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The Isomerization of 3,3-Dimethylbut-1-ene, 3-Methylcyclopent-1-ene, and Methylenecyclopentane over γ-Alumina

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Skeletal isomerization of 3,3-dimethylbut-1-ene (33DMB1) and double-bond migration of 3-methylcyclopent-1-ene (3MCP$^=$) and methylenecyclopentane (MCP) have been studied over γ-alumina. The activity for the isomerization of all three alkenes increases with increasing catalyst activation temperature. Addition of fluoride to the catalyst greatly increases its activity. Treatment of the γ-Al_2O_3 catalysts with H_2S results in some enhancement of activity for 33DMB1 and MCP isomerization but reduces activity for 3MCP$^=$ isomerization by ~90%. The importance of initial water content of the alumina on subsequent activity is discussed. It is concluded that skeletal isomerization of 33DMB1 and double-bond migration in MCP occur via carbonium ion intermediates on Brønsted acid centers whereas double-bond migration in 3MCP$^=$ occurs predominantly via π-allylic intermediates on Lewis acid sites.

INTRODUCTION

Isomerization reactions of alkenes over alumina have received considerable attention but there remains some controversy over their mechanisms (*1*). The skeletal isomerization of 3,3-dimethylbut-1-ene (33DMB1) to 2,3-dimethylbut-2-ene (23DMB2) and 2,3-dimethylbut-1-ene (23DMB1) proceeds via a carbonium ion mechanism (*2, 3*). The isomerization of but-1-ene to *cis*- and *trans*-but-2-ene over alumina appears to be very complex. Hightower and Hall (*4*), observing that the selectivity of the reaction depended on poisoning, method of catalyst preparation, pretreatment, and reaction temperature, concluded that different types of sites and/or reaction complexes were involved in each of the reaction paths for butene isomerization. Medema (*5*) studied but-1-ene isomerization at 373 K using aluminas activated at different temperatures and concluded that two mechanisms were operative. At high catalyst activation temperature, $T_a > 873$ K, the double-bond migration (DBM), proceeded via an intramolecular hydrogen transfer process while at lower activation temperatures, $T_a < 723$ K, a base-catalyzed mechanism involving π-allylic intermediates produced by allyl C–H dissociation was operative.

Recently it has been shown (*6*) that labeled propene undergoes DBM at 300 K via a dissociative mechanism involving π-allylic intermediates but at ca. 470 K it reacts via an associative mechanism involving carbonium ions.

As a result of their studies on small cyclic alkenes, Hightower and Hall (*7*) suggested that only those molecules having a three-carbon-atom chain, containing the double bond, which could appear concave when viewed from "outside" would undergo isomerization at reaction temperatures (T_r) of less than 373 K. For example, 1-methylcyclopent-1-ene (1MCP$^=$) only isomerized to methylenecyclopentane (MCP) and not to 3-methylcyclopent-1-ene (3MCP$^=$).

The present work is concerned with the

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isomerization of 33DMB1, 3MCP$^=$, and MCP over alumina and fluorided aluminas. The effect of activation temperature (T_a) on catalyst activity is described together with the effect of pretreating the catalyst with H_2S (a molecule recently shown to be a selective poison for reactions proceeding *via* π-allylic intermediates (*8*, *9*)). The importance of initial catalyst water content on activity is also demonstrated.

EXPERIMENTAL

The standard alumina (SA2165) used in this study was a Condea SB γ-alumina calcined in air at 773 K for 48 h (major impurities (ppm): C, 500; Cl, 56; Na_2O, 28; Fe_2O_3, 12; and SiO_2, <50; surface area, 214 $m^2\ g^{-1}$; particle size, 45 μm). Two fluorided aluminas were prepared from SA2165 by HF treatment, designated X312A, 1.55% fluoride, and X312B, 0.22% fluoride. Some experiments were performed using the uncalcined Condea SB (carbon content 3700 ppm; surface area, 296 $m^2\ g^{-1}$; particle size, 45 μm) and Kaiser SAS type γ-alumina STA234B (major impurities (ppm) C, 400; Na_2O, 162; Fe_2O_3, 271; SiO_2, <10; surface area, 261 $m^2\ g^{-1}$; particle size, 90–125 μm). All the aluminas were supplied by I.C.I. Petrochemicals Division.

