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Catalytic Sites for the Isomerization of 1-Butene Over Magnesium Oxide

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The nature of the isomerization reaction of 1-butene over MgO has been investigated. The selectivity (*cis/trans* ratio) and the isomerization rate were measured as a function of the catalyst pretreatment temperature which was varied from 300 to 900°C. The results show that the sites on MgO that are responsible for the isomerization reaction are dependent upon the pretreatment temperature and pass through a maximum concentration following pretreatment at 700°C. Constant activation energies and turnover rates indicate that the 1-butene isomerization site did not change in type as the pretreatment temperature was increased. The initial *cis/trans* ratio of the product 2-butene was found to be dependent upon the pretreatment and reaction temperature. Results from infrared studies indicate that butene was physically adsorbed on MgO and remained olefinic in character. A correlation was found to exist between the concentration of electron donors, presumably the strongly basic O^{2-} ions, and the 1-butene isomerization rate. The isomerization reaction may proceed via a concerted process on oxide ions of low coordination number.

INTRODUCTION

Catalytic isomerization of 1-butene over oxide catalysts (acid and base) has been extensively investigated in attempts to understand the mechanisms of catalytic isomerization of olefins. In the case of 1-butene, the reaction is a simple one in which 1-butene forms two products, *cis*- and *trans*-2-butene. The initial selectivity (ratio of *cis*- and *trans*-2-butene) and other kinetic data give information that can serve as a guide in determining the mechanism for the reaction.

Three mechanisms are generally proposed which have been correlated to different selectivity ranges. Initial *cis/trans* ratios which are less than one are usually found for 1-butene isomerization over metals (*1*). These results have been interpreted in terms of a radical mechanism in which the relative stability of the various conformations of the adsorbed butyl radical controls the ratio. Initial *cis/trans* ratios of unity are common when acid catalysts (silica–alumina) are employed, and carbonium ion intermediates are generally proposed (*2–6*). Initial *cis/trans* ratios that are greater than one are generally reported for the isomerization over basic catalysts (MgO, CaO), and the reaction is believed to proceed via a carbanion mechanism (*7–11*). The differences in the *cis/trans* ratios that were observed for acid and base catalysts were related to the structural differences of the reaction intermediates. The base-catalyzed reaction, proceeding via a highly unsaturated carbanion, might be expected to exhibit a greater stereoselectivity due to the restriction on rotation which is not present in the almost fully saturated carbonium ion.

Several investigators have studied the 1-butene isomerization reaction by infrared spectroscopy. Peri (*12*) studied the reaction on γ-alumina and showed that the adsorbed butene was olefinic in character and resembled liquid *cis*-2-butene. He suggested the adsorption of 1-butene may have occurred through coordination with exposed aluminum ions, possibly as a complex similar

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to those suggested by Winstein and Lucas (*13*) for metal–olefin coordination compounds. Infrared studies of adsorbed 1-butene on zinc oxide (*14*) have shown that the adsorbed butene forms a π-bonded allylic species which is believed to be the intermediate in the isomerization reaction.

Investigators who have studied the isomerization of 1-butene over MgO believe the reaction proceeds via a carbanion mechanism, possibly in a chain process, on basic sites of the catalyst. Shannon, Kemball and Leach (*10*) studied the co-isomerization of a mixture of "light" (C_4H_8) and "heavy" (C_4D_8) *cis*-2-butene over MgO. Their results showed that there was no loss of deuterium to the catalyst, and they concluded that both reactions, i.e., *cis/trans* isomerization and double bond migration occurred without appreciable isotopic mixing and possibly by a mechanism that was effectively intramolecular. Clark and Finch (*15*) have shown that only basic sites on the surface of MgO are involved in the isomerization of 1-butene. They suggested that the isomerization proceeds via an anionic mechanism in which catalytic acidity is not involved.

Krylov and co-workers (*16*) have investigated the basic properties of MgO by studying the adsorption and isotopic exchange of carbon dioxide on MgO and on partially dehydrated magnesium hydroxide surfaces. They established the presence of three types of basic centers at the surface of partially dehydrated magnesium hydroxide. These are described as (a) strongly basic O^{2-} centers which are transformed to CO_3^{2-} ions upon adsorption of CO_2, (b) strongly basic centers which were derived from O^{2-} ions that were adjacent to surface OH groups, and (c) surface OH groups which represented weakly basic centers.

