

Reactions of 3,3-Dimethylbut-1-ene with Deuterium Oxide or Deuterium Over Oxide Catalysts

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Exchange reactions of 3,3-dimethylbut-1-ene (I) with D_2O have been studied over four X-type zeolites, silica-alumina and magnesium oxide, and with D_2 over some of the catalysts. The isomerization of I, in the presence of D_2O or D_2 , to form 2,3-dimethylbut-1-ene (II) and 2,3-dimethylbut-2-ene (III) was also followed.

These reactions are useful in establishing the properties of oxide catalysts for reactions of olefins. For systems where carbonium ions are formed and where D^+ is readily available, e.g., zeolites with D_2O , isomerization of I to II and III is observed, accompanied by extensive exchange of the C_6 olefins. For systems which do not readily form carbonium ions, e.g., MgO with D_2 , the main reaction is the exchange of the vinyl hydrogen atoms of I without isomerization. The choice of D_2 or D_2O as the source of the labeling isotope has a profound effect on the character of the reaction observed with some of the catalysts.

INTRODUCTION

Exchange reactions of 3,3-dimethylbut-1-ene (I) with deuterium or deuterium oxide can be used to establish the properties of oxide catalysts for reactions of olefins, and to indicate the nature of the reactive intermediates formed on the catalyst surface.

The character of the exchange reactions will depend on whether or not the catalyst can bring about the formation of carbonium ions from the olefins. If these ions are formed isomerization is likely to occur by the reaction scheme shown in Fig. 1. The scheme involves the formation of a secondary carbonium ion which rearranges to the more stable tertiary ion and this, after loss of H^+ , leads to 2,3-dimethylbut-1-ene (II) and 2,3-dimethylbut-2-ene (III). Evidence

for this scheme was obtained by Pines and Haag (1) who showed that isomerization of the olefins produced by the dehydration of 3,3-dimethylbutan-2-ol increased with the acidity of the alumina used as catalyst, and was reduced by treatment of the alumina with a base. Thus, for catalysts giving rise to carbonium ions from I, Fig. 1 suggests that, if an adequate supply of deuterium is available as D^+ ions, any or all of the 12 hydrogen atoms in the C_6 olefin may be replaced but simultaneously with isomerization to form II and III.

On catalysts which do not readily form carbonium ions no isomerization of I is likely to occur and the rate of exchange of the three vinyl hydrogen atoms will probably be much faster than the exchange of the nine atoms in the methyl groups. This has been demonstrated by Hightower and Hall (2) for the exchange of I with deuterium on activated alumina at 301 K. They found no isomerization and no products containing four or more deuterium atoms.

In this investigation, we have carried out

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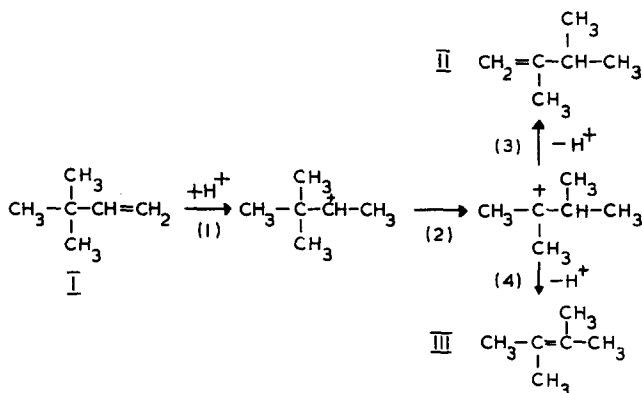


FIG. 1. The probable reaction scheme for the isomerization of 3,3-dimethylbut-1-ene (I) to 2,3-dimethylbut-1-ene (II) and 2,3-dimethylbut-2-ene (III).

some exploratory work on the reaction of I with deuterium or deuterium oxide on a series of oxide catalysts and examined the isotopic content of the combined C₆ olefins by mass spectrometry. In cases where products containing four or more deuterium atoms were observed, we have used gas chromatographic analysis in separate experiments, but under similar conditions, to confirm that isomerization of I to form II and III was occurring.

