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# Thermodynamics and Kinetic Effects in Platinum-Catalyzed *n*-Hexane Transformations

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Equilibrium concentrations of *n*-hexane, isohexanes, methylcyclopentane, and benzene have been calculated and compared with experimental conversion data in the presence of a platinum catalyst. The results can be interpreted in terms of equilibration between *n*-hexane and each of two types of intermediates leading to saturated $C_6$ products and benzene, respectively, at a hypothetical "effective surface hydrogen pressure" which is higher than that measured in the gas phase.

The yields of benzene, methylcyclopentane, and skeletal isomers produced over Pt black from $C_6$ alkanes are strongly influenced by the amount of gaseous hydrogen present: Lower hydrogen pressures favor benzene formation, whereas with more hydrogen present, isomers and methylcyclopentane predominate (*1–3*). It has been suggested that the methylcyclopentane vs benzene ratio, being dependent on hydrogen pressure, may ultimately be attributed to thermodynamic reasons (*4*). Christoffel *et al.* (*5*) have calculated that unsaturated products are formed on Pt from *n*-hexane in amounts higher than those corresponding to their equilibrium concentrations, due, obviously, to kinetic reasons.

Maxima observed in the yields of various products as a function of hydrogen pressure (*1*b, *3*, *6*) can be interpreted in terms of kinetics rather than thermodynamics. Nevertheless, we intended to compare experimental conversion data with those calculated for equilibrium.

Experiments have been carried out in a pulse-microcatalytic device, as described earlier (*1*, *7*). The unsupported platinum black catalyst used was identical to that of Ref. (*1*).

Log $K_p$ values were taken from Ref. (*8*). The calculations were carried out on a TPA-i electronic computer using a program described in Ref. (*9*) and modified to meet the requirements of constant pressure conditions (1 atm together with the helium content of the carrier gas).

The reactions to be considered from a thermodynamic point of view have first to be selected from the very large number of possible processes. We decided to neglect the formation of unsaturated products and [although they are thermodynamically favored (*5*)] dimethylbutanes, because of their very low yields under the conditions applied (*3*, *6*). Hydrogenolysis has also been left out of consideration. As opposed to Ref. (*5*), its yield was not negligible; this process, however, offered an irreversible "sink" for $C_6$ hydrocarbons (build-up reactions not occurring), so as far as it is a process independent of those forming $C_6$ products, its omission cannot

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TABLE 1

Comparison of *n*-Hexane Conversion with Equilibrium Concentrations at 600 K[a]

| $P_{H_2}$, initial (atm) | Composition (%) | | | $C_6$ selectivity (%) | | | Equilibrium concentration (within the $C_6$ fraction) (%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $<C_6$ | $C_6$ prod. | *n*-Hexane unreacted | Isomer[b] | MCP | Benzene | Alkane[c] | MCP | Benzene | $H_2$[d] |
| A. 600 K | | | | | | | | | | |
| 0 | 11.02 | 13.18 | 75.78 | 22.53 | 9.64 | 67.83 | 3.49 | 0.35 | 96.16 | 0.28 |
| | 12.66 | 14.26 | 73.08 | 22.37 | 8.13 | 69.50 | | | | |
| 0.045 | 13.46 | 15.14 | 71.40 | 37.12 | 11.82 | 51.06 | 5.30 | 0.48 | 94.22 | 0.31 |
| | 14.12 | 15.10 | 70.28 | 35.50 | 11.99 | 52.52 | | | | |
| 0.18 | 4.85 | 8.82 | 86.83 | 64.29 | 19.67 | 16.04 | 13.77 | 0.96 | 85.27 | 0.39 |
| 0.45 | 1.45 | 2.84 | 95.73 | 69.72 | 24.65 | 5.63 | 41.91 | 1.99 | 56.10 | 0.56 |
| 0.90 | 0.54 | 0.94 | 98.51 | 78.7 | 21.3 | — | 78.48 | 2.43 | 19.08 | 0.91 |
| B. 700 K | | | | | | | | | | |
| 0 | 28.28 | 27.33 | 44.39 | 2.23 | 0.44 | 97.33 | — | — | 100.00 | 0.29 |
| 0.045 | 30.12 | 22.25 | 47.65 | 2.11 | 0.49 | 97.39 | — | — | 100.00 | 0.32 |
| 0.28 | 43.13 | 25.43 | 31.44 | 2.75 | 0.55 | 96.70 | 0.01 | — | 99.99 | 0.43 |
| 0.45 | 37.52 | 29.18 | 33.14 | 9.12 | 1.56 | 89.31 | 0.05 | 0.01 | 99.94 | 0.64 |
| 0.90 | 31.77 | 26.06 | 40.02 | 20.49 | 4.03 | 75.48 | 0.21 | 0.04 | 99.75 | 0.93 |

