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# Characterization of Catalytic Lanthanum Oxide for Double Bond Isomerization of *n*-Butenes

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Lanthanum sesquioxide, when properly activated, is an extremely active catalyst for double bond migration in the *n*-butenes. The initial rate of 1-butene conversion on rehydrated $La_2O_3$ varies with final calcination temperature, and attains a maximum of $4.2 \times 10^{20}$ molecules/m$^2$/min at 0°C, following catalyst evacuation at 650°C. In the temperature range 0 to 50°C, the reaction is zero order in 1-butene for initial reactant pressures of 25 to 200 torr. A cumulative self-poisoning of the catalyst occurs at reaction temperatures due to adsorption of a strongly held, unreactive form of *n*-butene, but the latter is completely removed and activity restored upon subsequent rehydration and calcination. Initial *cis*-2-butene/*trans*-2-butene ratios are large (7 to 8 at 0°C), and the rates of reaction of both 2-butene isomers are much lower than that of 1-butene. Direct interconversion of *cis*- and *trans*-2-butene occurs very slowly or not at all on $La_2O_3$, and a reaction scheme for the three-component system is proposed. Active sites for 1-butene isomerization involve surface $O^{2-}$ ions in conjunction with adjacent defect structures such as anion vacancies. A difference of 4.2 kcal/mol between the apparent activation energies of *cis*- and *trans*-2-butene appearances suggests that formations of the two 2-butene isomers from the 1-butene reactant may occur on energetically and/or structurally dissimilar sites on $La_2O_3$.

## INTRODUCTION

Although considerable information is available about the catalytic and surface properties of the alkaline earth oxides (*1–5*), much less effort has been devoted to characterizing the fundamental catalytic behaviors of other basic oxides, particularly those of the rare earth elements. Empirical studies have demonstrated that lanthanide sesquioxides ($M_2O_3$) are effective and, in certain cases, extremely active catalysts for a variety of reactions, including alcohol dehydrations and dehydrogenations (*6, 7*), hydrocarbon and carbon monoxide oxidations (*8, 9*), decompositions of nitric and nitrous oxides (*10, 11*), and olefin hydrogenations (*12*).

These investigations, however, have been largely aimed at obtaining comparative kinetic data for the various oxides, and relatively few details have been reported about the identities, modes of generation, or surface concentrations of catalytically active sites on rare earth oxides, or about the natures of their interactions with adsorbed and/or reacting molecules. As part of a continuing study of the fundamental catalytic and surface properties of the lanthanide oxides, we have examined the behavior of $La_2O_3$, the most highly basic member of the sesquioxide series, as a catalyst for double-bond migration and *cis*/*trans* rotation in the *n*-butenes. This reaction, because of its often highly specific structural requirements when occurring on oxide catalysts, affords an opportunity to

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TABLE 1

Temperature Dependence of Surface Area and Phase Composition of Lanthanum Oxide Catalyst

| Final calcination temperature (°C)[a] | Surface area ($m^2/g$) | Phase(s) present |
|---|---|---|
| 25 | 19.2 | $La(OH)_3$ |
| 100 | 19.0 | $La(OH)_3$ |
| 150 | 17.9 | $La(OH)_3$ + LaOOH (tr.) |
| 200 | 16.3 | LaOOH |
| 300 | 14.5 | $La_2O_3$ + LaOOH (tr.) |
| 400 | 14.6 | $La_2O_3$ |
| 500 | 13.6 | $La_2O_3$ |
| 600 | 12.1 | $La_2O_3$ |
| 700 | 10.4 | $La_2O_3$ |
| 800 | 7.9 | $La_2O_3$ |

[a] Evacuation for 16 h at each temperature.

probe geometric restrictions and limitations on the behaviors of the active sites.

