

Alcohol dehydration. Isotope studies of the conversion of 3-pentanol

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Abstract

Three deuterated 3-pentanol and undeuterated 3-pentanol were converted using an alumina catalyst. Similar values of the kinetic isotope effect (KIE; k_H/k_D) were obtained for the rate of conversion of 3-pentanol and the rate of H(D) removal in forming the alkene products. The data support a catalytic dehydration mechanism that involves a concerted removal of H(D) from the $-\text{CH}_2-x\text{D}_x$ group and OH (or O) from the carbinol carbon and with a timing such that the transition state resembles neither a carbonion-like nor carbenium-like species. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The name of Tamaru spans catalysis work during essentially all of the 20th century. Shortly after the turn of the century, S. Tamaru studied with Haber for six years and participated in pioneering research on the synthesis of ammonia [1]. By 1960, Kenzi Tamaru was beginning his pioneering studies on dynamic heterogeneous catalysis [2–5], and his studies of ammonia synthesis and decomposition played a dominant role in this work. Another reaction that received K. Tamaru's special attention was the dehydrogenation and/or dehydration of formic acid. His in-situ infrared and deuterium isotopic studies were an important features of developing much knowledge of the mechanism of this reaction [5]. The present study emphasizes the

use of one of the techniques employed by Tamaru, deuterium tracer studies, in studying the mechanism for the catalytic dehydration of alcohol.

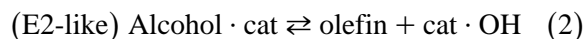
It has been shown by many workers that the hydrogen atom of the hydroxyl group of an alcohol can be readily exchanged with deuterium present in water. Furthermore, at temperatures below those where alumina catalyzes alcohol dehydration, it has been shown by infrared studies that the alcohol is adsorbed through rupture of the O–H bond of the hydroxyl group, and that an alkoxide species is formed by the reaction with the alumina surface (e.g., Ref. [6]). This implies that the first step of the interaction of an alcohol with the surface of a metal oxide catalyst involves a reversible reaction that is at, or near, its equilibrium position:



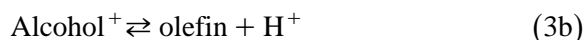
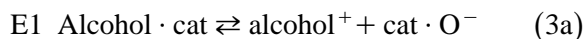
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The fact that alcohol dehydration, at least at pressures approaching 1 atm, is a zero order reaction implies that the surface is saturated with the alcohol–catalyst species denoted as $A \cdot \text{Cat}$ in Eq. (1) [7,8].

Thus, alcohol dehydration requires the surface complex, alcohol \cdot cat, be converted in either a concerted reaction (E2-like) or in a two-step reaction (E1):



or



The dehydration of alcohols have been shown to exhibit a kinetic isotope effect. For the E1 mechanism, a kinetic isotope effect requires that step 3b be rate-limiting since a C–D bond is not involved in reaction 3a. On the other hand, the concerted reaction must exhibit the same isotope effect for both the rate of alcohol conversion and the alkene formation step. These conclusions require that the adsorption–desorption steps be at, or very near, equilibrium; that is, the desorption of products is rapid compared to the rate-limiting step.

In order to study the mechanism, 3-pentanol- d_2 ($\text{CH}_3\text{CD}_2\text{CHOHCH}_2\text{CH}_3$), 3-pentanol- d_1 ($\text{CH}_3\text{CDHCHOHCH}_2\text{CH}_3$) and 3-pentanol- d_4 ($\text{CH}_3\text{CD}_2\text{CHOHCD}_2\text{CH}_3$) have been synthesized. If the adsorption step is the rate limiting step, the competitive conversion of labeled and unlabeled 3-pentanol would not exhibit an isotope effect; the relative amounts of the two reactants that are converted would be in the same ratio as they are present in the gas phase. If the E1 mechanism applies and step 3a is rate-limiting, there would be no kinetic isotope effect in the amounts of the labeled and unlabeled 3-pentanol that is converted. However, there would be an isotope effect in the formation of the alkene products from the carbenium ion produced from ($\text{CH}_3\text{CD}_2\text{CHOHCH}_2\text{CH}_3$) with the pathway leading to the production of $\text{CH}_3\text{CD}_2\text{CH}=\text{CHCH}_3$ occurring more rapidly

