Studies of *n*-Butene Isomerization over Sodium X Zeolite and Copper X Zeolite

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The kinetics of the isomerization of *n*-butenes was studied in a static reaction system over synthetic, crystalline, sodium silica-alumina, known as Na13X, and over a series of copper 13X zeolites prepared by partial exchange of the sodium.

It was shown that all samples were active for *cis-trans* isomerization and for double-bond shift. The results conformed to a triangular reaction scheme in which all possible reaction paths between the three-component mixture of isomers were parallel, reversible and first order. The relative rate constants were determined for Na13X at 305°C, and for all the Cu13X samples at 105°C; in all cases the relative amounts of products were kinetically controlled.

Na13X was active for *n*-butene isomerization, without skeletal rearrangement, over a temperature range 200–300°C. The course of reaction was in marked contrast to that reported for amorphous silica-alumina, in particular the Na13X exhibited a marked preference for double bond shift rather than *cis-trans* isomerization.

The partial replacement of sodium cations with cupric cations had a profound effect upon the reaction rate, activation energy, and stereoselective nature of the process; but this effect was not linear with percentage exchange. When the extent of exchange was below approximately 30% the Cu13X zeolites exhibited a very strong preference for the formation of *trans*-but-2-ene from but-1-ene, and an induction period was a characteristic feature. Such behavior was attributed to a radical type mechanism in which the active sites were the copper cations contained in the relatively inaccessible type I cation sites, and where reduction of cupric to cuprous ions was possible. These cuprous ions would be capable of forming unstable complexes with olefins.

When the extent of exchange was higher the reaction followed an entirely different course. There was preferential formation of the thermodynamically less stable *cis*-but-2-ene, and the reaction exhibited many of the characteristics typical of a carbonium ion type of mechanism. The production of the active sites responsible for such an ionic type of activity was explained in terms of the presence of cupric cations in surface cation sites of the lattice although the precise nature of such sites was uncertain.

INTRODUCTION

The use of crystalline molecular sieves of the X and Y type is potentially of great theoretical and practical importance (*1*, *2*). The work which has been recently reported in the fields of synthesis, structure, and catalytic properties of zeolites shows that they possess considerable advantages compared with amorphous silica-alumina catalysts. The cations can be readily exchanged and, as the activity is dependent on the nature of the cation in the sieve and also probably on the sites which the cations occupy in the sieve structure, a range of materials can be formed which will be catalytically active for such basic industrial processes as cracking, hydrocracking, reforming, isomerization, alkylation, etc.

Apart from the practical importance of

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such a range of catalysts, the process of cation exchange and the effect upon the catalytic activity can provide valuable insight into the nature of the active sites in such materials, and the mechanisms operative during catalytic reactions on their surfaces. The amount of data reported in the literature for such studies is rather limited and no definite conclusions have as yet been reached.

A very suitable reaction for such an investigation is the isomerization of *n*-butenes without skeletal rearrangement. The molecules are small and relatively simple and can be analyzed reliably by G.L.C. The catalytic isomerization of but-1-ene to *cis*-but-2-ene and *trans*-but-2-ene has been shown to occur generally in a stereoselective manner (*3*), and data of this type can provide information regarding the reaction mechanism. The reaction does not require extreme conditions and has a highly selective character, with no detectable side reactions. It can be regarded as a model reaction in olefin chemistry.

The isomerization of but-1-ene has been investigated over the sodium and ammonium forms of the 13Y zeolite (*4*), and over the calcium form of the 5A zeolite (*5*). However, the reaction does not appear to have been studied over crystalline Na13X although this material, which is produced in large amounts, is known to be catalytically active for other important reactions (*1, 2, 6*). There are no reports concerning the reaction over the copper zeolites although from the literature, mainly patents (*7, 8*), it would seem that such materials are catalytically active for other reactions. We therefore decided to investigate the effect of the degree of exchange of Cu^{2+} for Na^+ upon the but-1-ene isomerization reaction over the 13X zeolite after first examining the catalytic activity of the parent Na13X.

EXPERIMENTAL

Apparatus. A conventional Pyrex glass system was employed with a cylindrical reaction vessel of volume 102 cc. It was connected to a standard gas handling system which allowed the sample to be evacuated and the hydrocarbon to be introduced to various pressures (normally in the range 10–30 Torr). The reaction vessel temperature was controlled to within $\pm0.5°C$. Samples from the gas phase were periodically removed and analysed by G. L.C. with a 9-foot 20% acetonylacetone-Chromosorb P(60–80 mesh) column held at 0°C, which was used in conjunction with a flame ionisation detector and an integrator. The gas pressures in the dosing apparatus were measured with a mercury manometer, and no special precautions were taken to prevent the catalyst sample from coming into contact with mercury vapor.