Electron donor centers on metal oxides can be measured by adsorbing certain organic compounds on the surface of the oxides. The process involves an electron transfer from the donor center on the metal oxide to the adsorbed molecule. The concentration of the resulting paramagnetic ions can be measured by electron paramagnetic resonance spectroscopy. Tench and Nelson (*17*) used the method to verify the presence of anions that resulted when nitrobenzene, *m*-dinitrobenzene, and *sym*-trinitrobenzene were adsorbed on MgO pretreated at 1000°C. They identified the electron donor source as surface lattice oxygen ions.

Che, Naccache and Imelik (*18*) studied the adsorption of tetracyanoethylene (TCNE) on MgO that had been pretreated between 100 and 800°C. Using EPR techniques, they identified the adsorbed paramagnetic ions as $TCNE^-$. As the pretreatment temperature was increased from 100 to 800°C, the concentration of the radical anions passed through two maxima, one at 200°C and another at 700°C. The electron donor centers were associated with OH^- and O^{2-} ions of low coordination number; the hydroxyls being present on the surface of MgO at the lower pretreatment temperatures ($<300°C$). It is likely that the oxide ions which serve as electron donors are also strongly basic sites.

The purpose of this research was to investigate the nature of the active site for the isomerization of 1-butene over MgO using electron paramagnetic resonance spectroscopy, infrared spectroscopy, and kinetic data. The specific objectives were (a) to measure the overall rate constant, activation energy, and initial selectivity for the isomerization of 1-butene over MgO as a function of the catalyst pretreatment temperature; (b) to use EPR spectroscopy to measure the concentration of the basic O^{2-} ions on the surface of MgO as a function of the catalyst pretreatment temperature; and (c) to investigate the adsorption of 1-butene on MgO using infrared spectroscopy.

EXPERIMENTAL METHODS

Kinetic Studies

Catalyst preparation and pretreatment. The MgO catalyst used in this investigation was in the form of pellets. The preparation consisted of first boiling reagent grade MgO powder in deionized water for 2 hr. The resulting paste of $Mg(OH)_2$–MgO was extruded into pellets which were dried in air at 120°C for 12 hr and stored in glass vials.

All catalysts received the same standard pretreatment which consisted of slowly heating the sample under vacuum for 1 hr at each 100°C increment, starting at 200°C, to the final pretreatment temperature which ranged from 300 to 900°C. At the pretreatment temperature, or maximum degassing temperature, the catalyst was heated for an additional 2 hr. The pressure at the end of the pretreatment was always less than 3×10^{-5} Torr. The BET surface areas of the MgO pellets pretreated at 300, 500, 700, and 900°C were 218, 205, 113, and 83 m^2/g, respectively.

Reactant gas. Research grade 1-butene purchased from the Phillips Petroleum Company and C.P. grade 1-butene purchased from the Matheson Company were used as the reactant gas. When proper purification methods were employed, similar activity was obtained when using either gas.

Some of the lecture bottles of 1-butene that were purchased from the Matheson Company contained oxygen (approximately 1%) which caused rapid poisoning of the reaction. The oxygen could be removed by the freeze pumping technique which consisted of condensing small portions of 1-butene from the lecture bottle into glass columns at liquid nitrogen temperatures and pumping off any oxygen that may have been present in the residual gas phase. The liquid butene was returned to the lecture bottle by the same technique. The whole process was usually repeated 7 or 8 times before acceptable activities could be obtained.

Before passing the reactant gas over the pretreated catalyst, the gas was further purified by passing it through a column of activated Alcoa alumina at 0°C. The pretreatment of the alumina consisted of degassing it at 320°C for 3 hr. This purification step was included for the purpose of removing any water vapor from the butene which would not have been removed by the liquid nitrogen freeze–degassing process.

Experimental procedure. Two systems, one static and one flow, were employed to study the isomerization of 1-butene over MgO. For the static experiments, the reactor was a 500 cm^3 spherical Pyrex bulb which was connected through a 4 mm stopcock to the vacuum system. A glass side arm extended from the top of the bulb, through stopcocks, to a helium line. The catalyst was placed at the bottom of a 25 mm o.d. well which extended 3 in. below the bulb. The flow reactor (U-tube) was made from 6 mm o.d. quartz and was connected to the vacuum system through 6 mm stopcocks.

