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Hydrogenation and Hydrogenolysis. XIII.[1] The Hydrogenation of Ethyl 4-Methyl-1-cyclohexenyl Ether over Platinum Metal Catalysts

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The hydrogenation and hydrogenolysis of ethyl 4-methyl-1-cyclohexenyl ether (I) have been investigated with six unsupported platinum metals as catalysts at 25°C under atmospheric pressure of hydrogen. The hydrogenation of I in ethanol was accompanied by the formation of 4-methylcyclohexanone diethyl acetal (II), the extent of which depended on the nature of the catalyst metals. The ratio of the acetal formation to hydrogenation increased with respect to the catalyst metals in the sequence $\mathrm{Os}<\mathrm{Ru}<\mathrm{Ir}\ll\mathrm{Rh}<\mathrm{Pd}<\mathrm{Pt}$. The amount of the hydrogenolysis to give methylcyclohexane increased in the order $\mathrm{Pd}\cong\mathrm{Ru}\ll\mathrm{Os}<\mathrm{Rh}<\mathrm{Ir}\ll\mathrm{Pt}$ at an initial stage of the hydrogenation in ethanol. This order in hydrogenolysis was explained in terms of the action of the ionized hydrogen on the catalyst surface and the olefin isomerization activity of the catalyst metals. The stereochemistry of the hydrogenation of I was also studied and the results were interpreted on the basis of the proposed mechanism. I was also hydrogenated in *t*-butyl alcohol and isopropyl ether as solvents and, except in a few cases, the proportion of hydrogenolysis decreased with solvent in the order ethanol > *t*-butyl alcohol > isopropyl ether. The stereoselectivity in ether formation did not differ much among the solvents except over palladium.

Detailed studies on the catalytic hydrogenation of an enol ether seem rather few in the literature.[2-4] Howard and Brown, Jr.,[3] hydrogenated various acetals with supported platinum metal catalysts in the presence of hydrochloric acid and interpreted from the results that acetals hydrogenate *via* the corresponding enol ethers under the acidic conditions. Acke and Anteunis[4] hydrogenated some acetals and corresponding enol ethers, in relation to the study of the hydrogenation of cycloalkanones in acidic methanol, with Adams platinum as catalyst. They showed that in the presence of hydrochloric acid the products obtained on hydrogenation of acetals and enol ethers were almost the same and suggested that formation of these compounds would be responsible for the production of ethers and

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[1] Part XII: Y. Takagi, S. Ishii, and S. Nishimura, This Bulletin, **43**, 917 (1970).

[2] P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals," Academic Press Inc., New York (1967), p. 444.

[3] W. L. Howard and J. H. Brown, Jr., *J. Org. Chem.*, **26**, 1026 (1961).

[4] M. Acke and M. Anteunis, *Bull. Soc. Chim. Belges*, **74**, 41 (1965).

cycloalkanes on hydrogenation of the ketones in acidic methanol. It is also known from some examples in the literature that formation of alkanes on hydrogenation of enol ethers occurs over platinum, while this does not seem to occur with palladium.[2,4,5] However, no comparative study of the hydrogenation and hydrogenolysis of an enol ether over the six platinum metals seems to have ever been described and, especially, the nature of the rarer platinum metals in this reaction appears little known.

In this study, the catalytic hydrogenation and hydrogenolysis of ethyl 4-methyl-1-cyclohexenyl ether (I) over six unsupported platinum metals have been investigated in ethanol, *t*-butyl alcohol and isopropyl ether as solvents at 25°C and the atmospheric pressure of hydrogen. The properties of the six platinum metals have been compared mainly with respect to their activities for acetal formation in ethanol, their tendencies towards hydrogenolysis as well as their stereoselectivities in the formation of saturated ether. 4-Methylcyclohexanone diethyl acetal (II) has also been subjected to hydrogenation for comparison. We have been interested in the hydrogenation of I, because it is an important intermediate in the catalytic hydrogenation of ethyl *p*-tolyl ether, the results of which will be described in a forthcoming paper.[6]

Experimental

Materials. 4-Methylcyclohexanone Diethyl Acetal (II) was prepared by passing dry hydrogen chloride into a mixture of 4-methylcyclohexanone and ethyl orthoformate in absolute ethanol. Bp 96°C/21 mmHg; n_D^{20} 1.4347 (lit,[7] Bp 76—78°C/15 mmHg; n_D^{20} 1.4350).

