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# The Chemistry and Catalysis of the Toluene Hydrodealkylation Reaction

## II. Kinetic Analysis

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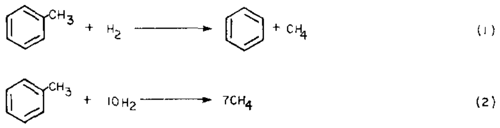
The toluene hydrodealkylation (THD) reaction may be considered to be a selective hydrogenolysis reaction since a single C–C bond is selectively broken in the presence of hydrogen. It was demonstrated, however, in the first paper of this series that the kinetic parameters and periodic trends observed for THD show little resemblence to those trends expected for typical paraffin hydrogenolysis reactions such as ethane hydrogenolysis. For example, the dependence of the THD reaction on hydrogen partial pressure for Group VIII metals varies from slightly negative on Pt and Pd to about first order on Os and Ru, whereas for these same metals the rate of ethane hydrogenolysis shows a strong negative dependence on hydrogen partial pressure. Reasons for these differences are presented in this present paper. A reaction sequence is presented that includes both C–C bond-breaking and product desorption steps in the overall reaction sequence. This analysis leads to a simple power rate law expression of the form:

$$r = kP_{\mathrm{Tol}}{}^{n}P_{\mathrm{H_2}}{}^{1-n(a+1)}.$$

The kinetic parameters presented in Part 1 of this series agree well with those predicted from this rate expression.

## INTRODUCTION

Hydrodealkylation of alkylaromatics to produce benzene is potentially an important process for benzene production. The hydrodealkylation reaction can be carried out either thermally or catalytically using a variety of catalysts including both oxides and supported metals. The simplest hydrodealkylation reaction is the reaction of toluene and $H_2$. This reaction may occur by the selective hydrodealkylation reaction to produce benzene and methane according to reaction (1) and/or by the total toluene hydrogenolysis reaction according to reaction (2) shown below. Supported Group VIII metals are known to be effective catalysts for reaction (1) and relatively ineffective catalysts for reaction (2). In the first paper (*1*) of this series, the specific activities and selectivities of one Group VIIB metal, Re, and all the Group VIII metals, except Fe and Co, were discussed. These results were compared where possible to the results of other workers for reaction (1), the toluene hydrodealkylation



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reaction, which for simplicity will be referred to as the THD reaction.

The THD reaction may be considered to be a selective hydrogenolysis reaction in the sense that a C–C bond is being selectively broken in the presence of $H_2$. However, as discussed in Part 1, the kinetic parameters and periodic trends observed for THD over most of the Group VIII metals show little resemblence to those trends expected for a typical paraffin hydrogenolysis reaction such as ethane hydrogenolysis. The reasons for these differences will be discussed in detail in this present paper. A reaction sequence will be proposed that, with simplifying assumptions, leads to a power rate law expression consistent with the kinetic results for the THD reaction presented in Part 1.

## DISCUSSION

The catalytic breaking of C–C bonds in the presence of $H_2$ is termed hydrogenolysis. Paraffin hydrogenolysis reactions have been the subject of extensive studies in heterogeneous catalysis. Perhaps the most widely studied hydrogenolysis reaction is the $H_2$–ethane reaction as follows:

$$C_2H_6 + H_2 \rightarrow 2\ CH_4. \qquad (3)$$

The Group VIIB and Group VIII metals are known to be active metal catalysts for reaction (3). Reaction (1), the THD reaction, is also a reaction in which a C–C bond is broken and may thus be thought of as a selective hydrogenolysis reaction. It might be expected then that the kinetics of the THD reaction would tend to resemble to some degree the kinetics observed for reaction (3), the ethane hydrogenolysis reaction. It was shown, however, in Part 1 of this present study that the THD kinetics do not in fact resemble the kinetics for ethane hydrogenolysis as reported by Sinfelt (*2*). It was shown in Fig. 2 of the preceding paper that there are substantial differences in the periodic trends of the metals for the two reactions. For ethane hydrogenolysis, the maximum activity is found at the Group $VIII_1$ metals, Ru and Os. In contrast, the most active metals for THD are the Group $VIII_2$ metals, Rh and Ir. Another important difference is the specificity of the metals for the two reactions. Ethane hydrogenolysis is quite specific to the metal in the sense that there is about a seven-order-of-magnitude range of activities between the most active metal, Os, and the least active metal, Pt. In contrast the metals are relatively insensitive toward the THD reaction. For these same metals, the range of activities is less than a factor of 200.

