

Kinetics and Mechanism of *n*-Butene Isomerization over Activated Lanthanum Oxide

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The catalytic behavior of lanthanum sesquioxide for double-bond isomerization of the *n*-butenes has been studied in the temperature range 0–50°C. Initial activity for individual conversions of all three *n*-butene reactants increases with increasing pretreatment temperature, due to removal of surface hydroxyls, attains a maximum following evacuation at ~650°C, and then declines with further increase in pretreatment temperature, due to decreases in surface anion disorder. Initial reaction rates of each isomer at 0°C are described by a Langmuirian rate equation of the form $\text{Rate} = kbP/(1 + bP)$, which reduces to a zero-order expression in the case of 1-butene reactant. Double bond migration in the *n*-butenes occurs very rapidly over La_2O_3 , but the rates of direct *cis* \rightleftharpoons *trans* interconversion are, by comparison, negligibly slow throughout the temperature range investigated, due possibly to the absence of surface sites that permit the necessary anti- π -allyl \rightleftharpoons syn- π -allyl rotation. As a result, although conversion of 1-butene involves characteristically high initial *cis/trans* product ratios, the sole primary product observed for both 2-butene reactants is 1-butene. Tracer studies employing the three perdeuterated *n*-butenes indicate that initial proton abstraction is the rate-determining step for each interconversion, and that the hydrogen transfer process involved in double-bond migration occurs via an intramolecular mechanism. Both directions of the one \rightleftharpoons *cis* interconversion are accompanied by a much larger initial H–D isotope effect (9 to 10) than those observed for the one \rightleftharpoons *trans* reaction (1 to 3), suggesting that the two reversible processes may proceed by dissimilar mechanisms or occur on different types of surface sites.

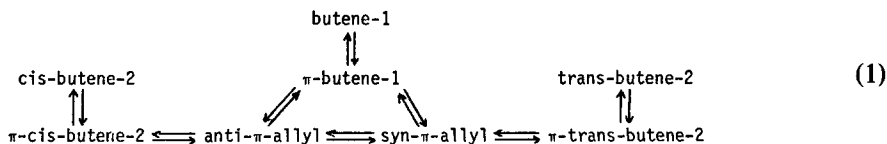
INTRODUCTION

Interconversion of the isomeric *n*-butenes has been extensively employed as a diagnostic reaction to probe the natures of catalytically active sites on a variety of basic metal oxides, including BaO (1), CaO (2), MgO (3), ThO₂ (4), and ZnO (5). These studies have established that certain distinct similarities in kinetic and mechanistic behaviors are commonly exhibited by basic oxides for this reaction. Most notable among these are an initially high and kinetically, rather than thermodynamically,

controlled selectivity to *cis*-2-butene from 1-butene reactant at low temperatures (<50°C), and an often marked dependence of activity and, in some cases, selectivity on catalyst pretreatment temperature and preparation method.

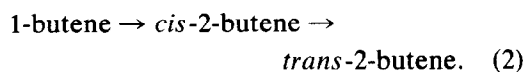
Explanations of the kinetic and selectivity behaviors of the isomerization process over these oxides vary, but most involve some modification of a mechanism in which initial abstraction of an allylic hydrogen from an adsorbed olefin species generates a π -allyl carbanion or radical intermediate. Representative of these suggested reaction schemes is that proposed by Kokes *et al.* for ZnO (5), and supported by detailed kinetic and spectroscopic measurements:

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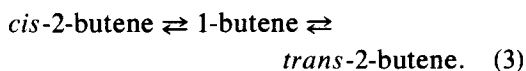


The associatively-adsorbed π -complex form of 1-butene, upon hydrogen abstraction, preferentially forms the anti- π -allyl intermediate, at the expense of the less stable syn- π -allyl species, causing the high (~ 13) initial *cis/trans* product ratio observed for 1-butene reactant over ZnO at 25°C. Direct interconversion of the syn- and anti- π -allyls, and, hence, of *cis*- and *trans*-2-butenes, was evident and was assumed to occur via a σ -allyl intermediate whose surface concentration was, however, too small to be detected spectroscopically. Although in the case of ZnO the rate of direct *cis* \rightleftharpoons *trans* interconversion is relatively small compared to those of the other possible pathways, reaction of *cis*-2-butene over certain other basic oxides, such as CaO pretreated at 700–900°C (2), results in preferential formation of *trans*-2-butene product.

Recently, several groups of investigators (6–9) have studied the catalytic behavior of basic lanthanum sesquioxide for interconversion of the *n*-butenes at low temperatures (0–50°C). Although the inherently very high isomerization activity of La₂O₃ has been recognized by all of these authors, conflicting opinions have been reported regarding the reaction mechanism and relative importances of the various interconversion pathways. Minachev and co-workers (6) have suggested the following scheme, in which *cis*-2-butene, generated from 1-butene reactant, is directly and irreversibly converted to *trans*-2-butene:



Our previously reported results (7) have indicated, however, that direct interconversion of the two 2-butene isomers appears to be negligibly slow over La₂O₃ at low temperatures, and that 2-butene equilibration occurs via a 1-butene intermediate:



Hall and Wasserman (9) and Tanabe *et al.*

(8) have concurred in essence with this conclusion, although the latter authors believe that a limited amount of direct *cis* \rightleftharpoons *trans* isomerization may occur during the early stages of 1-butene conversion.

The purposes of the present investigation have been to examine in greater detail the kinetics and mechanism of the catalytic interconversion of *n*-butenes over La₂O₃, to establish the relative rates of the various isomerization pathways in this system, and to elucidate the nature of the catalytically active surface sites involved.

EXPERIMENTAL METHODS

Materials

Preparation of catalytic La₂O₃ and a characterization of its pertinent physical and surface properties and dehydration/rehydration behavior have been reported previously (10). A 10-mg (dehydrated weight) charge of 30/40-mesh granules was used for all experiments involving 1-butene reactant, and a 100-mg sample size for those experiments employing *cis*- and *trans*-2-butene reactants. Catalyst pretreatment prior to each run involved overnight evacuation at 800°C to remove residual decomposed butene species and surface carbonates, followed by treatment with 100 Torr of circulating O₂ for 1 hr (with continuous removal of combustion products by an in-line trap maintained at –196°C) and subsequent evacuation for 1 hr at the same temperature. The sample was then rehydrated *in situ* to La(OH)₃ by exposure to an excess of gaseous, CO₂-free H₂O for 3 hr at 25°C, evacuated at the desired pretreatment temperature in the range 300–800°C for 16 hr to a residual pressure of <10^{–5} Torr, and then rapidly cooled to reaction temperature. Measured BET-N₂ surface areas of La₂O₃ samples prepared by this treatment sequence varied inversely with final pretreatment evacuation temperature, ranging from 15 m²/g at 300°C to 8 m²/g at 800°C.

