} + k_{xk} + K_{xy}k_{yj} + K_{xz}k_{zk}). \quad (25)$$

(vi) b_i consists of as many terms as the number of surface species formed from i immediately on the active sites

$$b_i = (b_i)_x + (b_i)_y + (b_i)_z + \ldots \quad (26)$$

(vii)

$$(b_i)_x = k_{ix}(1 + K_{xy} + K_{xz})/$$
$$(k_{xi} + k_{xj} + k_{xk} + K_{xy}k_{yj} + K_{xz}k_{zk}). \quad (27)$$

The extension of the validity of Langmuir-type initial rate equations to the catalytic interconversion of three components results in a generalization of the real meaning of the constants involved. The generalization listed under (ii)–(vii) permit the initial rate equation for any arbitrary transformation scheme to be set up directly; the constants for nonexisting steps or equilibria are to be simply omitted.

If the interconversion proceeds according to Scheme VI

$$a_{ij} = (a_{ij})_x = (k_{ij})_x(k_i)_x$$
$$= k_{xj}k_{ix}/(k_{xi} + k_{xj} + k_{xk} + 0) \quad (28a)$$

$$b_i = (b_i)_x$$
$$= k_{ix}(1 + 0)/(k_{xi} + k_{xj} + k_{xk} + 0) \quad (28b)$$

or according to Scheme VII if the surface reaction is rate-determining

$$a_{ij} = (a_{ij})_x = (k_{ij})_x(k_i)_x$$
$$= k_{xy}k_{ix}/(k_{xi} + 0) = k_{xy}K_{ix} \quad (29a)$$

$$b_i = (b_i)_x$$
$$= k_{ix}(1 + 0)/(k_{xi} + 0) = K_{ix}. \quad (29b)$$

DISCUSSION OF n-BUTENE ISOMERIZATION

Constants a_{ij} and b_i in Eq. (21) can be experimentally determined. Two groups of kinetic cases can be immediately distinguished from these values (8): if

$$a_{ij}/b_i = a_{kj}/b_k \quad (30)$$

then interconversion takes place via a common surface intermediate or an equilibrium mixture of surface intermediates; if

$$a_{ij}/b_i \neq a_{kj}/b_k \quad (31)$$

then this is not the case.

From a_{ij} and b_i the constants of elementary steps can be determined after appropriate substitution (see above for Schemes VI and VII Eqs. (28) and (29), respectively). Different substitutions may be satisfactory so that different schemes would seem applicable. This uncertainty can be eliminated by kinetic measurements carried out at different temperatures. From Arrhenius plots of calculated rate (and equilibrium) constants the energy changes of elementary steps can be determined. An energy scheme can be constructed by plotting the energy changes of successive steps. If the levels are realistic (i.e., the differences be-

tween the energy levels of the gaseous isomers determined kinetically are the same as those calculated from the thermodynamic equilibria), the corresponding conversion scheme is acceptable. Moreover, the energy levels relate to the species actually involved in the catalytic reaction, because they have been determined from kinetic data and not independently of the reaction, e.g., from adsorption only.

Some evaluation of the experiments will be presented.

H-Clinoptilolite

The initial conversion rates of the pure isomers were determined under conditions where both a_{ij} and b_i in Eq. (21) should be calculated, i.e., the order of reaction is between zero and unity (8). (In the following instead of symbols i, j, k the notation 1 (1-butene), 2 (cis-2-butene), 3 (trans-2-butene) will be used.) Values found in Ref. (8) are summarized in Table 1.

It is evident from the data that criterion (30) is satisfied within the experimental error (cf. respective data of Eqs. (30) and (31) in Tables 1 and 2). If the rate constants for Scheme VI are calculated from a_{ij} and b_i, using Eqs. (28) and the activation energies of the corresponding steps are determined from their Arrhenius diagrams, an acceptable energy scheme can be plotted. In Fig. 1 (a) the differences between the energy levels of pure isomers are equal to the enthalpy changes of the given transformation, (b) the energy level of the surface intermediate of each transformation is the same as expected for Scheme VI (which was only one of the possible conversion
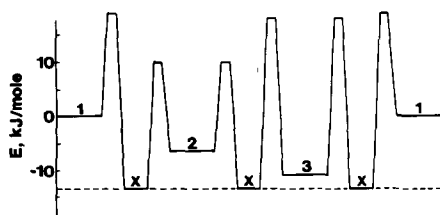

FIG. 1. Energy scheme of n-butene isomerization on H-clinoptilolite.