## EXPERIMENTAL METHODS

*Materials.* The preparation of catalytic lanthanum sesquioxide and a characterization of its pertinent physical and surface properties and dehydration/rehydration behavior have been reported previously (*13*). A 10-mg (dehydrated weight) charge of 30/40 mesh granules was used for all experiments. 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 oxygen for 1 h (with continuous removal of combustion products by an in-line trap maintained at −196°C) and subsequent evacuation for 1 h at the same temperature. The sample was then rehydrated *in situ* with an excess of $CO_2$-free $H_2O$ for 3 h at 25°C, and finally evacuated at the desired calcination temperature to a residual pressure of $<10^{-5}$ torr. This procedure resulted in a relatively nonporous, moderate surface area material that had quite reproducible activity (±2 to 4%) for the isomerization reaction. A summary of catalyst surface area and phase composition as a function of final calcination temperature is presented in Table 1.

1-Butene was Phillips research grade (99.9%), and was purified by passage through a column containing Linde 4A molecular sieve at 25°C, followed by three freeze-pumping cycles at −196°C, three condensation/evacuation/revaporization cycles at −78°C, and four distillations from −78 to −196°C, the center 90% cut being retained in each case. This lengthy purification method proved necessary because the small catalyst sample was extremely sensitive to minute traces of $CO_2$ and especially $H_2O$ in the butene reactant.

Oxygen was Airco high-purity grade (99.9%) and was purified before use by passage through a glass bead-filled trap at −196°C. Carbon dioxide was Linde instrument grade (99.99%) and was used without further purification. Deionized $H_2O$, used for catalyst rehydration during the pretreatment procedure, was freed of $CO_2$ by four distillations from 25 to −78°C, with final evacuation at the latter temperature to a residual pressure of $<10^{-4}$ torr. Complete removal of detectable $CO_2$ was verified by the absence of infrared bands due to $CO_3^{2-}$ species in the spectrum of an $La_2O_3$ sample that had been exposed to the treated $H_2O$.

*Apparatus.* All experiments were performed using a closed-loop, recirculation-type system that consisted of an all-glass circulation pump, a U-shaped quartz reactor containing the catalyst sample, and appropriate provisions for periodically removing 1 vol% samples by expansion for gas chromatographic analysis. Total system volume was 345 $cm^3$, 87% of which was contained in a spherical mixing vessel. Several check experiments were performed at the highest reaction temperature employed (51°C) to confirm that observed reaction rates were not limited by circulation pumping speed. Pretreatment furnace temperatures were maintained to ±1°C by a digital proportional band controller, and reaction temperatures in the range of 0 to 51°C were achieved with a thermostatted oil bath. The reaction system was connected via greased stopcocks to a conventional mercury-free high-vacuum gas-handling system. Gas pressures were measured in three overlapping ranges with an ionization gauge ($<10^{-3}$ torr), thermocouple gauge ($10^{-3}$ to 1 torr), and calibrated pressure transducer ($>1$ torr) whose digital output was accurate to $\pm 0.2\%$ of reading.

The three *n*-butene isomers were separated by gas–liquid chromatography, using a $\frac{3}{8}$ 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 reported by a digital integrator from the output of a hot-wire thermal conductivity detector, following appropriate corrections for differing thermal responses of the three components.

## RESULTS AND DISCUSSION

### *Activity Dependence on Calcination Temperature*

A characteristic feature of alkaline earth and other basic oxides is that their catalytic activities for certain reactions are often sensitive functions of prior calcination temperature and sample origin (*1*). The effect of final calcination temperature (following rehydration) on the specific activity of $La_2O_3$ for 1-butene isomerization was determined in a series of experiments at 0°C, with an initial 1-butene pressure of 100 torr in each case. The resulting initial conversion rates, normalized to account for the surface area variations shown in Table 1, are represented by the solid points in Fig. 1. Below 300°C, dehydration of $La(OH)_3$ and its LaOOH successor, formed during the pretreatment rehydration process, is incomplete (*13*), and the sample lacks measurable activity for the isomerization reaction. Activity begins to appear following evacuation at 300–350°C, when basic $O^{2-}$ ions become available on the dehydrated oxide surface, and increases to a maximum at ~650°C, above which a rapid decline occurs up to 800°C, the highest calcination temperature investigated. The general behavior is similar to that observed by Tanabe for the generation of 1-butene isomerization activity in alkaline earth oxides (*14*).