[a] 1 g Pt (~0.7 $m^2$ $g^{-1}$); carrier gas: 60 ml $min^{-1}$; 3-μl pulses.

[b] 2-Methylpentane + 3-methylpentane.

[c] 2-Methylpentane + 3-methylpentane + *n*-hexane.

[d] Hydrogen partial pressure (atm) in *complete* equilibration, considering the hydrogen content of carrier gas plus hydrogen given off during reaction.

influence the concentration of the latter ones.

Thus, the treatment will be confined to the following reactions:

$$n\text{-hexanes(nH)} \rightleftharpoons \text{2-methylpentane (2MP)} \rightleftharpoons \text{3-methylpentane (3MP)} \quad (1)$$

$$\text{hexanes} \rightleftharpoons \text{methylcyclopentane (MCP)} + H_2 \quad (2)$$

$$\text{hexanes} \rightleftharpoons \text{benzene (Bz)} + 4\ H_2 \quad (3)$$

As far as reactions with no changes in the number of carbon atoms are concerned, at any given temperature the equilibrium hydrogen pressure ($P_H$) is the only variable influencing the relative concentration of any hydrocarbon (or group of hydrocarbons):

$$\frac{P_i}{P_{HC}} = \frac{K_{p,i}}{P_H{}^{n,i}} \cdot \left(1 + \sum \frac{K_{p,i}}{P_H{}^{n,i}}\right)^{-1}. \quad (4)$$

Here $P_i$ denotes the partial pressure of the $i$-th component, $P_{HC}$ the total pressure of hydrocarbons equilibrated, $n,i$ the stoichiometric coefficient of hydrogen given off in the $i$-th reaction, and $K_{p,i}$ the equilibrium constant. A very important consequence of Eq. (4) is that equilibrium concentrations expressed this way are not affected by the initial hydrocarbon pressures, and therefore, they are not influenced by the pulse shape.

Table 1 summarizes the experimental results together with the equilibrium concentrations calculated. Outlet concentrations with respect to the total outflow are very far from equilibrium. Obviously, a large fraction of $n$-hexane has not been equilibrated with its products.

The comparison of product selectivities (total $C_6$ conversion regarded as 100%) shows that the observed concentrations of benzene are always lower, and those of methylcyclopentane and isomers (i.e., "saturated $C_6$ products") are higher than those expected in equilibrium under given hydrogen pressures. These concentrations as well as calculated equilibrium concentrations are plotted in Fig. 1 as a function of the final hydrogen pressure (cf. Table 1). The data indicate an equilibration between saturated and aromatic products provided that a hypothetical "effective