Catalysts. The Na13X catalyst (Linde Air Products) was treated (10 g) at room temperature with deionized water (50 ml) for 12 hr, then filtered, washed, and dried. It was stored over saturated $Ca(NO_3)_2$ solution in a desiccator at room temperature. Five samples containing various amounts of Cu^{2+} cation (by partial exchange of the Na^+) were prepared by treatment of the original Na13X with aqueous solutions of copper sulphate. After exchange the samples were washed, dried and stored as above. The degree of exchange (expressed at % age Na^+ replaced by Cu^{2+}) was determined by analysis of the copper sulfate solutions before and after the exchange procedure.

Some physical properties of the Na13X and copper exchanged catalyst are given in Table 1. The nomenclature adopted there will be used throughout the paper. The surface areas quoted were determined with a silica spring apparatus, using nitrogen as the adsorbate at liquid nitrogen temperature and employing the point B procedure in calculation. X-ray diffraction spectra (Phillips Diffractometer) were measured for all the solid catalysts before and after reaction, and after various outgassing conditions.

Reagents. The butenes (Matheson: CP grade) were purified before use by repeated low temperature distillation. Analysis by G.L.C. showed that the individual butenes then contained only negligible amounts of lower molecular weight compounds. Deu-

terium (Matheson) and hydrogen were purified by diffusion through palladium thimbles.

Experimental procedure. A 0.1-g portion of the zeolite catalyst was normally employed in an experiment. After degassing overnight at 10^{-6} Torr and 420°C the furnace temperature was adjusted to the required value and maintained there for 30 min before admission of the reactant gas. The gas was admitted by opening the reaction vessel to a mixing bulb (volume 373 cc), with an olefin pressure of approximately 20 Torr, for 15 sec. Samples, approximately 2% of the reaction mixture, were withdrawn from the reaction vessel at 5- to 10-min intervals over a period of normally 90–120 min, and immediately swept into the G.L.C. column.

In some cases further runs were carried out with the same catalyst sample after it had been outgassed at reaction temperature by pumping at 10^{-6} Torr. This was to examine the reproducibility of the catalyst, particularly with regard to (a) the stereoselectivity of the process, and (b) the course of the initial stages of the reaction.

RESULTS

Activity of Catalysts, Kinetic and Stereoselective Data

Table 1 indicates the temperature range over which the activity of each catalyst was studied. The lower temperature quoted corresponds to conditions under which

the but-1-ene conversion was approximately 5% after 90 min, the upper temperature to conditions under which the equilibrium mixture of but-1-ene, *cis*-, and *trans*-but-2-ene was approached after 90 min. With CuXV the conversion of but-1-ene at 105°C (the highest temperature investigated with this sample) was only 36% after 90 min; the temperature corresponding to equilibrium conditions after 90 min was therefore not measured.

Features of the but-1-ene isomerization typical of all the zeolite catalysts were: (a) The major products of the reaction were *cis* and *trans*-but-2-ene; (b) no isobutene (from skeletal isomerization) was detected; and (c) under certain conditions traces of cracking and dehydrogenation processes were detected. Figure 1 (a) illustrates the course of the reaction over the parent NaX sample at 305°C. The reaction over the various CuX samples followed the same general pattern, Figs. 1(b) and 1(c), but with important differences as described below.

The majority of the experiments were carried out with but-1-ene as starting material, but some were performed with *cis*-but-2-ene or *trans*-but-2-ene. The kinetic data were plotted according to the first-order equation:

$$- \log (x_t - x_e) = kt - \log x_e \qquad (1)$$

where x_e = equilibrium percentage of but-1-ene at the experimental temperature and x_t = percentage of but-1-ene at time t. The data for the parent NaX gave linear

TABLE 1
COMPOSITION AND PROPERTIES OF ZEOLITE CATALYSTS

Catalyst	% Na+ exchanged by Cu²+	Surface area (m²g⁻¹)		Temperature range[a] of activity (°C)
		Before reaction	After reaction	
NaX	0.0	870	872	228–305
CuXI	9.3	908	866	105–205
CuXII	37.0	877	787	72–115
CuXIII	62.2	818	635	14–90
CuXIV	68.5	811	684	18–80
CuXV	80.0	17.5	Not determined	0–105