1-Butene was Phillips research grade (99.9%), and *cis*- and *trans*-2-butenes were

Linde C. P. grade (99.0%). 1-Butene- d_8 (98 at.% D) was obtained from Merck, Sharp, and Dohme, Ltd. *Cis*- and *trans*-2-butene- d_8 were synthesized by isomerization of 1-butene- d_8 at 100°C over MgO that had been evacuated for 16 hr at 500°C. The two isomers were separated chromatographically and collected in individual traps at -196°C. All *n*-butene reactants were purified by vacuum distillation through a trap containing activated Linde 4A molecular sieve maintained at -78°C. Oxygen, used for catalyst pretreatment, was Airco high-purity grade (99.9%) and was further purified before use by passage through a trap at -196°C. Gaseous H₂O, used for catalyst rehydration during the pretreatment procedure, was taken from the vapor phase over a degassed, saturated solution of Ba(OH)₂ stored in a vacuum-tight vessel, which assured CO₂ removal via BaCO₃ precipitation.

Apparatus

All experiments were performed using the closed-loop recirculation-type batch reaction system (total volume = 345 cm³) that has been previously described (7). Except where otherwise noted, standard conditions employed for all runs involved an initial *n*-butene reactant pressure of 100 Torr and a reaction temperature of 0°C.

The three *n*-butene isomers were separated by gas-liquid chromatography using a 3/8-in. × 40-ft column containing 25 wt% propylene carbonate on 60/80-mesh Chromosorb W (acid-washed) and maintained at 0°C. Quantitative analyses were based on peak areas resulting from the output of a thermal conductivity detector, following appropriate corrections for differing thermal responses of the three components. The eluted butene isomers were collected, when necessary, in individual traps at -196°C for subsequent mass spectral analyses of deuterium contents. The latter were obtained using a quadrupole mass analyzer operated at an ionization potential of 25 eV. Calculations were based on parent-peak

heights, after calibrated corrections for fragmentation and isotopic carbon-13 contributions.

Infrared spectra were obtained with a Perkin-Elmer Model 399 spectrophotometer that was interfaced to a microcomputer-based data acquisition and processing system. The latter was used to apply ensemble averaging techniques for signal enhancement and noise reduction that were necessary in order to quantify the relatively weak absorption bands observed with the low-surface-area La₂O₃ samples. The quartz cell employed was of standard design, using KCl windows and containing a heated region into which the sample could be moved by a windlass arrangement for vacuum thermal treatment. Samples were prepared in the form of self-supporting pressed disks having an optical density of 20 mg/cm², and were subjected to the same dehydration/rehydration pretreatment procedure as that described above. All spectra were recorded in the double-beam transmission mode, using air as a reference, with the sample at ambient temperature.

RESULTS AND DISCUSSION

Effect of Catalyst Pretreatment Temperature

The marked dependence of the activity of La₂O₃ for 1-butene isomerization on prior pretreatment temperature has been described previously (7). Figure 1 summarizes the effect of pretreatment evacuation temperature of La₂O₃ on surface area-normalized initial rates of conversion at 0°C for each of the *n*-butene reactants. Measurable initial activity appears in all three cases only after evacuation at >300°C (corresponding to virtually complete bulk dehydration of La(OH)₃), increases with increasing evacuation temperature up to ~650°C, and then declines with further increase in pretreatment temperature. Such increases in catalytic activity for certain reactions with increasing temperature of evacuation are commonly observed for

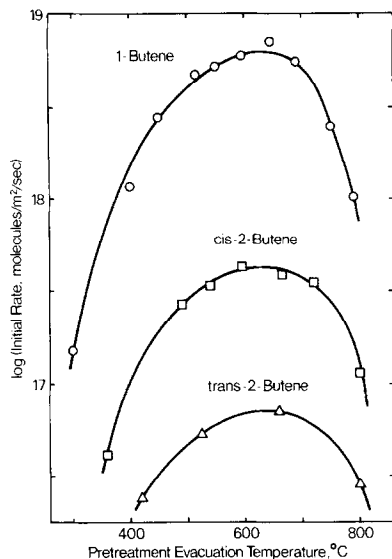


FIG. 1. Effect of catalyst pretreatment temperature on initial rates of conversion of *n*-butene reactants over La_2O_3 at 0°C .

many basic metal oxides, and have been variously ascribed to increasing removal of trace surface contaminants, such as carbonate ions, hydroxyl species, or adsorbed water (11), and to the generation of stoichiometric and/or structural defects, such as anion vacancies or disorders and exposed metal ions, that serve as catalytic sites (1, 7, 12).

Previous spectroscopic studies had suggested that measurable concentrations of surface hydroxyls do not exist on $\text{La}(\text{OH})_3$ -derived La_2O_3 following evacuation at $\geq 350^\circ\text{C}$ (10). Recent infrared measurements, however, employing computerized signal enhancement and noise reduction techniques, have confirmed the presence of surface hydroxyls on La_2O_3 up to considerably higher temperatures than had been previously supposed. Figure 2 shows the effect of pretreatment temperature on the integrated absorbance intensity of the O–H stretching band that appears at 3590 cm^{-1} on La_2O_3 . Complete disappearance of this band only occurs following evacuation at $600\text{--}650^\circ\text{C}$, coinciding closely with the pretreatment temperature range that results in

maximum initial activity for *n*-butene isomerization. Further confirmation of the importance of surface hydroxyls in determining catalytic activity was obtained from a separate experiment in which an La_2O_3 sample was pretreated in the usual manner, using a final evacuation temperature of 650°C . The catalyst was then exposed to an excess of gaseous H_2O for 3 hr at 400°C , in order to partially regenerate the surface hydroxyl layer (as confirmed by infrared spectral measurement), and finally evacuated for 16 hr at the same temperature. The resulting initial activity of the sample for 1-butene isomerization was identical to that of La_2O_3 pretreated at 400°C , rather than that of samples pretreated at 650°C . Concomitant with increasing removal of the surface hydroxyls was an increasing exposure of underlying La^{3+} ions. Accessibilities of the latter were probed by infrared spectra of adsorbed NH_3 , which coordinates exclusively to cationic sites on La_2O_3 and produces a deformation band at 1135 cm^{-1} .

