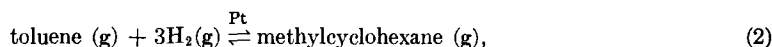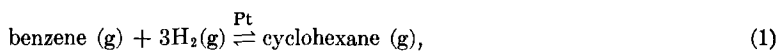# Competitive Hydrogenation of Benzene and Toluene and Dehydrogenation of the Corresponding Naphthenes over Platinum Wire

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Relative rates were measured for the reactions

$$\text{benzene (g)} + 3\text{H}_2\text{(g)} \overset{\text{Pt}}{\rightleftharpoons} \text{cyclohexane (g),} \tag{1}$$

$$\text{toluene (g)} + 3\text{H}_2\text{(g)} \overset{\text{Pt}}{\rightleftharpoons} \text{methylcyclohexane (g),} \tag{2}$$

occurring competitively on platinum wire. The experiments were done in a well-mixed flow reactor at 600–672°K and 4.4–24.9 atm. The catalyst was selective for the reactions shown; no other products were significant. The catalyst activity declined steadily during processing, and was restored periodically by hydrogen treatment.

The data are well represented by the theoretical expression

$$\frac{\mathfrak{R}_2}{\mathfrak{R}_1} = \left(\frac{k_2}{k_1}\right)_d \exp\left[\frac{E_2 - E_1}{R}\left(\frac{1}{T_d} - \frac{1}{T}\right)\right] \frac{[p_T p_{\text{H}_2}{}^3 - p_{\text{MCH}}/K_2]}{[p_B p_{\text{H}_2}{}^3 - p_{\text{CH}}/K_1]} \tag{3}$$

at all pressures, temperatures, and activity levels investigated. The 95% confidence intervals for the kinetic and equilibrium constants are

$$(k_2/k_1) = 0.578e^{\pm 0.055},$$

$$(E_2 - E_1)/R = 116 \pm 326 \text{ Kelvins,}$$

$$K_1 = 0.0196e^{\pm 0.05},$$

$$K_2 = 0.0063e^{\pm 0.05},$$

at the datum temperature T_d of 600°K. A value of 0.96 ± 0.06 was obtained for the common stoichiometric number of Reactions 1 and 2. Mechanistic implications of these results are discussed.

INTRODUCTION

This work is a continuation of research in our laboratory *(1–4)* on the platinum-catalyzed hydrogenation of benzene and dehydrogenation of cyclohexane. In the

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present work, toluene and methylcyclohexane are included in order to study two competing reactions. This multicomponent system is relevant to petrochemical operations, and allows demonstration of a robust method for investigating kinetics during catalyst deactivation.

The method used here was prompted by

the Yang–Hougen rate expression (5)

$$rate = \frac{(coefficient)(driving\ force)}{adsorption\ term} \quad (4)$$

for reactions with one controlling step, occurring on an ideal surface. If two such reactions occur competitively on the same *number* and *kinds* of sites, their adsorption terms cancel when the ratio of the overall rates is predicted. Relative rate measurements can then be used to study the numerators of the two rate expressions, independent of the adsorption term. Deactivation resulting from chemisorption can likewise be factored out, greatly facilitating kinetic interpretations.

EXPERIMENTAL METHOD

The rates of reaction were measured in a well-mixed flow system, consisting of a fixed-bed reactor and special recycle blower (6). The flow plan is shown in Fig. 1.

Hydrogen was fed to the recycle blower through a Deoxo unit, dryer, and rotameter. The mixed hydrocarbons were fed through a dryer, a guard bed of platinum–alumina for adsorption of catalyst poisons, a capillary flowmeter, and a vaporizer, before entering the hydrogen stream. All reactants were 99.9% pure or better; reactant and catalyst analyses are given in Ref. (6).

The catalyst was platinum wire, 99.979% pure, obtained from Mathey Bishop, Inc.; 365.8 m of 28.4-μm-diameter wire were used, giving a nominal surface area of 327 cm². Electron micrographs (6) of the catalyst after use indicate that the roughness factor was near unity for these experiments.