Mthyl 4-Methyl-1-cyclohexenyl Ether (I) was prepared by heating II with 0.1% anhydrous *p*-toluenesulfonic acid and distilling off ethanol under the pressure of about 100 mmHg.[7] The residue was then distilled fractionally under reduced pressure. Bp 76—76.8°C/26 mmHg; n_D^{20} 1.4590 (lit,[7] Bp 58—60°C/15 mmHg; n_D^{20} 1.4537). The purity of this preparation was almost 100% as analyzed by gas chromatography. For hydrogenation, the enol ether of 97.3% purity, containing 2.3 mol% of II and 0.4 mol% of 4-methylcyclohexanone, was used throughout the experiments.

Solvents. S.S.G. ethanol of the Wako Pure Chemical Industries was further dehydrated by refluxing with sodium metal and diethyl phthalate.[8] *t*-Butyl alcohol and Isopropyl ether were dehydrated with sodium metal and then carefully distilled.

Catalysts. Unsupported ruthenium, rhodium and palladium catalysts were prepared by reducing the corresponding metal hydroxides in water with hydrogen under atmospheric pressure (at room temperature for rhodium and palladium and at 40—50°C for ruthenium). Unsupported iridium catalyst was prepared by reducing iridium hydroxide in water for 40 min at 90°C under the hydrogen pressure of 80 kg/cm^2. Unsupported osmium catalyst was obtained by reducing osmium tetroxide in water for 40 min at 90°C under the hydrogen pressure of 60 kg/cm^2. Unsupported platinum catalyst was prepared by the following procedure: Adams platinum oxide was reduced in water for 10 min at room temperature and atmospheric pressure. The upper layer of water was removed by decantation and a new portion of distilled water was added, and then the reduction was continued further for 5 min. By this procedure satisfactory removal of alkaline substances was effectuated for Adams platinum oxide. The catalyst metals thus prepared were all well washed with distilled water and then dried in vacuum over silica gel.

Hydrogenation. The substrate (0.2 m*l*) was hydrogenated with 10—40 mg of the catalyst metal in 10 m*l* of the solvent at 25°C and the atmospheric pressure of hydrogen in a glass bottle shaken at about 300—350 strokes per minute.

Analysis of Reaction Mixture. The reaction mixture was taken into a microsyringe through a silicone gum stopper during the course of hydrogenation and subjected to gas-chromatographic analysis as soon as possible. A column of 10% PEG 20M on Chromosorb W (column dimensions: 0.3 cm × 3.75 m; column temperature: programmed at 2°C/min for 36—100°C and 4°C/min for 100—160°C) was used except for the product in isopropyl ether, which was analyzed using a column consisting of PEG 6000 (2.25 m) and Apiezon L (1.5 m). The peaks of the *cis* and *trans* isomers of ethyl 4-methylcyclohexyl ether were assigned according to those of corresponding methyl ether, the *cis* isomer of which was reported by Hückel and Kurz to be of smaller retention time.[9] Correctness of this assignment was confirmed by ethylating a *cis*-rich 4-methylcyclohexanol with sodium amide and ethyl iodide in benzene and subjecting the resulting *cis*-rich ether to gas chromatography.

Results

Hydrogenation in Ethanol as the Solvent. Hydrogenation of I in ethanol is accompanied by the formation of the acetal II, the extent of which largely depends on the nature of the catalyst metal used. The rate of hydrogenation of the acetal is in most cases much lower than that of I and the product from the acetal often differs from that obtained from I. Accordingly, the composition of the reaction mixture at initial stages of hydrogenation is not always similar to that of subsequent hydrogenation. Table 1 shows only the composition of the reaction mixture at a final stage of hydrogenation. The varying composition of the reaction mixture during the course of hydrogenation is shown in Figs. 1—6. The results of the hydrogenation of the acetal II is given in Table 2.

1) Hydrogenation over Ruthenium Catalyst (Fig. 1): The acetal formation was slow over this metal, the maximum amount of it being 20.3 mol% at 79.4% hydrogenation. Accordingly, the greater part of I was hydrogenated without the accompanying formation of the acetal. Hydrogenolysis occurred only to the extent of 2.8 mol% and the selectivity for formation of ethyl 4-methylcyclohexyl ether (IV) was very high (95 mol%), until the acetal began to hydrogenate at about 70% hydrogenation. The rate of hydrogenation after this became very small and the main product of hydrogenation was 4-methylcyclohexanol (V), which

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[5] H. H. Inhoffen, G. Stoeck, G. Kölling, and U. Stoeck, *Ann. Chem.*, **568**, 52 (1950).

[6] Presented at the 25th Symposium on Catalysis, Fukuoka, October, 1969. See also *Shokubai*, **11**, 149P (1969).

[7] U. Schmidt and P. Grafen, *Ann. Chem.*, **656**, 97 (1962). The boiling point for II and the refractive index for I reported by these authors appear too low.

[8] L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., Heath and Company (1955), p. 285.

[9] W. Hückel and J. Kurz, *Ann. Chem.*, **645**, 194 (1961).