Hence, although increasing temperature of evacuation undoubtedly leads to the formation of various surface defect structures on La_2O_3 (13), it is apparent that isomeriza-

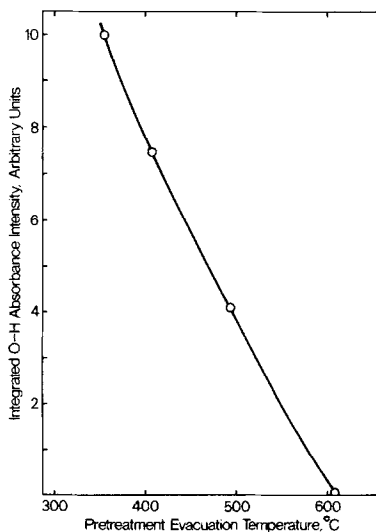


FIG. 2. Effect of pretreatment evacuation temperature on surface hydroxyl concentration for La_2O_3 .

tion sites are produced by the removal of surface hydroxyls, and probably involve the presence of both disordered surface anions and exposed underlying La^{3+} cations in acid-base pair-site configurations that the dehydroxylation process generates. The necessary participation of surface anions in the active sites has been demonstrated previously when it was shown that CO_2 , whose sole mode of interaction with La_2O_3 produces CO_3^{2-} species via reaction with surface O^{2-} ions (14), is an effective poison for *n*-butene interconversion (7). Despite widely different initial conversion rates of the various *n*-butene reactants following identical La_2O_3 pretreatment, the behaviors shown in Fig. 1 suggest, nevertheless, that the sites utilized by each of the three reactant isomers are either identical, or at least share a common feature that is similarly affected by variations in evacuation temperature. The decrease in activity observed in all three cases for pretreatment temperatures higher than $\sim 650^\circ\text{C}$ may be due to a decrease in surface disorder that results from the relatively high mobility of O^{2-} ions in lanthanide sesquioxides (15).

In view of the results presented in Fig. 1, all subsequent experiments described below employed La_2O_3 samples that had been pretreated using a final evacuation temperature of 650°C .

Isomerization Pathways

Occurrences of the various *n*-butene interconversion pathways over La_2O_3 were investigated by determining the selectivity exhibited by each *n*-butene reactant at various temperatures in the range 0 – 50°C . As shown by the results presented in Fig. 3, it is evident that isomerization of 1-butene is a parallel process, with both *cis*- and *trans*-2-butenes being primary products of the reaction throughout the temperature range investigated. Initial *cis/trans* product ratios are relatively large, characteristic of the behavior observed for most basic metal oxide catalysts. The decrease in initial *cis/trans* ratio with increasing reaction

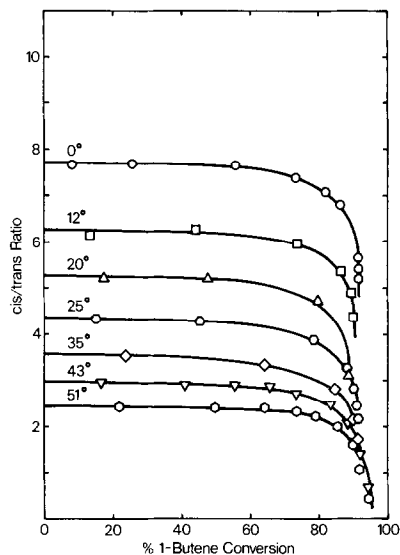


Fig. 3. *cis*-2-Butene/*trans*-2-butene product ratios as a function of 1-butene conversion over La_2O_3 at the indicated reaction temperatures.

temperature is due to the higher apparent activation energy of the one \rightarrow *trans* pathway compared to that of the one \rightarrow *cis* (*vide infra*). Maintenance of virtually constant *cis/trans* ratios up to very high ($\sim 80\%$) 1-butene conversions indicates that the rates of direct *cis* \rightleftharpoons *trans* interconversion are very small in comparison to that of 1-butene conversion, even at 50°C .

The latter conclusion is supported by the results of corresponding experiments that employed *cis*- and *trans*-butene reactants (Figs. 4 and 5, respectively). In contrast to the parallel isomerization pathways observed for 1-butene, conversions of both 2-butene reactants appear to be largely consecutive processes throughout the temperature range investigated. Initial *trans*/one and *cis*/one product ratios are zero in every case, with curves for all reaction temperatures in both figures having zero initial slope, indicating that the rates of *cis* \rightarrow *trans* and *trans* \rightarrow *cis* double bond rotation are negligibly slow compared to those of *cis* \rightarrow one and *trans* \rightarrow one double-bond migration. Thus, 1-butene is the sole measurable primary product from

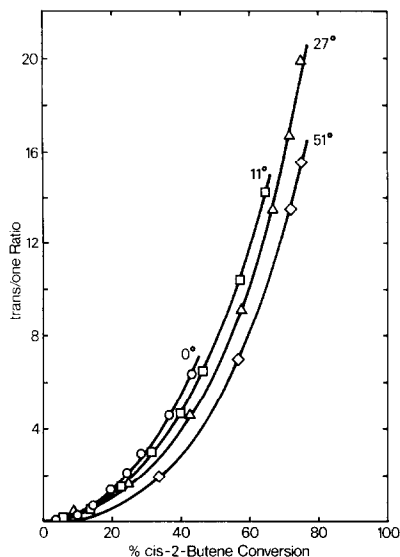


FIG. 4. *trans*-2-Butene/1-butene product ratios as a function of *cis*-2-butene conversion over La_2O_3 at the indicated reaction temperatures.

both 2-butene reactants, and appearance of the other 2-butene isomer in each case occurs principally by subsequent isomerization of 1-butene. The low-conversion data presented in the inset of Fig. 5 were obtained at 0°C using a 1-mg catalyst sample. Although the calculated uncertainty in measured *cis*/one product ratios for this experiment was $\pm 15\%$, the initial concave shape of the curve is evident. The rapid increases in *cis*/one product ratios at low conversions of *trans*-2-butene, compared to the much slower increases in *trans*/one ratios during *cis*-2-butene conversion (Fig. 4), reflect the relatively high rate of the $\text{one} \rightarrow \text{cis}$ pathway in comparison to that of the $\text{one} \rightarrow \text{trans}$ reaction, as shown in Fig. 3.