TABLE 1

Parameters in Eq. (21) of n-Butene Isomerization on H-Clinoptilolite[a,b]

Temperature (K)	a_{12}	a_{13}	a_{23}	a_{21}	a_{31}	a_{32}
	(in 10^{-7} mole g_{cat}^{-1} s^{-1} Torr^{-1})					
373	1.3	2.0	2.5	0.54	0.24	0.67
403	1.9	3.5	4.0	0.83	0.50	1.2
433	2.4	5.3	5.3	1.3	1.0	2.0

	b_1		b_2		b_3	
	r_{12}	r_{13}	r_{23}	r_{21}	r_{31}	r_{32}
			(in 10^{-2} Torr^{-1})			
373	1.00	0.96	1.30	1.38	0.64	0.57
403	0.76	0.76	1.00	1.00	0.60	0.60
433	0.52	0.53	0.67	0.79	0.68	0.72

	$\dfrac{a_{12}}{b_1} = \dfrac{a_{32}}{b_3}$[c]		$\dfrac{a_{23}}{b_2} = \dfrac{a_{13}}{b_1}$[c]		$\dfrac{a_{31}}{b_3} = \dfrac{a_{21}}{b_2}$[c]	
373	1.3	1.1	1.9	2.0	0.40	0.40
403	2.5	2.0	4.0	4.6	0.83	0.83
433	4.6	2.9	7.2	10.0	1.4	1.8

[a] From Ref. (8).
[b] 1 Torr = 133.3 N m^{-2}.
[c] Equation (30).

schemes following from the validity of Eq. (30)).

Ni-Clinoptilolite

Similar kinetic measurements were carried out on Ni-clinoptilolite (8). The experimental values are summarized in Table 2. As inequality (31) prevails, interconversion must proceed through different surface intermediates not in equilibrium with each other. Scheme VII realizes an appropriate situation if the surface triangle reaction steps are rate-determining. From the a_{ij} and b_i values the rate constants and the adsorption equilibrium constants are calculated according to Eqs. (29). From their temperature dependence the activation energies and the adsorption heats are determined and plotted in Fig. 2. The energy scheme is consistent again because the energy differences between the gas phase isomers differ only by 0.8–1.2 kJ/mol from the thermody-

TABLE 2

Parameters in Eq. (21) of n-Butene Isomerization on Ni-Clinoptilolite[a,b]

Temperature (K)	a_{12}	a_{13}	a_{23}	a_{21}	a_{31}	a_{32}
	(in 10^{-7} mole g_{cat}^{-1} s^{-1} $Torr^{-1}$)					
343	0.83	0.89	0.38	0.086	0.053	0.16
373	0.91	1.11	0.53	0.124	0.096	0.27
403	0.92	1.37	0.77	0.170	0.167	0.37

	b_1		b_2		b_3	
	r_{12}	r_{13}	r_{23}	r_{21}	r_{31}	r_{32}
	(in 10^{-2} $Torr^{-1}$)					
343	2.13	2.15	0.38	0.38	1.75	1.8
373	0.71	0.68	0.26	0.26	0.71	0.70
403	0.22	0.22	0.185	0.19	0.30	0.30

	$\dfrac{a_{12}}{b_1} \neq \dfrac{a_{32}}{b_3}$[c]		$\dfrac{a_{23}}{b_2} \neq \dfrac{a_{13}}{b_1}$[c]		$\dfrac{a_{31}}{b_3} \neq \dfrac{a_{21}}{b_2}$[c]	
343	0.39	0.09	1.00	0.42	0.030	0.23
373	1.3	0.39	2.0	1.6	0.135	0.48
403	4.2	1.23	4.1	6.2	0.56	0.90

[a] From Ref. (8).
[b] 1 Torr = 133.3 N m^{-2}.
[c] Equation (31).