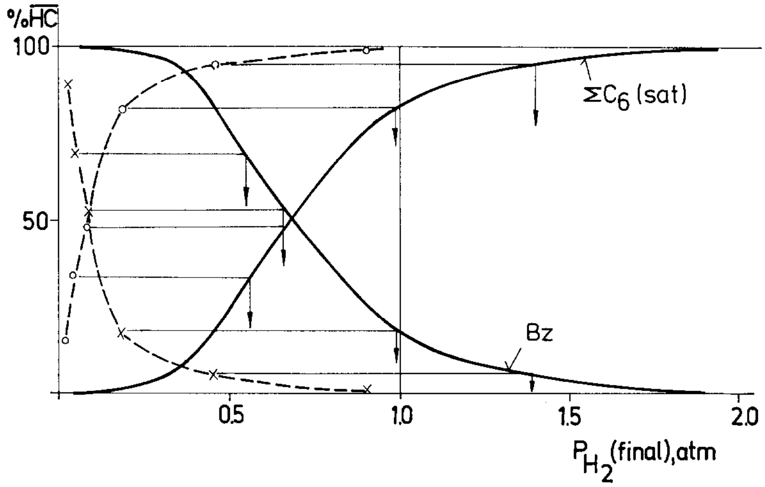

FIG. 1. Concentrations of saturated products (2MP + 3MP + MCP) and benzene as a function of the final hydrogen pressure. "Final hydrogen pressure" is defined in Table 2. Thick solid lines represent equilibrium curves calculated according to Eq. (4). Dashed lines denote experimental concentrations of benzene (X) and saturated $C_6$ products (O), respectively. Arrows indicate "effective surface hydrogen pressures" (see text and Table 2). Catalyst: 1 g platinum black; $T = 600$ K.

TABLE 2

Actual and Calculated Hydrogen Pressures in *n*-Hexane Conversion

| *T* (K) | Hydrogen pressure characteristic | Pressure (atm) | | | | |
|---|---|---|---|---|---|---|
| 600 | Hydrogen pressure in the carrier gas | 0 | 0.045 | 0.18 | 0.45 | 0.90 |
| | Final hydrogen pressure[a] | 0.04 | 0.08 | 0.19 | 0.46 | 0.90 |
| | "Effective surface hydrogen pressure"[b] | 0.56 | 0.7 | 1.0 | 1.4 | 2.0 |
| 700 | Final hydrogen pressure[a] | 0.10 | 0.13 | 0.24 | 0.50 | 0.91 |
| | "Effective surface hydrogen pressure"[b] | 1.5 | 1.7 | 2.0 | 2.5 | 3.5 |

[a] Hydrogen pressure in the pulse leaving the catalyst considering the hydrogen content of the carrier gas plus hydrogen given off in reactions at the conversion values measured. Rectangular pulse is assumed and chromatographic separation of the product is neglected.

[b] A hypothetic hydrogen pressure at which the observed amounts of benzene and $C_6$ saturated products would be in equilibrium with each other and hydrogen (see also Fig. 1).

surface hydrogen pressure" is assumed (Table 2) which is higher than that in the gas phase. Since the system in question is thermodynamically open (due to its flow-through character), *any equilibration must occur on the surface.* Two important conclusions can be drawn about the surface participants. First, the open character of the system (i.e., the continuous hydrogen supply by the carrier gas) ensures that such surface conditions might really occur. Various types of hydrogen sorbed on platinum have been detected by thermodesorption (*10, 11*) and radiotracer (*12*) studies.

The "effective surface hydrogen pressures" at 700 K are much higher as compared to gas phase ones than at 600 K (cf. Table 1). At 600 K a marked negative hydrogen order can be observed in the overall conversion. Both phenomena can be interpreted in terms of at least two types of sorbed hydrogen (*12*). The more strongly bonded species ("HaII") may be the one determining the ratio of the two surface intermediates. At 600 K, a considerable amount of another "HaI" species may also be present (*12*) and may serve as a supply for HaII but also may compete with hydrocarbons for active surface sites. At 700 K, only HaII should be considered. It is difficult to identify HaI and HaII unambiguously in terms of hydrogen types suggested in Refs. (*10*) and (*11*). Even the presence of more than two types of sorbed hydrogen cannot be excluded with gaseous hydrogen present.