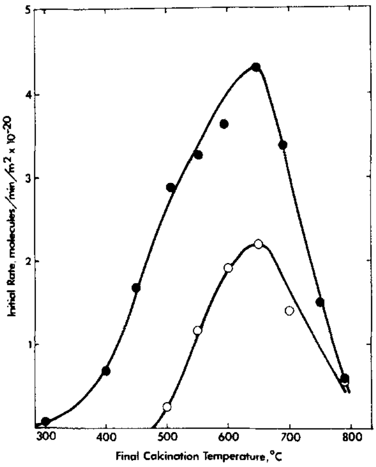


FIG. 1. Dependence of initial 1-butene reaction rate on final calcination temperature of $La_2O_3$, following pretreatment rehydration step. Solid points, normal pretreatment (see text); open points, sample exposed to excess $CO_2$ for 3 h at 25°C following rehydration and prior to final calcination.

Thermogravimetric studies have demonstrated that dehydration of $La(OH)_3$ is complete at 300°C (*13*), and supplementary infrared measurements have confirmed the absence of both surface and bulk hydroxyls in $La_2O_3$ evacuated above this temperature (*15*). Hence, the considerable increase in specific activity of the oxide in the calcination temperature range 300–650°C indicates that available surface $O^{2-}$ ions, although necessary participants, are not the sole components of the isomerization sites. It is likely that adjacent surface irregularities, such as anion vacancies, generated during vacuum calcination of the oxide, are required features of the active sites, and

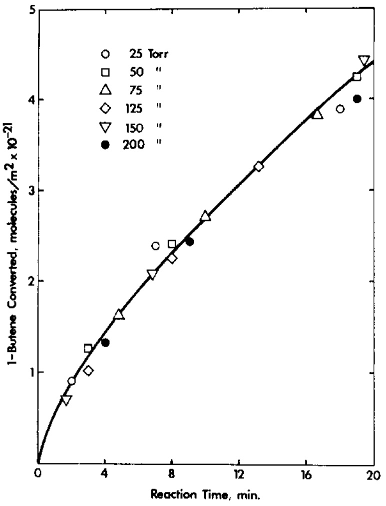


FIG. 2. 1-Butene conversion on $La_2O_3$ (calcined at 650°C) as a function of reaction time at 0°C for various initial reactant pressures.

may govern both the activity and structural specificity of the isomerization process (*vide infra*). Infrared (*15*) and $^{16}O$–$^{18}O$ isotope exchange studies (*16*) have previously suggested the existence of such anion vacancies on $La_2O_3$ that has been subjected to high-temperature evacuation. The decline in specific activity at calcination temperatures >650°C may be due to a decrease in the concentration of surface defect structures caused by an "annealing" effect.

Evidence for the necessary participation of surface $O^{2-}$ ions as components of the isomerization sites was obtained by repeating the above series of experiments under identical reaction conditions, but exposing the catalyst sample to an excess of carbon dioxide at 25°C, following the pretreatment rehydration step and prior to the final calcination. This procedure results in a surface concentration of seven to eight $CO_2$ molecules per 100 Å² on the trihydroxide, or approximately one $CO_2$ per surface $O^{2-}$ ion on the resulting oxide (*15*). The observed dependence of isomerization activity on calcination temperature is summarized by the open points in Fig. 1. In this case, measurable activity does not begin to appear until 450–500°C, but still reaches a maximum at calcination temperatures of ~650°C, above which a rapid decrease is again apparent up to 800°C.

These results correlate well with those of a previous infrared study which established that the sole mode of interaction of $CO_2$ with $La(OH)_3$ involves proton displacement from surface $OH^-$ ions and consequent formation of a complete monolayer of unidentate $CO_3^{2-}$ species (*15*). The latter persist on the sesquioxide surface following complete dehydration of the trihydroxide at 300°C, and do not begin to decompose until ~500°C. Increasing carbonate removal and consequent exposure of available surface $O^{2-}$ ions, together with surface defect generation, occur above the latter temperature, and are accompanied by a simultaneous appearance of isomerization activity. A considerable amount of surface $CO_3^{2-}$ remains, however, even at 650°C, and causes a lower maximum activity to be observed for "carbonated" samples (or for those previously exposed to atmospheric carbon dioxide) than is the case in the absence of adsorbed $CO_2$. Evacuation at 750–800°C is required to completely remove all surface $CO_3^{2-}$ structures (*15*), and, significantly, the initial isomerization rates observed for the two types of samples are virtually identical following calcination at 800°C.