TABLE 1. HYDROGENATION OF ETHYL 4-METHYL-1-CYCLOHEXENYL ETHER (I) CATALYZED BY PLATINUM METALS

Catalyst mg	Solvent	Reac. time (hr)	Hydrogenation[a)] (%)	Composition of reac. mixture,[b)] mol%						*Cis*/*trans*		Proportion of hydrogenolysis[c)] (mol%)
				I	II	III	IV	V	VI	IV	V	
Ru, 25	EtOH	18.7	94.9	0.0	5.1	0.0	76.0	16.4	2.7	1.45	2.04	2.80
Rh, 25	EtOH	3.7	98.6	0.0	1.4	0.0	59.5	30.8	8.3	4.09	3.10	8.45
Pd, 25	EtOH	18.3	96.3	0.0	3.7	0.0	96.0	0.0	0.3	10.0	—	0.30
Os, 25	EtOH	3.8	88.9	2.2	8.9	0.0	67.4	0.8	20.8	2.11	1.03	23.3
Ir, 25	EtOH	15.3	88.3	0.0	11.7	0.0	75.3	2.2	10.9	2.87	1.02	12.3
Pt, 25	EtOH	2.9	100.0	0.0	0.0	0.0	46.3	14.6	39.1	2.56	1.01	39.1
Ru, 10	*t*-BuOH	1.9	97.3	0.0	2.7	0.0	96.2	0.74	0.45	1.85	0.90	0.46
Rh, 10	*t*-BuOH	2.2	99.6	0.13	0.17	0.11	96.3	2.3	1.1	3.13	1.19	1.1
Pd, 10	*t*-BuOH	1.9	92.5	0.0	0.61	6.8	91.8	0.0	0.73	4.54	—	0.79
Os, 15	*t*-BuOH	2.3	97.8	0.37	1.9	0.0	87.3	1.3	9.1	1.85	1.02	9.3
Ir, 10	*t*-BuOH	0.8	97.7	0.15	2.2	0.0	91.8	0.96	5.0	2.50	0.78	5.1
Pt, 10	*t*-BuOH	1.2	100.0	0.0	0.0	0.0	40.1	1.46	58.4	2.55	4.65	58.4
Ru, 10	*i*-Pr_2O	0.2	97.8	0.0	2.2	0.0	96.8	0.92	0.14	1.66	1.13	0.13
Rh, 10	*i*-Pr_2O	0.7	100.0	0.0	0.0	0.0	94.6	5.1	0.34	3.56	2.65	0.34
Pd, 10	*i*-Pr_2O	2.6	79.6	0.43	5.2	14.8	79.6	0.0	0.06	5.27	—	0.08
Os, 15	*i*-Pr_2O	2.9	97.8	0.0	1.9	0.3	94.8	1.42	1.7	1.84	1.04	1.7
Ir, 10	*i*-Pr_2O	2.1	98.2	0.0	1.8	0.0	92.9	0.88	4.4	2.40	1.04	4.45
Pt, 10	*i*-Pr_2O	1.6	91.6	1.1	4.1	3.2	63.9	0.0	27.8	2.83	—	30.3

a) "Hydrogenation" in this Table (and also in Table 2 and Figs. 1—6) is given by $\dfrac{100 \times \text{mol (IV+V+VI)}}{\text{mol } \sum(\text{I}-\text{VI})}$.

b) I: Ethyl 4-methyl-1-cyclohexenyl ether; II: 4-Methylcyclohexanone diethyl acetal; III: 4-Methylcyclohexanone; IV: Ethyl 4-methylcyclohexyl ether; V: 4-Methylcyclohexanol; VI: Methylcyclohexane.

c) Proportion of hydrogenolysis is given by $\dfrac{100 \times \text{mol (VI)}}{\text{mol (IV+V+VI)}}$.

probably resulted from hydrogenation of 4-methylcyclohexanone (III) formed by the hydrolysis of I or II. This type of hydrolysis was difficult to be avoided although hydrogenation was performed in carefully dehydrated ethanol under dry hydrogen. The alcohol formation was not observed during a much faster hydrogenation of I at earlier stages. The hydrogenation of II under the same conditions was also very slow and the predominant product was the alcohol IV, as expected from the results of the hydrogenation of I.