than the one leading to $\text{CH}_3\text{CH}_2\text{CH}=\text{CDCH}_3$. Results obtained for the conversion of labeled alcohols with carbon tetrachloride and triphenyl phosphine are consistent with a mechanism that involves steps 3a and 3b [9]. If the reaction occurs by an E2-like mechanism, then there will be a common kinetic isotope effect for the conversion of the alcohol and the formation of the alkenes.

2. Experimental

3-Pentanol and 3-pentanone were obtained from Aldrich Chemical and were 99% pure (gas chromatographic (GC) analysis). Ethanol- d_2 and D_2O were purchased from CIL with 95 and 98% isotopic purity, respectively. These reagents were used without further purification.

2.1. 3-Pentanol- d_2

Concentrated H_2SO_4 (8 ml) was added dropwise to a mixture of 31 ml HBr (48%) and 10 g ethanol-1,1- d_2 . When the addition was completed, the mixture was distilled to produce 16.7 g ethyl bromide- d_2 (yield = 82.7% of theory). One crystal of iodine was added to a mixture of 70 ml anhydrous diethyl ether and 4.9 g of Mg turnings contained in a round bottomed flask fitted with a reflux condenser. A few drops of ethyl bromide- d_2 solution (15 g in 20 ml anhydrous diethyl ether) were added to the Mg–ether mixture. After the reaction started (about 5 min) the rest of the ethyl bromide- d_2 solution was added dropwise during about 40 min with continuous stirring and the stirring was continued 30 more min. Freshly distilled propanal (7.0 g; 48–50°C fraction) in 30 ml diethyl ether was added dropwise to the Grignard reagent. The mixture was stirred during the 40-min addition period. The reaction mixture was then cooled in an ice-bath, 10 ml of water was added and then the mixture was acidified by adding 3 M HCl to produce a final pH of 2–3. The organic layer

was separated and the aqueous layer extracted with ether (3 times, 100 ml total). The combined organic fraction was washed with water (3 times, 100 ml total) and dried over anhydrous magnesium sulfate. The organic layer was distilled to remove ether and then the alcohol fraction was collected (5.0 g). IR: 2102, 2182 and 3366 cm^{-1} bands. ^1H NMR: (chemical shift from tetramethyl silane) 0.95 (triplet and singlet of CH_3); 1.3–1.7 (multiplet of CH_2); 1.8 (singlet, OH) and 3.45 (triplet, from CH).

2.2. 3-Pentanone- d_4

A saturated $\text{D}_2\text{O}/\text{Na}_2\text{CO}_3$ solution was prepared from 32 g Na_2CO_3 and 60 ml D_2O and then 25 g 3-pentanone was added. The mixture was refluxed for 48 h., cooled to room temperature and the 3-pentanone- d_x was separated from the aqueous layer. After one exchange, GC–MS indicated that 72% of the H present in CH_2 groups was exchanged with deuterium. The exchange procedure was repeated 3 more times and about 18.5 g 3-pentanone- d_4 was obtained following the final exchange (yield, 74%). GC–MS analysis indicated that at least 98% of the CH_2 hydrogens had been exchanged with deuterium.

2.3. 3-Pentanol- d_4

3-Pentanone- d_4 (18 g) was dissolved in 30 ml diethyl ether and then 100 ml of 1 M solution of LiAlH_4 in diethyl ether was added dropwise with reflux. After completing the addition, the mixture was refluxed for 2 h, cooled to room temperature and then to about 0°C in an ice bath, and dilute (5%) aqueous sodium carbonate added dropwise to react with unconverted LiAlH_4 . The organic layer was collected and dried over magnesium sulfate. The organic layer was distilled to remove the diethyl ether and then the 3-pentanol- d_4 (11 g; yield = 61%). The ^2H NMR and ^1H NMR data indicate that the alcohol contained $100 \pm 2.0\%$ $-\text{CD}_2-$.

