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The Mechanisms of Dimethylbutene Isomerization over Alumina

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Reactions of dimethylbutenes over pure and chlorided γ-alumina have been studied in the presence of selective poisons and/or with various host molecules for deuterium label. The extent of H_2S poisoning has been used to determine the relative roles of π-allylic species and alkyl carbonium ions in the isomerization of the 2,3-dimethylbutenes on alumina at 273 K. The absence of poisoning by H_2S of skeletal isomerization of 3,3-dimethylbut-1-ene at 352 K is evidence that H_2S does not inhibit reaction through carbonium ions whereas it is known to poison activity involving π-allylic species. The isomerization of 3,3-dimethylbut-1-ene in the presence of suitably labeled alkenes showed that vinylic and allylic hydrogen atoms can equilibrate with Brønsted-acid-type hydrogen on alumina at about 273 K. But adsorbed vinyl species have been found to retard skeletal isomerization, suggesting identity, or at least close proximity, of the sites for Brønsted acid reactions and vinylic C–H exchange. Catalyst chloriding enhanced isomerization but retarded exchange of C–H bonds with D. The influence of activation temperature and of impurities is discussed for reactions of dimethylbutenes over alumina.

INTRODUCTION

The skeletal isomerization (SI) of 3,3-dimethylbut-1-ene (**I**), to 2,3-dimethylbut-1-ene (**II**) and 2,3-dimethylbut-2-ene (**III**), has been studied over alumina catalysts (*1*), partly as a test reaction for carbonium ion reactivity (*2*). However, the reported data show considerable disagreement both in regard to reaction rate and to the occurrence or otherwise of simultaneous exchange of C–H bonds with D_2. Hightower and Hall (*3*) reported that at 301 K, over γ-alumina activated at 803 K, **I** underwent exchange with D_2 limited to vinylic C–H bonds and without significant isomerization. Knözinger *et al.* (*4*) found that, even at 523 K, **I** neither isomerized nor exchanged with D_2 over η-alumina activated at 573 K; **II** isomerized to **III** over such a catalyst at 353 K, but incorporation of D from D_2 still did not occur. Scurrell *et al.* (*5*) showed that **I** isomerized to **II** and **III** at 328 K, over γ-alumina activated at 723 K, but that exchange with D_2 was very slow. It has been suggested (*5*) that impurities or minority sites might be responsible for the diversities of isomerization behavior, whereas activation temperature has been shown (*6*) to influence the development of alkene exchange activity, at least for propene.

The work reported here, using pure and chlorided γ-alumina, selective poisons, and the reactions of both **I** and **III** with several sources of deuterium, was undertaken to provide a better understanding of these reactions, particularly of their mechanisms. It is known that π-allylic reactivity on alu-

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mina can be poisoned by H_2S adsorbed at about 300 K; double bond migration (DBM) of both but-1-ene (*7*) and propene (*8*), involving π-allylic intermediates, may be poisoned by sufficient H_2S to cover about 5×10^{17} sites m^{-2}. The effects of H_2S on DBM of **III** have therefore been studied to decide on the relative role of π-allylic intermediates and tertiary carbonium ions in this reaction.

The use of alternative source molecules for D was recently emphasized (*8*) for alkene reactions over alumina if correct conclusions are to be reached on the relative role of intermolecular and intramolecular processes in isomerization. Here, D_2, perdeuteroethene, and perdeuteropropene have been used. CO_2 has been employed in some experiments to poison selectively dissociative adsorption of D_2 (*9*) and vinylic C–H bond activation (*6, 10*); the role of allylic hydrogen, produced from propene but not ethene and unaffected by CO_2 could be studied in this way. The effect of catalyst chloriding on the relative rates of exchange and isomerization has also been studied.

EXPERIMENTAL

Apparatus

A static reactor was used with periodic removal of gas samples either to a gas chromatograph (Perkin Elmer F11) or to a combined gas chromatograph–mass spectrometer (AEI MS20 Rapide). Mass spectrometric data were collected on a PDP11 dedicated computer as described previously (*11*). A 2m column of propylene carbonate on Chromosorb P, operated at about 295 K, was used to separate the dimethylbutene isomers.