Second, the hydrocarbon species participating in the equilibration must be surface ones; namely, those corresponding to the

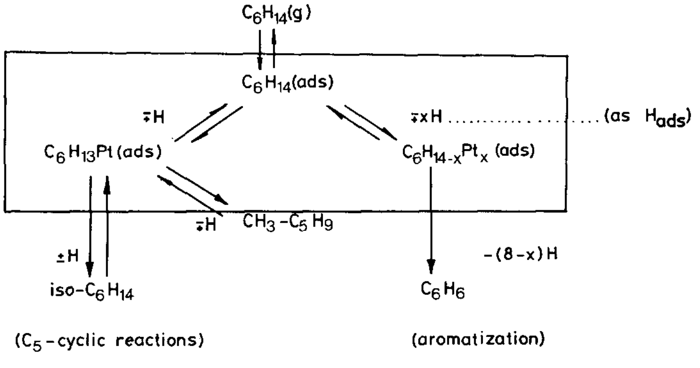

FIG. 2. Proposed reaction scheme for $C_5$- cyclic reactions and aromatization of *n*-hexane. Reactions in the box are considered in equilibrium.

precursors of saturated $C_6$ products and benzene, respectively. $C_6H_{14}$(ads) might correspond to the weakly adsorbed species assumed in Refs. (*21*) and (*22*); this may give either a half-hydrogenated surface species with a geometry suitable for $C_5$ cyclic reactions (including isomerization and $C_5$ ring closure and opening) as we suggested earlier (*3, 13*), or a more dissociated one for aromatization which occurs according to a stepwise mechanism via hexatriene (*7*). Their ratio is regulated by the amount of surface hydrogen (Fig. 2).[1] The two types of surface intermediates react further independently of each other (i.e., a kinetic barrier should be assumed between them). Their fate (desorption or further reaction) is governed mainly by kinetic and not thermodynamic factors.

The half-hydrogenated species for $C_5$ cyclic reactions should be identical to the "*C*" surface intermediate of cyclization and isomerization suggested by Barron *et al.* (*14*). We do not agree with the later work of this group which attributed a strongly dissociated character to "*C*" (*15*). This species reacts further independently of other intermediates. For example, the high concentrations of MCP can only be explained if we assume that isomerization and $C_5$ cyclization proceed as if no aromatization occurred. The "effective surface hydrogen pressures" corresponding to the i-$C_6$/MCP ratios measured are 0.13 ± 0.03 atm at 600 K and still higher (1.26 ± 0.18 atm) at 700 K, independent of the actual hydrogen pressure. The hydrogen content of the "*C*" surface complex may therefore belong to the surface complex, as suggested by Liberman (*16*), and not be in equilibrium with other sorbed H species. Also, the ratio of 2MP/3MP (1.72 ± 0.07 between 0.05 and 0.50 atm of $H_2$) does not correspond to the equilibrium value of 1.96 at 600 K and reflects the selective character of ring opening (*13, 17*).

This picture is consistent with our previous suggestions that saturated $C_6$ products and benzene represent the result of two basically different reaction possibilities (*1, 3, 6, 13, 18*). This is supported, among other things, by the entirely different self-deactivation characteristics of these two product groups (*18*). A serious consequence of this concept is that it may not be correct to treat $C_5$ and $C_6$ dehydrocyclization as principally identical reactions of intermolecular C–C bond formation (*14, 19, 20*). The differences lying in the nature of their surface precursors may be more pronounced than this apparent and mainly formal relationship.

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[1] When postulating two types of surface intermediates no restrictions are made about the exact character of the adsorption process leading to them. It is possible that a "reactive" (*23*) and a "dissociative" chemisorption compete. The former would occur on a site containing a hydrogen atom plus *z* adjacent "free" sites. This suggestion is analogous to the type of adsorption we propose for $C_5$ cyclic reactions.

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