All experiments were performed in a static system in a silica reaction vessel of ~380 cm^3 using $\sim 1.1 \times 10^{20}$ molecules of reactant, and ~200-mg samples of catalyst, except for the MCP reactions where ~10-mg samples were used. The "standard" pretreatment of the catalysts involved treatment with oxygen (9.3 kN m^{-2}) for 1 h at T_a followed by outgassing at T_a for 15 h. The catalyst was then cooled to T_r and the experiment performed. In some cases the catalyst was allowed to stand in a water-saturated atmosphere at 298 K for 3 days prior to the standard pretreatment. Surface areas of the catalysts as a function of T_a were determined by nitrogen adsorption at 77 K using the BET method.

Reaction products were analyzed using a Perkin–Elmer F11 gas chromatograph. A 3-m column of 10% OV 101 silicone oil on 80- to 100-mesh Chromosorb P operating at 353 K was used for 33DMB1 experiments, a 4-m column of 11.5% silicone fluid MS550 and 11.5% Bentone 34 on 80- to 100-mesh Chromosorb P operating at 343 K for 3MCP$^=$ experiments, and a 2-m column of 3% squalane on 80- to 100-mesh Chromosorb P operating at 423 K for MCP experiments.

Rate constants (k) were obtained from the first order equation,

$$\ln(x - x_e) = -100\ kt/(100 - x_e) + \ln(100 - x_e),$$

where x is the percentage of reactant remaining at time t and x_e is the equilibrium percentage of reactant. Initial rates (k_i) were obtained from the equation

$$k_i = kB/A,$$

where B is the number of molecules of reactant used and A is the surface area of the catalyst sample.

RESULTS

Isomerization of 33DMB1

The products of 33DMB1 isomerization were 23DMB2 and 23DMB1, and in all cases the initial product ratios (23DMB2/

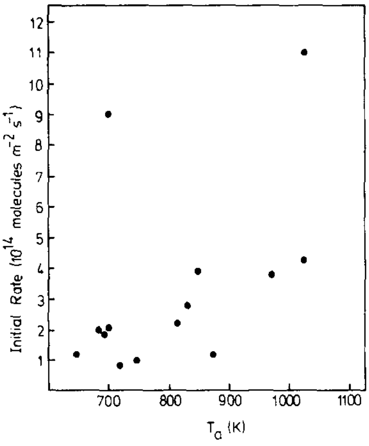


FIG. 1. Isomerization of 33DMB1 over SA2165. Catalyst activity at 426 K against activation temperature for catalysts activated in the standard manner.

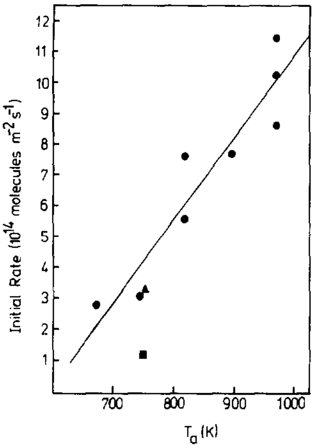


FIG. 2. Isomerization of 33DMB1 over various aluminas. Catalyst activity against activation temperature. ●, SA2165 treated with water prior to standard activation, $T_r = 426$ K; ▲, Condea SB, standard activation, $T_r = 392$ K; ■, STA234B, standard activation, $T_r = 392$ K.

23DMB1) were between 3.1 and 3.6, close to the equilibrium value of 2.7 at 426 K.

The variation of catalyst activity with T_a for reaction over the "standard" alumina SA2165 is shown in Fig. 1, where it can be seen that there is considerable variation in the measured rates. Figure 2 shows the variation of catalyst activity with T_a for SA2165 which had been allowed to stand in a water-saturated atmosphere for 3 days at 298 K prior to the "standard" pretreatment. It can be seen that the repeatability of results is much better using this catalyst, and that the catalyst activity increases with increasing T_a.