[a] The lowest temperature quoted corresponds to 5% of but-1-ene isomerization after 90 min, the higher temperature to the equilibrium mixture being approached after 90 min.
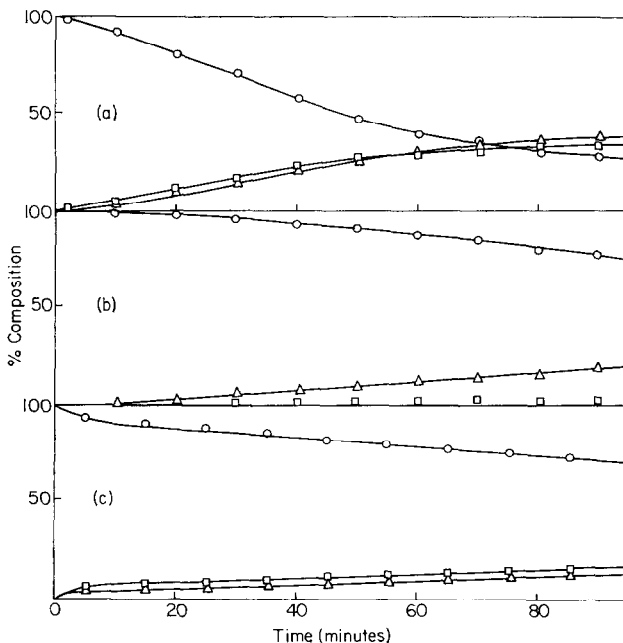
FIG. 1. The course of but-1-ene isomerization over various catalysts: (a) Over NaX at 305°C; (b) over CuXI at 127°C; (c) over CuXIII at 40°C. (○) Refers to but-1-ene; (□) to *cis*-but-2-ene; and (△) to *trans*-but-2-ene.

plots which on extrapolation to zero time intersected the $-\log (x_t - x_e)$ axis at values corresponding closely to $-\log (100 - x_e)$. This was regarded as a strong indication that the catalyst was not poisoned in the initial stages of the reaction. Similar plots for the CuXI and CuXII samples showed that the reaction accelerated in the early stages but gave a linear plot thereafter. With the other CuX samples the plots were again linear after the initial stages of reaction but extrapolation to zero time gave a value for $-\log (x_t - x_e)$ significantly below $-\log (100 - x_e)$ value. This indicated a poisoning effect with these materials; the effect was evident for only 5–10 min with CuXIII and CuXIV, but for a much longer period with CuXV.

It was established that with all the catalysts apart from CuXV, the equilibrium mixture of isomers could be obtained from each of the three, in accordance with reaction scheme 2, the time for equilibrium being characteristic of each isomer. From the equilibrium data (*9*), and the ex-

(2)
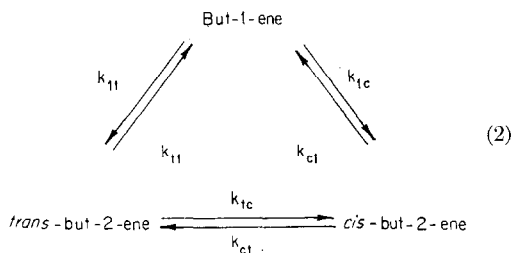
perimental data, the relative rate constants were calculated as listed in Table 2. It is a necessary requirement of the scheme that $k_{1c}k_{ct}k_{t1} = k_{1t}k_{tc}k_{c1}$. Haag and Pines (*10*) have derived rate equations based on reaction scheme 2 from which it was possible to calculate the concentration of each of the three isomers as a function of time in terms of the relative rate constants. Figure 2 shows that the experimental data for the isomerization on Na13X catalyst at 305°C fit closely on the theoretical curves calculated in this manner. The data of Table 2 also indicate the stereoselective nature of the isomerization in that the values of k_{1c}/k_{1t}, k_{ct}/k_{c1} and k_{tc}/k_{t1} are