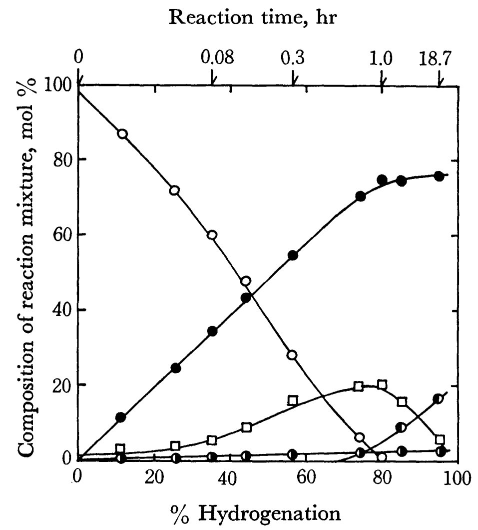


Fig. 1. The products in the hydrogenation of ethyl 4-methyl-1-cyclohexenyl ether (○) over ruthenium catalyst in ethanol at 25°C and 1 atm.
□ : 4-Methylcyclohexanone diethyl acetal
● : Ethyl 4-methylcyclohexyl ether
◐ : 4-Methylcyclohexanol
◑ : Methylcyclohexane

2) Hydrogenation over Rhodium Catalyst (Fig. 2): The acetal formation occurred to considerable extent during the hydrogenation of I with rhodium. The maximum amount of it formed was 44 mol% at 51% hydrogena-

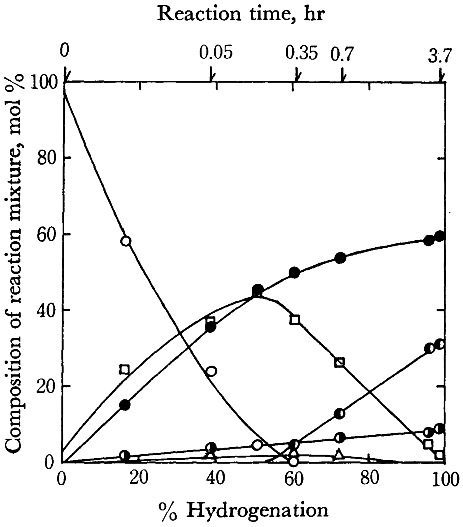


Fig. 2. The products formed in the hydrogenation of ethyl 4-methyl-1-cyclohexenyl ether over rhodium catalyst in ethanol at 25°C and 1 atm.
△: 4-Methylcyclohexanone. For other indications see Fig. 1.

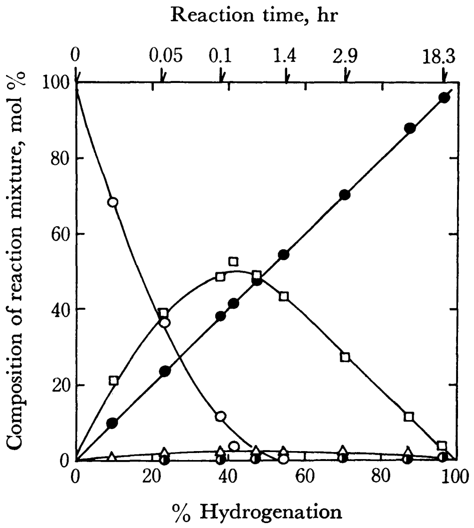


Fig. 3. The products formed in the hydrogenation of ethyl 4-methyl-1-cyclohexenyl ether over palladium catalyst in ethanol at 25°C and 1 atm. For indications see Figs. 1 and 2.

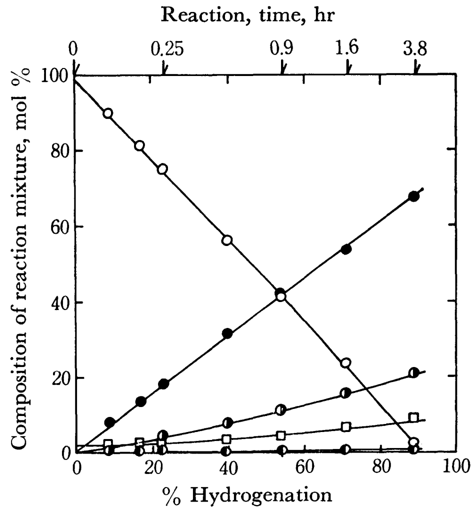


Fig. 4. The products formed in the hydrogenation of ethyl 4-methyl-1-cycohexenyl ether over osmium catalyst in ethanol at 25°C and 1 atm. For indications see Fig. 1.

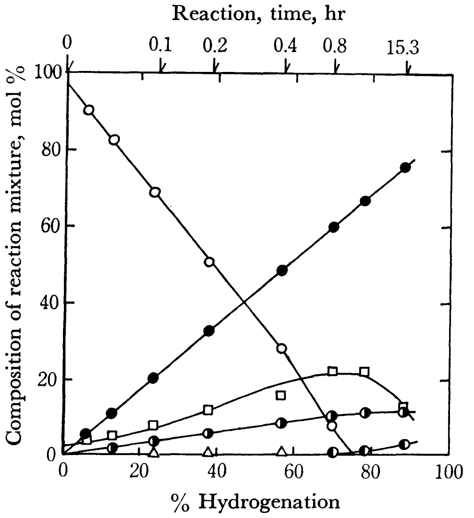


Fig. 5. The products formed in the hydrogenation of ethyl 4-methyl-1-cyclohexenyl ether over iridium catalyst in ethanol at 25°C and 1 atm. For indications see Figs. 1 and 2.