EXPERIMENTAL

The apparatus for the exchange reactions has been described by Kemball (3) and Kemball and McCosh (4). It consisted of a gas handling system with a reaction vessel (1.90 × 10⁻⁴ m³) connected to an A.E.I. MS 10 mass spectrometer by a fine capillary leak. Analyses of the isotopic content of the combined C₆ olefins were made using an ionizing beam of 18 V electrons. Isomerization was studied in a static system with a reaction vessel of the same size as for the exchange reactions. Samples from the gas phase above the catalyst were analysed on a 4 m glc column of hexan-2:5-dione on Chromosorb P at 273 K.

The catalyst samples and the pretreatment used in each case were identical to those reported for other catalytic studies. Details for the zeolites NaX, CaX (59% exchanged), CeX (36% exchanged) and NiX (40% exchanged) have been given by Cross, Kemball and Leach (5,6), for mag-

nesium oxide by Shannon, Kemball and Leach (7), and for silica-alumina (13% Al₂O₃) by McCosh and Kemball (8).

The olefins I, II and III were of purum grade from Fluka Ltd. and were all further purified and degassed before use by repeated trap-to-trap distillation. Deuterium and deuterium oxide were as used by Kemball and McCosh (4,9).

Fresh catalyst samples (0.1 g) were used in each experiment. For reactions of I with deuterium oxide, a pressure of 3.2 kN m⁻² of heavy water was admitted to the reaction vessel and condensed, and then a dose of olefin equivalent to a pressure of 0.53 kN m⁻² was added. The reaction vessel was allowed to warm up to room temperature and the furnace (preset at the desired reaction temperature) was raised around the vessel to start the reaction. For reactions of olefin with deuterium, again a 1:6 mixture was used but the olefin was condensed into the vessel and the deuterium expanded in to the required pressure from the gas handling line. The number of molecules of olefin in the reaction vessel was 2.5 × 10¹⁹ which corresponded to about one molecule per supercage with the zeolite catalysts.

Isomerization experiments were carried out with the same mixture of gases as used in the exchange runs.

RESULTS

The results from the exchange reactions were plotted according to the usual first

TABLE I
 EXCHANGE REACTIONS OF DIMETHYLBUTENES

No.	System ^a	Catalyst	Temperature (T/K)	k_0 ($k_0/\%$ min ⁻¹ 0.1 g ⁻¹)	M
1	I + D ₂ O	NaX	463	0.10	~10
2	I + D ₂ O	CeX	397	0.85	10.4
3	I + D ₂ O	CeX	423	1.74	10.4
4	I + D ₂ O	CaX	407	1.59	10.1
5	II + D ₂ O	CaX	369	~8	~0.8
6	III + D ₂ O	CaX	375	1.31	2.4
7	I + D ₂ O	NiX	406	1.57	10.2
8	I + D ₂ O	NiX	423	~6	~8
9	I + D ₂	NiX	383	0.44	0.97
10	I + D ₂ O	MgO	573	0.29	0.93
11	II + D ₂ O	MgO	567	0.16	1.02
12	III + D ₂ O	MgO	554	0.52	1.06
13	I + D ₂	MgO	393	~5	~0.7
14	I + D ₂ O	SiO ₂ /Al ₂ O ₃	345	0.16	9.8

^a I = 3,3-dimethylbut-1-ene, II = 2,3-dimethylbut-1-ene, III = 2,3-dimethylbut-2-ene.

order reversible equations, see Lake and Kemball (10), and the initial rates k_0 (% min⁻¹) and k_ϕ (D atoms entering 100 molecules min⁻¹) were obtained. The ratio of these rates $M = k_\phi/k_0$ gave the mean number of deuterium atoms acquired by each olefin molecule in the initial stages of the reaction. Table 1 shows values of k_0 and M for most of the exchange experiments. Any experiments showing unusual features are described below.

A typical result from the gas chromatographic study of the isomerization of I is

given in Fig. 2 which shows that the relative ratio of the amounts of III to II, R , did not change appreciably with time. Table 2 gives values for k_I (% min⁻¹), the initial rate of isomerization obtained from plotting according to a reversible first order equation, and also R for most catalysts.