The reactor (Fig. 2) was a tubular pressure fitting, thermally insulated and packed with a fixed bed of platinum wire. The wire was coiled in 3-m lengths and packed between two screens, giving a catalyst bed 7.6 cm long and 1.27 cm in diameter with a porosity of 0.976. The reactor and recycle loop were mounted in an electric oven to
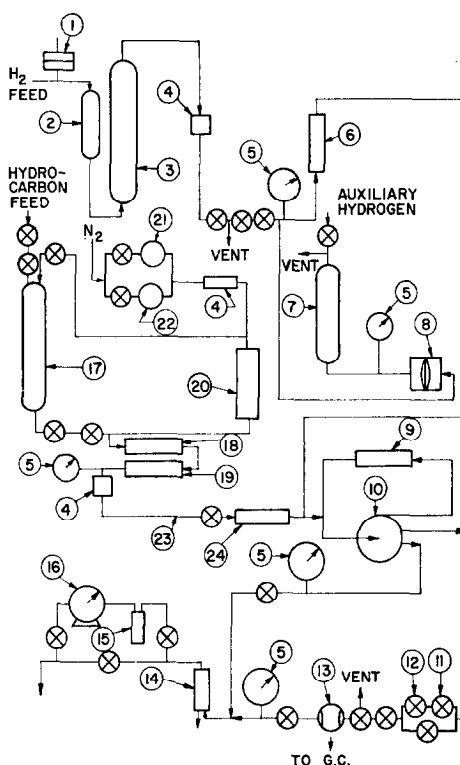

Fig. 1. Flow diagram. (1) Rupture disk, (2) deoxo unit, (3) dryer, (4) filter, (5) pressure gauge, (6) rotameter, (7) reference pressure chamber, (8) diaphragm switch, (9) reactor, (10) recycle blower, (11) solenoid valve, (12) metering valve, (13) sampling valve, (14) cold traps, (15) saturator, (16) wettest meter, (17) reservoir, (18) dryer, (19) guard reactor, (20) blowcase, (21) low-pressure regulator, (22) high-pressure regulator, (23) capillary tube, (24) vaporizer.

avoid any condensation of the reaction mixture. Recycle rates ranged from 6 to 24 moles/mole of fresh reactants.

The reaction products were analyzed by gas chromatography with hydrogen carrier and a thermal conductivity detector. Two columns in series were used, with 20% silicone oil D.C. 200 on 60- to 80-mesh chromosorb P in the first and 20% β,β'-oxydipropionitrile on 40- to 50-mesh chromosorb P in the second. The standard error of analysis (in mole percent of total hydrocarbons) was 0.4 for benzene and 0.6 for the other hydrocarbons.

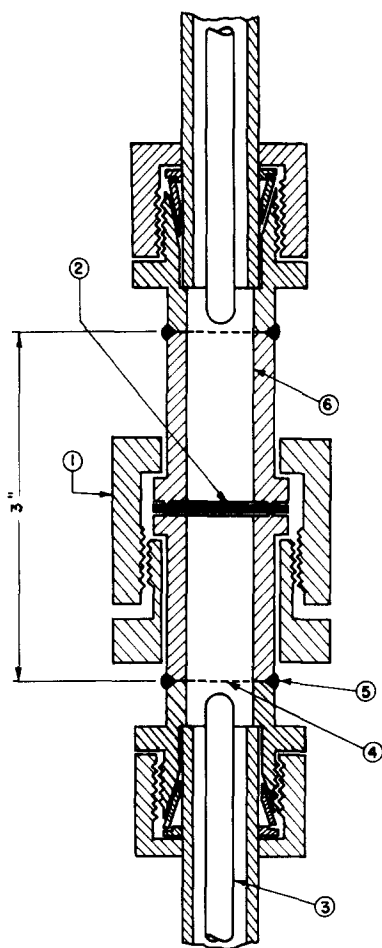Reaction rates were calculated from the

FIG. 2. Reactor. (1) Cajon 10 VCR fitting, (2) soft stainless gasket, (3) ¼-in.-i.d. thermowell, (4) retaining screen, (5) weld, (6) ½-in.-i.d. fitting.

feed rates and conversions. Mean reaction temperatures and partial pressures were calculated from the reactor inlet and outlet conditions, to correct for the small deviation from perfect mixing. Heat and mass transfer calculations by the methods in Ref. (7) indicated that the gas temperature and concentrations at the catalytic interface differed negligibly from the bulk stream conditions.

