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Hydrogenation and Hydrogenolysis. XII.[1] The Hydrogenation of Isomeric Dimethoxybenzenes with Platinum Metal Catalysts[*1]

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The catalytic hydrogenation and hydrogenolysis of isomeric dimethoxybenzenes over six platinum metals have been investigated at elevated temperature and pressure. The hydrogenolysis of methoxyl group occurred more extensively over Group $VIII_3$ metals than over Group $VIII_2$ metals. The *meta* isomer hydrogenolyzed to greater extent and gave smaller *cis/trans* ratio of dimethoxycyclohexane, than the *ortho* and *para* isomers. The greater tendency of the *meta* isomer toward hydrogenolysis supports the previously proposed explanation according to which the electron-releasing group at *meta* position would promote hydrogenolysis.

Only few studies have been described in the literature on the catalytic hydrogenation of dimethoxybenzenes and most of them are not comparative or not quantitative.[2-6] Smith and Thompson[5] studied the hydrogenation of various methoxybenzenes with Adams platinum and rhodium-on-alumina catalysts in acetic acid at 20—50°C under the initial hydrogen pressure of 40—60 psi. Their results indicated that the hydrogenolysis of methoxyl group was less extensive over the supported rhodium catalyst than over the platinum catalyst and that it increased with respect to the three isomers of dimethoxybenzene in the order *ortho*>*meta*>*para* over the platinum catalyst, while with the rhodium catalyst the *meta* isomer underwent slightly more hydrogenolysis than the *ortho* and *para* isomers.

In this study the catalytic hydrogenation and hydrogenolysis of isomeric dimethoxybenzenes over six platinum metals have been investigated at elevated temperature and pressure, mainly with the object to know the behaviors of the three isomers toward hydrogenolysis.

Experimental

Materials. Tokyo Kasei G. R. dimethoxybenzenes were purified by distillation. *o*-Dimethoxybenzene:

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[1] Part XI: S. Nishimura and H. Yoshino, This Bulletin, **42**, 499 (1969).

[*1] Presented partly at the Research Meeting of the Catalysis Society of Japan, Sendai, October, 1968.

[2] R. Amatatsu, *Nippon Kagaku Kwaisi*, **52**, 585 (1931).

[3] E. M. van Duzee and H. Adkins, *J. Amer. Chem. Soc.*, **57**, 147 (1935).

[4] R. H. Martin and R. Robinson, *J. Chem. Soc.*, **1943**, 491.

[5] H. A. Smith and R. G. Thompson, "Advances in Catalysis," Vol. 9, Academic Press Inc., New York, N. Y. (1957), p. 727.

[6] Y. Takagi, T. Naito and S. Nishimura, This Bulletin, **38**, 2119 (1965).

bp 105°C/26 mmHg, n_D^{25} 1.5316; *m*-dimethoxybenzene: bp 106.5°C/26 mmHg, n_D^{20} 1.5248; *p*-dimethoxybenzene: bp 110°C/26 mmHg, mp 55°C.

Catalysts. Unsupported ruthenium, rhodium, iridium and platinum catalysts were prepared by reducing the corresponding hydroxides in water at 80°C (at 30°C for platinum hydroxide) for 20 min under 80 kg/cm^2 of hydrogen. Unsupported osmium catalyst was prepared by reducing osmium tetroxide in isopropyl alcohol at 60°C for 20 min under 80 kg/cm^2 of hydrogen. The metals thus prepared were washed with distilled water until the filtrate became neutral and then dried in vacuum at room temperature. The palladium-on-carbon catalyst (5% Pd) was obtained from the Nippon Engelhard Co.

Hydrogenation. Dimethoxybenzene (0.1 mol) was hydrogenated in a 100-m*l* bomb of up-and-down stirring type driven electromagnetically, using 20 mg of unsupported catalyst at 80°C or 200 mg of the supported catalyst at 120°C under the hydrogen pressure of 80—100 kg/cm^2.