Zeolites—NaX, CeX, CaX and NiX

The character of the reaction between I and deuterium oxide was the same on all four zeolites. Very highly exchanged products with an average of 10 D atoms per

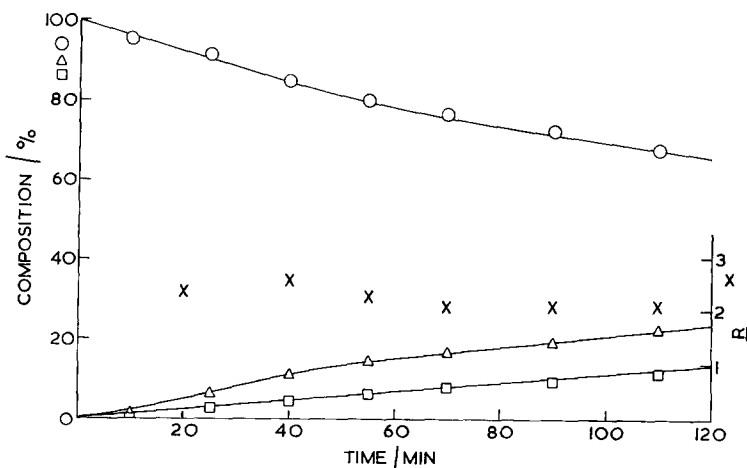


FIG. 2. The isomerization of 3,3-dimethylbut-1-ene over CaX at 403 K in the presence of deuterium oxide: O, I; □, II; △, III; X, ratio R of III:II.

TABLE 2
ISOMERIZATION OF 3,3-DIMETHYLBUT-1-ENE
IN THE PRESENCE OF D₂O

No.	Catalyst	Temperature (T/K)	k_t ($k_t/\%$ $\text{min}^{-1} 0.1$ g^{-1})	R
21	NaX	498	0.58	~1.5
22	CeX	395	0.16	2.7
23	CaX	403	0.35	2.2
24	NiX	403	0.06	2.8
25	MgO	575	0.03	1.2

C₆ molecule were formed initially in each case. These results implied that isomerization was occurring and this was confirmed by the data reported in Table 2. Rates of isomerization were within a factor of about four of the rates of exchange at the same temperature except for NiX on which isomerization was relatively slow.

The activity of the zeolites showed an expected variation with the charge on the cations. The sieves with divalent ions, CaX and NiX, had similar activities but NaX was much less active. The CeX zeolite, although only 36% exchanged, had comparable activity with the 59% exchanged CaX.

A typical initial product distribution, that for run 4, determined from plots of the amounts of the various isotopic olefins against time is shown in Table 3 which also includes a calculated binomial distribution with the same average deuterium content as the experimental distribution. While the two distributions are similar they are not in close agreement. On the other hand, the *final* distribution of products in fast exchange runs showed excellent agreement with the corresponding binomial distribu-

tion, as shown in Table 4 for run 8. Furthermore, the average deuterium content of the olefins was generally within 10% of the value expected for a random distribution of H and D atoms between the "olefin" and the "water."

Runs 4, 5 and 6 in Table 1 show that both II and III exchanged with heavy water at lower temperatures than I on CaX, and also that the character of the exchange was different. Both II and III showed much less tendency to undergo multiple exchange.

Very significant differences were observed between CaX and NiX as catalysts for the reaction of I with deuterium. With CaX no appreciable entry of D atoms into the olefin occurred below 561 K at which temperature C₆ olefin was observed to disappear and the mass spectra indicated that higher molecular weight compounds were being formed. With NiX, run 9 on Table 1, a stepwise exchange of I with D₂ occurred at least as rapidly as the multiple exchange with D₂O. The successive replacement of H by D at 383 K did not stop after three atoms had been exchanged and this indicated that isomerization was occurring. A subsidiary experiment confirmed that isomerization of I was rapid on NiX in the presence of D₂ at a somewhat higher temperature of 431 K.