We conclude, therefore, that Eq. (3) is an essentially correct qualitative representation of the interconversion of *n*-butenes over La_2O_3 in the temperature range $0\text{--}50^\circ\text{C}$. Evidently, either the apparent activation energies of the direct $\text{cis} \rightleftharpoons \text{trans}$ interconversion pathways are sufficiently large that these reactions are negligibly slow in the temperature range investigated, or surface sites that permit the

required $\text{anti-}\pi\text{-allyl} \rightleftharpoons \text{syn-}\pi\text{-allyl}$ rotation in Eq. (1) are absent on La_2O_3 . With regard to the latter possibility, it should be noted that previous studies by Tanabe and co-workers have suggested that double-bond migration and rotation reactions in the *n*-butenes occur on dissimilar kinds of catalytic sites on CaO (2). The type catalyzing only $\text{cis} \rightleftharpoons \text{trans}$ rotation interacted readily with NO at 25°C to produce an NO_2^{2-} surface species, as confirmed by ESR spectral measurements, while that promoting only double bond migration did not interact measurably with NO. It is significant, therefore, that, as reported in our previous investigation (7), we observed no ESR evidence for the formation of NO_2^{2-} following exposure to NO of an La_2O_3 sample that had been pretreated in the usual manner and then evacuated at any temperature in the range $300\text{--}800^\circ\text{C}$. Hence, sites on La_2O_3 that catalyze double bond migration in the *n*-butenes may involve surface O^{2-} ions that resemble the more weakly basic of the two types observed on CaO.

Reaction Kinetics

Kinetic behaviors of the four prevailing

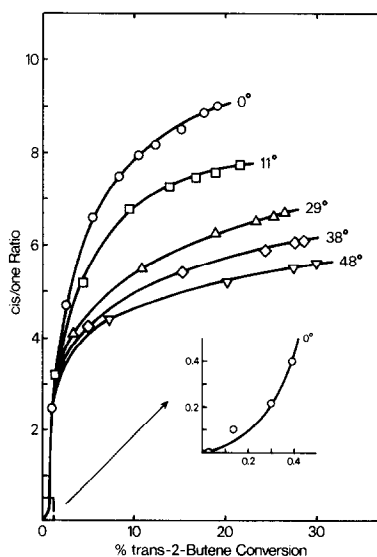


FIG. 5. *cis*-2-Butene/1-butene product ratios as a function of *trans*-2-butene conversion over La_2O_3 at the indicated reaction temperatures.

isomerization pathways were quantitatively established by measuring initial reaction rates at 0°C for each of the *n*-butene reactants at various initial pressures in the range 25–200 Torr. Reaction orders were obtained from the slopes of $\log R_i$ vs $\log P_i$ plots, according to:

$$R_i = kP_i^n \quad (4)$$

or

$$\log R_i = \log k + n \log P_i, \quad (5)$$

where R_i and P_i are the initial reaction rate and reactant pressure, respectively; k is the rate constant, and n is the reaction order with respect to pressure. As seen from the results in Fig. 6, initial rates of the two 1-butene reaction pathways are virtually pressure-independent, conforming to zero-order kinetics in the pressure range investigated and indicating that, at 1-butene pressure ≥ 25 Torr, the active sites catalyzing double-bond migration are essentially saturated with adsorbed reactant molecules at 0°C. By contrast, initial rates for *cis*- and *trans*-2-butene reactants exhibit marked pressure dependences, and illustrate the

much greater adsorption propensity at 0°C of 1-butene in comparison to those of both 2-butene isomers.

The fractional reaction orders observed for the 2-butene reactants suggest that kinetic data for all three reactant isomers may be represented by a Langmuirian rate expression of the form:

$$R_i = k \frac{bP_i}{1 + bP_i} \quad (6)$$

or

$$\frac{1}{R_i} = \frac{1}{kbP_i} + \frac{1}{k}, \quad (7)$$

where b is an adsorption/desorption equilibrium constant, and R_i , P_i , and k have the same meanings as in Eqs. (4) and (5). Appropriate plots of $1/R_i$ vs $1/P_i$ for *cis*- and *trans*-2-butene reactants at 0°C were quite linear, and their respective slopes and intercepts were used to derive the values of k and b that are summarized in Table 1 for the four isomerization pathways that prevail at this temperature. For sufficiently large values of b , Eq. (6) reduces to a zero-order expression, and may be used to describe the kinetics of the two reaction pathways for 1-butene conversion if b is larger than ~ 0.25 Torr⁻¹. The latter value (more than one order of magnitude greater than those for the two 2-butene reactants) would produce a variation in initial 1-butene reaction rate of <15% over the pressure range investigated, in agreement with the observed experimental results. It should be noted that the constant b decreases with increasing temperature, and, although all pressure-dependent kinetic data in the present study were obtained at 0°C, the kinetics of all four isomerization pathways are expected to approach first-order behavior at sufficiently high reaction temperature and low initial reactant pressure.

The apparent activation energies included in Table 1 were obtained from linear Arrhenius plots that were based on the initial reaction rates observed during the experiments summarized in Figs. 3, 4, and

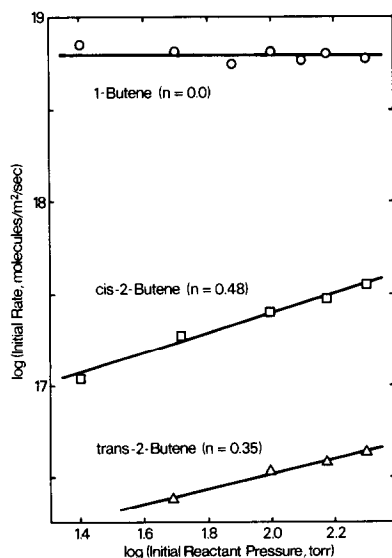


FIG. 6. Initial pressure dependences of *n*-butene reaction rates over La_2O_3 at 0°C; (n = reaction order with respect to pressure.)