PRELIMINARY EXPERIMENTS

Several preliminary hydrogenation runs were made at 14.6 atm and 533°K, with hydrogen and benzene as reactants in a 12:1 molar ratio. The results can be summarized as follows:

1. Reaction rates up to 10 mole hr^{-1} m^{-2} were observed initially on fresh or regenerated wire. These rates are comparable with initial values obtained by Quady (3) on finely ground platinum–alumina catalyst (and also based on platinum surface area).

2. The wire catalyst lost activity rapidly at first, and less rapidly with continued use. A five to tenfold decline in activity typically occurred in the first 8 hr, and a two to threefold decline in the next 8 hr.

3. The deactivation was slowed by each of the following measures: using desulfurized benzene (0.05 ppm S), reducing the total feed rate, and feeding the liquid benzene through a guard bed of platinum–alumina catalyst. These measures were continued in all subsequent experiments.

4. With the foregoing measures in effect, the reaction rate still declined, but approached a steady level (about 0.12 mole hr^{-1} m^{-2}) after 50 hr of operation at a benzene feed rate of 1.05 mole hr^{-1}. This reaction rate is somewhat lower than the stable level of 1.0 mole hr^{-1} m^{-2} for platinum on alumina indicated by Korbach's experiments (1, 8) at the same gasphase conditions. Such rates are believed typical of long-term operation at these conditions, but are too low for convenient measurement in the present apparatus.

5. Regenerations by mild oxidation (0.4% O$_2$ in N$_2$, 700°K, 1 atm, 8 hr) followed by reduction (H$_2$, 744°K, 14.6 atm, 72 hr) consistently restored full catalyst activity. Reduction alone was used later (H$_2$, 755°K, 18 atm, 48 hr) and proved comparably effective.

6. Cyclohexane and traces of cyclohexene were the only detectable reaction products.

The deactivation was attributed to chemisorbed feed impurities and coke precursors, removable by combustion or hydrogenation. Although these techniques restored the activity consistently, their repro-

ducibility was not sufficient for an absolute rate investigation. Therefore, in the following experiments, Reactions (1) and (2) were conducted competitively and their relative rates were used for the kinetic analysis.

MAIN EXPERIMENTS

The main test pattern was a 2^5 factorial design in the following variables:[2]

	Level 1	Level 2
p at 600°K	4.4 atm	6.1 atm
p at 672°K	20.0 atm	24.8 atm
H_2/HC	6	12
$x_B = 0.5 - x_{CH}$	0	0.5
$x_T = 0.5 - x_{MCH}$	0	0.5

Here p is the total pressure, H_2/HC is the molar ratio of the entering hydrogen and hydrocarbon streams, and x_i is the mole fraction of species i in the entering hydrocarbon stream. The liquid compositions were chosen to give data on the forward and reverse reactions at each combination of p, T, and H_2/HC.

The minimum pressure was determined by operability of the recycle blower, and the maximum pressure was determined by the rate of leakage from the seals on the blower shaft. The temperatures and intermediate pressures were selected to allow readily measurable conversions according to previous equilibrium data (1, 8, 9).

Each run in the design was conducted for 2 hr, and provided reaction rates over a range of catalyst activity. After each run, the catalyst was regenerated for 4 hr with hydrogen at 755°K and 21.4 atm. The following results were evident:

1. The catalyst remained highly selective. Reactions 1 and 2 accounted for all measurable products.
2. The ratio $\mathcal{R}_1/\mathcal{R}_2$ stayed constant during each run, even when both rates declined as much as fivefold.