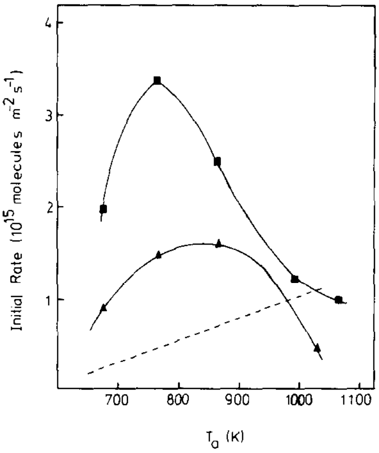


FIG. 3. Isomerization of 33DMB1 over standard and fluorided aluminas. Catalyst activity against activation temperature: ---, SA2165 at 426 K, catalyst water treated prior to standard activation; ▲, X312B (0.22% F) at 349 K; ■, X312A (1.55% F) at 293 K.

The variation of activity of the fluorided catalysts X312A and X312B with T_a is shown in Fig. 3, together with that of SA2165 for comparison. The behavior of the fluorided catalysts differs from that of SA2165 in that their activities both pass through a maximum as T_a increases. It is also evident from Fig. 3, taking into account the different reaction temperatures employed, that activity increases markedly with increasing fluoridation; in the case of catalysts activated at lower values of T_a, activity is enhanced by at least an order of magnitude. During the activation of the

TABLE 1

Effect of Catalyst Pretreatment with Various Alkenes on Subsequent Activity for 33DMB1 Isomerization over SA2165 at 423 K

T_a (K)	Alkene used for pre-treatment	Initial isomerization rate, k_i (10^{14} molecules m^{-2} s^{-1})	
		Standard catalyst	Pretreated catalyst
825	33DMB1[a]	3.0	2.7
841	33DMB1[b]	3.8	3.0
697	33DMB1[b]	2.2	1.7
777	Propene[b]	5.7	3.5
777	Ethene[b]	3.7	2.5
777	Propene[b]	2.4	1.2
769	Propene[c]	3.3	1.2
772	33DMB1[c]	2.9	0.5
778	Ethene[c]	—	3.0

[a] Alkene (1.5×10^{20} molecules) added at 708 K for 30 min, then pumped off at 708 K prior to cooling to 423 K. Catalyst black.

[b] Alkene (1.5×10^{20} molecules) added at 477 K for 30 min, then pumped off at 423 K. Slight catalyst discoloration.

[c] Alkene (1.5×10^{20} molecules) added at 778 K for 30 min, then pumped off at 423 K. Catalyst black.

fluorided catalysts at high T_a, etching of the reaction vessel was observed suggesting that loss of HF from the catalyst was occurring indicating that data for fluorided catalysts activated at high T_a should be treated with caution.

Also shown in Fig. 2 are some results obtained using a Condea SB alumina and a γ-alumina, STA234B. It will be noted that the reaction rates (allowing for temperature differences) are similar for the three aluminas.

Both SA2165 and the high-fluoride catalyst, X312A, showed deviations from first-order behavior at moderate conversions (ca. 30%), the deviations increasing with T_a for X312A, indicating catalyst poisoning. The low-fluoride catalyst, X312B, however, showed no deviation.

The effect on activity of pretreating the catalyst SA2165 with various alkenes is shown in Table 1. In all cases the catalyst was activated in the "standard" manner and the isomerization of 33DMB1 was performed. The catalyst was then treated with alkene as specified in Table 1 prior to reaction of a second dose of 33DMB1. In each case the catalyst activity was reduced but this reduction was not particularly great, in most cases around 50%, even when the alkene treatment resulted in black catalysts.