TABLE 1. RELATIVE RETENTION TIMES OF DIMETHOXYBENZENES AND THEIR HYDROGENATION PRODUCTS

Compound	Relative retention time
Cyclohexane	1.0
Methanol	1.2
Methoxycyclohexane	1.9
Cyclohexanone dimethyl acetal	3.4
trans-1,2-Dimethoxycyclohexane	3.8
cis-1,2-Dimethoxycyclohexane	4.8
o-Dimethoxybenzene	24.0
trans-1,3-Dimethoxycyclohexane	4.9
cis-1,3-Dimethoxycyclohexane	6.8
m-Dimethoxybenzene	27.3
trans-1,4-Dimethoxycyclohexane	5.3
cis-1,4-Dimethoxycyclohexane	6.3
p-Dimethoxybenzene	25.2

Analysis of Products. Hydrogenation products were analyzed by gas chromatography using 10% PEG 20M on 60—80 mesh Chromosorb W (column dimension: 3 mm × 2.25 m; column temperature: 128°C; carrier gas: helium at 70 m*l*/min). Relative retention times of dimethoxybenzenes and their hydrogenation products are summarized in Table 1. Table 2 summarizes the mol percent composition of reaction mixtures.

Results

Table 3 shows the amount of hydrogenolysis which occurred during hydrogenation of dimethoxybenzenes over platinum metal catalysts. The figures in the table are based on the amount of the cleaved methoxyl group. It is seen that in most cases the hydrogenolysis is more extensive over Group VIII$_3$ metals (osmium, iridium and platinum) than over Group VIII$_2$ metals (ruthenium, rhodium and palladium). It can also be seen that the *meta* isomer hydrogenolyzes more extensively than the *ortho* and *para* isomers with only one exception in osmium, where the *para* isomer underwent slightly more hydrogenolysis than the *meta* isomer. The greater tendency of the *meta* isomer toward hydrogenolysis is more prominent over Group VIII$_2$ metals than over Group VIII$_3$ metals.

Figures 1 and 2 compare the rates of hydrogenation of isomeric dimethoxybenzenes with ruthenium and rhodium catalysts, respectively. The decreasing

TABLE 2. MOL PERCENT COMPOSITION OF REACTION MIXTURE IN HYDROGENATION OF DIMETHOXYBENZENES OVER PLATINUM METAL CATALYSTS

Dimethoxybenzene	Catalyst	Reac. time (min)	Composition of reaction mixture, mol %				
			Dimethoxybenzene	Dimethoxycyclohexane	Methoxycyclohexane	Cyclohexane	Unidentified product
Ortho	Ru	39	0.0	98.5	1.5	0.06	—
Meta	Ru	74	0.0	81.8	16.9	0.2	1.2
Para	Ru	50	0.8	96.9	2.3	0.04	—
Ortho	Rh	55	0.0	98.9	1.0	0.1	—
Meta	Rh	120	2.4	87.0	7.6	0.7	2.2
Para	Rh	46	0.4	97.7	1.9	0.05	—
Ortho	Pd/C	120	80.1	19.2	0.6	0.03	—
Meta	Pd/C	120	75.4	20.0	4.0	trace	0.6
Para	Pd/C	120	64.3	34.0	1.6	0.08	—
Ortho	Os	60	28.9	67.5	3.3	0.3	—
Meta	Os	60	39.4	51.2	8.6	0.2	0.6
Para	Os	60	53.5	38.3	7.2	1.0	—
Ortho	Ir	90	15.3	79.0	4.6	1.1	—
Meta	Ir	160	12.4	61.9	23.4	1.5	0.9
Para	Ir	40	24.9	62.0	10.4	2.8	—
Ortho	Pt	60	86.9	12.6	0.5	0.01	—
Meta	Pt	60	89.0	9.9	0.9	0.07	0.06
Para	Pt	60	84.5	14.2	1.2	0.03	—

TABLE 3. AMOUNT OF HYDROGENOLYSIS IN HYDROGENATION OF DIMETHOXYBENZENES OVER PLATINUM METAL CATALYSTS

Catalyst	Hydrogenolysis, mol%[a]		
	Ortho	*Meta*	*Para*
Ru	1.6	17.5	2.4
Rh	1.2	9.4	2.0
Pd/C	3.3	17.0	4.9
Os	5.5	15.0	19.8
Ir	8.0	30.4	21.3
Pt	4.0	9.5	8.1

a) Mol% hydrogenolysis is given by:

$$\frac{\left[\begin{array}{l}\text{mol(methoxycyclohexane}\\ +\text{cyclohexane}\times 2)\times 100\end{array}\right]}{\left[\begin{array}{l}\text{mol(dimethoxycyclohexane}\\ +\text{methoxycyclohexane}+\text{cyclohexane)}\end{array}\right]}$$

rate during the hydrogenation of the *meta* isomer is noteworthy with both catalysts. This decrease in the rate is probably caused by the methanol produced by hydrogenolysis which occurs extensively in the case of the *meta* isomer. The addition of methanol to reaction mixture was found to retard the hydrogenation of *o*- and *m*-dimethoxybenzene with ruthenium catalyst as indicated in Fig. 1.[7]