KINETIC MODEL

Absolute rate theory (10) yields the rate expressions

$$\mathcal{R}_1 = k_1[(a_B a_{H_2}{}^3)^{1/\sigma_1} - (a_C/K_1)^{1/\sigma_1}]\phi_1, \quad (5)$$

$$\mathcal{R}_2 = k_2[(a_T a_{H_2}{}^3)^{1/\sigma_2} - (a_{MCH}/K_2)^{1/\sigma_2}]\phi_2 \quad (6)$$

for a thermodynamically ideal catalytic surface, if each overall reaction has a single rate-controlling step. Here σ_i is the stoichiometric number (11) of the controlling step in overall reaction i. The function ϕ_i, which includes the adsorption term of Eq. (4), is a product of thermodynamic activities common to the forward and reverse rate terms. For example, if the activated complex of Reaction 1 were $C_6H_{12}X$ and σ_1 were unity, then ϕ_1 would be a_X, whatever the identity of X.

The similarity of Reactions 1 and 2 suggests the hypotheses $\sigma_1 = \sigma_2 = \sigma$ and $\phi_1 = \phi_2$. Equations (5) and (6) then give the prediction

$$\frac{\mathcal{R}_2}{\mathcal{R}_1} = \frac{k_2}{k_1} \frac{[(a_T a_{H_2}{}^3)^{1/\sigma} - (a_{MCH}/K_2)^{1/\sigma}]}{[(a_B a_{H_2}{}^3)^{1/\sigma} - (a_{CH}/K_1)^{1/\sigma}]} \quad (7)$$

for the ratio of the rates when the two reactions occur together.

Use of Arrhenius forms for k_1 and k_2 gives

$$\ln\left(\frac{k_2}{k_1}\right) = \ln\left(\frac{k_2}{k_1}\right)_d$$
$$+ \left(\frac{E_2 - E_1}{R}\right)\left(\frac{1}{T_d} - \frac{1}{T}\right), \quad (8)$$

in which the subscript d denotes values at a datum temperature T_d. Integration of the Gibbs–Helmholtz relation gives the temperature dependence of the equilibrium constants:

$$\ln K_i = \ln K_{id} + \int_{T_d}^{T} \frac{\Delta H_i^0}{R} d\left(-\frac{1}{T'}\right)$$
$$i = 1, 2 \quad (9)$$

or

$$\ln K_i = \ln K_{id} + \left(\frac{\Delta H_{id}^0}{R}\right)\left(\frac{1}{T_d} - \frac{1}{T}\right)$$
$$+ \int_{T_d}^{T} \frac{\Delta H_i^0 - \Delta H_{id}^0}{RT'^2} dT' \quad i = 1, 2 \quad (10)$$

The integral in Eq. (10) can be calculated accurately enough from heat capacities given in (9); however, redetermination of K_{id} (and possibly ΔH_{id}^0) is worthwhile in view of previous comparisons (8).

REGRESSION CALCULATIONS

Equations (7), (8), and (10) were fitted to the data by minimizing the total sum of squares,

$$S = \sum_{h=1}^{N} \left[\ln\left(\mathfrak{R}_{2h}/\mathfrak{R}_{1h}\right)_{\text{obs}}\right.$$
$$\left. - \ln\left(\mathfrak{R}_{2h}/\mathfrak{R}_{1h}\right)_{\text{pred}}\right]^2, \quad (11)$$

taken over all test numbers, h. The variance

TABLE 1

Comparisons of k_2/k_1

T (°K)	Prediction from Regression 1	Prior observation and catalyst
423	$0.53\,e^{\pm 0.17}$	0.5, Ni–alumina (15)
303	$0.48\,e^{\pm 0.58}$	0.6, Adams Pt (16)

of $\ln\left(\mathfrak{R}_2/\mathfrak{R}_1\right)_{\text{obs}}$ was thus treated as uniform over the experimental region.

Test calculations of activities a_i from the virial expansion (12) with Kihara parameters from (13) showed that partial pressures p_i could be substituted for activities within the accuracy of the rate measurements; this was done in the calculations reported here. The Lewis–Randall mixture rule (14), employed in Ref. (6), overestimates the activity corrections and is not used in the present calculations. The regressions are summarized in Table 1.