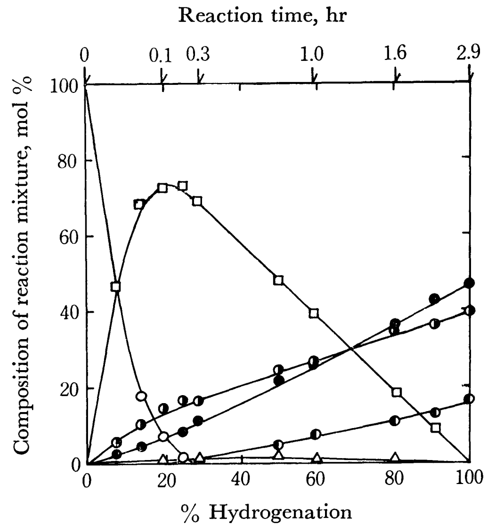


Fig. 6. The products formed in the hydrogenation of ethyl 4-methyl-1-cyclohexenyl ether over platinum catalyst in ethanol at 25°C and 1 atm. For indications see Figs. 1 and 2.

TABLE 2. HYDROGENATION OF 4-METHYLCYCLOHEXANONE DIETHYL ACETAL (II) WITH PLATINUM METAL CATALYSTS[a)]

Catalyst mg	Reac. time (hr)	Hydrogenation[b)] (%)	Composition of hydrogenation product, mol%			*cis/trans*	
			IV	V	VI	IV	V
Ru, 40	3.8	17.0	6.5	93.5	0.0	6.2	1.5
Rh, 40	3.4	99.8	10.1	88.3	1.7	4.7	2.5
Pd, 30	6.1	88.6	99.0	0.7	0.3	8.9	2.4
Os, 40	3.5	43.0	73.4	25.3	1.3	3.0	1.0
Ir, 40	4.3	6.2	100.0	0.0	0.0	8.1	—
Pt, 15	13.7	17.7	29.5	10.6	60.0	3.3	1.0

a) Acetal II (0.2 m*l*) was hydrogenated in 10 m*l* ethanol at 25°C under an atmospheric pressure of hydrogen.
b) See the footnote (a) in Table 1.

tion. Similarly as with ruthenium catalyst, hydrogenation became slow after about 50% hydrogenation at which the acetal formed began to be hydrogenated and formation of the alcohol increased suddenly. As shown in Table 2, the main product of the hydrogenation of II was also the alcohol IV. Hydrogenolysis occurred to a much greater extent than over ruthenium catalyst and it decreased during the hydrogenation from 10 mol% at the initial stage to 8.5 mol% at a final stage. Hydrogenolysis occurred to a much lesser extent in hydrogenation of II as seen in Table 2. The *cis/trans* ratio of ether IV formed from I was 4.1 which was rather great as compared with those by other platinum metals except palladium.

3) Hydrogenation over Palladium Catalyst (Fig. 3): Hydrogenation of I with palladium catalyst was accompanied by a rapid formation of II which amounted to 53 mol% at 41% hydrogenation. In contrast to the results with ruthenium and rhodium, the product of the hydrogenation of I did not differ much from that formed from the acetal II (see Table 2). Noteworthy features of the palladium-catalyzed hydrogenation are that hydrogenolysis occurred only to a slight extent (0.3 mol%) and the selectivity for the formation of ether IV was almost quantitative (99.7 mol%). The alcohol was not formed, although the ketone III was found in the reaction mixture in an amount of 2.3 mol% at the maximum in 41% hydrogenation. This is probably due to the fact that with palladium the ketone is hydrogenated to yield the ether IV as the predominant product as reported previously.[10] Another characteristic feature of the hydrogenation with palladium is a high stereospecificity in ether formation. The *cis/trans* ratio of the ether IV formed in ethanol was about 10 which was much greater than those obtained by other platinum metals.

4) Hydrogenation over Osmium Catalyst (Fig. 4).: Over this metal the acetal formation occurred to the least extent of the six metals investigated (8.9 mol% at 88.9% hydrogenation). The acetal formed appears not to be hydrogenated to any appreciable extent during hydrogenation as indicated by a linear increase of it with hydrogenation. Formation of the alcohol was also at a low level (0.86 mol%). Since the ketone III is readily hydrogenated to the alcohol V under these conditions, it seems that hydrolysis of I or II to give III did not occur or did only to a slight extent over osmium. Hydrogenolysis, however, occurred to considerable extent and the proportion of it increased from 8.2 mol% at an initial stage to 23 mol% at 88.9% hydrogenation.