It was also discussed in Part 1 that the reaction orders for the two reactions differ substantially. Figure 1A compares the orders of reaction with respect to hydrocarbon for both ethane hydrogenolysis and THD. While the periodic trends are similar for both reactions, the reaction orders for toluene are shifted to lower values for THD (zero to $\frac{1}{2}$ order) compared to ethane hydrogenolysis ($\frac{1}{2}$ to first order). Figure 1B

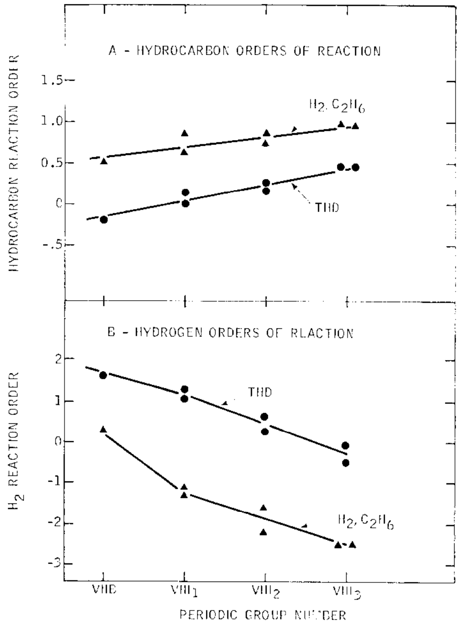

FIG. 1. Comparison of periodic trends of reaction orders for toluene hydrodealkylation and ethane hydrogenolysis. The ethane hydrogenolysis data is from reference (*2*).

compares the orders of reaction with respect to hydrogen for both reactions. Again the values for both reactions vary in a similar manner as one proceeds across the periodic table. However, the values of this parameter are strikingly different for the two reactions. For ethane hydrogenolysis, all values except for Re are strongly negative and vary from less than $-1$ to about $-2.5$. Re has a slightly positive value. In contrast, the values for THD vary from strongly positive for Re to only weakly negative for the Group $\mathrm{VIII}_3$ metals, Pd and Pt.

While the periodic trends of the reaction orders in general vary in a similar manner for both ethane hydrogenolysis and THD, there are important differences in magnitude and sign that need to be rationalized. To address this a brief review of the kinetic sequence for ethane hydrogenolysis proposed by Sinfelt (*3*) is useful. The kinetic results obtained for ethane hydrogenolysis have been interpreted by Sinfelt using the following reaction sequence:

$$C_2H_6 \overset{1}{\rightleftarrows} C_2H_5(\mathrm{ads}) + H(\mathrm{ads}) \tag{4}$$

$$C_2H_5(\mathrm{ads}) + H(\mathrm{ads}) \overset{2}{\rightleftarrows} C_2H_x(\mathrm{ads}) + aH_2 \tag{5}$$

$$C_2H_x(\mathrm{ads}) \overset{3}{\rightarrow} \text{adsorbed } C_1 \text{ fragments} \xrightarrow[\text{Fast}]{H_2} CH_4 \tag{6}$$