Regression 1 is a least-squares determination of all parameters in the model, except σ which is fixed at unity. The standard deviation of 0.070 is comparable with the repeatability of $\ln(\mathfrak{R}_2/\mathfrak{R}_1)$ in replicate measurements. The enthalpies of reaction are smaller than those of API (9); the latter values are preferred in view of the narrow temperature range and appreciable temperature rises (up to 7°K across the reactor) in our experiments.

A seven-parameter regression (not shown) with σ adjustable gave a slightly better fit, with 95% confidence limits of 0.96 ± 0.06 for this parameter. With this statistical evidence, σ was taken as unity in subsequent calculations.

Regression 2 of Table 1 is a four-parameter fit with σ, ΔH_{1d}^0, and ΔH_{2d}^0 maintained at their recommended values. The standard deviation is significantly larger than that of Regression 1, but the parameter values are considered more realistic. The small value of $(E_2 - E_1)$ is consistent with the expected similarity of the two reactions. Published measurements of k_2/k_1 in liquid-phase hydrogenation fall close to our results, as indicated in Table 1.

The equilibrium constants in Table 2 have quite narrow confidence intervals, and are smaller than the API (9) values, in common with other determinations (8, 17). Our estimate of K_{1d} in Regression 2 is close to the value predicted from Korbach's measurements (1, 8). Graphical com-

TABLE 2

Kinetic and Thermodynamic Constants at $T_d = 600°K$

	$\ln (k_2/k_1)_d$	$(E_2 - E_1)$	$\ln K_{1d}$	$\ln K_{2d}$	ΔH_{1d}	ΔH_{2d}	Sum of squares, S	Degrees of freedom	Regression standard deviation
Regression 1	−0.573 ±0.033[a]	630.[b] ±555.	−4.05 ±0.04	−5.21 ±0.04	−49165.[b] ±619.	−47638.[b] ±623.	0.390	80	0.070
Regression 2	−0.548 ±0.055	231. ±648.	−3.93 ±0.05	−5.06 ±0.05	52281[c]	51392[c]	1.417	82	0.131

[a] All indicated ranges are 95% confidence intervals based on the regression standard deviation, and on $\sigma = 1$ in Eq. (7).
[b] All energies are in calories per mole.
[c] Fixed values from Ref. (9).

parisons of results for K_1 and K_2 as functions of temperature are given in Figs. 3 and 4.

CONCLUSIONS

1. The constancy of $\mathfrak{R}_1/\mathfrak{R}_2$ during catalyst deactivation implies that reactions (1) and (2) use the same number and kinds of sites in their controlling steps.

2. The stoichiometric number $\sigma = 0.96$ ± 0.06 indicates that Reactions (1) and (2) each involve just one occurrence of a rate-controlling step. This result, with Eqs. (5) and (6), determines the reaction orders except for the functions ϕ_1 and ϕ_2.

3. The excellent fit of the data with Eq. (7) indicates that ϕ_1 and ϕ_2 are equal, as postulated. Hence, the two reactions have similar controlling steps. The smallness of our result for $(E_2 - E_1)$ is consistent with this conclusion.
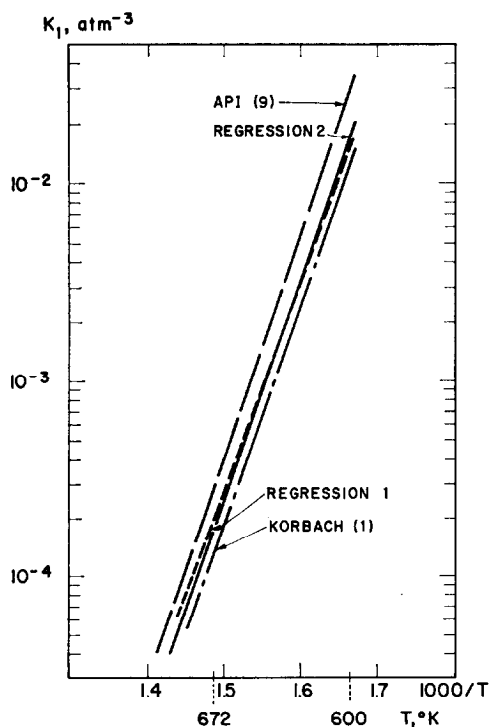
4. The competitive reaction method is