In the static experiments, a weighed sample of catalyst (1 to 10 mg) was placed in the well at the bottom of the reactor and was given the standard pretreatment. A cylindrical furnace which was placed around the quartz well could be maintained within ±1° of a given temperature by a Barber-Colman temperature controller. Following the pretreatment, the catalyst was allowed to cool to room temperature. The reaction temperature was maintained by placing a Dewar filled with water around the well of the reactor. Usually the reaction was carried out at room temperature, but when the activation energy was being determined, other temperatures were employed. The temperature variation during a run, which lasted approximately 2 hr, was less than 1½°C. Fifteen minutes were allowed for the catalyst to reach the reaction temperature, then 240 mm of purified 1-butene was added to the reactor. By manipulating the stopcocks in the side arm of the reactor, small amounts of gas could be removed during the reaction and allowed to pass into the helium stream for gas chromatographic analysis. A 2:1 ratio of dimethyl sulfolane to hexamethylphosphoramide on fire brick was used for the packing in a 20 ft chromatographic column prepared from ¼ in. copper tubing. Complete separation of the butene isomers was obtained when the column was maintained at 0°C.

In the flow experiments from 30 to 100 mg of catalyst was used. Before the catalyst was added, about 0.4 g of 6–16 mesh silica gel was added to the bottom of the reactor. The catalyst was then added to the one side of the reactor, followed by 0.1 g of silica gel. The purpose of the silica gel was to support the catalyst in a portion of the reactor that was of uniform diameter and to protect the catalyst from any stopcock grease vapor that might diffuse over the MgO during the pretreatment. After the catalyst received the standard pretreatment, 1-butene was continuously passed over the MgO. The reaction temperature, which ranged from 0 to 82°C, was maintained by placing a Dewar of water around the reactor. The concentration of the products was measured at different 1-butene gas flow rates. After a steady state condition was reached, 1 ml of the product gas was removed from the system with a plastic syringe and analyzed by gas chromatography. The overall rate constant, the isomerization rate, the initial selectivity, and the activation energy were determined for each pretreatment temperature (300, 500, 700, and 900°C).

Treatment of data. Several investigators who have studied *n*-butene isomerization over oxide catalysts have suggested that at low conversion the reaction follows first-order kinetics. Hightower and Hall (*5*) used a reversible first-order equation to describe the isomerization of 1-butene over alumina and silica–alumina. They showed that product distributions calculated using the real rate constants in the exact rate equations obeyed the following integrated first-order equation through at least 70% of the reaction:

$$2.303 \log[X_e - X] = -kt + 2.303 \log[X_e], \tag{1}$$

where X and X_e represent the percent conversion of 1-butene at time t and at equilibrium, respectively.

In this investigation, it was not possible to calculate the rate constants for the isomerization of 1-butene occurring in the static system because the effective volume of the reaction zone could not be determined, but reaction rates were calculated for both systems, as well as rate constants for the flow system. The reaction rate r_s for the isomerization of 1-butene in the static system was determined from the following equations

$$r_s = \frac{1}{w}\frac{dn_A}{dt} \quad \text{and} \quad r_s' = \frac{1}{s}\frac{dn_A}{dt}. \tag{2}$$

Here dn_A is the number of moles of 1-butene that had reacted in time dt; w is the weight of the catalyst; and s represents the surface area of the catalyst. The reaction rate at a given pressure was calculated by setting $dn_A/dt = \Delta n_A/\Delta t$ over a small increment of Δn (3.2% of 1-butene reacted). The corresponding value of Δt was evaluated from the straight line which was the best fit to the experimental data when the latter was plotted according to Eq. (1).

The overall first-order rate constants for the flow experiments were determined from Eq. (1) by plotting $\log[X_e - X]$ versus the reciprocal of the flow rate. In order to express the rate constants in units ($\mathrm{min}^{-1}\ \mathrm{g}^{-1}$) and ($\mathrm{min}^{-1}\ \mathrm{m}^{-2}$), the void volume of the catalyst bed was determined. The void volume was defined as the volume of gas that occupied the space in the catalyst bed, including the volume of the catalyst pores. The isomerization rate r_f for the flow experiments was calculated from the following equations:

$$r_f = \frac{F}{w}\frac{dn_A}{dV_v} = \frac{1}{w}\frac{dn_A}{dt} \quad \text{and} \quad r'_f = \frac{1}{s}\frac{dn_A}{dt}, \tag{3}$$

where F is the gas flow rate, dn_A represents the number of moles of 1-butene reacted, dt is the time required for the gas to pass through the element of volume dV_v, and w and s represent the weight and surface area of the catalyst, respectively.

The activation energy for the overall reaction, A → B, where A is 1-butene and B is 2-butene, was determined from the Arrhenius equation

$$k = Ae^{-E/RT}. \tag{4}$$

Here k is the overall first-order rate constant, A is the frequency factor which is proportional to the number of active sites available for reaction, E is the activation energy, R is the gas constant, and T is the absolute temperature.

The initial selectivity for each reaction, which is defined as the ratio of *cis*-2-butene to *trans*-2-butene, was determined by plotting *cis/trans* ratios against percent of 1-butene reacted and extrapolating back to 0% conversion.