TABLE 2

RELATIVE RATE CONSTANTS FOR n-BUTENE ISOMERIZATION OVER SODIUM AND COPPER X ZEOLITES

Catalyst	Temperature (°C)	Relative rate constants						Selectivities		
		k_{1c}	k_{c1}	k_{1t}	k_{t1}	k_{ct}	k_{tc}	k_{1c}/k_{1t}	k_{ct}/k_{c1}	k_{tc}/k_{t1}
NaX	305	1.00	0.61	0.91	0.36	0.10	0.06	1.10	0.16	0.17
CuXI	105	1.00	0.25	9.09	0.99	0.20	0.09	0.11	0.80	0.09
CuXII	105	1.00	0.25	1.94	0.21	0.21	0.09	0.52	0.84	0.43
CuXIII	105	1.00	0.25	0.89	0.10	0.52	0.23	1.12	2.08	2.30
CuXIV	105	1.00	0.25	0.79	0.09	0.37	0.16	1.27	1.48	1.78
CuXV	105	1.00	0.25	1.11	0.12	0.52	0.23	0.90	2.08	1.92

[a] The equilibrium data (9) corresponded to selectivities as follows: (a) at 305°C $k_{1c}/k_{1t} = 0.66$, $k_{ct}/k_{c1} = 2.51$ and $k_{tc}/k_{t1} = 1.64$; (b) at 105°C $k_{1c}/k_{1t} = 0.44$, $k_{ct}/k_{c1} = 9.23$ and $k_{tc}/k_{t1} = 4.06$.

different from those predicted from thermodynamic equilibrium data.

As mentioned previously, the isomerization on CuXI and CuXII catalysts showed an initial stage during which the rate of but-1-ene disappearance accelerated. The length of this induction period could be conveniently obtained by plotting the data in the form log $(x_0 - x_e/x_t - x_e)$ against time, where x_0 = but-1-ene concentration at zero time, and extrapolation in the manner illustrated in Fig. 3. Results obtained in this manner for CuXI and CuXII at various temperatures are given in Table 3, from which activation energies of 9.6 kcal

mole^{-1} for CuXI and 3.8 kcal mole^{-1} for CuXII are obtained. With CuXII a similar type of induction period was observed when the initial reactant was either cis-but-2-ene or trans-but-2-ene. In a few experiments with these catalysts in which the outgassing procedure was done with a vacuum of only 10^{-3} Torr rather than the customary 10^{-6} Torr induction periods much longer than those reported in Table 3 were observed.

Second runs on CuXI and CuXII catalysts (with evacuation for 2 hr after the first run) showed no induction periods, the first-order rate constants being the same
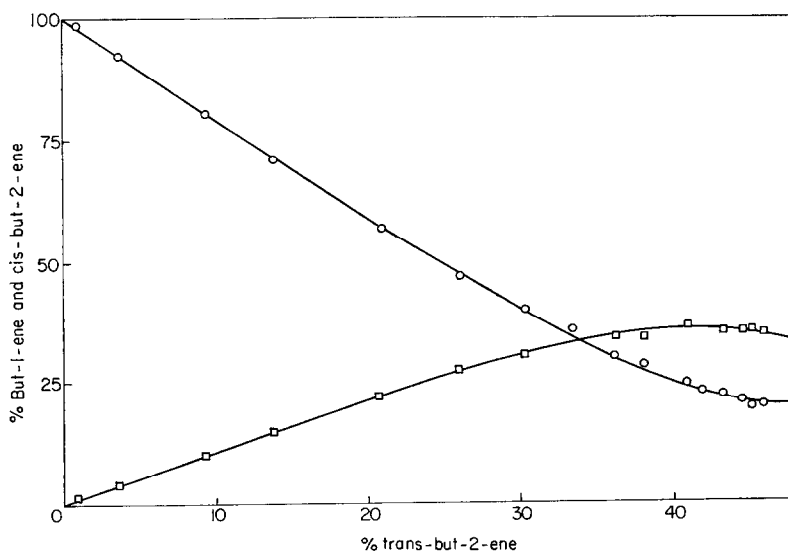