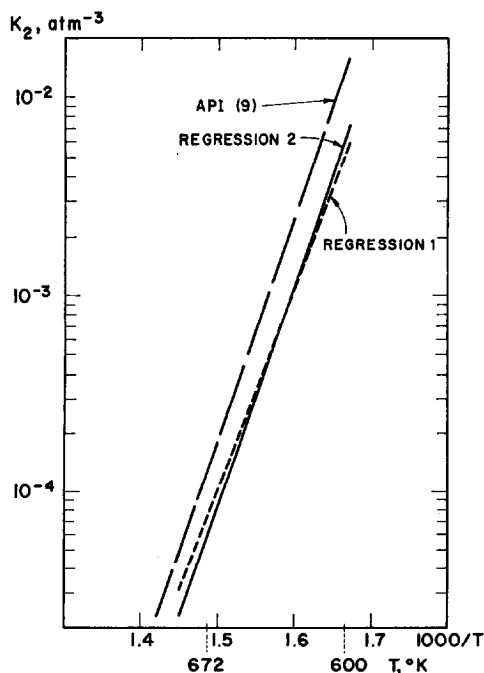FIG. 3. Results for equilibrium constant of Reaction (1).

FIG. 4. Results for equilibrium constant of Reaction (2).

useful for studying the reaction rate functions of multicomponent systems with steady or varying catalyst activity. The method also provides valuable information on catalyst selectivity. In the form used here, the theory is restricted by the assumptions of (i) an ideal surface and (ii) a single rate-controlling step for each overall reaction.

REFERENCES

1. Korbach, P. F., Ph.D. Thesis. University of Wisconsin, Madison (1962).
2. Weaver, R. H., Ph.D. Thesis. University of Wisconsin, Madison (1964).
3. Quady, D. E., Ph.D. Thesis. University of Wisconsin, Madison (1968).
4. Curtin, D. J., Ph.D. Thesis. University of Wisconsin, Madison (1972).
5. Yang, K. H., and Hougen, O. A., Chem. Eng. Prog. 46, 146 (1950).
6. Akyurtlu, J., Ph.D. Thesis. University of Wisconsin, Madison (1975).
7. Bird, R. B., Stewart, W. E., and Lightfoot, E. N., "Transport Phenomena," Chap. 21. Wiley, New York, 1960.
8. Korbach, P. F., and Stewart, W. E., Ind. Eng. Chem. Fundam. 3, 24 (1964).
9. API Research Project 44, National Bureau of Standards Circular. U.S. Department of Commerce, Washington, D.C. (1947).
10. Glasstone, S., Laidler, K. J., and Eyring, H., "The Theory of Rate Processes," Chap. 7. McGraw–Hill, New York, 1941.
11. Horiuti, J., J. Catal. 1, 199 (1962).
12. Hirschfelder, J. O., Curtiss, C. F., and Bird, R. B., "Molecular Theory of Gases and Liquids" (corrected printing with notes added). Wiley, New York, 1964.
13. Tee, L. S., Gotoh, S., and Stewart, W. E., Ind. Eng. Chem. Fundam. 5, 363 (1966).
14. Lewis, G. N., and Randall, M., "Thermodynamics." McGraw–Hill, New York, 1923.
15. Lozovoi, A. V., and D'yakova, M. K., J. Gen. Chem. (U.S.S.R.) 9, 895 (1939).
16. Smith, H. A., and Pennekamp, E. F. H., J. Amer. Chem. Soc. 67, 276 (1945).
17. Prigogine, I., Outer, P., and Herbo, Cl., J. Phys. Colloid Chem. 52, 321 (1948).