FIG. 2. Energy scheme of n-butene isomerization on Ni-clinoptilolite.

namical values and the energy level of the system is the same at the beginning and at the end of the isomerization cycle.

Silica–Alumina and Alumina

Hightower and Hall (9) found that n-butene isomerization on two commercial silica–aluminas (Houdry M-46, DSA-1) and on an alumina (GA-48) is first order in reactant. They determined the six phenomenological rate constants k_{ij} (see in Eq. (1))
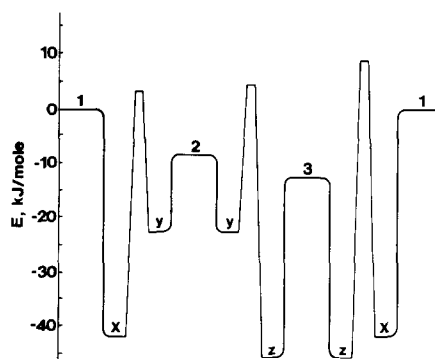
related to k_{12} ($k_{ij}' = k_{ij}/k_{12}$ in Table 3) and the differences between the phenomenological activation energies of parallel conversions (Table 4).

Because of the first order kinetics, $1 \gg b_i p_i^0$ in Eq. (21) and thus

$$k_{ij} = a_{ij} \qquad (\text{or } k_{ij}' = a_{ij}/k_{12}). \qquad (32)$$

It cannot be decided, therefore, whether criterion (30) or (31) is valid. Presuming that, in accordance with Ref. (9), interconversion takes place through a common surface intermediate (Scheme VI), we may calculate the relative adsorption rate constants $k_{i,r} = k_{i,r}'/k_{12}$ and the desorption probabilities $k_{r,i}^*$ from the phenomenological relative rate constants k_{ij}', using Eqs. (2) and (3) (Table 3).

A partly correct energy scheme of interconversion can be constructed with known levels of reacting isomers and differences between the activated sorption complexes

TABLE 3

Phenomenological Relative Rate Constants at 296 K (9); Derived Relative Adsorption Rate Constants and Desorption Probabilities

Catalyst	k_{12}'	k_{13}'	k_{23}'	k_{21}'	k_{31}'	k_{32}'	$k_{1,r}'$	$k_{2,r}'$	$k_{3,r}'$	k_{r1}^*	k_{r2}^*	k_{r3}^*
M-46	1.00	1.00	0.16	0.15	0.04	0.04	3.00	0.48	0.12	0.33	0.33	0.34
DSA-1	1.00	1.10	0.14	0.15	0.04	0.04	3.10	0.42	0.12	0.34	0.33	0.33
GA-48	1.00	0.16	0.67	0.15	0.0046[a]	0.17	1.20	4.9	0.20	0.032	0.834	0.134

[a] 0.01 in Ref. (9) is to be corrected for thermodynamic reasons ($k_{31}/k_{13} = K_{31}$).

TABLE 4

Phenomenological Activation Energy Differences of
Parallel Conversions According to Ref. (9)ᵃ

Catalyst	$E_{12}^{\ddagger} - E_{13}^{\ddagger}$	$E_{23}^{\ddagger} - E_{21}^{\ddagger}$	$E_{31}^{\ddagger} - E_{32}^{\ddagger}$
M-46	0	-3.3	+3.3
GA-48	-7.1	+7.1	0

ᵃ kJ/mol.

FIG. 4. Energy scheme of n-butene isomerization on alumina (GA-48 in Ref. (9)).

(Figs. 3 and 4). The latter are calculated from the data in Table 4, which reflect the temperature dependence of k_{ik}/k_{ij}.