In view of the results presented in Fig. 1, all subsequent experiments reported below were made using a rehydrated sample and a final pretreatment calculation temperature of 650°C.

### *Reaction Kinetics*

Kinetics of the double bond migration reaction of 1-butene over $La_2O_3$ were established by measuring absolute conversion levels as a function of reaction time in a series of experiments at 0°C in which initial reactant pressure was varied within the range 25–200 torr. As shown in Fig. 2, the rate of reaction during the early stages was essentially independent of initial 1-butene pressure, and the results may be represented by a single curve having an initial slope of $4.2 \times 10^{20}$ molecules/m$^2$/min. The implication of such zero-order kinetic behavior is that initial exposure of a fresh $La_2O_3$ sample to 1-butene results in the formation of a virtually inexhaustible reservoir of adsorbed molecules, or their derivatives, that is unaffected by residual gas phase reactant pressure. Double bond migration and subsequent desorption of 2-butene product molecules are followed by immediate reoccupation of the vacated surface sites by additional 1-butene molecules from the gas phase. These results are similar to those of Kokes *et al.* who observed that 1-butene isomerization on ZnO also occurs via zero-order kinetics (*17*). Unlike these authors, however, we were unable to detect infrared bands assignable to any chemisorbed form of 1-butene or reaction intermediate on the catalyst surface. The situation on $La_2O_3$ is evidently similar, in this regard, to that reported by Baird and Lunsford for 1-butene adsorption on MgO (*18*).

It should be noted that, even for the extreme assumption that every surface $O^{2-}$ ion may serve as an active site, the initial 1-butene reaction rate of $4.2 \times 10^{20}$ molecules/m$^2$/min at 0°C corresponds to a turnover number of 52 molecules/site/s. This value is about twice that observed on MgO (*18*) and is larger by a factor of 5000–10,000 than those obtained with $Al_2O_3$ (*19, 20*) and ZnO (*17*). If, as discussed in the previous section, isomerization sites on $La_2O_3$ consist of $O^{2-}$ ions in necessary conjunction with less frequently occurring surface features, such as anion vacancies, then the effective turnover numbers would be even larger.

TABLE 2

Initial 1-Butene Reaction Rates at 0°C for Successive Experiments Involving No Catalyst Pretreatment between Runs

| Experiment number | Initial 1-butene reaction rate (molecules/m$^2$/min $\times 10^{-20}$) |
|---|---|
| 1 | 4.39 |
| 2 | 3.21 |
| 3 | 2.34 |
| 4 | 1.51 |
| 5 | 0.93 |

The low-conversion curvature observed in the kinetic plot of Fig. 2 could not be removed, even by additional chromatographic purification of the 1-butene reactant, and is apparently due to a self-poisoning of the catalyst that is caused by the *n*-butene molecules themselves. This poisoning effect is independent of any residual concentration of surface carbonate species, and is cumulative and largely irreversible at typical reaction temperatures (<50°C). Table 2 summarizes, for example, the decline in initial rates observed for a series of 20-min runs at 0°C, in which the catalyst was merely evacuated for 10 min at 0°C between each 100-torr admission of 1-butene reactant. Identical results were obtained when the sample was evacuated for 1 h at 800°C between runs. In the latter experiments, the color of the catalyst became progressively darker following each evacuation, due to thermal decomposition of a strongly held, and presumably unreactive, form of *n*-butene. In all cases, however, complete recovery of original activity occurred when the catalyst was subjected to the normal pretreatment procedure.