Electron Paramagnetic Resonance Studies

The tetracyanoethylene was purified by recrystallization in 1,2-dichloroethane at 4°C. The colorless crystals were dried at 40°C and stored in a desiccator. Reagent grade benzene was first purified by distillation and then was stored under vacuum over type 4A molecular sieve which had been pretreated by heating under vacuum at 500°C for 8 hr.

Nearly saturated solutions of TCNE in benzene were prepared. Ten milliliters of the purified benzene was transferred to a mixing vessel which contained 0.1280 g of TCNE. The transfer was carried out under vacuum by first freezing the benzene in liquid nitrogen. The solid benzene was heated with a hot air gun, and the benzene vapor was condensed into the mixing vessel which was at liquid nitrogen temperature. The mixing vessel was calibrated so that exactly 10 ml of benzene would be transferred.

Approximately 0.1 g of MgO pellets was added to the bottom of a quartz sample tube. After the standard pretreatment, the sample tube was removed from the vacuum system, and the MgO pellets were transferred (by tapping the outside of the sample tube) to the quartz side arm. The sample tube was connected back to the vacuum system and approximately 2 ml of TCNE solution was allowed to flow into the sample tube. The sample tube was then removed from the vacuum system and tilted on its side so that the TCNE solution could come into contact with the MgO pellets that were in the quartz side arm. All spectra were obtained at room temperature with a Varian spectrometer operating at a resonance frequency of 9500 MHz. The spin concentration of $TCNE^-$ adsorbed on MgO was determined by comparing the second integral of the EPR curves for the sample and a standard 2,2-diphenyl-picryhydrazyl solution.

Infrared Experiments

The ir cell was constructed according to the design of Peri (*19*) and consisted of a Pyrex tube which contained silver chloride windows and a quartz side arm into which the sample could be transferred for the degassing treatment. A Beckman IR 12 spectrophotometer was used for the measurements. An attenuator screen was used for the reference cell and was adjusted for 90% transmission at 1300 cm^{-1} for the pretreated MgO.

The MgO sample, in the form of a paste, was spread in a thin layer over a platinum wire screen and was placed in the quartz side arm of the ir cell. After the sample received the standard pretreatment, the following spectra were recorded at 23°C: after MgO was pretreated, after 100 Torr of 1-butene was added, after the MgO sample was transferred to the quartz side arm (gas phase spectrum), and after the butene was evacuated.

The spectrum of the MgO sample when butene gas was present represented a combined gas phase plus adsorbed phase. Before the gas phase was recorded, a blank sample (ZnO on platinum screen) was placed in front of AgCl windows and adjusted until the base line of the gas phase spectrum appeared at approximately the same percentage transmission as the observed base line for the combined phase spectrum. Then, the difference in the observed intensities of the combined phase spectrum and the gas phase spectrum would represent (to a rough approximation) the spectrum of the isomer that was adsorbed on the surface of MgO.

RESULTS

Kinetic experiments. The results from the static experiments, given in Table 1, show that the isomerization rate at 26°C

TABLE 1

RESULTS FROM THE ISOMERIZATION OF 1-BUTENE OVER MAGNESIUM OXIDE IN THE STATIC SYSTEM

Temp (°C)		Isomerization rates[a,b]		
Pretreatment	Reaction	(moles g^{-1} min^{-1} × 10^{3})	(moles m^{-2} min^{-1} × 10^{5})	Initial[a] *cis/trans* ratio
300	26	1.1	0.5	7.0
350	26	3.7	1.7	4.6
400	26	7.1	3.3	3.7
500	26	42.2	20.6	1.7
400	0	4.6	2.1	4.7
500	0	17.7	8.7	3.9

[a] Av values.

[b] Corrected to a pressure of 1 atm.

increases with increasing pretreatment temperature. Before the static experiments were carried out, the maximum weight of catalyst that could be used at each pretreatment temperature without causing diffusion problems was determined. Diffusion or mixing problems existed when too large a weight of MgO was used, which would cause the rate of the reaction in the area of the catalyst (in the well) to be much faster than the rate at which the butene molecules could diffuse into and out of the well. This problem could be eliminated by reducing the weight of MgO until the observed rate of the reaction was also reduced by a proportional amount; i.e., until the rate per gram of catalyst remained constant. The maximum weights of MgO pretreated at 300, 400, and 500°C that could be used were 0.0130, 0.0080, and 0.0014 g, respectively. As the weight of catalyst was decreased in order to avoid diffusion problems, the probability of poisoning the catalyst was increased. Diffusional and poisoning problems limited the range of data that could be collected, and reaction rates could not be determined for MgO pretreated above 500°C. It was found that by going to a flow system, where a larger weight of catalyst could be used, the above problems could be avoided.

