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Yields of Methylcyclohexanone Intermediates in the Hydrogenation of Isomeric Cresols over Ruthenium and Palladium Catalysts[1]

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Isomeric cresols have been hydrogenated over ruthenium and palladium catalysts at elevated temperature and pressure. The yields of the methylcyclohexanone intermediates formed were estimated by application of a kinetic method. Hydrogenation with ruthenium catalyst gave 77, 61 and 60% of the ketone as the intermediate for *o*-, *m*- and *p*-cresol, respectively, while with palladium catalyst all isomeric cresols yielded the ketone intermediates quantitatively. The hydrogenation pathways leading to the formation of methylcyclohexanones were discussed. The stereochemistry of hydrogenation of isomeric cresols and methylcyclohexanones were also studied, and the results were interpreted on the basis of the estimated yields of the ketone intermediates.

It is known that cyclohexanones are produced as intermediates in the catalytic hydrogenation of phenols and the ketones produced often accumulate in considerable amounts in the course of hydrogenation.[2-4] Cresols may give stereoisomeric methylcyclohexanols on hydrogenation and the stereochemistry of the hydrogenation is closely related to the production and subsequent hydrogenation of the corresponding methylcyclohexanones formed as intermediates. Although some studies on the hydrogenation of isomeric cresols have recently been reported with rhodium and ruthenium catalysts,[5] and with a rhodium-platinum catalyst,[6] a more detailed study will be required for the quantitative interpretation of the results.

In previous papers,[7,8] we estimated quantitatively the yields of the methylcyclohexanone intermediates formed in the rhodium-catalyzed hydrogenation of isomeric cresols by application of the following three methods: (a) the stereochemistry of the hydrogenation of a cresol and the corresponding methylcyclohexanone, (b) initial yield method, (c) a kinetic interpretation of the product change

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

[2] G. Vavon and A. L. Berton, *Bull. Soc. Chim. Fr.*, [**4**]**37**, 296 (1925).

[3] F. Coussemant and J. C. Jungers, *Bull. Soc. Chim. Belges*, **59**, 295 (1950).

[4] H. A. Smith and B. L. Stump, *J. Amer. Chem. Soc.*, **83**, 2739 (1961).

[5] P. N. Rylander and D. R. Steele, *Engelhard Ind. Tech. Bull.*, **3**, 125 (1964).

[6] F. Zymarkowsky and G. Strippel, *Arch. Pharm.*, **297**, 727 (1964).

[7] Y. Takagi, S. Nishimura, K. Taya and K. Hirota, *J. Catalysis*, **8**, 100 (1966).

[8] Y. Takagi, S. Nishimura and K. Hirota, *ibid.*, **12**, 214 (1968).

during hydrogenation. Although the results obtained by the three methods did not differ much from each other and were in some cases in excellent accord, the kinetic method mentioned above seemed to be the most reliable and widely applicable to the estimation of the ketone intermediates, because of the quantitative nature of the method. In this study, therefore, the yields of the ketone intermediates formed in the ruthenium- and palladium-catalyzed hydrogenations of isomeric cresols have been determined by the kinetic method and the results compared with those obtained previously with rhodium catalyst. Stereochemistry of the hydrogenation has also been studied and interpreted on the basis of the estimated yields of the ketone intermediates.

Experimental

Materials. Cresols and methylcyclohexanones of G. R. grade of the Tokyo Kasei Kogyo Co. were used after fresh distillation through a 30 cm Vigreux column under reduced pressure. The cresols and methylcyclohexanones were sufficiently pure for the present purpose (more than 99% purity as judged from the analysis by gas chromatography of the hydrogenation products).

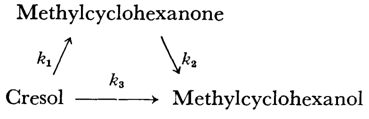
Catalysts. Ruthenium hydroxide used for hydrogenation was prepared by adding a slight excess of 10% sodium hydroxide solution to a 1% hot aqueous solution of ruthenium chloride.[9] The hydroxide catalyst was used without being prereduced to metals. For the palladium catalyst, 5% palladium-on-carbon of a commercial preparation (obtained from the Nippon Engelhard Co.) was used, since unsupported palladium was easily deactivated during hydrogenation under the present reaction conditions.