According to Eq. (28a)

$$a_{ij} = k_{ix}k_{xj}^{*} \qquad (33)$$

$$a_{ik} = k_{ix}k_{xk}^{*}. \qquad (34)$$

From Eqs. (32), (33), and (34)

$$k_{ik}/k_{ij} = k_{xk}/k_{xj}$$

hence

$$E_{ij}^{\ddagger} - E_{ik}^{\ddagger} = E_{xj}^{\ddagger} - E_{xk}^{\ddagger}. \qquad (35)$$

Consequently, $E_{jx}^{\ddagger} - E_{kx}^{\ddagger} - \Delta H_{jk}$ must result in the same differences (ΔH_{jk} is the enthalpy change of the overall reaction $j \rightarrow k$), which can be easily proved taking into account item (ii) in the preceding section, and Eq. (32)

$$a_{jk}/a_{kj} = K_{jk} = k_{jk}/k_{kj}$$

therefore,

$$-\Delta H_{jk} = -E_{jk}^{\ddagger} + E_{kj}^{\ddagger} \qquad (36)$$

and for the closed cycle of isomerization

$$-E_{jk}^{\ddagger} + E_{kj}^{\ddagger} + E_{ji}^{\ddagger} - E_{ki}^{\ddagger} = E_{ij}^{\ddagger} - E_{ik}^{\ddagger} \qquad (37)$$
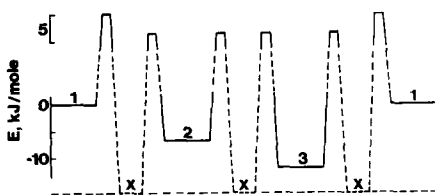
i.e., the sum of activation energy differ-

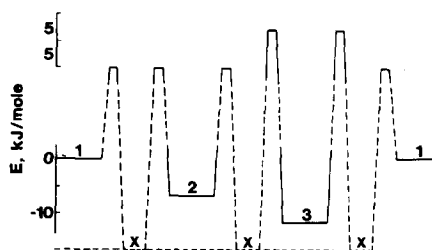FIG. 3. Energy scheme of n-butene isomerization on silica–alumina (Houdry M-46).

ences in Table 4 must be zero. According to Eq. (28a)

$$a_{ji} = k_{jx}k_{xi}^{*}$$

$$a_{ki} = k_{kx}k_{xi}^{*}$$

hence

$$E_{ji}^{\ddagger} - E_{ki}^{\ddagger} = E_{jx}^{\ddagger} - E_{kx}^{\ddagger} \qquad (38)$$

From Eqs. (35)–(38)

$$E_{xj}^{\ddagger} - E_{xk}^{\ddagger} = E_{jx}^{\ddagger} - E_{kx}^{\ddagger} - \Delta E_{jk}.$$

In Figs. 3 and 4 the energy level of the common surface intermediate is supposed to lie lower than that of the isomers as in Fig. 1 for H-clinoptilolite (or in Fig. 8 in Ref. (10) on a sulfonic acid ion-exchange resin).

Zinc Oxide

The isomerization of n-butenes on zinc oxide was found to be independent of the pressure of the reacting isomer (11, 12). At higher conversions the observed decline of the conversion curves (11, 12) is to be attributed to reverse reactions: for the composition an apparent first-order kinetics inevitably dominates the whole conversion range (see Eq. (1)). All the six zero-order rate constants k_{ij} have been determined and from their Arrhenius plots the corresponding activation energies $E_{ij}^{\ddagger}$ calculated (12) (Table 5).

According to Ref. (11), isomerization proceeds as follows: the n-butene isomers are adsorbed as π-complexes (1', 2', 3') on the "nonactive sites"; the interconversion of π-complexes takes place through π-allyl

Transformation	k_{ij}	$E^{\ddagger}_{ij}$
$1 \to 2$	18.0	32.6
$1 \to 3$	1.8	51.5
$2 \to 3$	5.4	64.0
$2 \to 1$	3.2	46.9
$3 \to 1$	0.6	45.2
$3 \to 2$	8.0	30.9

[a] kJ/mol.

complexes according to Scheme VIII where x and y are anti- and syn-π-allyl complexes on the "active sites."