Before collecting data from the flow experiment, the possibility of a diffusion problem through the pores of the catalyst was investigated in order to determine if pellet size had any effect on the reaction rate. This was accomplished by carrying out the reaction on MgO pellets of different sizes, but of the same weight. The results of similar rates indicated that pellet size did not affect the reaction rate.

TABLE 2
RESULTS FROM THE ISOMERIZATION OF 1-BUTENE OVER MAGNESIUM OXIDE IN THE FLOW SYSTEM[a]

Temp (°C)		Rate constants		
Pretreatment	Reaction	(min^{-1} g^{-1} $\times 10^{-2}$)	(min^{-1} m^{-2})	Initial *cis/trans* ratio
300	82	2.7	1.2	3.2
	53	1.3	0.6	5.2
	26	0.8	0.4	6.4
500	26	17.3	8.4	4.4
	15	11.4	5.6	5.4
	8	10.5	5.1	6.1
	0	8.8	4.3	6.2
700	26	93.2	82.5	3.0
	8	64.4	57.0	5.0
900	53	13.2	15.9	2.6
	32	9.6	11.6	6.4
	26	11.4	13.7	11.2
	16	6.2	7.4	11.2

[a] Av values.

The results for the overall first-order rate constants and initial *cis/trans* ratios from the flow experiments are given in Table 2. The results depicted in Fig. 1 show that as the pretreatment temperature was increased from 300 to 900°C the activity of the catalyst passed through a maximum at 700°C. The reaction rates and rate constants for the isomerization of 1-butene over MgO at 26°C as a function of the pretreatment temperature are summarized in Table 3. The initial *cis/trans* ratios varied from 2.6 to 11.2; the lower values corresponding to the faster reactions, while the higher values corresponded to the slower reactions. Some of the extrapolated values are questionable, especially the "initial" *cis/trans* ratios obtained on MgO pretreated at 700°C. The reaction was so fast that data could not be collected close enough to 0% conversion of 1-butene, therefore a considerable error could have existed in the extrapolation. Initial *cis/trans* ratios in excess of 15 were

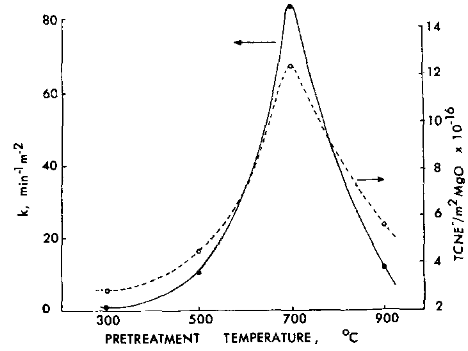

FIG. 1. Rate constants for the isomerization of 1-butene and the spin concentration of adsorbed TCNE$^-$ on MgO as a function of the catalyst pretreatment temperature.

TABLE 3

SUMMARY OF DATA FOR THE ISOMERIZATION OF 1-BUTENE OVER MgO AT 26°C IN THE FLOW SYSTEM, 1 atm

Pretreatment temp (°C)	Rate constants[a] (min^{-1} g^{-1} × 10^{-2})	Rate constants[a] (min^{-1} m^{-2})	Isomerization rates[a] (moles min^{-1} g^{-1} × 10^{3})	Isomerization rates[a] (moles min^{-1} m^{-2} × 10^{5})	Turnover no. (molecules site^{-1} sec^{-1})
300	0.8	0.4	1.0	0.4	1.2
500	17.3	8.4	38.9	18.9	35.0
700	93.2	82.5	67.1	59.5	44.5
900	11.4	13.7	35.4	42.6	64.6

[a] Av values.

observed on catalysts that were partially poisoned.

The results from the Arrhenius plots are shown in Table 4. It appears that the overall activation energy for the isomerization of 1-butene over MgO did not vary with pretreatment temperature. Although the deviation from the average as determined from the activation energies at 500°C was 0.3 kcal/mole, it was possible that a larger error could have existed. Trace amounts of impurities in the reactant 1-butene caused poisoning of the reaction which limited the amount of data that could be collected on each catalyst. Although rapid poisoning usually occurred after the fourth or fifth sampling, a smaller degree of poisoning could have been associated with the initial samples which would have affected the activation energy calculations. When determining the activation energies, it was possible to collect data at three reaction temperatures (one or two samples at each temperature) for MgO pretreated at 300, 500, and 900°C. The surface of MgO after pretreatment at 700°C was very sensitive to poisoning, and it was not possible to obtain data for more than one reaction temperature before poisoning occurred. Therefore, the activation energy for the reaction of 1-butene over MgO pretreated at 700°C was determined by obtaining the rate at two temperature (8 and 26°C) on separate catalysts.