### *Reaction Characteristics*

Double bond migration reactions of terminal olefins on basic oxide catalysts characteristically result in high initial *cis/trans* ratios among the primary internal olefin products (*14, 18*). This effect is a kinetic one that is governed by the often severe structural requirements of the active

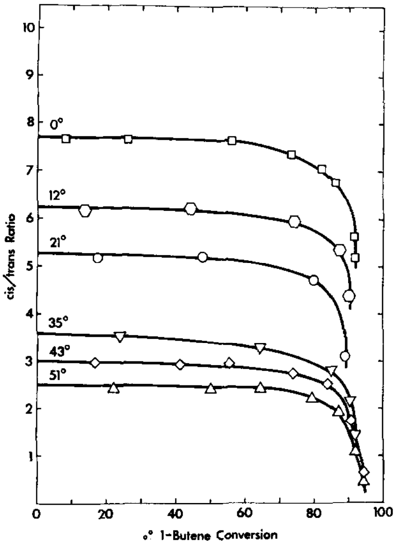


FIG. 3. The *cis/trans* ratios in 2-butene product as a function of 1-butene conversion at various reaction temperatures on $La_2O_3$.

sites on these materials and the necessary geometric limitations on their interactions with the various olefin isomers. On catalytic $\gamma$-$Al_2O_3$, for example, it is believed that reactant olefin molecules must "drape" themselves over active sites that are composed of an exposed $Al^{3+}$ ion and an adjacent $O^{2-}$ ion (*22-24*). The geometry of such a configuration favors generation of *cis* isomers in the product olefins. The initial product distributions of olefin isomerizations on such catalysts thus often differ considerably from those predicted solely on the basis of thermodynamic equilibrium considerations. After a sufficiently long reaction time, concentrations of the various olefin isomers will, of course, attain equilibrium values corresponding to the operational reaction temperature, regardless of any kinetic limitations imposed by the catalyst employed.

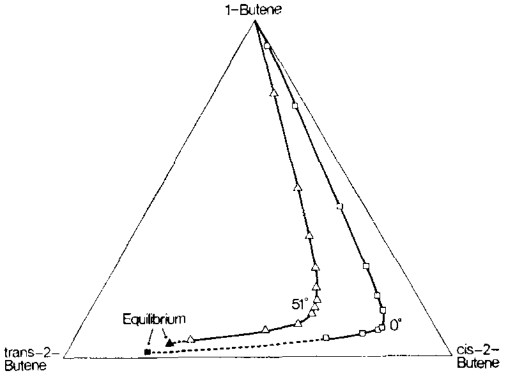


FIG. 4. Reaction profiles for 1-butene isomerization at 0 and 51°C on $La_2O_3$.

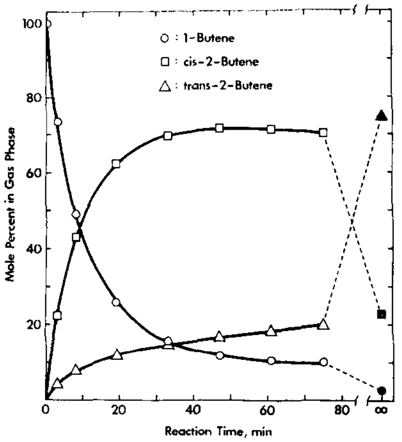
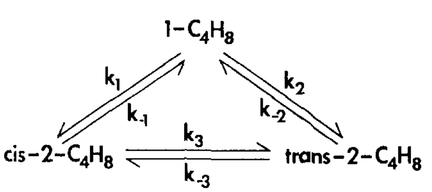


FIG. 5. Product distributions for 1-butene isomerization at 20°C on $La_2O_3$. Solid points represent thermodynamic equilibrium values for each isomer.

Figure 3 presents observed *cis/trans* ratios in the 2-butene product as a function of 1-butene conversion for several experiments in the temperature range 0 to 51°C, and complete reaction profiles for the 0 and 51°C runs are contained in Fig. 4. Profiles of the other runs lie between the two depicted in Fig. 4, but have been omitted for purposes of clarity. As expected, the initial *cis/trans* ratios at all temperatures are considerably greater than the corresponding thermodynamic equilibrium values, but decrease with increasing reaction temperature. Unlike the behavior typically observed with other basic oxide catalysts, however, the preponderance of *cis*-2-butene product over $La_2O_3$ remains uniformly large and virtually undiminished until very high (>80%) 1-butene conversions are attained. In addition, the final approach to thermodynamic equilibrium, involving primarily a redistribution of the *cis*- and *trans*-2-butene concentrations, occurs much more slowly than does the initial rapid conversion of 1-butene, as shown in Fig. 5, where the distributions of the three isomers are displayed for a typical experiment at 20°C. This behavior was observed in all experiments on $La_2O_3$, and was independent of the self-poisoning effect discussed in the preceding section.