2.4. 3-Pentanol- d_1

This alcohol was synthesized using the procedure for 3-pentanol- d_2 except that a diethyl ether solution of CH_3CDO was added to a propyl magnesium bromide Grignard reagent.

2.5. Catalyst

The alumina was prepared by the hydrolysis of aluminum isopropoxide and has been described previously [10]. Prior to use, the alumina was activated at 500°C overnight in flowing hydrogen.

2.6. Procedure

The conversion was effected in a plug flow reactor fitted with a thermowell extending to the center of the catalyst bed. About 20–30 ml of the reactor volume above the catalyst bed contained Pyrex glass beads to serve as a preheater section. A 10–15 mol% solution of deuterated or undeuterated 3-pentanol in 2-octanol was used as reactant. In the case of 3-pentanol- d_4 , however, an equal molar mixture of 3-pentanol- d_4 and 3-pentanol- d_0 was used as the reactant mixture. The conversion was effected at 190°C at atmospheric pressure without diluent. The liquid was added at a constant rate using a syringe pump. The liquid products were collected in a trap maintained at room temperature. For about 1-h period following the termination of pumping each reactant mixture, only helium was passed through the reactor to remove the vapors of the previous reaction mixture.

The percentage conversion was obtained from GC analysis using a DB-5 column. The reaction products were analyzed by GC–MS at 10 eV as well as by ^1H NMR and ^2H NMR. The amount of H and D can be calculated from the combined ^1H NMR and ^2H NMR data obtained when using methyl formate- d_1 as an internal standard.

3. Results and discussion

The isomerization of butene and pentene products may occur when butanol or pentanol is converted at pressures up to about 1 atm [10,11]. This isomerization reaction may redistribute the deuterium in the alkene products and obscure mechanistic details. It has been shown that 2-octanol is adsorbed strongly enough to essentially eliminate the alkene isomerization reaction at conversion levels of about 50% [10,11]. Thus, these studies were conducted, unless otherwise indicated, using a reaction mixture that consisted of about 10–15 mol% 3-pentanol and 85–90 mol% 2-octanol with a total alcohol pressure of 1 atm. In addition to limiting alkene isomerization, this experimental technique reduces the amount of the labeled alcohol needed for the study.

In order to determine the relative dehydration rates of 3-pentanol- d_0 , 3-pentanol- d_1 , 3-pentanol- d_2 and 3-pentanol- d_4 , 10 mol% of one of the 3-pentanols in 2-octanol was used as the reactant mixture. When the conversion of these mixtures is effected under the same conditions, the ratio of the conversion of 3-pentanol to 2-octanol can be utilized as a basis for obtaining the relative conversion rates of the 3-pentanols. These results are presented in Tables 1–4. The ratios of conversion were lower when deuterium was substituted for hydrogen and the conversion

data were essentially the same following the conversion of the deuterated pentanol as before the deuterated 3-pentanols were run (Table 1). The ratio for the conversion of 3-pentanol- d_0 /2-octanol is 0.79 ± 0.03 (0.72 ± 0.04 following conversion of the deuterated 3-pentanols) while these ratios are 0.66 ± 0.04 and 0.63 ± 0.4 for 3-pentanol- d_1 /2-octanol and 3-pentanol- d_2 /2-octanol, respectively. Using the relative conversion rates for the 3-pentanols, values of the kinetic isotope effect, k_H/k_D , can be calculated as 1.2 ± 0.1 for 3-pentanol- d_1 and 1.3 ± 0.1 for 3-pentanol- d_2 .

The products from the conversion of 3-pentanol are *cis*- and *trans*-2-pentene with little 1-pentene being formed (> 1%). As shown in Tables 4 and 5, the conversions ranged from 15 to 52%. The ratio of *cis*-/*trans*-2-pentene is about 2. Using the rate of formation of deuterium labeled and unlabeled *cis*- and *trans*-2-pentene, we calculate a value of k_H/k_D of 1.7 ± 0.2 . These values are slightly higher than were calculated when k_H/k_D was calculated from the conversion rates of the pentanols relative to 2-octanol.