TABLE 1

Kinetic Parameters for *n*-Butene Isomerization over La₂O₃ Fitted to the Rate Expression:
Rate = $kbP/(1 + bP)$

Reaction pathway	k $\left(\frac{\text{molecules}}{\text{m}^2\text{-sec}} \times 10^{-18}\right)^a$	b (Torr ⁻¹) ^a	E_a (kcal/mole) ^b
one → <i>cis</i>	5.65	>0.25	4.6
one → <i>trans</i>	0.73	>0.25	8.8
<i>cis</i> → one	0.69	0.016	6.2
<i>trans</i> → one	0.11	0.020	8.2

^a At 0°C.

^b In the reaction temperature range 0–50°C.

5. The difference in activation energy (viz., 1.6 kcal/mole) between the two directions of the one \rightleftharpoons *cis* interconversion is virtually identical, as expected, to the difference in standard enthalpy of formation of these two isomers. However, the corresponding $\Delta(\Delta E_a)$ for the one \rightleftharpoons *trans* interconversion (–0.6 kcal/mole) deviates considerably from the known $\Delta(\Delta H_f^\circ)$ of +2.8 kcal/mole for the two isomers. Such behavior has been reported previously for *n*-butene isomerization on ZnO (16), and may be due to the fact that the calculated apparent activation energies are based on *initial* conversion rates of each of the three isomer reactants, and involve coverage-dependent heats of adsorption. Since the initial surface condition, vis à vis relative one : *trans* coverages, is considerably different from that prevailing at equilibrium, the observed $\Delta(\Delta E_a)$ of the reversible pathway will not necessarily correspond to the enthalpy difference between the two isomers.

Hydrogen Transfer Mechanism and Kinetic Isotope Effect

Additional details regarding the mechanism of *n*-butene interconversion over La₂O₃ were obtained from tracer experiments in which approximately 1:1 mixtures of normal (d_0) and perdeuterated (d_8) forms of each of the three isomers were individually coreacted at 0°C. The results of these runs for 1-, *cis*-2-, and *trans*-2-butene

reactants are summarized in Tables 2, 3, and 4, respectively. The average deuterium contents shown in the last column of each table were calculated for each component from the following relationship:

Ave. No. D Atoms/Molecule

$$= \sum_i id_i, \quad (8)$$

where d_i is the fraction of all molecules of a particular isomer that contain i D atoms. It is evident from the data presented in these tables that isomerizations of all three *n*-butene reactants occur with negligible H–D redistribution, even at extents of reaction that correspond, as in the case of the last entry for *trans*-2-butene reactant in Table 4, to virtual thermodynamic equilibration. Thus, the hydrogen transfer step that necessarily accompanies double bond migration occurs over La₂O₃ via an intra-, rather than inter-, molecular mechanism. This conclusion is in agreement with that reported previously by Tanabe and co-workers for *n*-butene isomerization on La₂O₃ (8), and has been found to apply quite generally to most basic oxide catalysts for which the π -allylic carbanion mechanism of Eq. (1) is expected to be operative (16). Such behavior implies a complete localization of the abstracted proton on the O²⁻ ion component of the pair-site configuration during the double bond migration process.

TABLE 2

Isotopic Distributions of *n*-Butenes for Reaction of a 1 : 1 Mixture of 1-C₄H₈ : 1-C₄D₈ over La₂O₃ at 0°C

<i>n</i> -Butene isomer	Mole frac.	mole%									Ave. no. D atoms/molecule
		<i>d</i> ₀	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃	<i>d</i> ₄	<i>d</i> ₅	<i>d</i> ₆	<i>d</i> ₇	<i>d</i> ₈	
1-	1.000	46.3	0.0	0.0	0.0	0.0	0.0	2.7	11.0	40.0	4.13
<i>cis</i> -2-	0.000	—	—	—	—	—	—	—	—	—	—
<i>trans</i> -2-	0.000	—	—	—	—	—	—	—	—	—	—
1-	0.968	44.8	0.0	0.0	0.0	0.0	0.0	2.8	11.1	41.3	4.25
<i>cis</i> -2-	0.028	90.6	0.0	0.0	0.0	0.0	0.0	0.6	2.5	6.3	0.72
<i>trans</i> -2-	0.004	—	—	—	—	—	—	—	—	—	—
1-	0.945	42.5	0.0	0.0	0.0	0.0	0.0	2.9	11.5	43.1	4.43
<i>cis</i> -2-	0.049	—	—	—	—	—	—	—	—	—	—
<i>trans</i> -2-	0.006	84.9	0.0	0.0	0.0	0.0	0.0	1.1	3.5	10.5	1.15
1-	0.917	41.2	0.0	0.0	0.0	0.0	0.0	2.7	11.7	44.3	4.53
<i>cis</i> -2-	0.073	91.3	0.0	0.0	0.0	0.0	0.0	0.5	2.2	6.0	0.68
<i>trans</i> -2-	0.010	82.3	0.0	0.0	0.0	0.0	0.0	0.6	4.4	12.7	1.37
1-	0.886	39.3	0.0	0.0	0.0	0.0	0.0	3.2	12.3	45.1	4.67
<i>cis</i> -2-	0.101	92.0	0.0	0.0	0.0	0.0	0.0	0.4	2.1	5.4	0.62
<i>trans</i> -2-	0.013	86.8	0.0	0.0	0.0	0.0	0.0	0.8	3.2	9.1	1.00
1-	0.830	36.9	0.0	0.0	0.0	0.0	0.0	2.5	12.1	48.4	4.87
<i>cis</i> -2-	0.150	92.7	0.0	0.0	0.0	0.0	0.0	0.5	2.1	4.7	0.55
<i>trans</i> -2-	0.020	89.9	0.0	0.0	0.0	0.0	0.0	0.4	3.1	6.5	0.89
1-	0.823	36.8	0.0	0.0	0.0	0.0	0.0	3.3	12.6	47.3	4.86
<i>cis</i> -2-	0.157	93.0	0.0	0.0	0.0	0.0	0.0	0.6	2.1	4.3	0.53
<i>trans</i> -2-	0.020	88.8	0.0	0.0	0.0	0.0	0.0	0.4	2.7	8.0	0.86
1-	0.797	34.8	0.0	0.0	0.0	0.0	0.0	3.3	13.0	48.9	5.02
<i>cis</i> -2-	0.180	92.6	0.0	0.0	0.0	0.0	0.0	0.2	1.9	5.3	0.57
<i>trans</i> -2-	0.023	88.8	0.0	0.0	0.0	0.0	0.0	0.6	2.8	7.8	0.86
1-	0.787	34.2	0.0	0.0	0.0	0.0	0.0	3.3	13.3	49.2	5.06
<i>cis</i> -2-	0.188	92.0	0.0	0.0	0.0	0.0	0.0	0.4	2.1	5.5	0.69
<i>trans</i> -2-	0.025	89.0	0.0	0.0	0.0	0.0	0.0	0.6	2.7	7.8	0.85
1-	0.760	33.0	0.0	0.0	0.0	0.0	0.0	3.5	13.5	50.0	5.16
<i>cis</i> -2-	0.212	90.7	0.0	0.0	0.0	0.0	0.0	0.3	2.6	6.3	0.71
<i>trans</i> -2-	0.028	87.1	0.0	0.0	0.0	0.0	0.0	0.6	3.1	9.3	0.99
1-	0.640	23.9	0.0	0.0	0.0	0.0	0.0	3.8	14.8	57.4	5.86
<i>cis</i> -2-	0.318	88.8	0.0	0.0	0.0	0.0	0.0	0.4	3.0	7.8	0.86
<i>trans</i> -2-	0.042	85.7	0.0	0.0	0.0	0.0	0.0	1.1	3.6	9.6	1.08
1-	0.490	11.9	0.0	0.0	0.0	0.0	0.0	4.3	16.8	66.9	6.79
<i>cis</i> -2-	0.451	79.9	0.0	0.0	0.0	0.0	0.0	0.9	5.0	14.2	1.54
<i>trans</i> -2-	0.059	80.8	0.0	0.0	0.0	0.0	0.0	1.3	4.7	13.3	1.46

