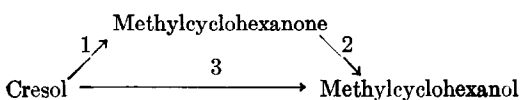


The Yields of Methylcyclohexanone Intermediates in the Rhodium-Catalyzed Hydrogenation of Isomeric Cresols as Estimated by a Kinetic Method

In a previous paper (1), we have reported that isomeric cresols afforded about 61–70% yields of the corresponding methylcyclohexanones as intermediates when each cresol was hydrogenated over a rhodium catalyst at 80°C and 80–100 kg/cm² of hydrogen pressure. The method of estimation of the ketone intermediates was based on the stereochemistry of hydrogenation of a cresol and the corresponding methylcyclohexanone.

In this paper, the yields of the ketone intermediates have been estimated by a kinetic method from the changes in the concentrations of the ketones in the course of hydrogenation (2, 3). The results on each cresol are shown in Fig. 1.

The hydrogenation of cresol to methylcyclohexanol will proceed by the following two simultaneous reaction paths: the one via methylcyclohexanone and the other not via the ketone. The intermediates in the reaction path 3 will be various unsaturated



alcohols which hydrogenate much more rapidly than cresol does, while the methylcyclohexanone produced by the path 1 hydrogenates rather slowly over rhodium under the present reaction conditions and accumulates in considerable amount in the course of hydrogenation. If it is assumed that the establishment of the adsorption-desorption equilibria is fast with respect to the hydrogenation of cresol and methylcyclohexanone, the change in the concentration of the ketone, C_2 , may be given by Eq. (1), on the assumption of the Langmuir-Hinshelwood mechanism and taking the original concentration of cresol as unity (see Ref. 2, Sections II and III, and Ref. 3).

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

C_1 is the concentration of cresol, the k_i 's are the rate constants for the corresponding reaction paths, and $K = k_2 b_2 / (k_1 + k_3) b_1$, where b_1 and b_2 represent the adsorption coefficients of cresol and methylcyclohexanone, respectively. Differentiating Eq. (1) with respect to C_1 and putting the resulting expression equal to zero, we obtain the concentration of cresol at which the ketone intermediate becomes maximum, which is denoted as $(C_1)_m$ and is given by Eq. (2).

$$(C_1)_m = K^{1/(1-K)} \quad (2)$$

Hence, the maximum concentration of the ketone intermediate, $(C_2)_{max}$, is given by Eq. (3).

$$(C_2)_{max} = \left(\frac{k_1}{k_1 + k_3} \right) K^{K/(1-K)} \quad (3)$$

By evaluating $(C_1)_m$ and $(C_2)_{max}$, which were obtained experimentally (see Table 1), into Eqs. (2) and (3), we obtain approximately the values of $k_1/(k_1 + k_3)$ and K . It is obvious that $k_1/(k_1 + k_3)$ is the proportion of the cresol which was hydrogenated to methylcyclohexanone of all the cresol converted. The yields of the ketone intermediates thus obtained are listed in Table 1, together with the corresponding values of K . Although the values of $k_1/(k_1 + k_3)$ and K can be obtained simply as described above, these values may be evaluated more accurately in such a way that, by choosing the most proper values of $k_1/(k_1 + k_3)$ and K in Eq. (1), the curve given by the equation may represent the real variation in the concentration of the ketone most closely. The yield of the ketone and K thus obtained are given in Table 1, and the corresponding