Hydrogenation. Hydrogenation was carried out without solvent at 80°C for ruthenium catalyst and at 120°C for palladium catalyst under a hydrogen pressure of 80—100 kg/cm^2. Cresol (0.1 mol) was hydrogenated with 20 mg of ruthenium hydroxide or with 300 mg of supported palladium in a 100 m*l* bomb equipped with an agitator driven up and down.

Analysis of Products. The reaction mixture was analyzed directly by gas chromatography (detector: hydrogen flame ionization type; column dimension: 3 m by 0.4 cm OD; stationary phase: 10 wt% diglycerol on 60 mesh firebrick; temperature: column 80—95°C, detector 80—95°C; carrier gas: nitrogen at 90—100 m*l*/min).

Results

The hydrogenation of cresol to methylcyclohexanol will proceed through two simultaneous reaction pathways: one *via* methylcyclohexanone and the other not *via* the ketone as indicated below.



Scheme 1

As shown in a previous paper on the rhodium-catalyzed hydrogenation,[8] concentration of the ketone (C_2) varying during hydrogenation may be given by Eq. (1) in which C_1 is the concentration of cresol, k_i's are the rate constants for the respective reaction pathways in Scheme 1, and $K = k_2b_2/(k_1+k_3)b_1$ where b_1 and b_2 represent the adsorption coefficients of cresol and methylcyclohexanone, respectively. The yields of the ketone intermediates and the values of K were obtained by finding the most suitable values of $k_1/(k_1+k_3)$ and K in such a way that the following equation, when these values are substituted into it, may represent the actual variation of the concentration of the ketone with the least deviation.

$$C_2 = \frac{k_1/(k_1+k_3)}{K-1}(C_1 - C_1{}^K) \qquad (1)$$

The yields of the methylcyclohexanone intermediates and the values of K thus obtained are summarized in Table 1, along with those for the rhodium-catalyzed hydrogenation obtained previously. The theoretical curves given by Eq. (1) showing the variation in the concentration of the ketone are compared with a set of experimental values in Figs. 1,2 and 3 for the hydrogenation of *o*-, *m*- and *p*-cresol, respectively. The data for the rhodium-catalyzed hydrogenation are reproduced in the figures for comparison. The ratios of the adsorption coefficients (b_2/b_1) can be evaluated from the values of K and the ratios of the rate constants of methylcyclohexanone and cresol $[k_2/(k_1+k_3)]$.[*1]

TABLE 1. ESTIMATION OF METHYLCYCLOHEXANONE INTERMEDIATE BY KINETIC METHOD IN HYDROGENATION OF CRESOL WITH PLATINUM METAL CATALYSTS OF GROUP VIII$_2$

Cresol	Catalyst	Yield of the ketone inter -mediate, mol%[a]	K	$\frac{k_2}{k_1+k_3}$	$\frac{b_2}{b_1}$
Ortho	Ru	77	0.98	0.14	6.9
Meta	Ru	61	2.25	3.05	0.74
Para	Ru	60	3.50	1.54	2.3
Ortho	Pd/C	100	0.94	1.71	0.57
Meta	Pd/C	100	1.07	1.50	0.65
Para	Pd/C	110	1.60	2.31	0.50
Ortho	Rh[b]	55	0.07	0.09	0.78
Meta	Rh[b]	52	0.25	0.53	0.47
Para	Rh[b]	54	0.30	0.39	0.77

a) Given by $100k_1/(k_1+k_3)$.
b) Reproduced from Ref . 8.

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

[*1] These were obtained from the initial rates of hydrogenation of methylcyclohexanone and cresol under the same conditions.