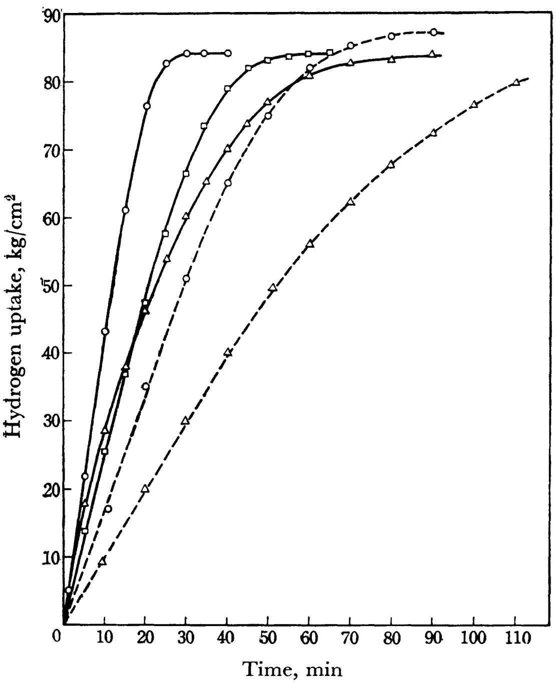

Fig. 1. Hydrogenation of dimethoxybenzenes with ruthenium catalyst: the effect of the addition of methanol.
—○—: *o*-Dimethoxybenzene; ---○---: *o*-Dimethoxybenzene and 0.8 m*l* methanol; —△—: *m*-Dimethoxybenzene; ---△---: *m*-Dimethoxybenzene and 0.5 m*l* methanol; —□—: *p*-Dimethoxybenzene

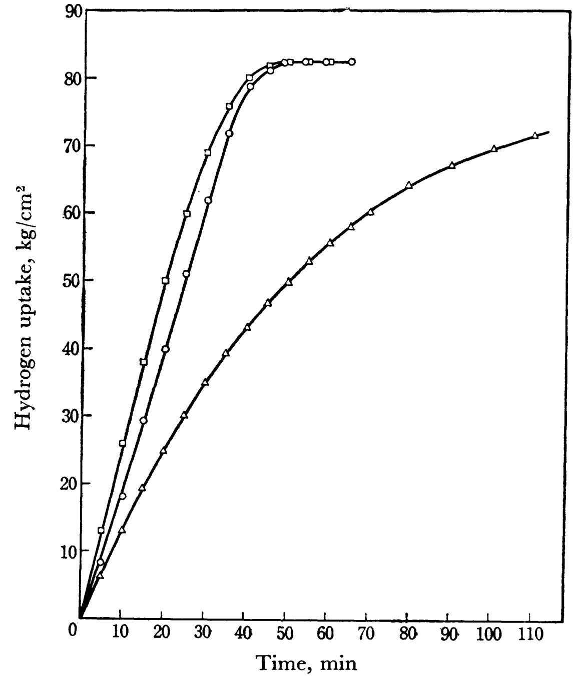

Fig. 2. Hydrogenation of dimethoxybenzenes with rhodium catalyst.
—○—: *o*-Dimethoxybenzene; —△—: *m*-Dimethoxybenzene; —□—: *p*-Dimethoxybenzene

TABLE 4. PERCENT *cis* ISOMER IN DIMETHOXYCYCLOHEXANE FROM HYDROGENATION OF DIMETHOXYBENZENE WITH PLATINUM METAL CATALYSTS

Catalyst	*cis*-Dimethoxycyclohexane, %		
	1,2-	1,3-	1,4-
Ru	82	73	80
Rh	87	67	81
Pd/C	86	56	64
Os	90	73	80
Ir	92	77	82
Pt	91	73	81

Table 4 summarizes the percent *cis* isomer in the dimethoxycyclohexane formed in hydrogenation of the corresponding dimethoxybenzene. It is of

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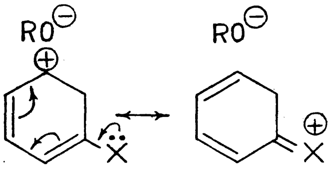
[7] This retardation caused by methanol is probably due to the formation of dimethyl acetals which may result from the addition of methanol to vinyl type ethers formed during hydrogenation. A small amount of cyclohexanone dimethyl acetal has been detected in the product from *m*-dimethoxybenzene. Formation of a considerable amount of 4-methylcyclohexanone diethyl acetal has been observed in hydrogenation of ethyl *p*-tolyl ether over a rhodium catalyst in ethanol, with a decreasing rate in the course of the hydrogenation [S. Nishimura, M. Uramoto and T. Watanabe, *Shokubai*, **11**, 149 (1969)].

interest that formation of *cis* isomer is greater in the *ortho* and *para* isomers than in the *meta* isomer.