TABLE 2

Effect of Catalyst Pretreatment with H_2S on Subsequent Activity for Alkene Isomerization over SA2165

Alkene	T_a (K)	T_r (K)	Rate (10^{15} molecules m^{-2} s^{-1})	
			Untreated	H_2S treated[a]
33DMB1	975	426	1.01	3.02
33DMB1	675	426	0.28	0.54
$3MCP^=$	773	391	0.69	0.034[b]
$3MCP^=$	773	355	0.25	0.012[b]
$3MCP^=$	973	355	1.47	0.099[b]
$3MCP^=$	773	355	0.25	0.13[c]
MCP	674	263	4.4	4.3
MCP	674	263	4.4	5.3[d]
MCP	975	263	46.4	53.8
MCP	975	263	46.4	79.0[d]
MCP	975	263	46.4	10.6[c]
MCP	1030	263	68.7	12.6[c]

[a] H_2S (~7.4 × 10^{17} molecules m^{-2}) added to freshly activated catalyst at T_r unless otherwise stated.

[b] Isomerization of $3MCP^=$ performed on catalyst prior to addition of H_2S and fresh dose of reactant.

[c] Isomerization of second dose of alkene on same catalyst, H_2S treatment omitted.

[d] H_2S added at 372 K.

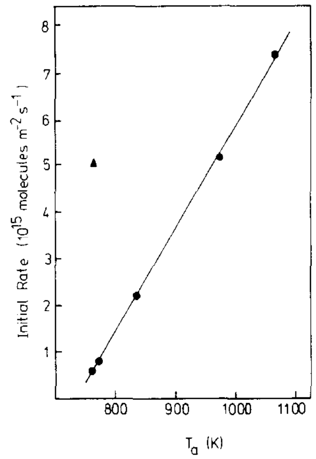


FIG. 4. Isomerization of $3MCP^=$ over SA2165. Catalyst activity at 391 K against activation temperature. ▲, activity of X312B (0.22% F) at 391 K.

Pretreatment of the catalyst SA2165 with H_2S enhances its activity for 33DMB1 isomerization as shown in Table 2. This enhancement in activity is two- to threefold.

Isomerization of 3MCP$^=$

The variation of activity of SA2165 with T_a for the isomerization of $3MCP^=$ to $1MCP^=$ is shown in Fig. 4. Catalyst activity increases with increasing T_a and the extent of increase is similar to that observed for 33DMB1 isomerization (Fig. 2). The result of one experiment using the fluorided catalyst, X312B, is also shown, and, as with 33DMB1, activity is increased by fluoridation, in this case by about an order of magnitude.

The result of performing a second isomerization over the same catalyst after removal by pumping of the first dose of reactant is shown in Table 2. In this case, activity is only ~50% of that shown for a first run. Also shown in Table 2 is the effect on activity of pretreating the catalyst with H_2S. In contrast to 33DMB1 isomerization, H_2S reduces activity for $3MCP^=$ isomerization by ~90%.

Isomerization of MCP

Catalysts used for MCP experiments were pretreated with water prior to the "standard" pretreatment. The variation of activity of SA2165 for the isomerization of $MCP^=$ to $1MCP^=$ with T_a is shown in Fig. 5. Activity increases with increasing T_a, particularly at higher temperatures, but the overall increase is similar to those observed for 33DMB1 and $3MCP^=$.

The effect on activity of pretreating the catalyst SA2165 with H_2S is shown in Table 2. There is little or no effect on isomerization activity for H_2S adsorption at 263 K though there could be slight activity enhancement when the H_2S is adsorbed at 372 K. Table 2 also shows the effect of a prior isomerization of MCP: activity for the second dose is reduced to about 20% of the initial activity.

Effect of Water

When the isomerizations of 33DMB1 and MCP were performed over catalysts taken from the bulk sample and activated in the "standard" manner, repeated reactions over different portions activated at a single T_a gave very poorly repeatable rate data. If, however, the catalyst was left to stand in a water-saturated atmosphere for 3 days at 298 K prior to the "standard" pretreatment, the repeatability was greatly improved (compare Figs. 1 and 2).

Differential thermal analysis of ~200-mg samples of catalyst taken from the bulk sample (~300 g) over the temperature range 293–873 K showed differences in their wa-

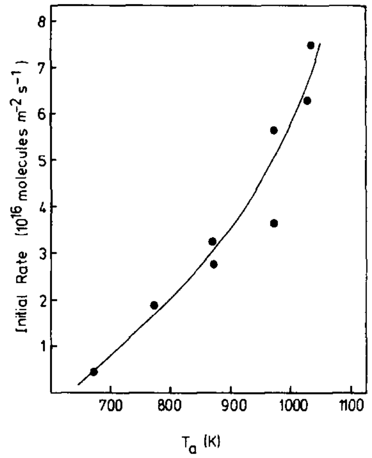


FIG. 5. Isomerization of MCP over SA2165. Catalyst activity at 263 K against activation temperature.

