LETTER TO THE EDITOR

Comment on Shawn D. Lin and M. Albert Vannice on "Hydrogenation of Aromatic Hydrocarbons over Supported Pt Catalysts"

In a recently published series (1–3) S. D. Lin and M. A. Vannice reported on hydrogenation of benzene and toluene over supported Pt and Pt-powder catalysts. They proposed a model for the reaction mechanism based on the following main assumptions (3):

—H_2 adsorbs dissociatively on sites different from those adsorbing benzene (or toluene);

—the aromatic reactant molecule is adsorbed in part via C–H bond dissociation;

—the rate-determining step of the hydrogenation (RDS) is the addition of the first H atom to the aromatic reactant, adsorbed nondissociatively.

The authors found that only the model based on these assumptions could fit the reaction kinetic data obtained for hydrogenation of benzene. The reliability of data obtained from kinetic constants on hydrogen adsorption and enthalpies indicated also the validity of the proposed mechanism. The observed (1) two levels of steady-state activity of benzene hydrogenation were accepted as an indication of formation and stability of H-deficient aromatic species, these species being coke precursors. Besides kinetic data, some H–D exchange and TPD data were also cited in support of the proposed model.

Here, we pursue the authors' suggestions with some independent data obtained earlier in our laboratory and published only in part. These relate to the adsorption of hydrogen and benzene on Pt black (specific surface-2.5–9.1 m^2/g, mean particle size = 31–35 nm for different samples) and to the hydrogenation and dehydrogenation of 6-membered hydrocarbon ring compounds.

Isotope dilution analysis data indicate (4) the two types of adsorption (chemisorption) of benzene on Pt black: It was found that irreversibly adsorbed 14-C labelled benzene (temperature range 383–543 K, atmospheric pressure) could be desorbed by inactive benzene in part only, while the remaining part could be desorbed in a H_2 stream in the form of cyclohexane and benzene. This advocated the existence of associative and dissociative forms of irreversibly adsorbed benzene.

The amount of benzene adsorbed irreversibly (423 K, $P = 1$ atm) was 8% of the maximally adsorbed quantity, whereas the percentage of benzene desorbed by H_2 only was less than 6% of the irreversibly adsorbed one (5).

Special measurements indicated that not more than 2–3% of benzene adsorbed irreversibly remained on the surface. The amount of this strongly held species increased continuously.

These data support the view expressed in Ref. (1) that benzene adsorbs in two forms and produces in part coke also. It is remarkable, however, that irreversibly adsorbed benzene—even in the absence of H_2 and at 760 Torr—did not exceed 20% of the benzene adsorbed at 15 Torr (5). This explains the standard activity of hydrogenation of benzene at a substantially lower (317–356 K) temperature range than that observed by Lin and Vannice.

Whereas the above-mentioned data related to the adsorption on Pt black at higher temperatures (383–543 K), IR studies carried out in our institute indicated that CD bond(s) dissociated after adsorption of C_6D_6 (6). Introduction of perdeutero-benzene resulted in C–D stretching of adsorbed C_6D_6, CD_2 bands due to self-deuteration, C–H bands indicating H–D exchange between surface hydrogen and C_6D_6, and OD bands due to exchange between C_6H_6 and Si–OH of the support.

Radioactive tracer experiments, carried out with 1 : 1 mixtures of benzene 14-C + 1,3 cyclohexadiene, in the presence of fresh Pt black catalyst at 464 K, indicated that the specific radioactivity of cyclohexane was an order of magnitude higher than that of cyclohexadiene (7). This supports the assumption made by Lin and Vannice of a rate-determining role of the first H addition to benzene. (Our data relate to higher temperature. Calculation indicates, however, that the conversion rates of benzene and cyclohexadiene hydrogenation on our catalyst could become equal at 350 K, if the activation energy of cyclohexadiene hydrogenation exceeds that of benzene with 7 kcal/mol. This is unlikely because of the higher—with 5.6 kcal/mol—exothermicity of hydrogenation of cyclohexadiene in comparison with benzene.)

From these radioisotope tracer experiments it follows also that the cyclohexene intermediate was avoided during hydrogenation of benzene: the ratio of specific radioactivities of cyclohexane/cyclohexene was 0.08 in the case of fresh Pt black; the main reaction path was the random addition of H atoms. This is in accordance with the direct dehydrogenation of cyclohexane: the radioactivity of cyclohexene produced by dehydrogenation of cyclohexane 14-C + cyclohexene mixtures on fresh Pt black did not exceed 5–6% of that of benzene (8).