5) Hydrogenation over Iridium Catalyst (Fig. 5): The acetal formation was not rapid, but somewhat faster than over osmium and ruthenium (24 mol% at 75.1% hydrogenation). Hydrogenolysis was 14.8% at the initial stage and decreased to about 12% towards the end of hydrogenation. The decrease in the proportion of hydrogenolysis may be due to the participation of the hydrogenation of II formed, since II was hydrogenolyzed to much lesser extent as seen in Table 2. A small amount of the alcohol V was produced after the hydrogenation of II began.

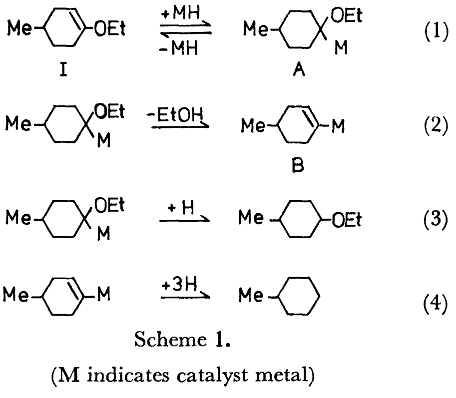
6) Hydrogenation over Platinum Catalyst (Fig. 6): The acetal was formed most rapidly over platinum. It amounted to 73 mol% at 24.8% hydrogenation. It is also noteworthy that hydrogenolysis occurred most extensively of the six platinum metals studied (71.6% at an initial stage and 39.1% at the end of hydrogenation). About 15 mol% of the alcohol V was formed along with 46 mol% of the ether. The ratio of the alcohol to the ether was almost the same with that obtained in hydrogenation of II (see Table 2). Thus the most part of the hydrogenation of I in ethanol is the same with that of II, but at the initial stage of hydrogenation a definitely more extensive hydrogenolysis was observed.

Hydrogenation in t-Butyl Alcohol and Isopropyl Ether as Solvents. The hydrogenation of I was performed in these solvents in order to see the behavior of I under the lack of formation of the acetal and also the effect of the solvent polarity. The results are given in Table 1. The acetal formation was observed only slightly except when hydrogenolysis occurred extensively. Hydrolysis to yield the ketone V occurred over rhodium, palladium and platinum catalysts. Except in a few cases the proportion of hydrogenolysis decreased with the solvents in the order ethanol>*t*-butyl alcohol>isopropyl ether. The *cis/trans* ratio of ether IV formed did not differ much among the three solvents except in hydrogenation over palladium where a definite decrease in the ratio was observed from in ethanol to in *t*-butyl alcohol and isopropyl ether.

Discussion

As illustrated in Figs. 1—6, hydrogenation of the enol ether I in ethanol is accompanied by the formation of the acetal II which results from the addition of ethanol to I. The ratio of the acetal formation to hydrogenation is indicated by the initial slope of the curves which show the amounts of the acetal varying with the extent of hydrogenation. The values of this ratio for the six platinum metals are in the following sequence: osmium (0.06)<ruthenium (0.11)<iridium (0.26)≪rhodium (1.28)<palladium (1.87)<platinum (5.76). Thus, the six metals can be classified into two groups. Osmium, ruthenium and iridium belong to the group which catalyzes the acetal formation only weakly, while rhodium, palladium and platinum to the other group which catalyzes it efficiently. The addition of ethanol to I is an acid-catalyzed reaction. The action of the platinum metals to catalyze this addition is probably due to the presence of the adsorbed hydrogen which is ionized on the catalyst surface. It was previously shown that acetal is formed rapidly in the hydrogenation of cycloalkanones over some platinum metals in methyl or ethyl alcohol and also that the acetal formation is greatly depressed in the absence of hydrogen.[10]

With respect to hydrogenolysis, platinum was definitely more active than any other platinum metals. On the other hand, palladium and ruthenium showed only poor tendency towards hydrogenolysis. At an initial stage of hydrogenation of I in ethanol, the proportion of hydrogenolysis was in the following sequence for the six platinum metals: palladium≅ruthenium≪osmium<rhodium<iridium≪platinum (see Table 3). It is to be noted that palladium showed the lowest activity for hydrogenolysis although the same metal is known to be highly active for the hydrogenolysis of benzyl- and allyl-type ethers.[11]



Scheme 1.
(M indicates catalyst metal)

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[10] S. Nishimura, T. Itaya, and M. Shiota, *Chem. Commun.*, **1967**, 422.