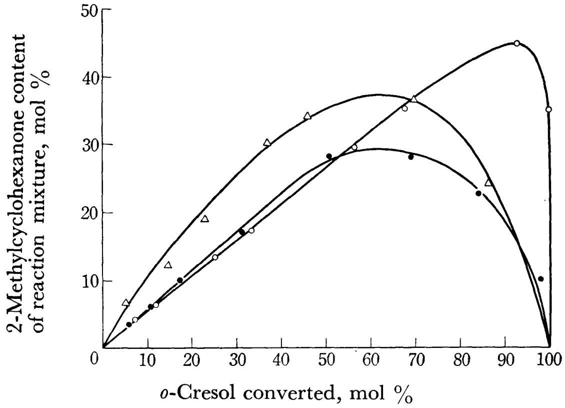


Fig. 1. 2-Methylcyclohexanone intermediate formed in hydrogenation of o-cresol over Ru, Rh and Pd/C catalysts as a function of the conversion of the cresol; temp., 80°C for Ru and Rh; 120°C for Rd/C; hydrogen press., 80—100 kg/cm^2. Experimental values in the Figure are a set of results obtained by separate experiments in each hydrogenation:
● Ru; ○ Rh; △ Pd/C. ——: Theoretical curve given by Eq. (1).

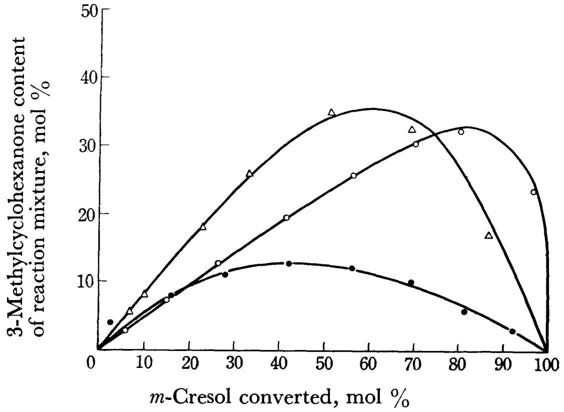


Fig. 2. 3-Methylcyclohexanone intermediate formed in hydrogenation of m-cresol over Ru, Rh and Pd/C catalysts as a function of the conversion of the cresol. For other indications see Fig. 1.

They are also listed in Table 1. The stereoisomeric compositions of the methylcyclohexanols produced by hydrogenation of cresols and methylcyclohexanones under comparable conditions are summarized in Table 2, along with those for the rhodium-catalyzed hydrogenation.

Discussion

It has been shown by the kinetic method that the rhodium-catalyzed hydrogenation of isomeric cresols yielded 52—55% of methylcyclohexanones as intermediates.[8] The yields obtained by the other two methods ranged between 43—66%. For the formation of the ketone intermediates in large amounts, we have suggested an explanation which is based on the assumptions that all dihydrocresols are produced from parent cresols in equal probability and that unsaturated ketones or their enols formed

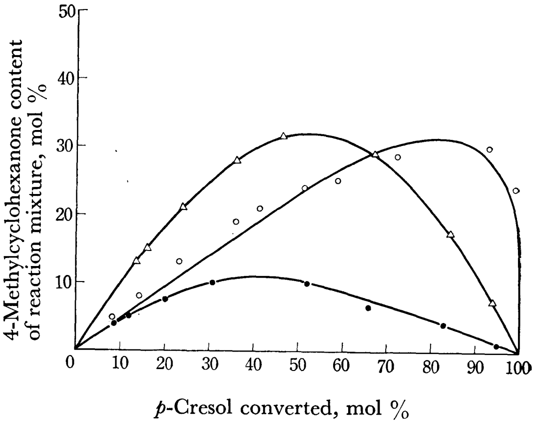


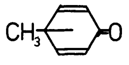
Fig. 3. 4-Methylcyclohexanone intermediate formed in hydrogenation of p-cresol over Ru, Rh and Pd/C catalysts as a function of the conversion of the cresol. For other indications see Fig. 1.