TABLE 4

ACTIVATION ENERGIES AS A FUNCTION OF PRETREATMENT TEMPERATURE, FLOW SYSTEM

Pretreatment temp (°C)	*E* (kcal/mole)
300	4.7
500	4.3
	4.1
	4.8
700	4.4
900	4.4

EPR experiments. The concentration of the TCNE radical ions adsorbed on MgO as a function of the pretreatment is given in Table 5 and Fig. 1. As the catalyst pretreatment temperature was varied from 300 to 900°C, the concentration of adsorbed TCNE$^-$ ions passed through a maximum at 700°C.

Infrared results. The infrared spectra recorded in the frequency range of 2000 to 1200 cm^{-1} for MgO that was pretreated at

TABLE 5

SPIN CONCENTRATION OF TCNE$^-$ ON MgO AS A FUNCTION OF THE CATALYST PRETREATMENT TEMPERATURE

Pretreatment temp of MgO (°C)	Spins of TCNE$^-$/g MgO × 10^{-18}	Spins of TCNE$^-$/m^2 MgO × 10^{-16}
300	8.6	4.0
	8.0	3.7
500	11.0	5.4
	11.2	5.5
700	14.0	12.4
	16.2	14.3
900	5.1	6.2
	5.9	7.1

500°C are shown in Fig. 2. Curve 1 shows the spectrum of MgO recorded before 100 Torr of 1-butene was added, and Curve 2 shows the spectrum 20 min after 1-butene was added. The following peaks were observed in this combined phase: a small broad peak at 1845 cm^{-1}; a sharp intense peak at 1645 cm^{-1} which contained shoulders at 1660 and 1655 cm^{-1}; and a broad band that appeared in the range of 1600 to 1300 cm^{-1} which contained peaks at 1510, 1460, 1445, 1420, 1385, and 1330 cm^{-1}. The infrared bands representing the physically adsorbed species were determined by subtracting out the background spectrum (Curve 1) and the gaseous phase spectrum that included the ZnO blank (Curve 3) from the spectrum of the combined phases (Curve 2). The resulting spectrum of the adsorbed species is shown in Curve 4. Infrared bands at 1650, 1460, 1420, and 1390 cm^{-1} represent the adsorbed species. The adsorbed species were easily removed by a 10 min evacuation via a liquid nitrogen trap (Curve 5). The prominent peaks that were observed for the combined phase, the gaseous phase, and the adsorbed phase spectra are compared to the literature values for gaseous *n*-butenes in Table 6.

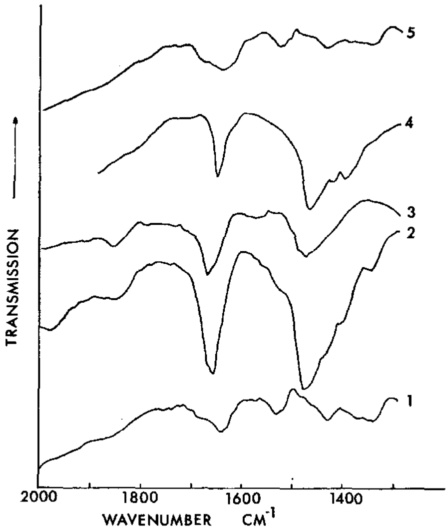

FIG. 2. Infrared spectra, in the region of 2000 to 1200 cm^{-1}, on MgO pretreated at 500°C before and after the addition of 100 Torr of 1-butene. The following spectra were recorded: (1) of MgO after pretreatment, (2) of MgO 20 min after the addition of 100 Torr of 1-butene, (3) gas phase plus ZnO blank taken 1 hr after the addition of 1-butene, (4) spectrum of adsorbed species on MgO determined by substracting Curves 1 and 3 from Curve 2, (5) of MgO after the gas was evacuated for 10 min via a liquid nitrogen trap.

TABLE 6

COMPARISON OF OBSERVED INFRARED PEAKS TO LITERATURE VALUES OF CHARACTERISTIC FREQUENCIES FOR THE *n*-BUTENES

Experimental frequencies (cm^{-1})			Characteristic frequencies		
Combined phase Curve 2	Gas phase Curve 3	Adsorbed phase Curve 4	1-Butene	*Trans*-2-butene	*Cis*-2-butene
1845	1845		1830[a]		
1660	1660				1660(w)
		1650			
1655					
1645	1645		1645		
1510					
	1480				
	1462				
1460		1460			
1420		1420	1420		
1385		1390			
1330					
	1270		1297	1302	

[a] Very strong ir band at 1830 cm^{-1} results from an overtone of the out-of-plane deformation frequency (912 cm^{-1}) of 1-butene.