H-D isotope effects observed during these tracer experiments provide additional mechanistic information and details about the modes of site utilization by the four

prevailing interconversion pathways. "Light"/"Heavy" ratios were calculated from the tabulated data for each reactant and product isomer according to

TABLE 3

Isotopic Distributions of *n*-Butenes for Reaction of a 1:1 Mixture of *cis*-2-C₄H₈: *cis*-2-C₄D₈ over La₂O₃ at 0°C

<i>n</i> -Butene isomer	Mole frac.	mole%									Ave. no. D atoms/molecule	
		<i>d</i> ₀	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃	<i>d</i> ₄	<i>d</i> ₅	<i>d</i> ₆	<i>d</i> ₇	<i>d</i> ₈		
1-	0.000	—	—	—	—	—	—	—	—	—	—	—
<i>cis</i> -2-	1.000	53.4	0.0	0.0	0.0	0.0	0.0	1.8	9.7	35.1	3.60	
<i>trans</i> -2-	0.000	—	—	—	—	—	—	—	—	—	—	
1-	0.009	89.8	0.0	0.0	0.0	0.0	0.0	0.7	3.0	6.3	0.76	
<i>cis</i> -2-	0.991	57.1	0.0	0.0	0.0	0.0	0.0	1.5	8.8	32.6	3.32	
<i>trans</i> -2-	—	—	—	—	—	—	—	—	—	—	—	
1-	0.015	87.8	0.0	0.0	0.0	0.0	0.0	0.8	3.3	8.1	0.93	
<i>cis</i> -2-	0.985	55.3	0.0	0.0	0.0	0.0	0.0	1.7	9.1	34.0	3.46	
<i>trans</i> -2-	—	—	—	—	—	—	—	—	—	—	—	
1-	0.040	87.7	0.0	0.0	0.0	0.0	0.0	0.9	3.8	7.6	0.93	
<i>cis</i> -2-	0.955	55.9	0.0	0.0	0.0	0.0	0.0	1.5	9.0	33.6	3.41	
<i>trans</i> -2-	0.005	93.8	0.0	0.0	0.0	0.0	0.0	0.3	2.0	3.9	0.47	
1-	0.056	81.8	0.0	0.0	0.0	0.0	0.0	1.4	5.5	11.3	1.37	
<i>cis</i> -2-	0.931	54.7	0.0	0.0	0.0	0.0	0.0	1.8	9.2	34.3	3.50	
<i>trans</i> -2-	0.013	95.1	0.0	0.0	0.0	0.0	0.0	0.6	1.7	2.6	0.37	
1-	0.060	78.9	0.0	0.0	0.0	0.0	0.0	1.1	5.7	14.2	1.60	
<i>cis</i> -2-	0.922	54.4	0.0	0.0	0.0	0.0	0.0	1.7	9.3	34.6	3.52	
<i>trans</i> -2-	0.018	96.0	0.0	0.0	0.0	0.0	0.0	0.3	1.5	2.2	0.30	
1-	0.064	73.9	0.0	0.0	0.0	0.0	0.0	1.9	7.1	17.0	1.98	
<i>cis</i> -2-	0.913	53.6	0.0	0.0	0.0	0.0	0.0	1.7	9.4	35.3	3.58	
<i>trans</i> -2-	0.023	96.2	0.0	0.0	0.0	0.0	0.0	0.3	1.2	2.2	0.28	
1-	0.067	71.0	0.0	0.0	0.0	0.0	0.0	2.1	7.8	19.2	2.20	
<i>cis</i> -2-	0.905	53.3	0.0	0.0	0.0	0.0	0.0	2.0	9.7	35.0	3.60	
<i>trans</i> -2-	0.028	95.5	0.0	0.0	0.0	0.0	0.0	0.4	1.5	2.5	0.33	
1-	0.069	68.2	0.0	0.0	0.0	0.0	0.0	2.0	8.4	21.4	2.42	
<i>cis</i> -2-	0.900	53.1	0.0	0.0	0.0	0.0	0.0	1.8	9.5	35.6	3.62	
<i>trans</i> -2-	0.031	95.3	0.0	0.0	0.0	0.0	0.0	0.2	1.6	2.8	0.35	
1-	0.075	64.7	0.0	0.0	0.0	0.0	0.0	2.3	8.9	24.1	2.69	
<i>cis</i> -2-	0.886	53.9	0.0	0.0	0.0	0.0	0.0	1.9	9.6	34.6	3.55	
<i>trans</i> -2-	0.039	95.5	0.0	0.0	0.0	0.0	0.0	0.1	1.5	2.9	0.34	
1-	0.076	63.1	0.0	0.0	0.0	0.0	0.0	2.3	9.1	25.4	2.81	
<i>cis</i> -2-	0.880	53.6	0.0	0.0	0.0	0.0	0.0	1.7	9.5	35.2	3.58	
<i>trans</i> -2-	0.044	95.3	0.0	0.0	0.0	0.0	0.0	0.4	1.6	2.7	0.35	
1-	0.078	59.1	0.0	0.0	0.0	0.0	0.0	2.8	9.9	28.3	3.12	
<i>cis</i> -2-	0.864	53.6	0.0	0.0	0.0	0.0	0.0	1.6	9.5	35.3	3.59	
<i>trans</i> -2-	0.058	94.9	0.0	0.0	0.0	0.0	0.0	0.3	1.6	3.1	0.38	
1-	0.078	58.3	0.0	0.0	0.0	0.0	0.0	2.6	9.9	29.2	3.18	
<i>cis</i> -2-	0.863	52.5	0.0	0.0	0.0	0.0	0.0	1.9	9.7	35.9	3.66	
<i>trans</i> -2-	0.059	93.8	0.0	0.0	0.0	0.0	0.0	0.8	1.8	3.6	0.46	