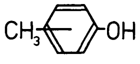
TABLE 2. STEREOCHEMISTRY OF HYDROGENATION OF CRESOL AND METHYLCYCLOHEXANONE WITH PLATINUM METAL CATALYSTS OF GROUP VIII$_2$

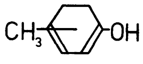
Catalyst	Cresol or cyclohexanone	Composition of methylcyclohexanol, % From cresol *cis*	*trans*	From ketone[a] *cis*	*trans*
Ru	Ortho or 2-methyl	60	40	58	42
Ru	Meta or 3-methyl	56.5	43.5	51	49
Ru	Para or 4-methyl	59.5	40.5	53	47
Pd/C	Ortho or 2-methyl	54	46	54	46
Pd/C	Meta or 3-methyl	62	38	62	38
Pd/C	Para or 4-methyl	46	54	45	55
Rh[b]	Ortho or 2-methyl	78	22	64	36
Rh[b]	Meta or 3-methyl	64	36	49	51
Rh[b]	Para or 4-methyl	73	27	70	30

a) The mean of the values obtained by hydrogenating the respective ketone in phenol and cyclohexanol solutions under the same conditions as used for the hydrogenation of the corresponding cresol.
b) Reproduced from Ref. 7.

are preferentially converted to saturated ketones on further hydrogenation. According to these assumptions, all isomeric cresols should give the ketone intermediates in 67% yield. It was pointed out that the yields estimated on the rhodium-catalyzed hydrogenation were close to this value and that they were nearly the same for *o*-, *m*- and *p*-cresol. As seen from Table 1, the yields of the ketone intermediates obtained with ruthenium catalyst are even more close to the value 67%, and the assumptions mentioned above also appear to hold for the ruthenium-catalyzed hydrogenation. It is to be noted that *o*-cresol gave a considerably greater yield of the ketone (77%) than *m*- and *p*-cresol (60—61%) over ruthenium. In the palladium-catalyzed hydrogenation all isomeric cresols gave quantitative yields of the ketone intermediates.[*2] Obviously the assumption that all dihydrocresols are produced in equal probability does not hold with this metal. It might be possible that over palladium cresol is hydrogenated in the keto form (I) rather than in the enol form (II) or it is hydrogenated through the selective formation of the dihydro intermediate (III). The hydrogenation of I or III is expected to give the saturated ketone quantitatively.[*3]


(I)


(II)


(III)

From Table 1 it will also be seen that the values of K are in the order with respect to catalyst metals, rhodium<palladium<ruthenium for every isomeric cresol. With respect to the three isomers of cresol the values of K decrease in the order, para>meta>ortho for any catalyst metal. The ratio b_2/b_1 is not always in the same order as K. It is of interest that the ratio is the smallest for hydrogenation of *m*-cresol both on rhodium and ruthenium catalysts.

A rather large yield of the ketone intermediate obtained in hydrogenation of *o*-cresol with ruthenium catalyst is supported by a small difference in the stereoisomeric compositions of the methylcyclohexanols formed from *o*-cresol and from 2-methylcyclohexanone (see Table 2). The results in Table 2 also indicate that the ketone intermediates are produced quantitatively in hydrogenation with palladium catalyst, because the methylcyclohexanols of the same stereoisomeric composition were obtained in the hydrogenation of cresols and the corresponding methylcyclohexanones, and thus support the conclusion deduced by the kinetic method. The results also indicate that the adsorption-desorption equilibrium was completely established in the formation and hydrogenation of the ketone intermediate on the surface of the palladium catalyst.

[*2] Nearly quantitative formation of cyclohexanone has also been reported recently on the hydrogenation of phenol with a palladium-carbon catalyst in acetic acid at 50°C under the hydrogen pressure of 1 atm [M. Matsumoto, T. Suzuki and S. Suzuki, *Kogyo Kagaku Zasshi*, **72**, 881 (1969)].

[*3] The possibility that the methylcyclohexanone intermediates are formed through the production of allyl type alcohols, followed by isomerization to the ketones, is excluded, because the hydrogenolysis product (methylcyclohexane), which would result from the allyl type alcohols, was not found in the products of the palladium-catalyzed hydrogenation.