Discussion

The kinetic data shows that the isomerization of 1-butene over MgO proceeds very rapidly at moderate temperatures. The isomerization rate over MgO was approximately 100 times faster than the rate over γ-alumina under similar conditions (6). The constant activation energy of 4.5 ± 0.5 kcal/mole indicates that the most active sites did not change in type as the pretreatment temperature was varied from 300 to 900°C. The reaction rate, however, was found to pass through a maximum at a pretreatment temperature of 700°C. A similar rate maximum at 600°C was observed by Tanabe, Yoshii and Hattori for 1-butene isomerization over CaO (*11*).

The initial *cis/trans* ratios, being greater than one, suggest that a basic type mechanism is operative. It is clear from the data that the initial *cis/trans* ratios are also a function of the pretreatment and reaction temperature; yet, the uncertainties in the extrapolation to 0% conversion cast some doubt on the validity of an apparent minimum at 700°C. The higher *cis/trans* ratio after pretreatment at 900°C compared to 300°C is significant. A decrease in the *cis/trans* ratio as a function of pretreatment temperature was reported for CaO (*11*).

The results of the spin concentration of $TCNE^-$ adsorbed on MgO show that the concentration of electron donor sites also passed through a maximum at 700°C. This is in good agreement with the results of Che, Naccache and Imelik (*18*). It is believed that the majority of the electron donor sites were O^{2-} ions that had a low coordination number, but it was possible that on MgO pretreated at 300°C a small concentration of OH^- ions could have been present on the surface and acted as donor sites.

Assuming that the concentration of active sites is equivalent to the concentration of $TCNE^-$ ions, one can calculate a turnover number (molecules reacting $site^{-1}$ sec^{-1}) as given in Table 3. The results of this calculation suggest, as did the activation energy data, that the reaction site did not change in type, but only varied in concentration as the pretreatment temperature was varied. Considering the errors that are involved in the rate measurements and in spin concentrations, an error of ± 15 molecules $site^{-1}$ sec^{-1} in the turnover rate was possible. Thus, the turnover rate on MgO pretreated at 500, 700, and 900°C remained essentially constant (Table 3). The lower rates per site at 300°C may be the result of some $TCNE^-$ ions being formed on OH^- groups rather than on O^{2-} ions.

Adler (20) has pointed out that the free O^{2-} ion is unstable by 9 eV, and it is stabilized in a crystalline solid by the Madelung potential which is on the order of 20 eV for a totally divalent material. It is doubtful, therefore, that an oxide ion lying above the plane of the surface would be stable when coordinated to only one magnesium ion. On the other hand, oxide ions on the edges or corners of a cube are stable. It is interesting to note that the number of O^{2-} ions which occupy the corners of a MgO cubic lattice approximately 100 Å square (*21*) compare very closely to the number of sites responsible for $TCNE^-$ radical formation. It is reasonable that the corner O^{2-} ions are the sites for TCNE reduction and are related to the active site for 1-butene isomerization. The corner O^{2-} ions, which have a lower coordination number than the other lattice oxide ions, would be the most basic and probably would be capable of abstracting an allylic hydrogen from adsorbed butene.

A mechanism similar to that proposed by Gerberich and Hall (*22*) for 1-butene isomerization over γ-alumina may be adapted to the present situation. We propose that 1-butene adsorbs on an exposed oxide ion as shown in Fig. 3. The basic oxide ion aids in removing an allylic proton and transferring it to the terminal methylene group. During this transfer step the π-allylic carbanion is held in the *cis* configuration by the electrostatic interaction between the terminal carbon atoms and two magnesium cations (Fig. 3c). It is important to note that the diameter of the oxide ion (2.64 Å) is slightly smaller than the separation between terminal carbons (2.74 Å), thus allowing the molecule to drape over the ion. The interaction between the carbons and the two magnesium ions is much less favorable when