[11] See for instance Ref. 2, p. 433.

The mechanism of the hydrogenation and hydrogenolysis of an enol ether appears not enough known. Probably, the half-hydrogenated state of I is the one which results from the addition of a hydrogen (or proton) to the C–2 carbon of I (A in Scheme 1), as assumed by Acke and Anteunis.[4] If the affinity of the carbon (or carbonium ion) and the catalyst metal is not strong in the resulting half-hydrogenated state, step (1) in Scheme 1 will readily be reversed and in this case the removal of ethanol from the half-hydrogenated state will not occur so easily. On the other hand, such affinity between the intermediate A and the catalyst metal is sufficiently strong, the reversal of step (1) would be inhibited and, rather, elimination of ethanol to give the adsorbed intermediate B would be favored [step (2)]. If we assume that the affinity mentioned above is expressed in terms of the olefin isomerization activity of the metal,[12] it is expected that hydrogenolysis will occur more easily over such metals which are less active in olefin isomerization. Since elimination of ethanol by step (2) would be promoted by acid and, accordingly, by the ionized hydrogen on the catalyst surface, hydrogenolysis will occur more extensively over such metals which can catalyze the acetal formation effectively on hydrogenation of I in ethanol. The activities of the six platinum metals in the acetal formation (r_1) and those in olefin isomerization (r_2) are summarized in Table 3. The value of r_2 was obtained in the hydrogenation of 1-octene in isopropyl alcohol at 25°C under an atmospheric pressure of hydrogen, using the unsupported metals prepared by the same methods as used for the catalysts in this study.[13] Thus we can expect that the extent of hydrogenolysis observed in the hydrogenation of an enol ether would increase with increasing value of r_1/r_2 which is also given in Table 3. For the six platinum metals the value of r_1/r_2 is in the following sequence: Pd$\cong$Ru$\ll$Os$<$Rh$<$Ir$\ll$Pt. It is seen that this sequence is in excellent accord with that obtained in the proportion of the hydrogenolysis which occurred at the initial stage of the hydrogenation of I in ethanol (see Table 3). Thus, the very low activity of palladium catalyst towards hydrogenolysis may be due to its weak affinity for the carbon atom as expressed by its unusually high olefin isomerization activity. The low activity of ruthenium in the hydrogenolysis may be explained by the poor action of the ionized hydrogen on that metal. The extremely high activity of platinum towards the hydrogenolysis will result from its properties as expressed by both of the high activity in the acetal formation and the low activity in the olefin isomerization.

TABLE 3. ACETAL FORMATION AND OLEFIN ISOMERIZATION ACTIVITIES OF PLATINUM METAL CATALYSTS AND THEIR TENDENCY TOWARDS HYDROGENOLYSIS IN HYDROGENATION OF ENOL ETHER I

Catalyst	Ratio of acetal formation to hydrogenation[a] (r_1)	Ratio of olefin isomerization to hydrogenation[b] (r_2)	$\frac{r_1}{r_2}$	Proportion of hydrogenolysis in hydrogenation of I (mol%)[a]
Ru	0.11	0.12	0.92	1.9
Rh	1.28	0.125	10.2	10.0
Pd	1.87	2.05	0.91	1.1
Os	0.06	0.0093	6.45	8.2
Ir	0.26	0.025	10.4	14.8
Pt	5.76	0.025	230	71.6

a) These values were obtained at the initial stage of the hydrogenation of I in ethanol.

b) The ratio r_2 was obtained in the hydrogenation of 1-octene in isopropyl alcohol at 25°C under atmospheric presence of hydrogen and is given bv the ratio of isomerized 2-octene to octane at about 20% conversion of 1-octene.

The results of the stereochemistry of hydrogenation of I seem consistent with the mechanism described in Scheme 1. The hydrogenation of I over palladium catalyst is noteworthy in that *cis*-ether IV is formed with a high stereospecificity. If the rate-determining step over this metal is assumed to be formation of the saturated ether [step (3)], just as postulated in the hydrogenation of cycloolefins,[14] the preceding steps, including the adsorption of I to the catalyst, would be easily reversed as supposed by its weak affinity toward unsaturation. Under these circumstances, possible half-hydrogenated states A_c, A_t and A_t' (see Fig. 7) will be equilibrated on the catalyst surface. Since the most stable one of them will be A_c, this will predominate at equilibrium and *cis*-ether will be formed in excess *via* A_c, if the rate constants for hydrogenation of them do not differ much among them. In this connection, it is of interest to note that hydrogenation of 1,4-dimethyl-1-cyclohexene, which has a methyl group instead of the ethoxyl group in I, gives the *trans* isomer as major product in the hydrogenation with palladium catalyst.[15] This result may be explained by the assumption made be Siegel and Smith that decreasing stabilities of various possible half-hydrogenated states are in the order primary$>$secondary$>$tertiary with respect to the carbon adsorbed on the catalyst surface.[14] On hydrogenation of I, the electromeric effect of the ethoxyl group will direct the first addition of hydrogen (or proton) to the C–2 carbon and this leads to the preferential formation of the half-hydrogenated state A. This assumption is strongly supported by the fact that hydrogenation of 3-