Materials

Most experiments involved a nominally pure γ-alumina (SAS: Kaiser SAS, BET area 226 m^2 g^{-1}, described previously (*10*)), but some were carried out with a chlorided γ-alumina (UM: Universal Matthey, code L-1043, 0.3% Cl, surface area 260 m^2 g^{-1}). Dimethylbutenes were obtained from the Aldrich Chemical Company, perdeuteroethene and -propene from Merck, Sharp, and Dohme (>99 at% D purity) and all gases were subjected to repeat freeze–pump–thaw cycles prior to use.

Catalyst Activation

The catalysts were used in about 150 mg lots and, unless stated otherwise, were first heated to 723 K under vacuum prior to treatment with 9.3 kPa O_2 for 45 min at 723 K before evacuation at 723 K under a pressure of about 200 μPa (Macleod gauge) for about 16 h.

Catalyst Poisoning

The required amounts of H_2S and CO_2 were computed from reported values of site densities (*7*) for π-allylic DBM and vinylic C–H exchange, respectively; 7.9×10^{17} H_2S m^{-2} and 2.5×10^{17} CO_2 m^{-2} were used, assuming complete, irreversible adsorption under reaction conditions. The appropriate quantities were expanded into contact with the active catalysts at reaction temperature before admitting the reaction mixture (4 kPa dimethylbutene with 20 kPa D_2 or about 4 kPa C_3D_6 or C_2D_4).

RESULTS

Unpoisoned SAS Alumina

A 1:5 molar ratio mixture of **I** with D_2 (Table 1: Experiment I-1) underwent exchange about 50 times faster than SI on SAS alumina at 352 K. Isomerization was limited to the production of **II** and **III** which were produced in equilibrium proportions (*12*). Exchange in **I** was limited to the three vinylic hydrogens; there was no detectable [$^2H_4$]-3,3-dimethylbut-1-ene even after 400 min reaction at 352 K (Table 2). Agreement of observed and binominal distribu-

TABLE 1

Exchange and Isomerization Rates for Dimethylbutenes over Alumina Activated at 723 K

Experiment	Reaction mixture	Reaction temperature (K)	Catalyst	Rate of	
				Exchange of reactant (10^{14} molecules $s^{-1}m^{-2}$)	Isomerization of reactant (10^{14} molecules $s^{-1}m^{-2}$)
I-1	I + D_2	352	SAS	39.6	0.84
I-2	I + D_2	352	SAS + CO_2	<0.3	2.26
I-3	I + C_3D_6	352	SAS	31.4	<0.02
I-4	I + C_3D_6	352	SAS + CO_2	~0.3	0.59
I-5	I + C_2D_4	352	SAS	2.0	<0.02
I-6	I + C_2D_4	352	SAS + CO_2	<0.3	0.18
I-7	I + D_2	352	UM	9.9	7.41
I-8[a]	I	352	SAS + H_2S	—	0.84
I-9[a]	I	352	SAS[b]	—	0.37
III-1	III + C_3D_6	273	SAS	—	13.0
III-2	III + C_3D_6	273	SAS + CO_2	—	23.0
III-3[a]	III	293	SAS	—	25.0
III-4[a]	III	293	SAS + H_2S	—	4.2
III-5[a]	III	273	SAS[b]	—	46.9
III-6[a]	III	273	SAS[b] + H_2S	—	46.9
III-7[a]	III	273	UM	—	45.7
III-8[a]	III	273	UM + H_2S	—	25.5

[a] Experiments in the absence of "hydrogen" or other diluent.