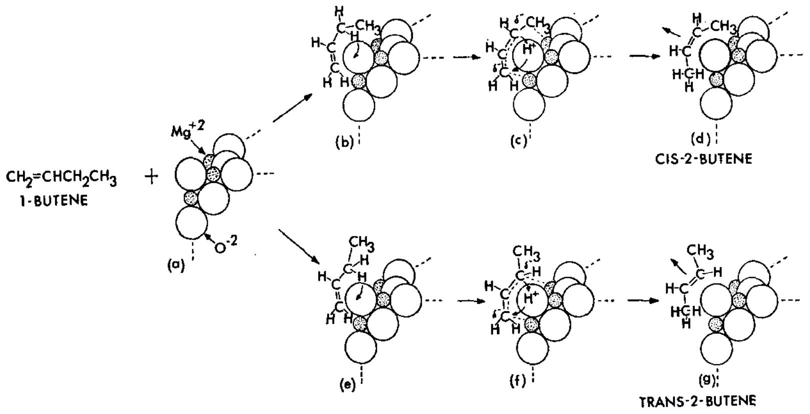

Fig. 3. Mechanism for the isomerization of 1-butene over MgO.

the molecule is adsorbed in the *trans* configuration (Fig. 3f).

The π-allylic carbanion may either be a true intermediate or it may be present as a transition state. If the latter case is true one may argue that the activation energy required to pass through this transition state is somewhat less than the energy required for the *trans* configuration. This would, of course, explain the high *cis/trans* ratio which was observed, as well as the decrease in the *cis/trans* ratio with an increase in the reaction temperature.

The variation in *cis/trans* ratio with pretreatment temperature and sample poisoning is more difficult to explain in terms of a single active site. It may be that other sites on the surface are mainly responsible for the conversion of *cis*- to *trans*-2-butene, and that these sites are destroyed either by pretreatment at 900°C or by poisoning.

The rate maximum at 700°C is probably due to the availability of the corner oxide ions. Since these are the most basic sites on the surface, they would likely be the last to lose their protons in the formation of water. As the outgassing temperature is increased, more of these corner ions would become available for interaction with the butene; however, at higher temperatures the surface begins to sinter. These opposing factors apparently yield a maximum concentration of corner oxide ions at about 700°C.

Dent and Kokes (*14*) studied the adsorption of 1-butene on ZnO and concluded that adsorbed butene formed a π-bonded allylic species. They observed four bands in the double bond stretching region, three of which were assigned to adsorbed species. A band at 1650 cm^{-1} was assigned to gaseous 1-butene, while peaks at 1630 and 1610 cm^{-1} were assigned to π-complexes of 2-butene and 1-butene, respectively. Bands in the region of 1550–1570 were believed to be due to a π-allyl species.

In this investigation, there was no evidence for the formation of adsorbed π-complexes or a π-allylic species, but peaks were observed which represented an adsorbed olefinic species. The peaks at 1660 and 1645 cm^{-1} that were observed in the combined phase spectra (Fig. 2, Curve 2) are assigned to the C=C stretching frequencies of *cis*-2-butene and 1-butene, respectively. The broad band in the region of 1600 to 1300 cm^{-1} is due to the CH deformation stretching frequencies of gaseous and physically adsorbed butenes. The broad band at 1845 cm^{-1} that was observed in the combined phase, as well as in the gaseous phase, is assigned to an overtone of the out-of-plane deformation frequency (912 cm^{-1}) of 1-butene. The peaks at 1650, 1460, 1420, and 1390 cm^{-1} (Curve 4), which represented the adsorbed species, indicated that the adsorbed butene was olefinic in character. Bands that were observed in the frequency range of 4000 to 2600 cm^{-1} were attributed to gaseous 1-butene, *cis*-2-butene, and *trans*-2-butene. It is possible that the higher pressures of 1-butene (100 Torr) used in this research could have broadened certain peaks and made detection of a π-bonded allylic species impossible. Dent and Kokes used lower gas pressures (8 Torr) in their investigation. If the π-allyl species described in Fig. 3 is a short-lived intermediate or a transition state, it may not be possible to observe it by infrared spectroscopy.

CONCLUSIONS

1. The results from the kinetic experiments demonstrate that the sites responsible for the isomerization of 1-butene over MgO were dependent on the pretreatment temperature and passed through a maximum concentration at 700°C as the pretreatment temperature was varied from 300 to 900°C.
2. The initial *cis/trans* ratios indicate that the isomerization reaction proceeded via a carbanion mechanism.
3. The consistency in the activation energies and in the turnover rates indicates that the active site for 1-butene isomerization did not change in type as the pretreatment temperature was varied.
4. Results from the infrared studies show that most of the butene was physically adsorbed on the surface of MgO and remained olefinic in character.
5. The results from the adsorption of TCNE on MgO show that the concentration of the reducing sites on MgO varied directly with the isomerization rate over the pretreatment temperature range. It is believed that the O^{2-} ions located on the corners of the cubic oxide lattice are the reducing sites for TCNE and are also related to the active site for the isomerization of 1-butene.

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