JOURNAL OF CATALYSIS 8, 100–104 (1967)

LETTERS TO THE EDITORS

The Hydrogenation of *o*-, *m*-, and *p*-Cresols with a Rhodium Catalyst

It has been known that cyclohexanones are produced as intermediates in the catalytic hydrogenation of phenols (*1–4*). Accordingly, the stereochemistry of hydrogenation of isomeric cresols must be closely related to the production of the corresponding methylcyclohexanones. Although studies on the stereochemistry of the hydrogenation with supported rhodium and ruthenium catalysts and with a rhodium-platinum catalyst have recently been reported (*4*, *5*), a more detailed study will be required for the quantitative interpretation of the results.

We have investigated changes in the amounts of the products in the course of the hydrogenation of isomeric cresols as well as changes in the stereoisomeric composition of methylcyclohexanols produced, using a rhodium hydroxide-black catalyst (*6*). The hydrogenation was carried out without using any solvent under such conditions as to be able to depress the probable occurrence of isomerization of the products or intermediates, namely, at a relatively low temperature (80°C) and a high hydrogen pressure (80–100 kg/cm^2). Under these conditions, no isomerization of *cis* and *trans* alcohols was observed and the hydrogen transfer reaction between the alcohol and the ketone occurred only very slightly. Although all runs were carried out at the same range of hydrogen pressure, the effect of varying hydrogen pressure on the stereochemistry was found to be rather small in the range of 10–120 kg/cm^2 of hydrogen pressure. For the analysis of reaction mixtures, gas chromatography of high sensitivity was always used (column dimensions: 3 m by 0.4 cm OD; stationary phase: 10 wt% glycerol on 60-mesh firebrick; temperatures: column, 95°; detector, 95°; carrier gas: nitrogen at 90–100 ml/min).

The results obtained with *o*-, *m*-, and *p*-cresols are shown in Fig. 1, 2, and 3, respectively. *o*-Cresol gives the largest yield of the ketone intermediate of the three cresols, probably because the rate of hydrogenation of 2-methylcyclohexanone is especially very slow. It may be considered that the change in the *cis/trans* ratio of the methylcyclohexanol produced during the hydrogenation is caused by the circumstance that the proportion of the alcohol formed via the ketone intermediate to the total amount of the alcohol produced varies during the reaction, since accumu-

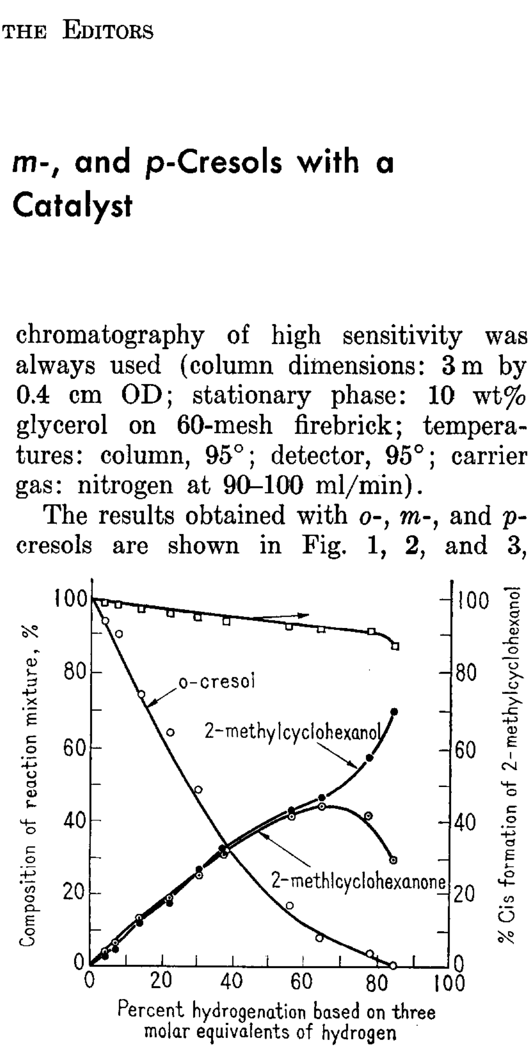


FIG. 1. Hydrogenation of *o*-cresol.