TABLE 4

Isotopic Distributions of *n*-Butenes for Reaction of a 1:1 Mixture of *trans*-2-C₄H₈:*trans*-2-C₄D₈ over La₂O₃ at 0°C

<i>n</i> -Butene isomer	Mole frac.	mole%									Ave. no. D atoms/molecule
		<i>d</i> ₀	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> ₃	<i>d</i> ₄	<i>d</i> ₅	<i>d</i> ₆	<i>d</i> ₇	<i>d</i> ₈	
1-	0.000	—	—	—	—	—	—	—	—	—	—
<i>cis</i> -2-	0.000	—	—	—	—	—	—	—	—	—	—
<i>trans</i> -2-	1.000	48.5	0.0	0.0	0.0	0.0	0.0	2.8	11.5	37.2	3.95
1-	0.003	—	—	—	—	—	—	—	—	—	—
<i>cis</i> -2-	0.007	83.2	0.0	0.0	0.0	0.0	0.0	1.0	4.8	11.0	1.28
<i>trans</i> -2-	0.990	48.2	0.0	0.0	0.0	0.0	0.0	2.7	11.6	37.5	3.98
1-	0.004	—	—	—	—	—	—	—	—	—	—
<i>cis</i> -2-	0.020	87.1	0.0	0.0	0.0	0.0	0.0	1.0	4.3	7.7	0.97
<i>trans</i> -2-	0.976	46.8	0.0	0.0	0.0	0.0	0.0	2.9	11.8	38.6	4.08
1-	0.005	67.2	0.0	0.0	0.0	0.0	0.0	2.0	8.6	22.2	2.50
<i>cis</i> -2-	0.031	87.9	0.0	0.0	0.0	0.0	0.0	0.8	4.1	7.1	0.91
<i>trans</i> -2-	0.964	45.9	0.0	0.0	0.0	0.0	0.0	2.7	12.0	39.4	4.15
1-	0.007	69.7	0.0	0.0	0.0	0.0	0.0	1.9	8.2	20.2	2.31
<i>cis</i> -2-	0.043	89.4	0.0	0.0	0.0	0.0	0.0	1.2	3.5	5.9	0.79
<i>trans</i> -2-	0.950	46.1	0.0	0.0	0.0	0.0	0.0	2.9	12.0	39.1	4.14
1-	0.008	65.2	0.0	0.0	0.0	0.0	0.0	2.0	9.1	23.8	2.66
<i>cis</i> -2-	0.051	88.7	0.0	0.0	0.0	0.0	0.0	0.9	3.9	6.4	0.85
<i>trans</i> -2-	0.941	43.5	0.0	0.0	0.0	0.0	0.0	2.8	12.3	41.4	4.34
1-	0.009	72.1	0.0	0.0	0.0	0.0	0.0	2.2	7.9	17.8	2.11
<i>cis</i> -2-	0.066	88.2	0.0	0.0	0.0	0.0	0.0	1.3	4.1	6.3	0.87
<i>trans</i> -2-	0.925	43.8	0.0	0.0	0.0	0.0	0.0	2.8	12.3	41.1	4.32
1-	0.014	72.1	0.0	0.0	0.0	0.0	0.0	2.9	9.2	15.8	2.08
<i>cis</i> -2-	0.120	81.7	0.0	0.0	0.0	0.0	0.0	1.5	6.5	10.3	1.37
<i>trans</i> -2-	0.866	42.7	0.0	0.0	0.0	0.0	0.0	3.1	12.3	41.9	4.40
1-	0.019	56.6	0.0	0.0	0.0	0.0	0.0	3.6	13.2	26.7	3.27
<i>cis</i> -2-	0.176	62.5	0.0	0.0	0.0	0.0	0.0	2.6	11.9	23.0	2.83
<i>trans</i> -2-	0.805	44.3	0.0	0.0	0.0	0.0	0.0	3.0	11.8	40.9	4.28
1-	0.023	44.9	0.0	0.0	0.0	0.0	0.0	3.7	15.2	36.2	4.18
<i>cis</i> -2-	0.216	54.6	0.0	0.0	0.0	0.0	0.0	2.9	13.4	29.1	3.44
<i>trans</i> -2-	0.761	46.2	0.0	0.0	0.0	0.0	0.0	2.4	11.6	39.7	4.14

$$\frac{\text{“Light”}}{\text{“Heavy”}} = \frac{\sum_{i=0}^3 d_i + \frac{1}{2}d_4}{\frac{1}{2}d_4 + \sum_{i=5}^8 d_i} = \frac{d_0}{d_6 + d_7 + d_8}, \quad (9)$$

where the latter equality is valid in the present case since H–D redistribution does not occur, and are presented as a function of conversion of the appropriate *n*-butene

reactant in Figs. 7, 8, and 9. The zero-conversion intercept of each curve represents the primary H–D isotope effect in those cases where the isomer is a primary product of the converted reactant, i.e., both 2-butenes from 1-butene reactant and 1-butene from the two 2-butene reactants. The significant initial increases in “Light”/“Heavy” ratios that occur for most of the product isomers prior to the expected continuous declines are unusual