These observations suggest two important features of the *n*-butene isomerization process on $La_2O_3$: (i) The rates of reaction of *cis*- and *trans*-2-butene are much slower than that of 1-butene, and (ii) direct interconversion of the two 2-butene isomers occurs very slowly or not at all on this catalyst. Preliminary results obtained from experiments using *cis*- and *trans*-2-butene reactants have supported both of these conclusions. The initial rates of reaction observed for the two isomers at 0°C were approximately equal, but were only 5 to 7% that of 1-butene on a similarly activated catalyst. Furthermore, the only *initial* product observed with both 2-butene reactants was 1-butene.

On most olefin isomerization catalysts for which quantitative data are available (*21, 25, 26*) the approach to equilibrium of the three *n*-butene isomers may be represented by the triangular scheme:



Scheme 1

in which all six rate constants are finite. On $La_2O_3$, however, $k_3$ and $k_{-3}$ are evidently negligibly small compared to the other four rate constants, and the overall reaction scheme is best represented as:

$$\text{cis-2-}C_4H_8 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{1-}C_4H_8 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{trans-2-}C_4H_8$$

Scheme 2

where, at 0°C for a rehydrated sample calcined at 650°C, the four rate constants $k_1$, $k_2$, $k_{-1}$, and $k_{-2}$ have the approximate *initial* values of 3.7, 0.5, 0.3, and $0.2 \times 10^{20}$ molecules/m$^2$/min, respectively.

Scheme (2) differs from that proposed by Minachev and co-workers (*27*), who believe that *trans*-2-butene formation from 1-butene over $La_2O_3$ occurs in a stepwise fashion through a *cis*-2-butene intermediate. This postulate, however, was based only on the results of experiments using 1-butene reactant, and implies the appearance of *cis*-2-butene as the sole initial product of 1-butene isomerization, with subsequent generation of *trans*-2-butene as a secondary reaction product. The latter observation is inconsistent with both our and their experimental results.

Although the characterization studies described here do not yet permit detailed conclusions to be drawn about the behavior of the active sites on $La_2O_3$, certain general features are apparent. The high initial selectivity to *cis*-2-butene that occurs at $\leq$51°C with the 1-butene reactant indicates the existence of considerable kinetic and geometric restraints on the nature and/or mode of operation of the isomerization sites on $La_2O_3$ that may be similar to those commonly observed on other basic oxide catalysts for this reaction. Tanabe and co-workers, for example, have recently identified two types of basic sites (i.e., $O^{2-}$ ions) of differing strengths that are generated on the surface of CaO by vacuum calcination (*28*). The weaker of these two types, formed at 500–600°C, catalyzes only double bond migration, but not *cis*/*trans* rotation, in the *n*-butenes, and is insufficiently basic to cause formation of $NO_2^{2-}$ species upon exposure to gaseous

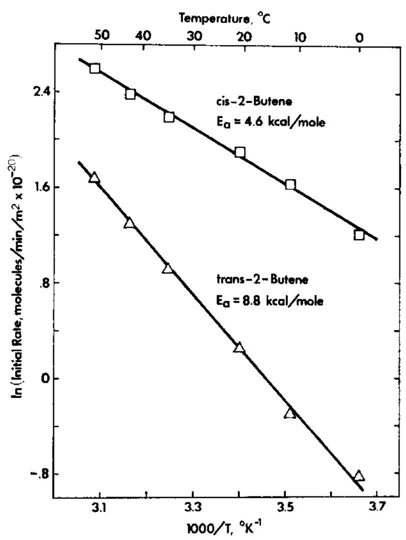


FIG. 6. Arrhenius plots for the rates of formation of *cis* and *trans*-2-butenes from 1-butene reactant on $La_2O_3$.