MgO

Magnesium oxide was a poor catalyst for the exchange of all three olefins with heavy water and for the isomerization of I in the presence of D₂O but all these reactions did take place slowly at ca. 570 K. Exchange with each olefin was stepwise and with I, the successive replacement of H by D did

TABLE 3
INITIAL PRODUCTS FROM RUN 4 (TABLE 1)

	d_6	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}	M_D^a
Expt	2	3	5	8	27	29	26	10.4
Binomial ^b	0.2	1.1	4.5	13.5	27.5	34.0	19.2	10.4

^a M_D is the average number of deuterium atoms in the products. For initial products it should be equivalent to the value of M (10.1) determined from the rates k_p and k_0 .

^b The binomial distribution is calculated on the assumption that all 12 atoms in the olefin are exchangeable and that the average composition is 10.4 D and 1.6 H.

TABLE 4
 DISTRIBUTION OF PRODUCTS FROM RUN 8 (TABLE 1) AFTER 120 MINUTES

	d_0	d_1	d_2	d_3	d_4	d_5	d_6
Expt	0.4	1.1	3.3	5.1	16.0	22.0	21.8
Binomial	0.1	0.5	2.6	7.7	15.3	21.5	22.0
	d_7	d_8	d_9	d_{10}	d_{11}	d_{12}	M_D
Expt	16.3	9.4	3.5	1.0	0.2	0.1	5.61
Binomial	16.5	9.1	3.5	0.9	0.1	0.0	5.61

not stop after three atoms had reacted. The compound III appeared to react slightly faster than I or II.

In contrast to the results with deuterium oxide, the exchange of I with deuterium occurred rapidly at moderate temperatures, run 13 in Table 1. A fast experiment at 423 K is shown in Fig. 3. The exchange was

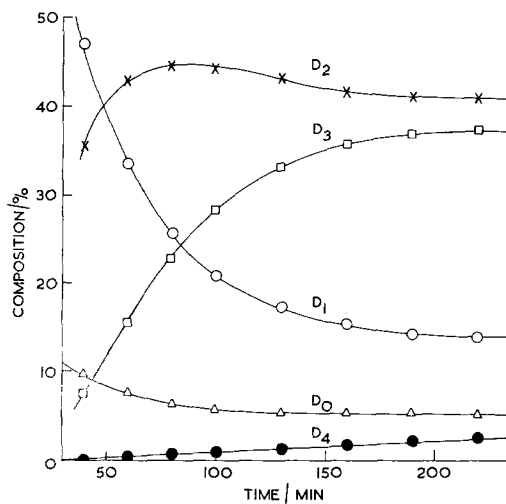


FIG. 3. The exchange of 3,3-dimethylbut-1-ene with deuterium on MgO at 423 K: Δ , d_0 ; \circ , d_1 ; \times , d_2 ; \square , d_3 ; \bullet , d_4 .

stepwise, three atoms being replaced quickly but compounds with four or more D atoms appearing more slowly. Table 5 shows that a product distribution from this experiment agreed much more closely with a binomial distribution calculated for three exchangeable hydrogen atoms than for 12 such atoms.

Rates of exchange of the different groups of hydrogen atoms in this first experiment were estimated by methods similar to those described by Harper, Siegel and Kemball (11). To obtain the rate of exchange of the fourth and subsequent hydrogen atoms ϕ_B was defined by:

$$\phi_B = \sum_{i=4}^{i=12} (i-3)d_i / \sum_{i=3}^{i=12} d_i,$$

where d_i is the percentage of olefin containing i deuterium atoms at time t . A plot of ϕ_B against time was linear as shown in Fig. 4a and gave a value of 0.030 atoms per 100 molecules min^{-1} for k_{ϕ_B} . To obtain the rate of exchange of the first three hydrogen atoms, ϕ_A was defined by:

$$\phi_A = d_1 + 2d_2 + 3 \sum_{i=3}^{i=12} d_i$$

 TABLE 5
 PRODUCTS DURING RUN 13 (TABLE 1)

	d_0	d_1	d_2	d_3	d_4	d_5	M_D
Expt	6.4	25.6	44.5	22.9	0.6	0.0	1.857
Binomial ^a	13.3	29.2	29.4	18.0	7.4	2.2 etc.	1.857
Binomial ^b	5.6	26.9	43.8	23.7	—	—	1.857

^a Assuming 12 exchangeable atoms.