TABLE 3

Summary of Olefin Isomerization Reactions over γ-Alumina SA2165

Olefin	Relative rate[a]	Influence of T_a over 300° range	Influence of fluoriding	Influence of H_2S adsorption	Catalyst activity remaining after pretreatment with olefin (%)
33DMB1	1	×4	Very high	×2–3	~90–20[b]
$3MCP^=$	~10	×6	×10	×0.1	~50[c]
MCP	$>10^4$	×7	Too fast to measure	~same or small increase	~20[c]

[a] Assuming activation energies of 40 kJ mol^{-1} to extrapolate rates for $3MCP^=$ and MCP to 426 K (T_r for 33DMB1 experiments).

[b] Pretreatment with various olefins at various temperatures (Table 1).

[c] Pretreatment consisted of an isomerization run (Table 2).

ter contents and evidently these differences persisted even after the activation treatment used. By treating small samples of the catalyst with a water-saturated atmosphere prior to activation these differences were largely eliminated presumably giving a more repeatable surface before, and thus also after, activation and consequently better repeatability of the rate data.

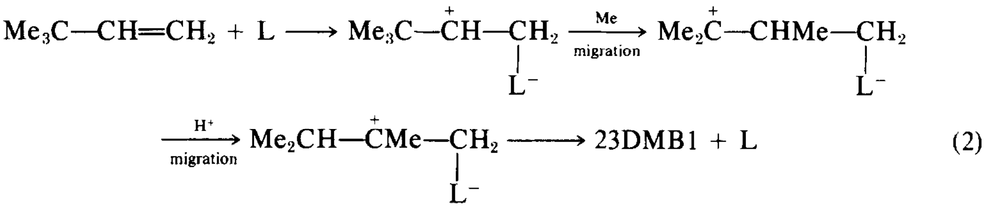
All the results described above are summarized in Table 3.

DISCUSSION

Potentially, there are two carbonium ion mechanisms (one involving proton addition (1) and the other Lewis acid induced (2)) and an allyl mechanism (proton abstraction (3)).

The skeletal isomerization of 33DMB1 proceeds via carbonium ion intermediates (*2, 3*) and here there are two possible pathways, (1) and (2):

$$\mathrm{Me_3C{-}CH{=}CH_2 \xrightarrow{H^+} Me_3C{-}\overset{+}{C}H{-}CH_3 \xrightarrow[\text{migration}]{Me} Me_2\overset{+}{C}{-}CHMe_2 \xrightarrow{-H^+} 23DMB1 + 23DMB2,} \qquad (1)$$

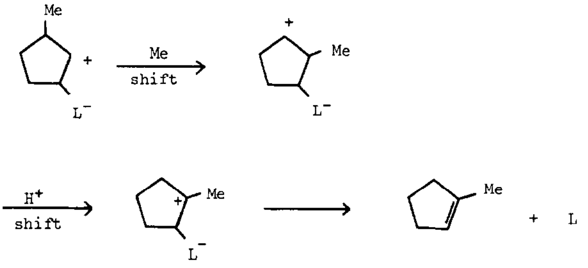


$$\mathrm{Me_3C{-}CH{=}CH_2 + L \longrightarrow Me_3C{-}\overset{+}{C}H{-}\underset{L^-}{C}H_2 \xrightarrow[\text{migration}]{Me} Me_2\overset{+}{C}{-}CHMe{-}\underset{L^-}{C}H_2 \xrightarrow[\text{migration}]{H^+} Me_2CH{-}\overset{+}{C}Me{-}\underset{L^-}{C}H_2 \longrightarrow 23DMB1 + L} \qquad (2)$$

(L = Lewis acid site).