[b] Catalyst activated at 948 K.

tions for three exchangeable hydrogens (Table 2) throughout reaction implies no appreciable preferential exchange of the terminal compared with the internal vinylic hydrogen. Exchange in products **II** and **III** was very extensive; although **I** contained on average about two D per molecule after 100 min (Fig. 1), **II** and **III** produced from **I** contained about 8.5 D per molecule on average at this time (Fig. 2) and the deuterium distribution agreed with binomial over all 12 hydrogen atoms. **II** and **III** attained an equilibrium distribution of deuterium even after about 50 min reaction (Fig. 2) which suggests strongly that D was incorporated during isomerization itself and not by subsequent vinylic exchange of the products, although it must be added that the rate of exchange of **I** was slightly limited by bulk diffusion effects under these conditions (*13*).

Exchange between **I** and C_3D_6 (Table 1: Experiment I-3) occurred at a similar rate to that with D_2 but, surprisingly, that with C_2D_4 (Experiment I-5) was significantly slower. Both C_3D_6 and C_2D_4, however, greatly inhibited the rate of SI of **I**.

DBM of **III** to give **II** (Table 1: Experiment III-1) occurred readily at about 70 K lower temperatures than SI of **I**. Extrapolation of the rates for DBM of **III** from 273 to 352 K indicated that this reaction was about 250 times faster than SI of **I** at 352 K.

SAS Alumina Poisoned by CO_2

CO_2 was found completely to poison exchange with D_2 and with C_2D_4 of both **I** and products **II** and **III** at 352 K (Table 1: Experiments I-2 and I-6; Figs. 1 and 2). Interestingly, CO_2 consistently enhanced the rates of SI of **I** and of DBM of **III** (Experi-

TABLE 2

Deuterium Product Distributions Obtained from Reaction of (I) over Alumina Activated at 723 K

Experiment	Amount of each dimethylbutene present (%)	Reaction time (min)	Product distribution (%)												
			[$^2H_0$]	[$^2H_1$]	[$^2H_2$]	[$^2H_3$]	[$^2H_4$]	[$^2H_5$]	[$^2H_6$]	[$^2H_7$]	[$^2H_8$]	[$^2H_9$]	[$^2H_{10}$]	[$^2H_{11}$]	[$^2H_{12}$]
I-1	I 98	27	14.2	32.8	38.5	14.6	0.0								
		27[a]	11.7	36.7	38.2	13.2	0.0								
	I 79	403	2.1	13.4	46.6	37.8	0.0								
	II[c] 2	403								17.2	16.3	15.2	26.8	24.5	0.0
	III 19	403						2.1	8.2	16.1	26.6	23.8	16.8	6.4	0.0
		403[b]				0.2	0.8	3.0	8.1	16.0	28.2	23.8	16.6	7.0	1.3
I-2	I 75	185	100.0												
	II 2	185	100.0												
	III 23	185	100.0												
I-3	I 100	140	11.2	34.7	39.1	15.1	0.0								
I-4	I 87	327	98.8	1.2	0.0										
	II[c] 1	327	64.7	32.3	3.1	0.0									
	III 12	327	59.2	31.8	8.6	0.3	0.0								
I-6	I 96	330	100.0												
	II <1	330	100.0												
	III 4	330	100.0												
I-7	I 93	14	81.9	17.2	1.5	0.0									
	III 6	14	10.5	30.2	29.8	19.2	10.0	0.5	0.0						

[a] Binomial distribution for three exchangeable hydrogens.

[b] Binomial distribution for 12 exchangeable hydrogens.

[c] Due to the small amounts of **II** produced, no significance is attached to the difference in product distribution for **II** and the more accurate data for **III**.