NO at 25°C. The stronger types of sites, on the other hand, generated by evacuation at 700–900°C, promote only *cis*/*trans* rotation in the 2-butenes, and interact readily with NO at 25°C to produce $NO_2^{2-}$ entities, as confirmed by ESR spectral measurements. In view of these results, it is significant that, consistent with the apparent lack of direct *cis*-2-butene $\rightleftarrows$ *trans*-2-butene interconversion on $La_2O_3$, 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 evacuated at any temperature <800°C. It is possible, therefore, that the sites on $La_2O_3$ that catalyze double bond migration in the *n*-butenes may involve $O^{2-}$ ions of the weaker, "normal" type observed on CaO.

An important additional feature, however, is reflected by the observed decrease in initial *cis*/*trans* product ratio with increasing reaction temperature (Fig. 3), which implies that the apparent activation energy of the pathway by which *trans*-2-butene is formed from 1-butene exceeds that involved in *cis*-2-butene formation. Assuming the validity of Scheme (2) above, it is possible to separately determine these two activation energies. Figure 6 contains Arrhenius plots for the rates of appearance in the gas phase of the two 2-butene isomers, calculated from the extrapolated initial *cis*/*trans* ratios of Fig. 3 and the total initial rates of 1-butene conversion at each temperature. The 4.2 kcal/mol difference between the two apparent activation energies obtained from these plots is considerably larger than the value (~1 to 2 kcal/mol) that would be expected solely on the basis of differing steric effects of the two isomers deriving from a common intermediate, and suggests the occurrence of separate reaction pathways and intermediates for the formation of the two 2-butenes.

An alternative possibility is that the respective formations of *cis*- and *trans*-2-butene from 1-butene may occur on structurally and/or energetically dissimilar surface sites on $La_2O_3$. Support for the latter postulate was obtained by performing an additional series of 1-butene isomerization experiments at various temperatures in the

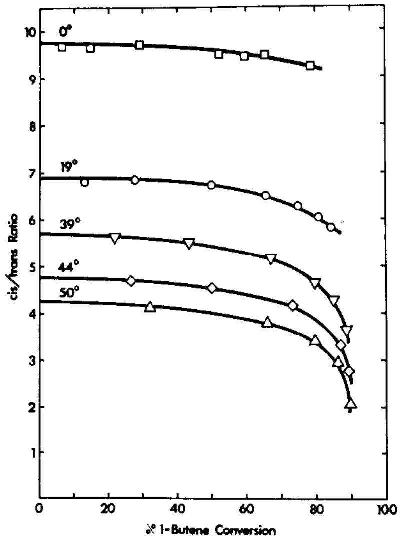


FIG. 7. The *cis*/*trans* ratios in 2-butene product as a function of 1-butene conversion at various reaction temperatures on $La_2O_3$ that had been partially poisoned by preadsorbed $CO_2$.

range 0 to 50°C, but using an $La_2O_3$ sample that had been partially poisoned by preadsorbed $CO_2$ and calcined at 650°C to correspond to the maximum point on the lower curve in Fig. 1. The resulting *cis/trans* product ratios (Fig. 7) were considerably larger at all reaction temperatures than those observed with a "clean" $La_2O_3$ sample (Fig. 3), and indicate a greater deactivating effect of $CO_2$ on the "*trans*-forming" sites than on the "*cis*-forming" sites. Furthermore, despite the lower total rates of 1-butene conversion on the poisoned catalyst, the apparent activation energies for the formation of the two 2-butene isomers were virtually identical to those shown in Fig. 6 for the unpoisoned sample. The poisoning effect of surface $CO_3^{2-}$ structures resulting from $CO_2$ adsorption thus appears to be one of simple site blockage, with no apparent effect on the mechanism or pathway of the isomerization process.

Further studies are currently underway with the aim of quantitatively refining the kinetics and energetics of *n*-butene isomerization over $La_2O_3$ and of elucidating the nature of the hydrogen-transfer step that accompanies this reaction.

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