^b Assuming only three exchangeable atoms.

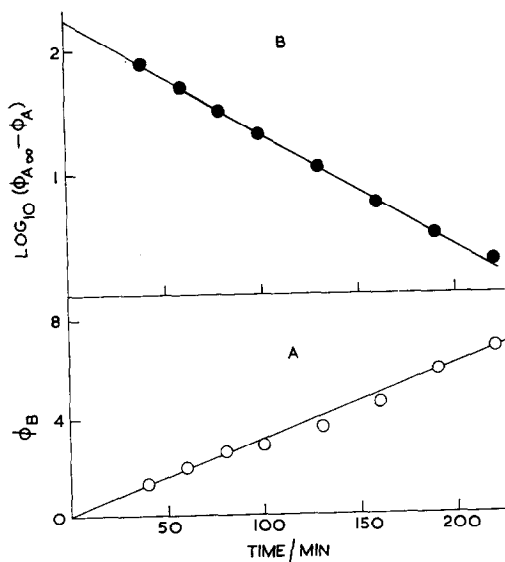


FIG. 4. Kinetic plots for results from Fig. 3: (a) ϕ_B representing exchange of the 4th and subsequent hydrogen atoms; (b) $\log_{10}(\phi_{A_\infty} - \phi_A)$ for the exchange of the first three atoms.

A plot was then made according to the first order reversible equation:

$$\log_{10}(\phi_{A_\infty} - \phi_A) = -k_{\phi_A}t/2.303\phi_{A_\infty} + \log_{10}\phi_{A_\infty}$$

and a straight line was obtained using $\phi_{A_\infty} = 217$ as shown in Fig. 4b. The derived value of k_{ϕ_A} was 4.7 D atoms per 100 molecules min^{-1} , i.e., about 150 times faster than the rate for the fourth and subsequent hydrogen atoms.

In contrast to the slow isomerization of I on MgO at high temperatures, a very rapid interconversion of II and III took place on this catalyst at room temperature in the presence of deuterium oxide. A preliminary exchange experiment of II with D_2 on MgO at room temperature indicated a very rapid reaction with stepwise character.

SiO_2/Al_2O_3

The character of the reaction between I and deuterium oxide on SiO_2/Al_2O_3 was identical with that found for the zeolites but the reaction occurred at an appreciable rate at the comparatively low temperature of 345 K.

An attempt to follow the reaction of I with deuterium was unsuccessful. Traces of exchanged olefins were observed at 293 K but the main process involved the disappearance of the C_6 olefins with the formation of higher molecular weight products, i.e., results similar to those found for CaX at 561 K.

DISCUSSION

Although the technique used in the present work gave the isotopic composition for the combined C_6 olefins and not the values for the separate isomers a number of useful conclusions emerge. Two main factors appear to have a critical influence on the character of the exchange reactions of I on oxide catalysts—the ability of the catalyst to form carbonium ions and the nature of the source of the heavy hydrogen, i.e., D_2 or D_2O .

Reactions with D_2O

On the catalysts expected to form carbonium ions, i.e., the four zeolites and silica-alumina, extensive exchange of I occurred accompanied by isomerization. On magnesium oxide which is not likely to form carbonium ions readily, these reactions were catalyzed only slowly even at high temperatures.

Some of the features about the isomerization of I are worthy of note. The reaction was limited to the products shown in Fig. 1 and no evidence was obtained for the formation of the methylpentenes as observed by Pines and Haag (1). The production of these compounds may require higher temperatures, more strongly acid sites or, alternatively, their formation may be inhibited by the excess water used in our experiments. The equilibrium ratios of the two olefins III and II are 2.8, 1.7 and 1.2 at temperatures of 400, 500 and 600 K, respectively (12). The results for R in Table 2 show that the isomerization of I gave the two products in ratios close to the equilibrium values.