The kinetic isotope effect was also obtained from data generated during the competitive conversion of an equal molar mixture of 3-pentanol- d_0 and 3-pentanol- d_4 . In separate experiments it has been shown that there is no detectable exchange between unconverted 3-penta-

Table 1

The conversion of a mixture of 3-pentanol- d_0 (about 10 mol%) and 2-octanol with an alumina catalyst at 190°C

Time (min)	3-Pentanol conversion (mol%)	2-Octanol conversion (mol%)	Conversion C ₅ ol/ conversion C ₈ ol
419	26.2	34.6	0.757
461	25.0	32.9	0.760
521	36.0	43.1	0.835
547	35.2	43.7	0.806
569	34.5	44.0	0.784
Average			0.788 ± 0.033
1155 ^a	32.9	47.5	0.692
1176	31.4	45.5	0.690
1195	35.2	45.0	0.783
1215	33.1	45.8	0.724
Average ^a			0.722 ± 0.043

^aData following return to same conditions following the conversion of deuterated 3-pentanols with 2-octanol.

Table 2

The conversion of a mixture of 3-pentanol- d_1 (about 10 mol%) and 2-octanol with an alumina catalyst at 190°C

Time (min)	3-Pentanol- d_1 conversion (mol%)	2-Octanol conversion (mol%)	3-C ₅ ol/2-C ₈ ol	k_H/k_D
711	36.0	53.1	0.677	1.16
728	31.8	45.2	0.704	1.12
741	28.9	46.6	0.621	1.27
770	29.2	44.8	0.651	1.21
814	30.8	45.5	0.676	1.17
840	28.9	44.0	0.656	1.20
Average			0.664 ± 0.028	1.2

Table 3

The conversion of a mixture of 3-pentanol- d_2 (about 10 mol%) and 2-octanol with an alumina catalyst at 190°C

Time (min)	3-Pentanol- d_2 conversion (mol%)	2-Octanol conversion (mol%)	3-Pentanol- d_2 /2-octanol	k_H/k_D
962	15.0	23.3	0.644	1.22
973	28.8	49.4	0.582	1.35
987	31.3	51.9	0.603	1.31
999	32.8	48.1	0.682	1.16
Average			0.628 ± 0.044	1.30 ± 0.1

nol- d_0 and D₂O; thus, exchange will not impact the relative rates of conversion of the alcohols. Unfortunately, the GC columns we utilized were

unable to separate 3-pentanol- d_0 and 3-pentanol- d_4 sufficiently for a reliable measure of the conversion of the two alcohols even though

Table 4

The conversion of a mixture of 3-pentanol- d_1 (about 10 mole%) and 2-octanol with an alumina catalyst at 190°C

Time on stream (min)	552	566	576	962	973	987	999
Pump rate (ml/h)	9.7	9.7	9.7	2.5	2.5	2.5	2.5
Catalyst amount (g)	1.5	1.5	1.5	0.5	0.5	0.5	0.5
Pentanol conversion (%)	51.8	43.3	32.7	15.0	29.0	31.3	32.8
<i>t</i> -2-Pentene (%)	31	31	26	32	30	27	24
k_H/k_D , <i>trans</i>	1.61	1.62	1.45	1.67	1.88	1.97	1.54
<i>c</i> -2-Pentene (%)	69	69	74	68	70	73	76
k_H/k_D , <i>cis</i>	1.97	1.48	1.64	1.76	1.55	1.51	1.66
k_H/k_D , GC-MS	1.91	1.52	1.64	1.73	1.65	1.63	1.97
k_H/k_D , NMR	1.68	1.69	1.62	2.63	1.42	1.97	1.93

Table 5

Isotope selectivity for the dehydration of an equal molar mixture of 3-pentanol- d_0 and 3-pentanol- d_4 with alumina (0.9 g; pump rate = 2.5 ml/h) at 190°C