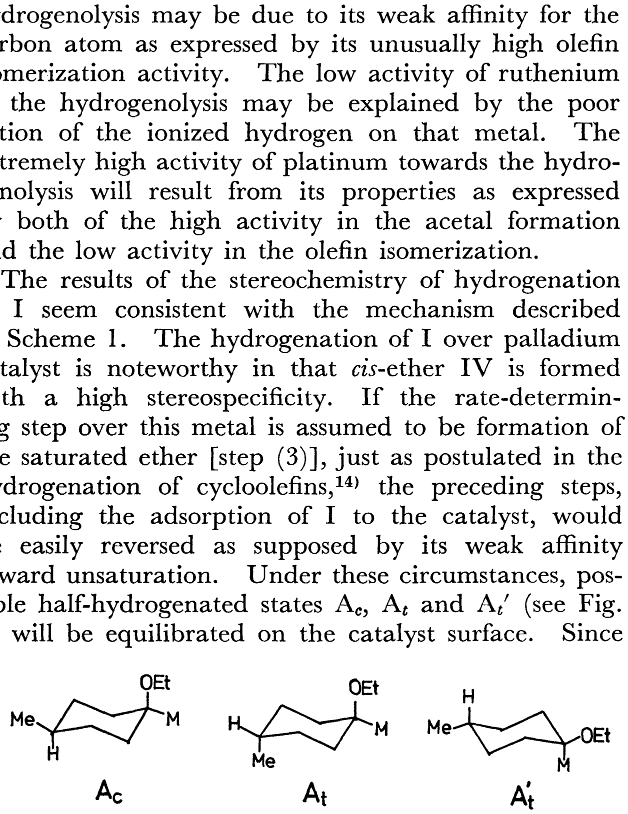

Fig. 7. Conformations of half-hydrogenated state A (M indicates catalyst metal).

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[12] G. C. Bond and P. B. Wells, *Advan. Catal.*, **15**, 91 (1964).

[13] Unpublished data by S. Nishimura and H. Nagamatsu.

[14] S. Siegel and G. V. Smith, *J. Amer. Chem. Soc.*, **82**, 6087 (1960).

[15] J.-F. Sauvage, R. H. Baker, and A. S. Hussey, *ibid.*, **83**, 3874 (1961).

methylcyclohexanone diethyl acetal (VII) in ethanol with palladium catalyst gave rise to *trans*-ether predominantly.[16] The acetal VII is probably hydrogenated *via* the corresponding enol ethers and over palladium the enol ethers are also expected to give the *trans*-ether in excess, as supposed from the comparison of the results obtained with palladium catalyst on their 4-methyl analogues (see Tables 1 and 2).

The stereoselectivity was much lower over the other platinum metals, although always *cis*-ether was formed in greater amount than *trans*-ether. It appears that the nature of the solvents does not have much influence on the stereochemistry of hydrogenation except with palladium. Over the metals other than palladium, the step which determines the stereochemistry of ether formation may be either adsorption of enol ether I or formation of the half-hydrogenated state, as postulated in the platinum-catalyzed hydrogenation of cycloolefins.[17]

It has been considered that acetals are hydrogenated *via* the corresponding enol ether in the presence of acid.[3,4] Although this reaction pathway will probably be true also in the absence of acid, hydrogenation of acetal II was in most cases much slower than that of enol ether I. This is also seen by the fact that I is hydrogenated at much greater rates in *t*-butyl alcohol and isopropyl ether than in ethanol (see Table 1). Since at an equilibrium in ethanol II is in a much greater amount than I, slow hydrogenation of II may be due to a slow formation of I by elimination of ethanol from I on the catalyst surface. It is also suggested that II is adsorbed to the catalyst much more weakly than I, since hydrogenation of II appears not to occur until almost all of I has disappeared as seen in Figs. 1—6. Slow hydrogenation of II also leads to the product considerably different from that obtained by hydrogenation of I and yields the saturated ether of a greater *cis*/*trans* ratio than formed from I, with the exception of the hydrogenation over palladium where almost the same product was formed on hydrogenation of I and II.

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[16] unpublished results.

[17] S. Siegel and G. V. Smith, *J. Amer. Chem. Soc.*, **82**, 6082 (1960).