Employing standard assumptions the above sequence leads to the following rate equation:

$$r = k_3K^nP_E{}^nP_H{}^{-na}, \tag{7}$$

where $P_E$ = ethane partial pressure, $P_H$ = hydrogen partial pressure, $K$ = equilibrium constant for $C_2H_6 \rightleftarrows C_2H_x(\mathrm{ads}) + aH_2$, and $a = (6 - x)/2$. Equation (7) represents the rate of reaction of ethane as a power rate law. The derivation of Eq. (7) predicts only negative values of hydrogen order since the value of $n$ is constrained to be in the interval $0 < n < 1$. For metals such as Re and Fe, where the experimental values for hydrogen order are positive, Sinfelt (*2*) suggests that the rate-determining step may involve the hydrogenative desorption of monocarbon fragments rather than the C–C bond-breaking step used to derive Eq. (7). Equation (7) has been very successful in correlating observed and calculated values of the $H_2$ order of reaction [see reference (*3*)] for those metals with negative orders of reaction with respect to $H_2$.

A kinetic treatment for THD similar to that employed by Sinfelt for ethane hydrogenolysis would lead to the following reaction sequence:

$$\phi\text{–}CH_3 \overset{K}{\rightleftarrows} \phi\text{–}CH_x(\mathrm{ads}) + aH_2 \tag{8}$$

$$\phi\text{–}CH_x(\mathrm{ads}) \overset{k_1}{\rightarrow} \text{Products} \tag{9}$$

By using assumptions similar to those used by Sinfelt (*3*) the following rate expression for THD can be derived:

$$r = k_1K^nP_T{}^nP_H{}^{-na}, \tag{10}$$

where $0 < n < 1$, $a = \frac{1}{2}$, 1, or $\frac{3}{2}$ with $a = (3 - x)/2$. Equation (10) predicts that the $H_2$ partial pressure dependence is always zero or negative depending on the experimental value of $n$. For THD the only metals that experimentally show negative values for $H_2$ order of reaction are Pt and Pd. Using the experimental value for toluene order of $n = 0.47$ and assuming the best value of $a$ to be $\frac{1}{2}$, the above expression gives a calculated value for $H_2$ order of $-0.24$ which lies between those observed experimentally for Pt and Pd. Nevertheless, the predicted negative $H_2$ order of reaction is inconsistent with the observed positive values with most of the metals which strongly suggests a different reaction sequence must be operative for THD.

It appears then that a typical hydrogenolysis reaction sequence does not satisfactorily explain the observed kinetics of the THD reaction. Therefore a modified reaction sequence is proposed as follows:

$$\phi\text{-}CH_3 + M^* \overset{K_T}{\rightleftarrows} \phi\text{-}CH_x\text{-}M^* + aH_2 \quad (11)$$

$$\phi\text{-}CH_x + M^* \xrightarrow{k_1} CH_x\text{-}M + \phi\text{-}^* \quad (12)$$

$$\phi\text{-}^* + H_2 \xrightarrow{k_2} \text{benzene} \quad (13)$$

$$CH_x\text{-}M + H_2 \xrightarrow{k_3} CH_4 \quad (14)$$

In the above sequence M* is a special site or ensemble of metal sites capable of chemisorbing toluene. Equation (11) represents the equilibrium dissociative chemisorption of toluene. Only the alkyl hydrogen atoms are assumed to be involved in this chemisorption step. This is reasonable in view of the $H_2$ exchange studies reported by Horrex *et al.* (*4*) where it was shown that the alkyl hydrogens exchanged more rapidly than the phenyl hydrogens over most metals. Therefore, by assuming the benzene ring remains intact the possible values of *a* become $\frac{1}{2}$, 1, or $\frac{3}{2}$ depending on the extent of dehydrogenation of the alkyl group.

The proposed THD kinetic sequence presented above differs from the ethane hydrogenolysis reaction sequence principally in the steps involving the hydrogenation of the hydrocarbon fragments [Eqs. (13) and (14)]. For ethane hydrogenolysis Sinfelt (*2*, *3*) assumes this step to be fast compared to the C–C bond-scission step and hence kinetically nonlimiting. Sinfelt also points out that in the case of those metals (Re and Fe) for which Eq. (7) does not represent the correct interrelationship between hydrogen order and ethane order, the rate-determining step may shift from C–C bond scission to methane desorption. Frennet *et al.* (*5*) has suggested that in ethane hydrogenolysis methane desorption may be rate determining for many of the Group VIII metals. This controversy has been long-standing and has yet to be resolved. It is a clear example of the ambiguities that may frequently surround a kinetic analysis of a complex reaction.