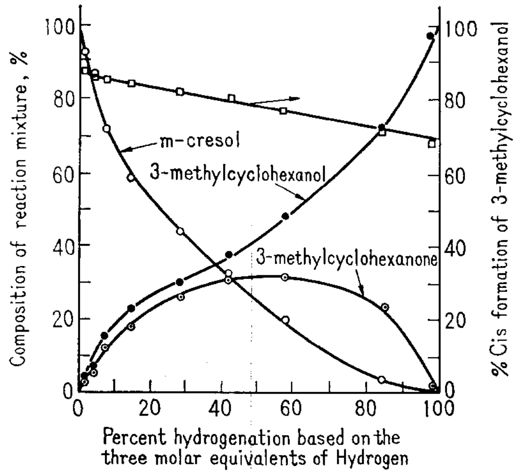


FIG. 2. Hydrogenation of *m*-cresol.

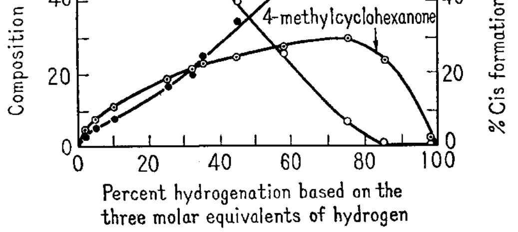


FIG. 3. Hydrogenation of *p*-cresol.