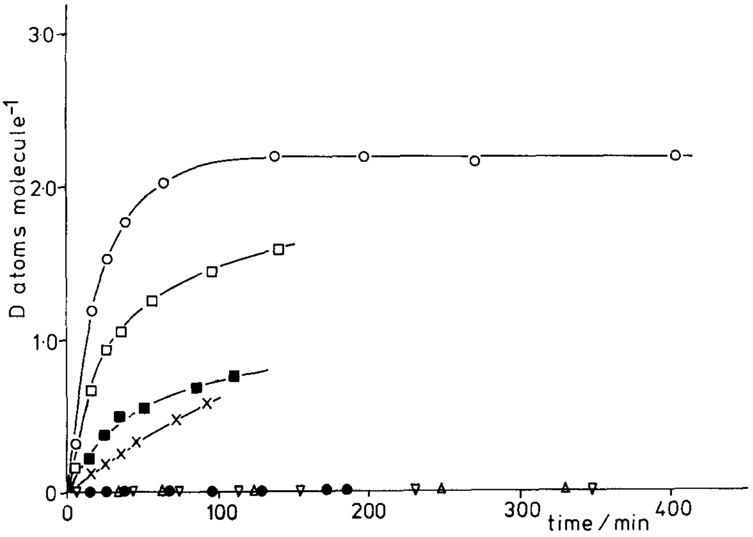

FIG. 1. Deuterium incorporation into 3,3-dimethylbut-1-ene (I) : ○, SAS with D_2; □, SAS with C_3D_6; ■, UM with D_2; ×, SAS with C_2D_4; ●, SAS plus CO_2 with D_2; △, SAS plus CO_2 with C_2D_4; ▽, SAS plus CO_2 with C_3D_6.

ment III-2), the effect on SI being more marked in the presence of C_2D_4 (factor >9) than in that of D_2 (factor about 3). Similar observations were made using C_3D_6 (Experiment I-4; SI enhanced by factor >25) as for C_2D_4 with the important exception that some incorporation of deuterium into products **II** and **III** was observed at 352 K (Fig. 2 and Table 2: Experiment I-4). DBM of **III** in the presence of C_3D_6 on CO_2 poisoned SAS, however, proceeded without exchange at 273 K.

SAS Alumina Poisoned by H_2S

Rate of SI of **I** was unaffected by H_2S adsorption (Table 1: Experiments I-1 and I-8) as expected for a reaction occurring via carbonium ion intermediates. The effect of H_2S on rate of DBM of **III** was influenced

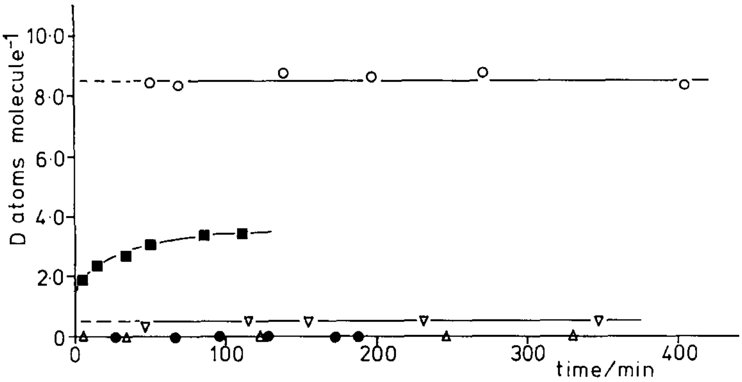

FIG. 2. Deuterium incorporation into product 2,3-dimethylbut-2-ene (III) in reaction of 3,3-dimethylbut-1-ene (I) : ○, SAS with D_2; ■, UM with D_2; ●, SAS plus CO_2 with D_2; △, SAS plus CO_2 with C_2D_4; ▽, SAS plus CO_2 with C_3D_6.

by catalyst activation temperature; after activation at 723 K, H_2S reduced the rate to about 17% its value on unpoisoned SAS (Experiment III-4) whereas following activation at 948 K it had no effect even when sufficient H_2S was used to produce a pressure ot about 100 Pa in the reactor. The predominant mechanism for DBM of **III** therefore appears to change as activation temperature is varied.

UM Alumina

After activation at 723 K and with reaction at 352 K, SI of **I** was about nine times faster over UM than over SAS (Table 1: Experiments I-1 and I-7), whereas exchange with D_2 was about four times slower on UM, thus making the rates of SI and exchange comparable over UM. Exchange of **I** was still limited to the three vinylic hydrogens, whereas again the products had a high deuterium content; over the first 100 min of reaction, **I** contained an average of about 0.4 D per molecule, whereas for products **II** and **III** the figure was about 3 (Figs. 1 and 2). It seems clear from Fig. 2 that on average about two D per molecule were being incorporated into products during their formation as exchange of neither reactants nor products was limited by bulk diffusion in this case (*13*).