We can avoid this discrepancy if we assume that the rate of benzene hydrogenative desorption [Eq. (13)] is slow relative to the hydrogenation of the monocarbon species [Eq. (14)]. Thus if we assume that $k_3 > k_2$ and further assume that $\phi$–* is the most abundant surface species, we can write the following expression for the concentration of $\phi$–*:

$$\phi - * = \frac{\left(\frac{K_T k_1}{k_2}\right)\left(\frac{P_T}{P_H{}^{a+1}}\right)}{\left(\frac{K_T k_1}{k_2}\right)\frac{P_T}{P_H{}^{a+1}}}, \quad (15)$$

where $K_T =$ equilibrium constant for toluene adsorption. Over a restricted range of pressures this expression can be approximated by a simpler expression using the well-known approximation of the expression $ax/(1 + ax)$ by the expression $bx^a$:

$$\phi\text{–}^* = bP_T{}^n P_H{}^{-n(a+1)}, \quad (16)$$

where $0 < n < 1$, and $b$ is a constant. The rate of reaction is given by:

$$r = k_2(\phi\text{–}^*)P_H, \quad (17)$$

and substituting from Eq. (16) gives:

$$r = k_2 b P_T{}^n P_H{}^{1-n(a+1)}. \quad (18)$$

Equation (18) represents the rate of benzene formation as a power rate law. In this treatment $n$ is constrained to be in the range $0 < n < 1$. That is, $n$ is always zero or positive. Thus the kinetic expression is not rigorously valid for Re since experimentally $n = -0.17$ for Re. Nevertheless, this value for Re is only slightly below zero and is not seriously inconsistent with the assumed reaction sequence. At the lower limit of $n = 0$ the order of reaction with respect to $H_2$ should be near 1 and independent of the value of "*a*" chosen. At the upper limit of $n = 1$, the order of reaction with respect to $H_2$ would be negative and vary from about $-0.5$ to $-1.5$ depending on the best value of "*a*" chosen. For the Group VIII metals it is possible to estimate the $H_2$ order of reaction based on the ob-

TABLE 1

Comparison of Calculated $H_2$ Partial Pressure Dependence to Experimental Partial Pressure Dependence

| | $r = kP_T^nP_H^m = kP_T^nP_H^{1-n(a+1)}$ | | | |
|---|---|---|---|---|
| Catalyst (% M/$\gamma$-$Al_2O_3$ | $n_{Expt.}$ | $m_{Expt.}$ | Best "$a$"[a] | $m_{calc} = 1 - n(a+1)$ |
| 1% Ru | 0.16 | 1.03 | $\frac{1}{2}$ | 0.76 |
| 1% Rh | 0.23 | 0.20 | $\frac{3}{2}$ | 0.43 |
| 1% Pd | 0.47 | −0.39 | $\frac{3}{2}$ | −0.18 |
| 2% Os | 0.01 | 1.23 | $\frac{1}{2}$ | 0.98 |
| 2% Ir | 0.15 | 0.49 | $\frac{3}{2}$ | 0.63 |
| 2% Pt | 0.47 | −0.06 | $\frac{3}{2}$ | −0.18 |
| 5% Ni | 0.34 | −0.15 | $\frac{3}{2}$ | 0.15 |

[a] The parameter "$a$" is defined by Eq. (11) in the text. Possible values, which represent the degree of dehydrogenation of the methyl group on toluene, are $\frac{1}{2}$, 1, and $\frac{3}{2}$.

served value of toluene order, $n$, in Eq. (18) by assuming a value of "$a$" to give the best fit to data. This procedure is carried out in Table 1. In general the fit to data is reasonable. Of particular significance is the fact that the use of this reaction sequence allows the derivation of a kinetic expression that correctly predicts both the slightly negative values of $H_2$ order for Pt and Pd and the near first-order dependence for Ru and Os.