(a) If the adsorption equilibrium $i \rightleftharpoons i'$ is established, the equation of the initial rate of overall transformation is similar to Eq. (21), the initial pressure p_i^0 is only to be substituted by the initial coverage $\vartheta_{i'}^0$:

$$r_{ij}^0 = r_{i'j'}^0 = \frac{a_{i'j'}\vartheta_{i'}^0}{1 + b_{i'}\vartheta_{i'}^0} \qquad (39)$$
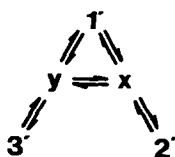
where

$$\vartheta_{i'}^0 = \frac{K_i p_i^0}{1 + K_i p_i^0}.$$

The rate equation reflects the zero-order kinetics when (aa) $1 \ll b_{i'}\vartheta_{i'}^0$, i.e., the reaction is of zero order in $\vartheta_{i'}^0$ and then

$$r_{ij}^0 = \frac{a_{i'j'}}{b_{i'}} = k_{ij} \qquad (40)$$

or (ab) $1 \ll K_i p_i^0$; $\vartheta_{i'}^0 = 1$, i.e., the reaction is of zero order in p_i^0 and then

$$r_{ij}^0 = \frac{a_{i'j'}}{1 + b_{i'}} = k_{ij} \qquad (41)$$

SCHEME VIII

if $1 \gg b_i$, due to item (ii) in the preceding section

$$a_{i'j'}/a_{j'i'} = k_{ij}/k_{ji} = \overline{\vartheta_{j'}}/\overline{\vartheta_{i'}}$$

(where $\overline{\vartheta}$ is coverage by π-complex when the surface reactions are in equilibrium) which was presumed in Ref. (12).

(b) The equilibrated surface transformations represented in Scheme VIII seem improbable, because the zero-order form of Eq. (21)

$$r_{ij}^0 = \frac{a_{ij}}{b_i} = k_{ij} \qquad (42)$$

defines a_{ij}/b_i and criterion (30) should be valid, i.e., $k_{ij} = k_{kj}$, which contradicts the experiments (Table 5).

Equations (40) and (41) do not allow the determination of six $a_{i'j'}$ and three $b_{i'}$, nine unknowns from six k_{ij}, which would provide a basis for further calculations required for the elucidation of the mechanism.

It can be observed, however, that the formation of the π-complex of 1- and cis-2-butene seems to be similar, whereas that of π-trans-2-butene is different:

$$E^{\ddagger}_{21} - E^{\ddagger}_{31} = 1.7 \text{ kj/mol}$$

$$E^{\ddagger}_{12} - E^{\ddagger}_{32} = 1.7 \text{ kJ/mol}$$

$$E^{\ddagger}_{23} - E^{\ddagger}_{13} = 12.5 \text{ kJ/mol}.$$

CONCLUSIONS

Equation (21) is of general validity and gives an insight into the mechanism of interconversion.

If both constants a_{ij} and b_i are known from six initial rates measured isothermally at different pressures, it can be decided whether the overall transformations in the six directions proceed via a common surface intermediate perhaps via an equilibrium mixture of surface intermediates (case a) or not (case b).

From six $a_{ij} - $ s and three $b_i - $ s—after appropriate substitution—nine rate (and equilibrium) constants can be determined with the exception of the equilibrium con-

stants of surface reactions, which always appear inseparably (see Eqs. (25) and (27)). If more constants are involved in the conversion scheme assumed, the six $r_{ij}^0 = f(p_i^0)$ functions are not sufficient any more, complementary data are needed, e.g., the coverage(s) of the active sites. For case (a) three adsorption and three desorption rate constants, for case (b) three adsorption equilibrium constants and six surface reaction constants can be determined at most. Since such calculations based on a_{ij} and b_i values are always possible, the reality of the conversion scheme is to be verified: from Arrhenius plots of the constants the energy changes of the successive steps must result in an acceptable energy scheme.

The reaction investigated is sometimes not of a fractional order expressed by Eq. (21), but of first or of zero order. For first-order kinetics, distinction between cases (a) and (b) is impossible; if there is other evidence for distinguishing, in case (a) adsorption rate constants and desorption probabilities; in case (b) surface reaction rate constants and relative adsorption constants can be calculated. For zero-order kinetics it is possible to distinguish case (a) from (b): in case (a) the reaction rate is equal to the desorption rate constant, in case (b) to the surface reaction rate constant.

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