FIG. 2. Comparison of the experimental data ((○) for but-1-ene and (□) for cis-but-2-ene) for NaX at 305°C with the theoretical curves (full lines) predicted by Haag and Pines (10).
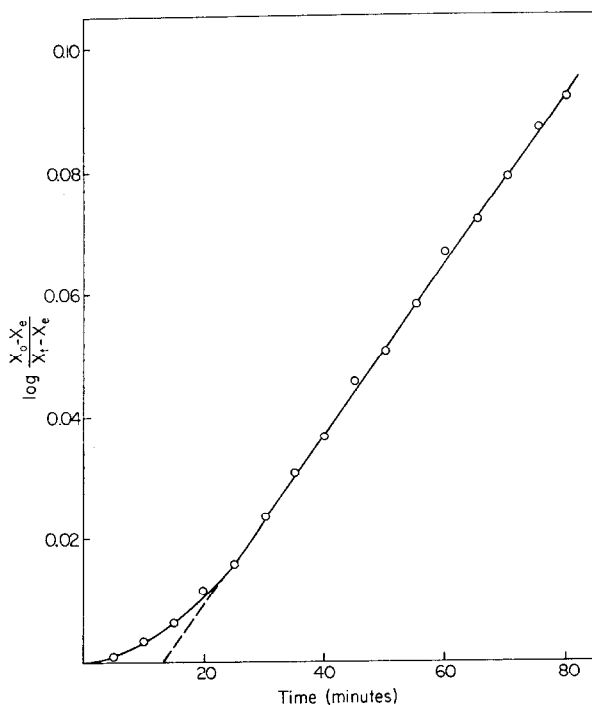
FIG. 3. First-order plot of data for but-1-ene disappearance over CuXI at 127°C, indicating the induction period.

as those in the first runs. Pretreatment of the catalysts with hydrogen (at 20-mm pressure) at reaction temperature (100–200°C) during 1 hr followed by evacuation had no effect on the length of the induction period in subsequent runs. However, if the catalysts were pretreated with hydrogen at the normal outgassing temperature (420°C) for 24 hr before evacuation the induction period was eliminated.

During normal outgassing conditions the CuXI and CuXII samples changed in color from a very light blue to a very light green—and then during reaction changed

further to grey-blue (with some areas of brown). The samples when kept after reaction under vacuum maintained their color, if kept in contact with air however they reverted to a light-blue appearance. The hydrogen pretreatment at 420°C resulted in a color change from very light-blue to pink.

Experiments with cupric oxide showed that it was not active for but-1-ene isomerization in the temperature range 0–200°C where the copper zeolites were active. However, at 252°C, 6.6% conversion of the but-1-ene occurred after 90 min, and in

TABLE 3
CHARACTERISTICS OF INDUCTION PROCESS FOR CuXI AND CuXII

	Temp (°C):	105	115	127	138	149	171
CuXI	Induction period (min)	21.0	16.5	12.5	8.5	6.5	3.5
	Temp (°C):	73	86	95	105	114	
CuXII	Induction period (min)	40.0	34.0	30.0	26.0	18.5	

[a] Arrhenius plots of these data gave values for the activation energy of the induction process of 9.6 kcal mole^{-1} for CuXI and 3.8 kcal mole^{-1} for CuXII.

contrast to the zeolites the cupric oxide showed some dehydrogenation activity since the reaction products consisted of 2.3% butadiene, 2.6% *cis*-but-2-ene, and 1.7% *trans*-but-2-ene. There was some evidence of partial reduction to copper metal during the reaction. No significant change in activity was found when the oxide sample was pretreated with hydrogen (at 20 Torr pressure) at 420°C for 24 hr.

Rates of reaction (in % min⁻¹) and activation energies are given in Table 4 for conditions where the percentage conversion was low. For CuX catalysts, the rates are for regions immediately following any induction or initial poisoning periods. For the CuXV catalyst the rates are uncertain due to the prolonged poisoning effect and furthermore, the Arrhenius plot was not linear over the full range of temperatures investigated. The table shows that the copper zeolite catalysts fall into three distinct groups: (a) Samples CuXIII and CuXIV which exhibit very similar behavior in all aspects; (b) samples CuXI and CuXII which differ somewhat in temperature range but show similar activation energies; and (c) the CuXV sample which has very different characteristics.