DBM of **III** was about three times faster over UM than over SAS at 273 K (Table 1: Experiments III-1 and III-7). The activity was poisoned by H_2S to about 45% its value on UM alone; the smaller effect with UM compared with SAS suggests that catalyst chloriding also influences mechanism.

DISCUSSION

The reactions to be considered are those of SI of **I**, DBM of **II** and **III** and exchange of C–H bonds with deuterium. Consider exchange of **I** first. At 352 K, **I** was found to exchange with D_2, C_2D_4, and C_3D_6 but in all cases only three hydrogens were labile. This is in agreement with Hightower and Hall (*3*) and implies, as supported by the poisoning effect of CO_2, that only the vinylic hydrogen in **I** was readily exchangeable. We did not detect any difference in exchange rate between the terminal and internal vinylic hydrogen but it is possible that the comparison of exchange data with binomial distributions is, in this case, a less sensitive test than NMR spectroscopy which was used by Hightower and Hall.

The independence of the rate of SI of **I** (Table 1: Experiment I-8) of the presence of H_2S is good evidence that carbonium ion reactions at about 350 K on alumina are not poisoned by H_2S. Thus, we may regard the poisoning effect of H_2S as a selective probe into mechanism; complete poisoning implies isomerization involving π-allylic species (*7*, *8*), whereas no poisoning implies isomerization most probably through carbonium ions (*14*). Thus, over SAS activated at 948 K, DBM of **III** does not involve π-allylic intermediates, whereas on SAS activated at 723 K about 83% activity involves such species. It implies that in the former case about 100%, and in the latter about 17% reactivity occurs through carbonium ion intermediates on alumina even at a reaction temperature of 273 K. Interestingly, the reactivity of carbonium ions in SI was almost unaffected by an increase in activation temperature (Experiment I-1 and I-9), whereas their reactivity in DBM was enhanced about 20-fold (Experiments III-4 and III-6). The mechanism of alkene isomerization on alumina seems to depend on the structure of the reactant with involvement of tertiary carbonium ions in cases where they can be formed by protonation of the alkene. Thus, but-1-ene isomerization at about 300 K on alumina proceeds almost exclusively via a dissociative mechanism with π-allylic intermediates, whereas **III**, isobutene, and methylenecyclopentane, all with the ability to form tertiary carbonium ions upon protonation, isomerize via an associative mechanism with carbonium ion intermediates at about 300 K on alumina

(*14*). Hightower and Hall (*15*) suggested that facile isomerization via allylic intermediates occurred only with alkenes that possess a three-carbon atom chain, including the double bond, which could appear concave when viewed from outside the molecule. It was suggested that such isomerization required the alkene to drape over a surface oxide ion in order for intramolecular, dissociative DBM to be possible. Apart from the ambiguous case of linear alkenes, all those molecules cited by Hightower and Hall (*15*) as fulfilling this criterion could also form tertiary carbonium ions. We suggest therefore, that when such ion formation is possible, the Brønsted acid character of alumina is sufficient to produce them at about 300 K and that they will then make a significant contribution to isomerization at this temperature.