TABLE 1

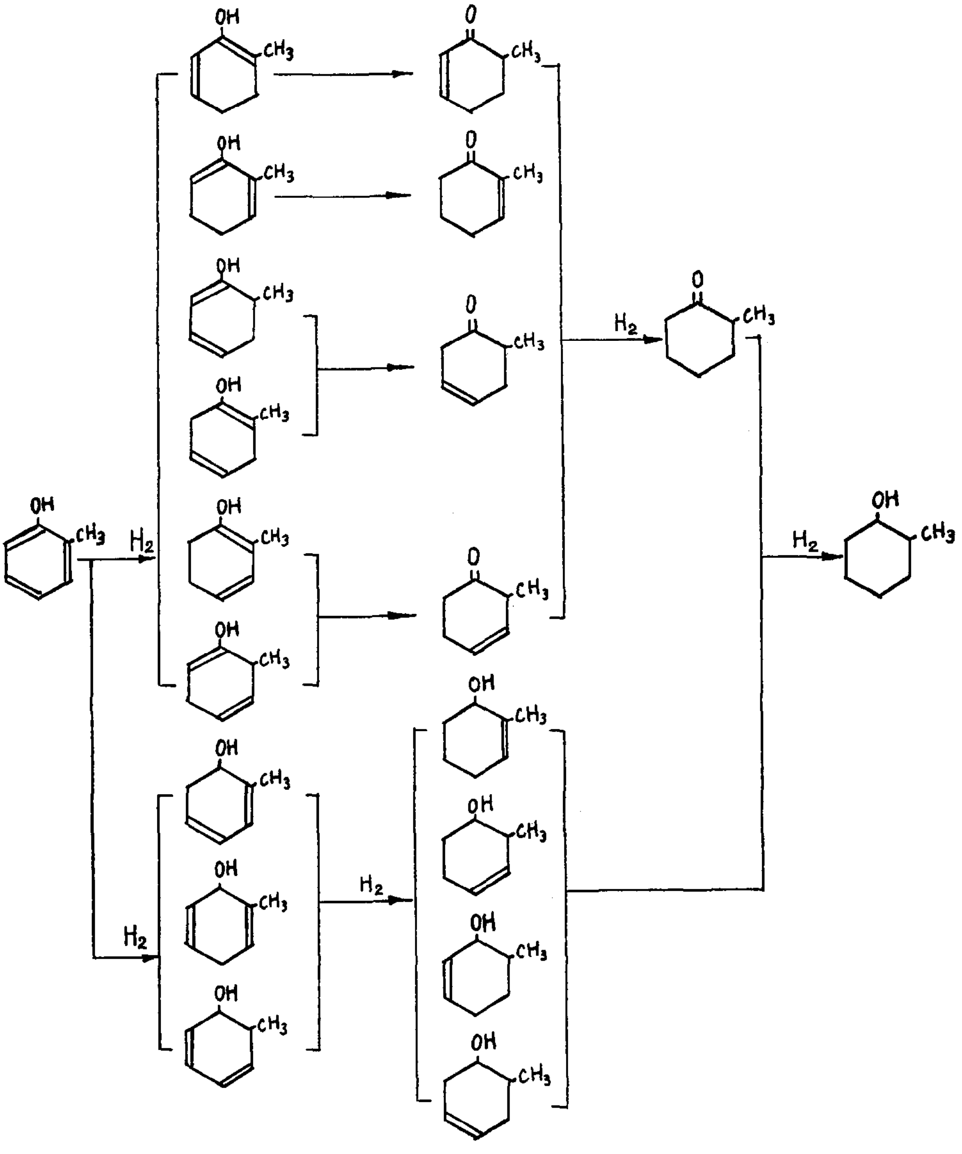
HYDROGENATION PRODUCTS OF CRESOLS WITH RHODIUM CATALYST

Compound	% Hydrogenation based on 3 moles equivalent of hydrogen	Composition of reaction mixture (%)			
		Methylcyclohexanol		Methylcyclohexanone	Cresol unreacted
		Cis	*Trans*		
o-Cresol	84	59	11	30	0
m-Cresol	100	64	36	0	0
p-Cresol	100	73	27	0	0

lation of the ketone and disappearance of the cresol will increase the proportion of the catalyst surface covered with the ketone. The ratio of the rate of formation of the alcohol via the ketone to that of the alcohol formed directly from cresol may be given by $k_1b_1C_1/k_2b_2C_2$, where k_1 is the rate of hydrogenation, b_1 the adsorption coefficient, and C_1 the concentration, of the ketone, and k_2, b_2, C_2 refer to those of cresol. Since, at the initial stage of the hydrogenation, C_2 is far greater than C_1, and k_2 is also much greater than k_1, the ratio $k_1b_1C_1/k_2b_2C_2$ is considered to be very small at the initial stages if a great difference between the adsorption coefficients does not exist, and should be reduced to zero at extrapolation to 0% hydrogenation. Thus, it may be considered that the methylcyclohexanol formed at the very first stage of the hydrogenation does not contain any alcohol formed via the ketone intermediate. If it is assumed that the saturated ketone formed is mostly desorbed from the catalyst surface and then hydrogenated to the alcohol, we can calculate the amount of the methylcyclohexanone formed as the intermediate in the hydrogenation of cresol on the basis of the *cis* yield of the methylcyclohexanol produced (Table 1), together with the following *cis* yields of the alcohol: the *cis* yield of the alcohol at the initial stage of the hydrogenation which was obtained by extrapolating the curve showing changes in the *cis/trans* ratio of the alcohol formed during the reaction, and the *cis* yield of the alcohol formed via the ketone intermediate which was obtained by hydrogenating the respective methylcyclohexanone in phenol and cyclohexanol solutions under the same conditions as used for the hydrogenation of cresol (Table 2). For instance, in the case of *o*-cresol, the yield of intermediate ketone may be calculated as follows, using the values of Tables 1 and 2:

$$64X + 100(70 - X) = 84 \times 70, \quad \text{hence} \quad X = 31\%$$

where X is the percentage of the alcohol which is produced via the ketone at 84% hydrogenation. Since the product at that hydrogenation contains 30% of the ketone



Scheme 1. Hydrogenation of *o*-cresol.

(see Table 1), the yield of the total ketone intermediate becomes

$$31 + 30 = 61\%$$

The yields of the ketone intermediates obtained by similar calculations for *m*- and *p*-cresols are given in Table 2.