From Table 4 it is clear that sample CuXIV is the most active. The activity of

TABLE 4

KINETIC DATA FOR BUT-1-ENE ISOMERIZATION OVER SODIUM AND COPPER X ZEOLITES

Catalyst	Reaction Temp. (°C)	Rates (% per min per 0.1 g of hydrated catalyst)			Activation energy for but-1-ene disappearance (kcal mole⁻¹)
		But-1-ene Disappearance	*Trans*-but-2-ene Appearance	*Cis*-but-2-ene Appearance	
NaX	228	0.054	0.028	0.026	
	235	0.073	0.038	0.035	
	241	0.099	0.050	0.049	
	252	0.137	0.072	0.065	20.8
CuXI	105	0.088	0.005	0.083	
	115	0.144	0.014	0.130	
	127	0.246	0.020	0.226	14.8
	136	0.344	0.041	0.303	
	149	0.656	0.075	0.581	
CuXII	73	0.063	0.023	0.040	
	86	0.160	0.064	0.096	16.7
	95	0.309	0.140	0.169	
	105	0.520	0.284	0.336	
CuXIII	21	0.087	0.050	0.037	
	30	0.130	0.070	0.060	12.6
	40	0.258	0.135	0.123	
	50	0.488	0.282	0.206	
CuXIV	31	0.141	0.072	0.069	
	40	0.270	0.140	0.130	
	50	0.484	0.276	0.208	12.3
	60	0.825	0.425	0.400	
CuXV	6	0.076	0.033	0.043	
	31	0.135	0.079	0.056	
	54	0.193	0.085	0.108	3.9
	71	0.273	0.118	0.155	

[a] The initial charge of but-1-ene in the reaction vessel varied between 3×10^{19} and 7×10^{19} molecules, depending upon the reaction temperature and the actual pressure used.

this catalyst in exchange reactions between n-butenes and deuterium was therefore examined. A but-1-ene-D_2 mixture (1:3) was reacted at 60°C for 60 min, after which the products were separated by G.L.C. and analyzed with a mass spectrometer. It was concluded that the catalyst was relatively inactive for the exchange reaction since only 0.8% of the but-1-ene, 1.1% of the trans-but-2-ene, and 1.4% of the cis-but-2-ene had exchanged with deuterium.

Physical Examination of Catalysts

X-ray examination showed that all the CuX catalysts, apart from CuXV, had the same, well defined structure as the parent NaX. The structure of the latter was unchanged after use, but with the CuX catalysts minor changes in the values of 2_θ and in relative peak intensities were found, indicating small changes in lattice dimensions. Similar, more pronounced, changes were found for the CuXII catalyst after pretreatment wth hydrogen, and after the most severe pretreatment conditions there was evidence of the formation of copper metal. The diffraction pattern of the CuXV sample showed that the lattice structure of the zeolite had been completely destroyed during preparation.

The nitrogen adsorption experiments gave surface areas as shown in Table 1. Except for CuXV, whose area was 18 m^2g^{-1}, all the catalysts had areas between 800–900 m^2g^{-1} before use. After use, the NaX value was unchanged, but significant decreases in area were found for the CuX samples in line with the minor changes in lattice structure.

DISCUSSION

Our results show that the parent NaX is active for the isomerization, without skeletal rearrangement, of n-butenes in the range 228–305°C, which is higher than that required for the same reaction on conventional amorphous silica-alumina catalysts (9, 11). Weisz and Frilette (12, 13) reported that the crystalline NaX was more active than the amorphous silica-alumina catalysts for the cracking of n-paraffins.

The principal feature of their results for the cracking of n-decane, 1-decane, and cumene was the small amount of branched-chain compounds in the products at 470°C. Our results are in accordance to the extent that in spite of the relatively high temperature range no processes other than positional and geometrical isomerization of the n-butenes could be detected. Turkevich et al. (4) have reported that the sodium 13Y sieve is not active for the isomerization but their work was confined to the temperature range 0–125°C.

The partial exchange of the sodium cation in NaX with cupric cation has a profound effect upon the activity for the n-butene isomerization. With all the CuX samples investigated the temperature range over which the reaction occurred at a measurable rate was lowered relative to the parent NaX (see Table 1). In general, with increasing copper content the observed temperature range decreased but the relationship was not linear. The temperature range reported for CuXV was similar to that normally found for amorphous silica-alumina, and although the reaction proceeded at a measurable rate at room temperature at which equilibrium was rapidly established was well above 100°C.

A more quantitative assessment of relative activity for the isomerization was obtained by a comparison of the rate of but-1-ene disappearance over all the samples at the same temperature. At 105°C, at which temperature the rate of disappearance of but-1-ene over NaX was considered to be zero the relationship shown in Fig. 4 is obtained. A similar picture, although the absolute values are lower, emerges when the rate of cis-but-2-ene disappearance at 105°C (in cases where cis-but-2-ene was the initial reactant) is plotted against percentage copper exchange.

The anomalous position of the CuXV sample can be understood since this catalyst did not have the zeolite structure and had a comparatively low surface area. The catalyst sample can be regarded as essentially an amorphous silica-alumina material containing some copper. The low activity

exhibited by CuXV showed that the zeolite structure was a necessary requirement for appreciable catalytic activity with the copper-exchanged zeolites.