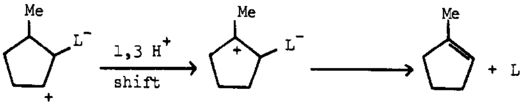
In mechanism (1) the alkene is protonated via the catalyst surface, the proton, coming from either Brønsted acid sites or adsorbed alkene fragments, undergoes methyl migration and then loses a proton to give either of the two products 23DMB1 or 23DMB2. Mechanism (2) involves adsorption of the alkene onto a Lewis acid site followed by two rearrangements and release of product 23DMB1. The skeletal rearrangement step in mechanism (1) is likely to be facile as the 1,2-methyl shift transforms a secondary carbonium ion to a tertiary. The same is true for the methyl shift in the Lewis acid route (2) as the formation of a tertiary carbonium ion would counteract the unfavorable charge separation. Note that for 33DMB1 there are no α-H atoms so that the allyl route is not possible here.

For 3MCP$^=$, the Brønsted mechanism is available, involving formation of a secondary carbonium ion. Two Lewis mechanisms are possible but both unlikely. The first, (3), involves a 1,2-methyl shift without the incentive of forming a tertiary center and with the need for charge separation.



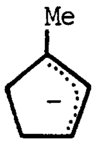
(3)

The second, (4), involves a 1,3 proton shift though it does also involve the formation of a tertiary center.

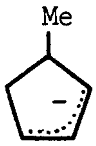


(4)

The allyl mechanism is possible (and if it occurs would be expected to lead to the formation of some 4MCP= because ions (5) and (6) have very similar stabilities). Note that these are convex allyls.

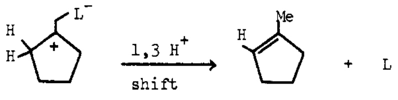


(5)

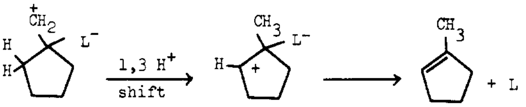


(6)

For MCP, the Brønsted mechanism involves formation of a tertiary carbonium ion, but the Lewis routes are unlikely as they would require either a 1,3 shift (7) or a 1,3 shift and a primary carbonium ion (8).



(7)



(8)

The allyl route would proceed via a concave carbanion. These preliminary considerations are summarized in Table 4.

Consideration of the results presented in this paper indicates preferences for some of these possibilities. In all cases studied here using alumina SA2165, catalyst activity increased as T_a increased, the increase being perhaps slightly less for 33DMB1 than for 3MCP= and MCP.

There is doubt whether or not the surface hydroxyl groups of alumina show Brønsted acidity. Dewing *et al.* (*10*) and Pearson (*11*) both claim to have detected the presence of Brønsted centers on alumina while Knözinger (*12*) has concluded that an alumina surface possesses no such species.

It is therefore possible that surface hydroxyl groups act as proton sources for the mechanism shown in Eq. (1). The number of surface hydroxyl groups, and thus the number of potential proton sources, will decrease as T_a increases, suggesting that, if these groups are important, activity should decrease on increasing the catalyst activation temperature. However, Peri (*13*) has shown that the heat of adsorption of water on alumina increases with dehydroxylation of the surface and this, taken together with the report (*14*) that Brønsted acidity increases with Al–OH bond strength, suggests that the acidity of surface hydroxyl groups would increase as T_a increases, i.e. as their number decreases. It is known (*8*) that the number of catalytically active sites on alumina constitutes only a very small fraction of the surface and so the increase in acidity of the remaining surface hydroxyl groups may well be the dominant factor,

TABLE 4

Possible Routes for Alkene Isomerization

Alkene	Brønsted	Lewis	Allyl
33DMB1	Yes; 2° → 3° → 23DMB1 + 23DMB2	Yes	No
3MCP=	Yes; 2°	Unlikely energetically	Yes; convex
MCP	Yes; 3°	Unlikely; 1,3 shift required	Yes; concave

thus suggesting an increase in activity as T_a increases.