The estimated yields obtained here are supported, at least in the case of *o*- and *p*-cresol, by the fact that the initial yields of methylcyclohexanones versus methylcyclohexanols obtained by extrapolation are 58% and 66% for *o*- and *p*-cresol, respectively, although a somewhat smaller value (about 40%) was obtained for *m*-cresol.

If we assume that all kinds of dihydrocresols are produced in equal amounts in the hydrogenation of cresols (7)* and that

---

* Cf. ref (7). These authors assumed in the platinum-catalyzed hydrogenation of isomeric xylenes that all tetrahydroxylenes are produced in equal amounts. This means that dihydroxylenes must be produced also in equal amounts.

unsaturated ketones or their enols formed are preferentially hydrogenated to saturated ketones, as illustrated in Scheme 1 in the case of *o*-cresol, it may be calculated that the hydrogenation of cresols will give 67% yield of methylcyclohexanone as the intermediate. It will be noted that this value does not differ so much from those estimated from the present stereochemical results.

TABLE 2
ESTIMATED YIELDS OF METHYLCYCLOHEXANONE INTERMEDIATES

Compound	Yield of *cis* isomer of methylcyclohexanol (%)		Estimated yield of methylcyclohexanone intermediate (%)
	At initial stage of hydrogenation	Formed in hydrogenation of methylcyclohexanone[a]	
o-Cresol	100	64	61
m-Cresol	87	49	61
p-Cresol	80	70	70

[a] Mean values of the results obtained in phenol and cyclohexanol solutions.

REFERENCES

1. VAVON, G., AND BERTON, A. L., *Bull. Soc. Chim. France* **37**, 296 (1925).
2. COUSSEMANT, F., AND JUNGERS, J. C., *Bull. Soc. Chim. Belges* **59**, 295 (1950).
3. SMITH, H. A., AND STUMP, B. L., *J. Am. Chem. Soc.* **83**, 2739 (1961).
4. RYLANDER, P. N., AND STEELE, D. R., *Engelhard Ind. Tech. Bull.* **3**, 125 (1964).
5. ZYMALKOWSKY, F., AND STRIPPEL, G., *Arch. Pharm.* **297**, 727 (1964).
6. TAKAGI, Y., NAITO, T., AND NISHIMURA, S., *Bull. Chem. Soc. Japan* **38**, 2119 (1965).
7. SIEGEL, S., SMITH, G. V., DMUCHOVSKY, B., DUBBEL, D., AND HALPERN, W., *J. Am. Chem. Soc.* **84**, 3136 (1962).

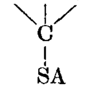
YUZURU TAKAGI†
SHIGEO NISHIMURA‡
KAZUO TAYA†
KOZO HIROTA†

† *The Institute of Physical and Chemical Research*
Bunkyo-ku, Tokyo, Japan
and
‡ *Department of Industrial Chemistry*
Tokyo University of Agriculture and Technology
Koganei, Tokyo, Japan

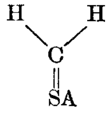
Received October 11, 1966; revised February 20, 1967

Hybridization of the Carbon Atom in Chemisorbed Hydrocarbon Species

Hybridization of the carbon atom of some small symmetric chemisorbed hydrocarbon species can readily be described by application of the group theory. This theory was applied by us to the adsorbed methyl radical (I) and the αα-diadsorbed methylene radical (II),



(I)



(II)

where SA represents a surface atom.

By representing each hybrid orbital by a vector pointing in the appropriate direction and using the rule that the character of the corresponding reducible representation equals the number of vectors which have not shifted by the symmetry operation, we found that for (I) (symmetry group C_{3v}) $\Gamma_\sigma = 2A_1 + E$. The four atomic orbitals necessary for constructing the set of four hybrid orbitals, must consist of two orbitals of A_1 symmetry and one of E symmetry. Using the character table, we found for the carbon atom the A_1 orbitals s, p_z, and d_{z^2} and the E orbitals (p_x, p_y), $(d_{x^2-y^2}, d_{xy})$, and