Figure 4 illustrates that relatively little increase in catalytic activity occurs until the percentage exchange exceeds approximately 30%, whereafter activity rises sharply. Similar behavior has been observed for the dehydration of formic acid on a series of NaX sieves partially exchanged with magnesium (14). The shape of the curve can be explained in terms of the three different types of cation site available in the zeolite lattice. Type I sites are in the center of the hexagonal prisms in the zeolite lattice whereas sites II and III occupy surface positions on the inner walls of the structure and hence are more readily accessible. If in the exchange process Cu^{2+} ions enter the type I sites preferentially then little increase in catalytic activity might be expected until sufficent exchange had occurred to allow Cu^{2+} ions to occupy sites II and III. Further-

more, the relatively high outgassing temperature used (420°C) could assist Cu^{2+} ion migration to type I sites. Infra-red work (15) has indicated that bivalent calcium ions prefer to fill type I sites first and electron spin resonance results (16) indicate a similar site preference for bivalent manganese; nothing has however been reported about the site preference of Cu^{2+} ions.

The isomerization on all the samples studied obeyed first order kinetics; compare acidic oxide catalysts (9–11). It has been suggested (17, 18) that the reaction might have some consecutive reaction type character, but, as Fig. 2 showed, our results agree closely with the reaction scheme (2) in which all possible reaction paths are parallel, reversible and first order.

Table 4 shows that the activation energies decrease nonlinearly with increasing percent copper content. The values emphasize that the four crystalline CuX samples can be split into two groups, since
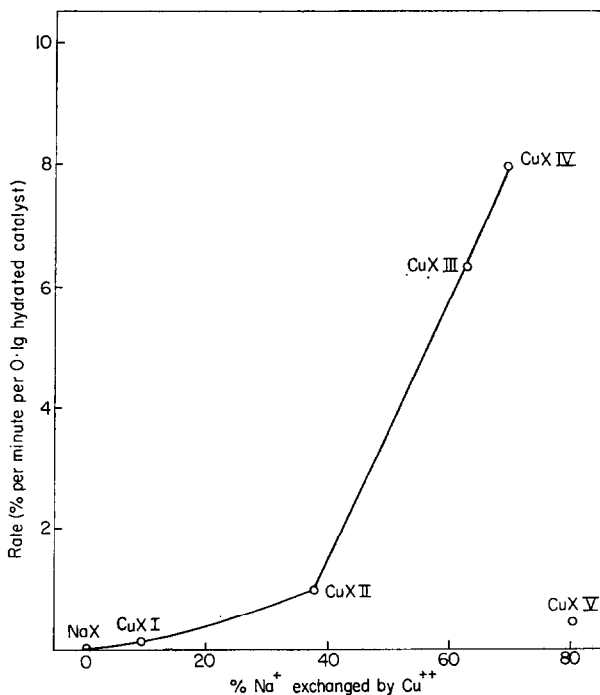

FIG. 4. The effect of the extent of exchange of Na^+ by Cu^{2+} on the rate of disappearance of but-1-ene at 105°C.

CuXI and CuXII have values which are 3–4 kcal mole^{-1} higher than those for CuXIII and CuXIV. For the latter pair the activation energies are similar to those reported for amorphous silica-alumina (11, 18–21). Again the CuXV data are anomalous.

Since the isomerization on all the catalysts gave a product distribution different to that predicted from thermodynamic equilibrium data (see Table 2), it was concluded that the reaction was kinetically controlled. The selectivities shown by the various catalysts, however, were very different. For example, the equilibrium data at 105°C predict a value for k_{1c}/k_{1t} of 0.44 whereas the experimental values varied from 0.11 for CuXI to 1.27 for CuXIV.

Detailed examination of the relative reaction rates calculated for NaX showed that the fastest processes in the triangular reaction scheme were those in which but-1-ene was converted into cis- and trans-but-2-ene, whereas the interconversion of the but-2-ene stereoisomers were the slowest processes. The conversion of either of the stereoisomers to but-1-ene was appreciably faster than the interconversion process. The NaX catalyst was thus more active for the double-bond shift reaction than for geometrical isomerization.

Comparison of the relative rate constants for the CuX samples with those for NaX revealed some marked differences. With CuXI the most important feature was the marked preferential formation of trans-but-2-ene from but-1-ene, as shown in Fig. 1(b). CuXI did not show such a preference for the double-bond shift process as NaX. The data for CuXII were similar to those for CuXI although the preferential formation of trans-but-2-ene from but-1-ene was less marked.