It is also possible that a highly dehydrated alumina surface can interact with olefin in such a way as to provide protons. This is supported by a recent report (*15*) of the equilibration of vinyl hydrogen atoms of 33DMB1 with Brønsted centers on alumina. This alternative source of protons is likely to increase with increasing exposure of Al^{3+} and O^{2-} species, thus suggesting an increase in activity with increasing T_a for mechanism (1).

Thus, an increase in catalyst activity with increasing T_a for mechanism (1) can be explained by the relative importance of some or all of the above factors.

The increase in surface Al^{3+} species, Lewis acid sites, would be expected to increase catalyst activity if mechanism (2) was operative. Likewise, as a π-allylic mechanism is thought to involve adjacent Al^{3+} and O^{2-} species (*1*), catalyst activity would be expected to increase with increasing T_a for mechanism (*3*).

Thus, the similarity in the catalyst activity versus T_a curves does not permit a discrimination between the active centers involved.

More informative were the studies involving catalyst pretreatment with H_2S. It has been shown that H_2S adsorbs onto exposed Al^{3+} ions on the alumina surface and that dissociation of the molecule occurs (*16, 17*). It has also been shown (*8, 9*) that H_2S is a selective poison for isomerization reactions proceeding via π-allylic intermediates while not destroying Brønsted activity.

The number of isomerization sites on alumina was calculated to be $\sim 5.3 \times 10^{17}$ m^{-2} (*8*), and so in the present study $\sim 7.4 \times 10^{17}$ molecules H_2S m^{-2} were added to the catalyst which may be expected substantially to poison allyl and perhaps Lewis sites. H_2S was shown to reduce catalyst activity (by ~90%) for $3MCP^{=}$ isomerization, but to enhance the activity for 33DMB1 and MCP isomerizations. One may surmize from this and Table 4 that $3MCP^{=}$ isomerizes predominantly via a π-allylic mechanism while 33DMB1 and MCP isomerize via carbonium ion mechanisms.

The fact that 3MCP seems to isomerize via a π-allylic intermediate is perhaps a little surprising in view of the suggestions of Hightower and Hall (*7*) that only molecules having a three-carbon-atom chain, containing the double bond, which could appear concave when viewed from "outside" would undergo isomerization at $T_r < 373$ K. In this study the isomerization of $3MCP^{=}$ takes place at 355 K near the limit proposed by these authors. The behavior of $3MCP^{=}$ also contrasts with that of MCP which isomerizes very much more rapidly and is not retarded by H_2S adsorption. We conclude that in this case the Brønsted mechanism operates, particularly favored because of the involvement of a tertiary carbonium ion.

The small enhancement of catalyst activity for the isomerization of 33DMB1 and perhaps also MCP by H_2S can be explained by a mechanism involving Brønsted-type sites, as dissociative chemisorption of H_2S on an alumina surface could give rise to new active sites of this type. The observed enhancement would also seem to discount mechanism (2) for 33DMB1 isomerization, as the necessary Lewis acid sites would be destroyed. This rate enhancement is in contrast to observations made using a Kaiser SAS γ-alumina (15) where no change in rate was observed on treating the catalyst with H_2S.

In all cases of 33DMB1 isomerization, the initial product ratios (23DMB2/23DMB1) were between 3.1 and 3.6, somewhat in excess of the equilibrim value of 2.7 at 426 K. This indicates that 23DMB1 is not the initial sole product, which is further evidence against the Lewis site mechanism for the isomerization of this olefin.

A qualitative idea of relative rates of various olefin isomerization mechanisms over alumina can be obtained by considering the results presented in this paper for

SA2165. Taking into account not only the measured reaction rates but also the different reaction temperatures employed, the relative rates of isomerization on SA2165 are MCP $\gg$ 3MCP$^=$ $>$ 33DMB1 (see Table 3). This leads to a tentative general statement that, on an alumina catalyst, the relative isomerization activities for different olefinic structures are: olefins capable of isomerization via a tertiary carbonium ion $\gg$ olefins capable of isomerization via an allyl $>$ olefins incapable of forming an allyl or a tertiary carbonium ion but capable of protonation to a secondary carbonium ion.