If the benzene hydrogenative desorption step [Eq. (13)] is important, then there could possibly be some relationship between THD and reactions in which benzene or other aromatics are products such as in cyclohexane dehydrogenation. Sinfelt *et al.* (*6*) have studied the kinetics of the dehydrogenation of methylcyclohexane to form toluene over Pt/$Al_2O_3$ catalyst. In their analysis, the authors treated the reaction as a series of irreversible steps as follows:

$$M \xrightarrow{k_1} T_a \tag{19}$$

$$T_a \xrightarrow{k_2} T, \tag{20}$$

where M = methylcyclohexane; $T_a$ = absorbed toluene, and T = toluene. An important aspect of the overall kinetics was the desorption step of the product, toluene. In a similar manner, Sinfelt *et al.* (*7*) considers the desorption of benzene to be the rate-determining step for cyclohexane dehydrogenation over Cu–Ni alloy catalysts of widely varying copper contents. The significance of these results is that under appropriate conditions and in particular with aromatic products, the rate of reaction may depend in part on the strength of interaction of the aromatic nucleus with the metal surface.

The methylcyclohexane and cyclohexane dehydrogenation studies were carried out at temperatures greater than 300°C. With the exception of Pt and Pd, the ethane hydrogenolysis studies of Sinfelt, on the other hand, were conducted at temperatures well below 300°C. It is possible that at the higher temperatures used for THD (300°C and greater), the hydrocarbon fragments would interact more strongly with the metals. This could cause the hydrogenative desorption of the hydrocarbon fragments to become kinetically important in a manner similar to the dehydrogenation studies of Sinfelt *et al.* discussed above. If these hydrogenative desoprtion steps are kinetically important, the specificity of the noble metals for THD might resemble the general features of hydrogenation reactions carried out over noble metals.

Two hydrogenation reactions have been extensively discussed in the literature. One reaction is the hydrogenation of ethylene to form ethane, and the second reaction is the hydrogenation of cyclopropane to form propane. Schmit and van Reijen (*8*) have reported specific activities for $C_2H_4$ hydrogenation over most of the Group VIII metals supported on $SiO_2$. Grant *et al.* (*9*) have studied a Re/$SiO_2$ catalyst for $C_2H_4$ hydrogenation. Figure 2A shows the relative specific activities (Rh activity = 1) of the silica-supported Group VIII metals for ethylene hydrogenation. Within the Group VIII metals studied, there is only about a three-orders-of-magnitude difference in activity and within the Group VIII noble metals only about a two-orders-of-magnitude difference in activity. Re/$SiO_2$ is reported (*9*) to be much less active than the Group VIII metals. There are several general comments to be made. First, the specificity of the metals, particularly the Group VIII noble metals, is relatively weak for this hydrogenation reaction. Second, the most active catalyst is Rh for this reaction.

Dalla Betta *et al.* (*10*) have reported the specific activities of the Group VIII noble metals/$SiO_2$ for cyclopropane hydrogenation. Their results are shown in Fig. 2B as relative specific activities (Rh = 1.0). The similarities of the periodic trends between ethylene (Fig. 2A) and cyclopropane (Fig. 2B) are obvious. In both cases Rh is the most active metal. For both reactions the specificity of the noble metals is relatively low (two to three orders of magnitude). Figure 2C shows the relative specific activities (Rh = 1.0) of the Group VIII noble metals for THD. The periodic trends of the second period metals (Ru, Rh, Pd) for THD are generally similar to the two hydrogenation reactions shown in Fig. 2. In the third period the trend in activity of Ir for THD is reversed to that observed for the two hydrogenation reactions. Most importantly, however, for all three reactions the specificity of the Group VIII noble metals is much weaker than for ethane hydrogenolysis discussed above. Also for all three reactions Rh has the highest specific activity.