Alumina catalyzes vinylic C–H exchange and DBM of **III** at 352 K. The marked increase in D content on reaction from **I** to **II** and **III** may now be considered. As indicated, the results strongly suggest that D may be incorporated during isomerization itself rather than through facile, diffusion rate limited vinyl exchange of **II** and **III** once these have been produced. However, it is not possible to decide unambiguously upon the mechanism for D incorporation during isomerization from the reported data. Two alternatives may be envisaged: (a) It may occur during the rapid, severely diffusion influenced, subsequent DBM of the first formed gas phase product of SI of **I**; over SAS, DBM of **III** was about 250 times faster than SI of (I) at 352 K. (b) The tertiary carbonium ion (TCI), $(CH_3)_2$-CH–$C^+(CH_3)_2$, produced from SI of **I** and believed important in DBM of **II** and **III** might take part in many interconversions of the type **III** $\rightleftharpoons$ (TCI) $\rightleftharpoons$ **II** before a product molecule finally desorbs. In both cases, intermediates in DBM must be able to exchange H for D. When C_3D_6 was used as source of D on CO_2 poisoned SAS, that is when only allylic D was available (*10*) (Experiment I-4), limited product deuterium incorporation still occurred at 352 K but not at 273 K when **III** was used as reactant. Thus, principally vinylic but also some allylic D must have been able to exchange with that hydrogen associated with intermediates in DBM. This implies that such D could exchange with catalyst hydrogen at Brønsted centers.

The retarding influence of ethene and propene upon rate of SI of **I** (reduction by factors >40) was unexpected. SI is believed to involve carbonium ions and while these ions formed from propene might adsorb as strongly as those from **I**, there should not be any such competition from ethene. In addition, CO_2 enhanced the rate of SI of **I**. This effect was initially thought to reflect increased catalyst acidity in presence of CO_2, but the fact that relative enhancement was much greater when ethene or propene was present was unexpected. A consistent explanation for all the above is that vinyl dissociatively adsorbed alkene, inhibited by CO_2, is a poison for SI. This conclusion is supported by our observation that vinylic D can exchange with Brønsted-acid-type hydrogen and suggests close proximity (or possible identity) of the sites for vinylic exchange and Brønsted acid activity. This suggestion is not contrary to previous evidence as exchange sites are believed to be associated with structural OH groups (*7*) and, indeed, very early work by Hindin and Weller (*16*) correlated hydrogenation, since concluded to involve carbonium ion intermediates (*17*), with exchange activity. One picture of the active site for exchange/Brønsted acid activity would involve O^{2-}, Al^{3+}, and OH^- ions; vinyl dissociative adsorption of C_2D_4 would produce OD^-, $(Al$–$C_2D_3)^{2+}$, and OH^- which would then provide D^+ or H^+ as Brønsted acids and give C_2D_3H as exchange product. CO_2 would adsorb on O^{2-} or OH^- only and so might therefore enhance SI by inhibiting $C_2D_3^-$ formation on Al^{3+}.

Consider now the influence on these reactions of catalyst chloriding. The relative reactivity for SI and exchange of **I** with D_2 at 352 K was reduced from about 50 to about 1 on chloriding, the assumption being made that chlorided SAS would have been very similar in reactivity to UM. The decrease in exchange activity may be understood in terms of blockage of exchange sites on the surface by Cl, whereas activity for SI was enhanced due to increased acidity, as found previously (*18*) for fluorided alumina which behaved similarly to silica–alumina. The fact that H_2S poisoning indicated a greater involvement of carbonium ion activity in DBM over UM than over SAS activated at 723 K is in agreement with the latter notion. Deuterium was again found to be incorporated into **II** and **III** upon their formation from **I**. In this case the effect was certainly not due to vinyl exchange alone but still the precise mechanism of incorporation upon isomerization is not clear as was discussed above.

Alumina activation temperature is now known to affect the rates for C–H exchange with D (*6*, *10*), the rates of both SI and DBM, and the importance of carbonium ions in DBM. Acid impurities (Cl, F) are known to decrease exchange rate whereas they enhance acid properties for isomerization; conversely, basic impurities, particularly Na, will have a detrimental effect on SI. These factors go a long way towards rationalizing the reported diversities of alumina catalysis. In the case of dimethylbutenes, the present data from SAS are very similar to those found by Hightower and Hall (*3*) in that exchange was much faster than SI at 352 K. The low activation temperature (573 K) used by Knözinger *et al.* (*4*) most probably explains the low activity of their catalyst, especially the lack of activity for SI and vinyl exchange. The rather different results from the work of Scurrell *et al.* (*5*) may be explained if the reactions of **I** are particularly prone to acidic and basic trace impurities.

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