Time (min)	Conversion (%)	<i>t</i> -2-Pentene (%)	k_H/k_D	<i>c</i> -2-Pentene (%)	k_H/k_D
60	7.42	36.3	2.77	63.7	2.11
85	7.55	29.1	2.86	71.0	2.42
110	7.34	25.9	2.17	74.1	2.05
140	7.50	25.0	2.26	75.0	2.19
Average			2.5 ± 0.4		2.2 ± 0.2

3-pentanol- d_0 and 3-pentanol- d_{10} could be analyzed with nearly baseline separation with the column used. The data in Table 5 show a kinetic isotope effect of 2.5 ± 0.4 for the formation of *trans*-2-pentene and 2.2 ± 0.2 for *cis*-2-pentene formation. These results are reasonably consistent with the value of 1.7 calculated based upon the k_H/k_D values obtained from the conversion of 3-pentanol- d_2 .

The results obtained during this study show that using 10 eV GC-MS provides an accurate measure of the relative abundance of the molecular ions of the deuterated and undeuterated alkenes. Furthermore, the results obtained from ^1H NMR and ^2H NMR, using methyl formate- d_1 as an internal standard, provides a reliable measure of the H/D content and permits the calculation of reliable k_H/k_D values.

The present data show that similar kinetic isotope effects, k_H/k_D , are obtained when these values are calculated from alcohol conversion and from alkene formation data. Thus, the same rate limiting step is involved in both the conversion of the alcohol and in determining the alkene formation. Thus, the dehydration of an alcohol with an alumina catalyst cannot involve an irreversible rate limiting step (reaction 1) nor an E1 (reactions 3a and 3b) mechanism. Thus, the current data are consistent with the dehydration occurring with an E2-like type of reaction. Thus, the loss of water occurs by the loss of H and OH (or O) from the alcohol molecule in a concerted sequence. Furthermore, the values of k_H/k_D are large so that the transition state cannot resemble the formation of either a carbanion or carbenium ion. If dehydration in-

involved the loss of a proton from $-\text{CH}_2-$ to a significant extent to produce a carbanion-like intermediate, we would expect that the kinetic isotope effect would be small. Likewise, if the loss of the OH (or O) occurred to a significant extent to produce a transition state that was carbenium-like, we would have expected no, or very small, kinetic isotope effect. Thus, by elimination of ionic or ionic-like transition states, we conclude that the alcohol dehydration catalyzed by alumina occurs through a concerted reaction mechanism with the loss of both H and OH (or O) occurring at, or nearly at, the same time. This conclusion is consistent with the concerted $\text{S}_{\text{N}}2$ reaction mechanism we obtained for the conversion of various alcohols to the corresponding ethers using an alumina catalyst [12].

References

- [1] K. Tamaru, in: J.R. Jennings (Ed.), *Catalytic Ammonia Synthesis*, Plenum, New York, 1991, pp. 1–18.
- [2] K. Tamaru, *Trans. Faraday Soc.* 57 (1961) 1410.
- [3] K. Tamaru, 3rd Int. Congr. Catalysis, Vol. 1, 1965, pp. 664–675.
- [4] K. Tamaru, *Acc. Chem. Res.* 21 (1988) 88–94.
- [5] K. Tamaru, *Dynamic Heterogeneous Catalysis*, Academic Press, New York, 1978.
- [6] R.G. Greenler, *J. Chem. Phys.* 37 (1962) 2041.
- [7] J.H. de Boer, R.B. Fahim, B.G. Linsen, W.J. Visseren, V.F.N.M. de Veesschauwer, *J. Catal.* 7 (1967) 163.
- [8] S. Chokkaram, B.H. Davis, *J. Mol. Catal. A: General* 118 (1997) 89.
- [9] H.A. Dabbagh, T.-S. Huang, B. Franzus, B.H. Davis, *Tetrahedron* 47 (1991) 949.
- [10] B.H. Davis, *J. Org. Chem.* 37 (1972) 1240.
- [11] B.H. Davis, *J. Catal.* 58 (1979) 493.
- [12] B. Shi, B.H. Davis, *J. Catal.* 157 (1995) .