The ability of magnesium oxide to bring about the rapid interconversion of II and

III at room temperature contrasts with the low activity of this catalyst for the isomerization of I at 575 K. This marked difference was expected. I will only isomerize if carbonium ions are formed so magnesium oxide is a poor catalyst. II and III can be interconverted by mechanisms involving either radicals or carbanions in addition to the scheme in Fig. 1 which involves tertiary carbonium ions. Magnesium oxide has been shown to be a very effective catalyst for the isomerization of the *n*-butenes and the evidence suggested carbanion intermediates (7). Thus, the rapid interconversion of II and III on this catalyst may well occur through an allyl carbanion formed by loss of H^+ from either olefin.

An unusual feature of the exchange experiments of I with heavy water on the catalysts forming carbonium ions was the exceptionally high amounts of multiple exchange. It was thought that this might be due to the zeolite structure retaining the C_6 olefins in the supercages for sufficiently long to enable the multiple exchange to occur but the evidence suggests that other factors are important as well. Firstly, the same extensive multiple exchange was observed on silica-alumina and secondly, the other C_6 olefins (II and III) underwent exchange in a normal manner involving mainly stepwise replacement of H by D over CaX. A comparison of runs 4, 5 and 6 in Table 1 shows that II and III were also more readily exchanged than I and this is to be expected in terms of Fig. 1. The exchange of either II or III should be able to take place readily through the reversible formation of a tertiary carbonium ion on the zeolite catalysts provided deuterium is available as a D^+ species, and this exchange should be accompanied by interconversion of II and III. The facile exchange of II and III may contribute to the multiple character of the exchange reaction observed with I as reactant. At the somewhat higher temperatures required to form the secondary carbonium ion from I the reactions represented by 3 and 4 in Fig. 1 should be occurring rapidly in both directions. Consequently several interconversions between II and III with loss of H

and gain of D at each stage may then occur before either II or III leave the catalyst.

Reactions with D_2

The differences between the reactions of I with deuterium and with deuterium oxide are marked but they depend on the catalyst.

Virtually no exchange was observed with deuterium on either CaX or on silica-alumina before the C_6 olefin was converted to other products. Both these catalysts are known to be relatively inefficient for the exchange of H_2 and D_2 (4,8), and so the absence of exchange was not surprising. It seems likely that for these two catalysts, and probably also for NaX and CeX, the presence of heavy water plays a dual role. It provides an ample supply of deuterium for acquisition by the olefin as a D^+ ion and it inhibits the type of reaction leading to the disappearance of the C_6 olefin.

The choice of D_2 as opposed to D_2O made relatively little difference with NiX which is known to be a good catalyst for H_2/D_2 exchange (4). The exchange of I was slightly faster with D_2 than with D_2O , and it is probable that this was also the case for isomerization but the evidence is not complete. The main difference was that exchange with D_2 was stepwise and exchange with D_2O was multiple. Probably D_2 was less effective than D_2O in NiX in providing a sufficient supply of D^+ to sustain the multiple character of the exchange process.

The really striking differences between D_2 and D_2O were found with magnesium oxide, which is known to have activity for H_2/D_2 exchange at moderate temperatures (13). With D_2 , a rapid exchange of three hydrogen atoms in I occurred at temperatures 200K lower than the slow reaction observed with D_2O in magnesium oxide. The fast process was accompanied by a very much slower exchange of the other hydrogen atoms. The fast process almost certainly involves adsorbed intermediates which are not carbonium ions. The very slow process could be due to reversible dissociation of the C-H bonds in the methyl groups attached to the quaternary carbon

atom of I or to isomerization of I to II and III via carbonium ions. Further work is needed to decide between these possibilities. Why is the rapid exchange of the three hydrogen atoms of I not observed with D_2O ? Either it is a poison for this kind of exchange or it is not capable of providing the appropriate kind of D species for reaction with the adsorbed olefin.

Our results for the exchange of I with D_2 on magnesium oxide are not unlike those found by Hightower and Hall (2) for the same reaction on alumina at 301 K but with two minor differences. Firstly, our data showed no marked difference in rate of exchange between the first two hydrogen atoms and the third. Secondly, we observed a slow exchange beyond $-d_3$ which was not found with alumina.

It is possible that results at lower temperatures on magnesium oxide would be more similar to those that have been reported for alumina.

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