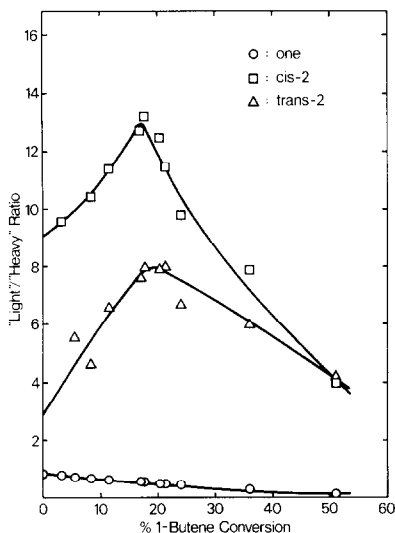


FIG. 7. "Light"/"Heavy" ratios of *n*-butene isomers as a function of conversion for reaction of a 1:1 mixture of 1-C₄H₈: 1-C₄D₈ over La₂O₃ at 0°C.

and may be due to the known self-poisoning effect of the *n*-butenes on La₂O₃ (7). If a heterogeneous array of active isomerization sites were available initially on the catalyst surface, for example, then differing isotope effects might prevail for the various reactions occurring on structurally or energetically dissimilar types of sites. Partial self-poisoning by essentially irreversibly adsorbed butene reactant or product molecules could result in deactivation of certain sites and cause a gradual change in the overall observed isotope effect. Under the isothermal conditions employed, such a phenomenon would be time-, rather than conversion-, dependent, and this was indeed the experimental observation.

Despite the possible occurrence of such poisoning behavior, certain fundamental differences between the principal isomerization pathways are evident. As shown in Figs. 7 and 8, the one \rightleftharpoons *cis* interconversion is accompanied by a large initial kinetic isotope effect ($k_H/k_D = 9$ to 10), indicating that the rate-limiting step in both directions is proton abstraction by a surface O²⁻ ion to form the π -allylic carbanion intermediate, which presumably then coordinates to

a neighboring exposed La³⁺ ion. Furthermore, the magnitude of the isotope effect suggests that such proton abstraction is essentially complete. The one \rightleftharpoons *trans* interconversion (Figs. 7 and 9), on the other hand, occurs with a much smaller initial isotope effect ($k_H/k_D = 1$ to 3), suggesting that a more covalently bonded allylic species may be generated in this case, or that these pathways consist of a more complex sequence of reactions that is characterized by more than one rate-determining step (17).

An alternative explanation for these disparate isotope effects is that the two reversible interconversions may occur predominantly on surface sites of La₂O₃ that, although similarly affected by pretreatment conditions, are not identical in every respect. Possible distinguishing features might involve, for example, differing accessibilities of underlying cations or extents of local anion disorder that influence site basicity and, consequently, the mode of proton abstraction. This view is supported by earlier results which have demonstrated that partial poisoning of La₂O₃ by adsorbed

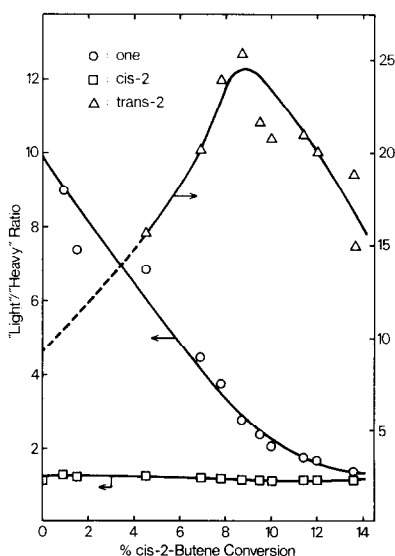


FIG. 8. "Light"/"Heavy" ratios of *n*-butene isomers as a function of conversion for reaction of a 1:1 mixture of *cis*-2-C₄H₈: *cis*-2-C₄D₈ over La₂O₃ at 0°C.

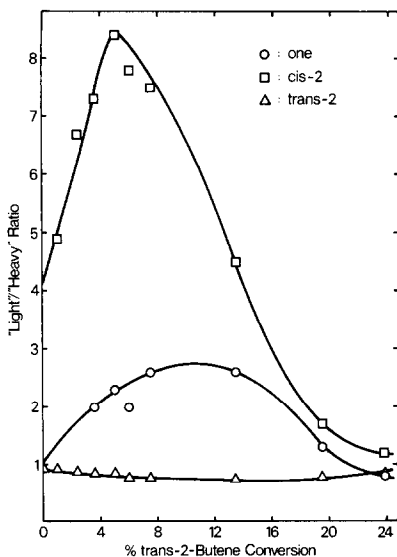


Fig. 9. "Light"/"Heavy" ratios of *n*-butene isomers as a function of conversion for reaction of a 1:1 mixture of *trans*-2-C₄H₈:*trans*-2-C₄D₈ over La₂O₃ at 0°C.

CO₂ results in significant increases in *cis/trans* product ratios from 1-butene reactant at all temperatures in the range 0–50° (7). Although the rates of both the one → *cis* and one → *trans* pathways were reduced by the resulting CO₃²⁻ complexes, the latter was affected considerably more than the former.

CONCLUSIONS

The catalytic behavior of La₂O₃ for *n*-butene isomerization resembles those exhibited by most other basic oxides for this reaction, but involves certain unusual features as well. Initial activity is a sensitive function of prior pretreatment temperature, due to surface hydroxyl removal and changes in local anion disorder, and attains a maximum for all three *n*-butene reactants following evacuation at ~650°C. Proton abstraction to form a presumably π-allylic carbanion intermediate is the rate-determining step of each interconversion process, and the hydrogen transfer step that necessarily accompanies double bond migration occurs via an intramolecular mechanism. Both 2-butene isomers are pri-

mary products of 1-butene conversion at all temperatures in the range 0–50°C, and initial *cis/trans* product ratios are characteristically large (~8 at 0°C). However, although the rates of double bond migration are very high, those of direct *cis* ⇌ *trans* interconversion are, by comparison, extremely slow in the same temperature range, possibly due to the absence of sites on La₂O₃ that permit the required anti-π-allyl ⇌ syn-π-allyl rotation to occur. As a result, the sole primary product observed for both 2-butene reactants at 0–50°C is 1-butene. Furthermore, the one ⇌ *cis* and one ⇌ *trans* reactions are accompanied by significantly different initial H–D isotope effects (9–10 vs 1–3, respectively), suggesting that the two reversible interconversions may involve dissimilar mechanisms or occur on distinguishably different types of surface sites.

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