Addition of fluoride to the catalyst increases activity for both 33DMB1 and 3MCP$^=$ isomerization (Figs. 3 and 4), an effect also observed for other isomerization reactions (*18*). In the case of 33DMB1, if one assumes Brønsted sites, then this is readily explainable by the inductive effect of surface fluoride increasing hydroxyl-group acidity. This argument would still apply if the proton source was olefin fragments on the surface, but would not be expected to enhance the rate of mechanism (2) as the primary mode of fluoride binding is to Lewis acid sites (*19*) preventing reactant access. In view of this binding it is surprising that fluoride enhances activity for 3MCP$^=$ isomerization. One possibility is that fluoride enhances the hydroxyl-group acidity sufficiently to enable an alternative carbonium ion mechanism to operate here, one that would involve a secondary carbonium ion, as well as allowing a π-allylic mechanism to operate on remaining Lewis acid sites.

In contrast to the standard alumina SA2165, the fluorided aluminas showed a maximum in activity with T_a for 33DMB1 isomerization. The fall in activity at high T_a may be due to loss of HF from the surface during the outgassing procedure. However, the highly fluorided catalyst, X312A, showed considerable deviation from first-order behavior, especially at high T_a, suggesting poisoning of the catalyst. No such effect was observed for X312B. On examination of the activities of X312A and X312B over 1 h of reaction (Fig. 6), it can be seen that X312B still shows a peak in activity whereas X312A does not, its activity falling off rapidly with increasing T_a. If, then, the increased activity with fluoride content is due to increased acidity, then one explanation of the increased poisoning of X312A may be that the catalyst becomes acidic enough to product surface oligomerization of 33DMB1, the products of which remain on the surface and poison the active sites.

Though the behavior of these fluorided catalyst is complex in detail, it is clear that fluoridation increases enormously the activity for carbonium ion reactions.

Pretreatment of alumina SA2165 with various alkenes had surprisingly little effect on 33DMB1 isomerization, even when severe blackening of the catalyst resulted. It seems, therefore, that hydrocarbon residues deposit on sites different from those used for isomerization reactions or that, as discussed above, adsorbed fragments can act as proton sources.

It is interesting to contrast the variation of catalyst activity (SA2165) versus T_a of the reactions presented here with terminal vinyl–hydrogen exchange and reactions involving σ-allyl species over alumina. Studies using labeled propene (*20, 21*) have shown that for terminal vinyl exchange

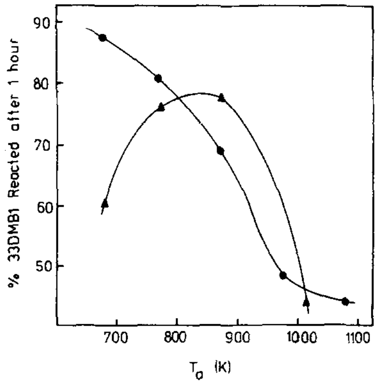


FIG. 6. Isomerization of 33DMB1 over fluorided catalysts. %33DMB1 reacted after 1 h against activation temperature: ●, X312A at 293 K; ▲, X312B at 349 K.

(involving a 1-propenyl intermediate, $\underset{*}{C}D{=}CH{-}CH_3$; * indicates a bond to the surface), catalyst activity shows a sharp peak with increasing T_a, whereas for methyl–hydrogen exchange (involving σ-allyl intermediates, $CD_2{=}CH{-}\underset{*}{C}H_2$) catalyst activity shows a very broad maximum as T_a increases. In the cases reported in this paper, concerning π-allylic and carbonium ion mechanisms, activity rises as T_a increases; no maximum is observed over the temperature range studied.

In conclusion, our results suggest that, over γ-alumina SA2165, 33DMB1 and MCP isomerize via carbonium ion mechanisms whereas $3MCP^{2-}$ isomerizes via a π-allylic mechanism. The similarities of the activity versus T_a curves for all three reactions suggests that there is a factor common to each reaction, for instance, the involvement of Lewis acid sites. These are necessary for the π-allylic mechanisms and may make some contribution to a carbonium ion mechanism.

H_2S, while poisoning sites involved in a π-allylic pathway, can enhance the rate of reactions involving carbonium ions.

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