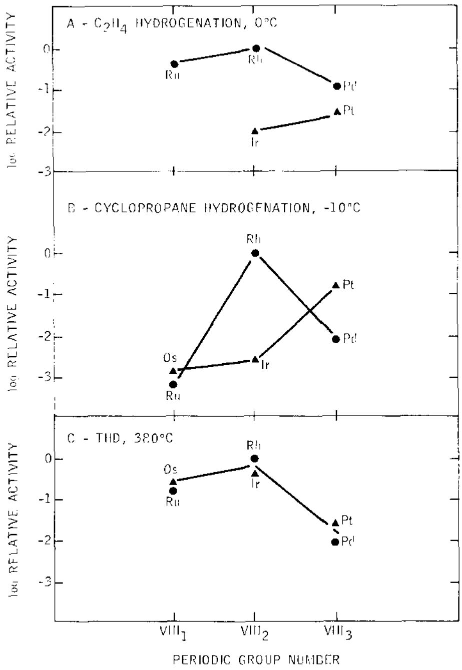

FIG. 2. Comparison of periodic trends of Group VIII noble metals for hydrocarbon hydrogenation reactions and the toluene hydrodealkylation reaction. The ethylene hydrogenation data are from reference (*8*), and the cyclopropane data are from reference (*10*).

There is unfortunately little quantitative information on the specific activities of Group VIII metals for the hydrogenation of benzene. The information that is readily available is reported by Bond (*11*) as follows:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Relative activity on $Al_2O_3$ | Rh > | Ru | >Pt | >Pd | | | |
| Log *k* at ca. 47°C | 0 | −1.0 | −1.01 | — | | | |
| Relative activity on $SiO_2$ | Pt | >Rh | > Ru | >Pd | >Co | >Ni | >Fe |
| Log *k* at ca. 100°C | +0.4 | 0 | −0.1 | −0.2 | −1.1 | −1.2 | −2.3 |

For the alumina-supported metals, Rh is the most active metal with Pt approximately one order of magnitude lower in activity. For the $SiO_2$-supported metals, Pt is slightly higher in activity compared to Rh. For the metals on either support the specificity for benzene hydrogenation is quite low, being only one to two orders of magnitude from the most active metal Rh (Pt) to the least active metals. These results again point to Rh as among the most active of the Group VIII metals for hydrogenation reactions.

From the results discussed above, it is apparent that the THD reaction is similar in many respects to typical hydrogenation reactions. The most significant similarity is the weak specificity of the Group VIII metals for THD and hydrocarbon hydrogenations compared to the very strong specificity of the Group VIII metals for hydrogenolysis reactions. The comparisons made above all point to rhodium as the most active metal for THD and hydrocarbon hydrogenation reactions.

Ethane hydrogenolysis is considered to be a demanding reaction whereas hydrogenation reactions are classified as facile reactions (*10*). We have previously reported (*12*) that within a factor of 2 the specific activity of Rh for THD is insensitive to the support and to the metal dispersion. These results classically define THD over rhodium to be a facile reaction. Once again THD resembles hydrogenation reactions more than hydrogenolysis reactions.

The THD reaction thus appears to occupy an intermediate position between hydrogenolysis and hydrogenation reactions. The kinetic parameters of Pt and Pd resemble somewhat typical hydrogenolysis reactions which is reasonable as they are the least active noble metals for breaking C–C bonds. Therefore the C–C bond-breaking step [Eq. (12)] may well be rate-determining for these metals. At the other extreme, Ru and Os are among the most active metals for C–C bond breaking; therefore it is plausible that for these metals the product desorption step [Eq. 13)] may have become rate-determining. The near first-order dependence in hydrogen observed for these metals supports this notion. Finally, Rh and Ir occupy an intermediate position and may well represent an optimum balance in the relative rates of the hydrogenolysis and hydrogenation steps in the above reaction sequence. Thus the THD reaction over Group VIII metals has kinetics characteristic of both hydrogenolysis and hydrogenation reactions.

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