Discussion

The results shown in Table 3 clearly indicate that *m*-dimethoxybenzene hydrogenolyzes more readily than the *ortho* and *para* isomers. This conclusion is also true when the rates of formation of hydrogenolysis products (*cf.* Ref. 1) are compared. Although osmium caused slightly less hydrogenolysis in the *meta* isomer than in the *para* isomer, the same conclusion can also be obtained in this case if we compare the rate of formation of hydrogenolysis products which is greater for the *meta* isomer than for the *para* isomer. The greater tendency of the *meta* isomer toward hydrogenolysis has also been observed in the hydrogenation of methoxy- and ethoxyanilines with ruthenium catalyst and for this an explanation based on the ionic cleavage of the carbon-oxygen bond has been proposed.[1] According to this explanation the electron-releasing group at the *meta* position may stabilize the transition states of carbonium ion character when the allyl type ethers formed on the catalyst undergo hydrogenolysis, as shown below in one example of dihydro intermediates.



The same effect may also be expected in the allyl type tetrahydro intermediates. In *m*-dimethoxybenzene both methoxyl groups can take part in such stabilization of the transition states leading to hydrogenolysis products and therefore the tendency of the *meta* isomer toward hydrogenolysis is expected to be more pronounced in dimethoxybenzenes than in methoxyanilines. The results in Table 3 which are in accord with this expectation may provide a strong support to the explanation proposed previously. It is to be noted that the more extensive hydrogenolysis in the *meta* isomer was not observed or less pronounced in the hydrogenation of dimethoxybenzenes in acetic acid.[8]

Another important factor which may have an effect on the relative amount of hydrogenolysis between *ortho*, *meta* and *para* isomers is the probability of the formation of allyl type ethers from parent aromatic compounds.[9] It will be difficult, however, to discuss on this point from the data now available and further detailed studies are needed for this purpose.

The stereochemistry of hydrogenation of dimethoxybenzenes is noteworthy in that the *meta* isomer gave smaller yields of the *cis* isomer than the *ortho* and *para* isomers, when compared with the hydrogenation of isomeric xylenes where formation of *cis* isomer decreases in the order *ortho*>*meta*>*para*.[10] It might be possible that the extensive hydrogenolysis in *m*-dimethoxybenzene would decrease the *cis* content of the resulting dimethoxycyclohexane, if the hydrogenolysis of the methoxyl group would occur by the S_N2 type mechanism.[11] But this fails to account for the results with osmium catalyst in which the *meta* isomer underwent less hydrogenolysis than the *para* isomer, whereas the *cis* content of dimethoxycyclohexane was smaller in the *meta* isomer.

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[8] The *meta* isomer hydrogenolyzes to less extent than the *ortho* and *para* isomers in the rhodium-catalyzed hydrogenation of methoxy- and ethoxyanilines in isopropyl alcohol added by one equivalent of acetic acid (S. Nishimura and Y. Takagi, Abstracts of the Research Meeting of the Catalysis Society of Japan, p. 31, Sendai, October, 1968). In *t*-butyl alcohol differences in the amount of hydrogenolysis are small between three isomers of methoxy- or ethoxyaniline [S. Nishimura, H. Uchino and H. Yoshino, This Bulletin **41**, 2194 (1968)].

[9] Hydrogenolysis in vinyl type ethers may also be possible over some platinum metals. But the contribution of this type hydrogenolysis seems not important, especially in hydrogenation with Group $VIII_2$ metals, and was not considered here (Unpublished observations; *cf.* also Ref. 10, p. 444).

[10] See, for instance, P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals," Academic Press Inc., New York, N. Y. (1967), p. 324.

[11] *Cf.* a) S. Nishimura and K. Mori, This Bulletin, **36**, 318 (1963). b) R. K. Callow and G. A. Thompson, *J. Chem. Soc.*, **1964**, 3106. c) S. Mitsui and Y. Nagahisa, *Chem. Ind.* (London), **1965**, 1975 and references cited therein.