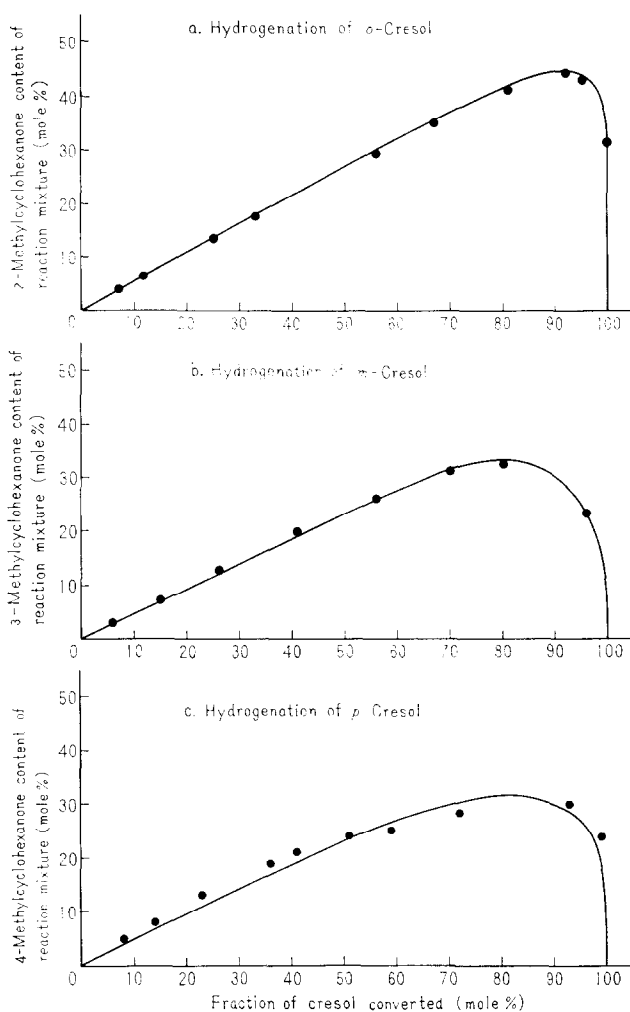


FIG. 1. Methylcyclohexanone formed in hydrogenation of cresol over rhodium catalyst as a function of the conversion of cresol; temp., 80°C, H₂ press., 80–100 kg/cm². ●, Methylcyclohexanone content of reaction mixture; the points shown are a set of results of separate experiments. —, Change in the concentration of methylcyclohexanone as given by Eq. (1).

TABLE I
YIELDS OF METHYLCYCLOHEXANONE INTERMEDIATES IN HYDROGENATION
OF CRESOL WITH RHODIUM CATALYST

Cresol	$(C_1)_m$ (mole %)	$(C_2)_{max}$ (mole %)	K in Eq. (2)	$\frac{100k_1}{k_1 + k_3}$ in Eq. (3)	K evaluated from Eq. (1)	$\frac{k_2}{k_1 + k_3}$	$\frac{b_2^a}{b_1}$	Yield of ketone intermediate (mole %)		
								By kinetic method ^a	By stereo- chemistry ^b	By initial yield method
Ortho	5–10	45	0.06–0.15	53–63	0.07	0.090	0.78	55	60	58
Meta	19–24	32	0.33–0.47	56–62	0.25	0.535	0.47	52	61	43
Para	11–16	29	0.15–0.25	40–46	0.30	0.39	0.775	54	63	66

^a Calculated from the value of the K evaluated by Eq. (1).

^b These values are slightly corrected from those reported previously according to the % hydrogenation based on the gas chromatographic analysis.

curves when these values are substituted into Eq. (1) are shown in Fig. 1. It will be seen that the changes in the concentrations of methylcyclohexanones obtained experimentally are in good agreement with those given by the equations, especially for *o*- and *m*-cresols, throughout the course of hydrogenation. From the value of K and the ratio of the rate constants of methylcyclohexanone and cresol, $k_2/(k_1 + k_3)$,* the ratio of the adsorption coefficients of the ketone and cresol, b_2/b_1 , can be calculated, which is also included in Table 1. It will be seen that the small value of K for *o*-cresol is mostly due to the kinetic factor, rather than to the difference in the strength of adsorption between *o*-cresol and 2-methylcyclohexanone.

When the yields of the ketone intermediates obtained by the present kinetic method are compared with those obtained previously by the stereochemistry of the hydrogenation and by the extrapolation of the yield of the ketone versus saturated alcohol to the initiation (see Table 1), it will be seen that, in general, differences in the results are not great and the yields of the ketone intermediates lie mostly between 50% and 65%. It is noteworthy that the yields of 2-methylcyclohexanone estimated by the three methods are all closely consistent with each other, as was expected, since the rate of the hydrogenation of 2-methylcyclohexanone was very small

* These were obtained from the initial rates of hydrogenation of methylcyclohexanone and cresol, respectively, under the same conditions.

and the three methods of estimation could all be applied more accurately in this case.¹

It is of interest that the yields of the ketone intermediates are nearly the same for three isomeric cresols. This may suggest that the steric factor does not concern with the steps which determine the yields of the ketones and seems also to be in line with the assumption made previously that all kinds of dihydrocresols are produced in equal probability (1).

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¹ The yields of the ketone intermediate obtained by the initial yield method are too small for *m*-cresol and too great for *p*-cresol. One reason for this may be that the method is concerned only with the initial states of hydrogenation which may not always be alike with the subsequent states of hydrogenation.

The Migration of Metal Ions in Zeolite-Y as Revealed by ESR of Cu²⁺

The zeolite used in this investigation was a zeolite of type Y with a unit cell composition according to Na₃₆(AlO₂)₅₆(SiO₂)₁₁₂·196 H₂O. Prior to introduction of Cu²⁺ the zeolite samples were ion-exchanged with Mg²⁺,

Zn²⁺, or La³⁺. Representative numbers are 18 Mg²⁺, 12 Zn²⁺, and 13 La³⁺ per unit cell. The number of copper ions amounts to 0.3 per unit cell. Dehydration was carried out in air or oxygen: 8 hr at 110°C in air, 8 hr at 200°C