The statistical probability of cyclohexene formation from benzene would be 0.4 at random addition. The obtained values for the ratio of radioactivities were substantially lower for all metals investigated (0.01 for Fe, 0.27 for Os). This can be explained with oriented (meta) H addition, with hindered desorption of cyclohexene, or with the more favorable thermodynamics of production of cyclohexane from benzene in comparison with that of cyclohexene. The nonfavored position of stepwise hydrogenation and the substantially higher—in comparison with benzene—rate of hydrogenation of cyclohexene suggest the rate-determining role of the addition of the first H, in accordance with kinetic data obtained by Lin and Vannice (3). This can probably be caused by the breakdown of the aromatic system at the addition of the first H to the associatively adsorbed benzene.

It is of interest to compare/combine adsorption data obtained by kinetic and direct adsorption measurements for Pt black with those obtained by Lin and Vannice. Besides gravimetric adsorption measurements of benzene and cyclohexane (4), volumetric ones of H_2 (10) were carried out. Adsorption equilibrium constants of benzene, cyclohexane, and hydrogen were derived from kinetic equation of cyclohexane dehydrogenation in binary mixtures of cyclohexane with argon and with benzene, cyclohexane, or hydrogen (10, 11). The pre-exponential term in

$$K_a = K_a^0 \exp\left[-\frac{\Delta H}{RT}\right] \qquad [1]$$

and the calculated (from temperature dependence of "kinetic" adsorption constants) adsorption enthalpy values are collected in Table 1. Isosteric adsorption enthalpies and pre-exponents of Langmuir adsorption constants are also indicated in Table 1.

The isosteric adsorption enthalpies substantially differ from the values calculated from kinetic data and refer to the catalytically active part of the surface. The "kinetic" enthalpy falls in the range of the isosteric values (28–9 kcal/mol range θ: 0.14–0.7). The absolute value of the isosteric adsorption enthalpy of H_2 is higher than the integral value determined (12) for Pt/Al_2O_3, applied by Lin and Vannice. In accordance with this, the "kinetic" value

TABLE 1

Enthalpy Values and Equilibrium Constants (Pre-exponentials) of Adsorption Determined by Kinetic and Direct Adsorption Methods on Pt Black

Substance	$-\Delta H$		$K_a^0 k P_a^{-1}$	
	Kinetic	Isosteric	Kinetic	Isotherm
Hydrogen	25.9	32.1	1.95×10^{-12}	1.04×10^{-14}
Benzene	22.9	9.3	5.8×10^{-11}	1.83×10^{-5}
Cyclohexane	12.6	7.7	3.97×10^{-7}	2.90×10^{-7}

for the Pt black exceeds by 10–12 kcal the value for Pt/Al_2O_3.

We can apply the concept of quasihomogenous surfaces developed by Balandin (13) for a rough estimation of the value of the adsorption constants of benzene for Pt/Al_2O_3 applied by Lin and Vannice. In accordance with this concept the ratio of adsorption coefficients of two different adsorbates remains constant for catalytically active sites of different activity of a surface. Consequently:

$$\frac{(K_H)Pt_I}{(K_H)Pt_{II}} = \frac{(K_A)Pt_I}{(K_A)Pt_{II}}. \qquad [2]$$

From the ratio of the adsorption constants of H on the two (ours and Lin and Vannice's) catalysts we obtain K_A for Pt/Al_2O_3: 21.5 and 3.2 atm^{-1} at 317 and 356 K.

For enthalpy of adsorption and surface C–H dissociation we obtain −11 and −13 kcal, whereas for the activation energy of the RDS we obtain 29 kcal, as the temperature dependence of the kK_A gives 18 kcal for $E + \Delta H_A$, the sum of the activation energy of RDS and the enthalpy of benzene adsorption. The enthalpy values of the adsorption and surface C–H dissociation seem to be real, considering the value of the enthalpy of condensation (8.1 kcal/mol) of benzene. The high activation energy is disputable, but this is a consequence of the high $E + \Delta H_A$ value. We should bear in mind, however, the substantial energy loss connected with the collapse of aromatic system caused by H addition.

Summing up, we can state that independent studies of adsorption, reaction mechanism, and kinetics support the assumptions made by Lin and Vannice with regard to the model of hydrogenation of benzene.

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