With catalysts CuXIII and CuXIV at all temperatures cis-but-2-ene was formed in preference to trans-but-2-ene, not only in excess of the equilibrium ratio but, also in absolute amount (see Fig. 1(c)). Also the k_{ct}/k_{c1} and k_{tc}/k_{t1} ratios were greater than unity, so these samples exhibited a preference for geometrical isomerization

rather than double bond shift. The relative rate constants for the CuXV sample were similar to those for CuXIII and CuXIV.

The preferential formation of the thermodynamically less stable cis isomer from but-1-ene has been shown by many authors to occur on both basic and acidic catalysts, whereas preferential cis-trans isomerization rather than double bond shift is a feature of acidic catalysts (3). For such catalysts it is generally accepted that the mechanism is ionic, involving a carbanion on basic catalysts and a carbonium ion on acidic catalysts. Catalysts CuXIII and CuXIV exhibit behavior characteristic of acidic catalysts and it is concluded that a carbonium ion mechanism was operative. Furthermore, the initial poisoning period, the loss of surface area, the temperature range and the activation energies measured for these samples are typical of acidic-type solid catalysts.

A carbonium ion type of mechanism has been proposed by other workers (1, 2) to explain the activity of multivalent cation molecular sieves but the nature of the active sites responsible is still uncertain. Three types of site have been proposed: (a) Bronsted acid sites; (b) Lewis acid sites; and (c) sites near the strong electrostatic fields surrounding the multivalent cations. The carbonium ion activity of CuXIII and CuXIV may be due to either type (a) or (c) sites. Under the outgassing conditions used the zeolite samples will still contain residual water and surface-bound hydroxyl groups. Since for the highly exchanged CuX samples a certain proportion of the cupric cations must be present in the surface cation sites II and III, the formation of Bronsted acid type active sites from a mechanism such as $Cu^{2+} + H_2O \rightleftharpoons Cu(OH)^+ + H^+$ is feasible. The presence of cupric cations in the surface cation sites could also lead to type (c) sites.

In studies of olefin isomerization catalysed by complex transition metal catalysts (22, 23) preferential formation of the trans isomer has also been observed and a radical type mechanism has been proposed in such cases. An induction pe-

riod was frequently a feature of the reaction. Since the behavior of such catalysts is very similar to that of CuXI and CuXII, for the latter a radical mechanism is also suggested. With CuXI and CuXII it was noted that the *cis/trans* ratio decreased with decreasing temperature. The catalytic activity of the alkali cation forms of molecular sieves are generally thought to be of radical type; e.g., reference (*13*). Our results for *n*-butene isomerization over NaX, which are in marked contrast to those which have been reported for amorphous silica-alumina, support such a radical type of mechanism.

Apart from the strong preferential formation of *trans*-but-2-ene from but-1-ene the CuXI and CuXII samples exhibited an induction period before first-order kinetics were obeyed. Such an induction period is typical of oxidation-reduction processes and it seems possible that with these samples, where the copper may be mainly in relatively inaccessible cation sites, a reduction of Cu^{2+} to Cu^+ is occurring. It is known (*24*) that Cu^+ forms unstable complexes with olefins, and the formation of such an intermediate can be envisaged as follows:

$$Cu^{2+} \xrightarrow{H} Cu^+ \qquad \text{(i)}$$

$$Cu^+ + \text{Olefin} \rightarrow \text{Unstable complex} \qquad \text{(ii)}$$
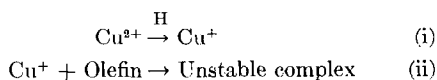
If the rate determining step was the reduction process then the observed temperature dependence of the length of the induction period could be explained since the production of hydrogen in trace amounts (from dehydrogenation and/or cracking) will increase with increasing temperature. Thus, the reduction would be facilitated and the induction period shortened.

Our experiments with hydrogen pretreatment support the suggestion that it is the reduction process which is responsible for the induction period. The fact that no induction period occurred in second runs with but-1-ene also suggests that the induction process is concerned with the formation of active sites, and that the time required for the but-1-ene to reach such

sites is not rate determining. The general observations of color changes and instability in the presence of air support such a reaction scheme. We therefore suggest that the unstable complex between Cu^+ and butene is playing an important role in the heterogeneous catalysis with these particular CuX zeolites, and hence that there are certain similarities with homogeneous catalytic processes involving complexes of transition metals.

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