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LETTER TO THE EDITORS

Benzene Hydrogenation Kinetics over Iron Catalysts: Comment on the Reaction Model of Ki J. Yoon and M. Albert Vannice

In their recent paper on benzene hydrogenation over a number of supported and unsupported iron catalysts, Yoon and Vannice (*1*) reported that a single Langmuir–Hinshelwood rate expression of the form

$$r_0 = k'p_{H_2}{}^3p_B/(1 + K_Bp_B)^2 \qquad (1)$$

provided a satisfactory fit of the data from 12 different catalysts. This expression predicted the maximum in activity observed at 473 K with the supported and at 493 K with the unsupported iron catalysts and provided an explanation of this behavior.

On the other hand, the rate expression proposed by Badilla-Ohlbaum *et al.* (*2, 3*) correlated the data from a singly promoted iron synthetic ammonia catalyst to within ±3% but was not able to predict the maximum in rate observed, in this case, at about 456 K. This expression,

$$r = \frac{kK_BK_H{}^3p_Bp_{H_2}{}^3}{(1.0 + K_Bp_B + (K_Hp_{H_2})^{1/2})^7} \qquad (2)$$

suggests that the rate-controlling step involves the simultaneous reaction of three molecules of dissociatively adsorbed hydrogen with one molecule of adsorbed benzene. Although the involvement of such a large number of species in a rate-controlling step may seem unlikely, a second expression proposed by Badilla-Ohlbaum for consideration (*2*) was even more unlikely, suggesting as it did the rate-controlling reaction of the adsorbed benzene molecule with three molecules of associatively adsorbed hydrogen. While this other equation fitted the data equally well over the same temperature range (403 to 453 K), it, too, did not predict the activity maximum. Indeed, in both cases, a change in mechanism was proposed to account for this phenomenon.

We have applied the Yoon/Vannice rate expression (*1*) to Badilla-Ohlbaum's kinetic data (*2*) and we can report that it correlates his experimental results extremely well (again, to within ±3%) over the entire temperature range. That is, the expression fits the data both above and below the rate maximum. Equation (1) was first linearized to the form $Y = A + BX$ with respect to both p_B and p_{H_2} as the independent variable, a particularly useful procedure since data had been collected at both constant hydrogen partial pressure and variable benzene partial pressure and vice versa. Thus, for p_{H_2} constant, the expression

$$\left(\frac{p_{H_2}{}^3p_B}{r_0}\right)^{1/2} = \frac{1}{(k')^{1/2}} + \frac{K_B}{(k')^{1/2}}\,p_B$$

resulted while for constant p_B, the expression became

$$(r_0)^{1/3} = \left(\frac{k'p_B}{(1 + K_Bp_B)^3}\right)^{1/3} p_{H_2}.$$

Values of A and B were determined by a linear least-squares data fit at eight temperatures (403 to 463 K in 10 K increments) and from these, K_B and k' (where $k' = kK_EK_H{}^3$ (*1*)) were calculated.

Figure 1 illustrates the successful correlation of the data by the Yoon/Vannice expression. The effect of temperature on K_B is shown in Fig. 2.

The same linearization procedure was applied to Eq. (2) to give results in the same form. The activation energy and the entropies and enthalpies of adsorption of both benzene and hydrogen had been determined by Badilla-Ohlbaum (*2*) and are

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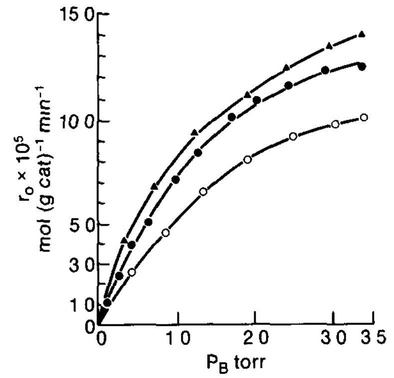

FIG 1 Effect of benzene partial pressure on initial rate (hydrogen partial pressure = 790 Torr) Experimental data points (○) 403 K, (●) 443 K, (▲) 463 K (—) Predicted bv Eq (1)

given, in Table 1, for comparison with the values determined for his data using Eq (1) and the values from Yoon and Vannice (*1*)

We note that, while the absolute values of $\Delta H_B{}^0$ and $\Delta S_B{}^0$ determined for the synthetic ammonia catalyst with Eq (1) are 39 and 17% greater, respectively, than are the values obtained with Eq (2), these values are still significantly lower than those reported by Yoon and Vannice (*1*)

A similar plot to Fig 2, that is, of the effect of temperature on K_B, appears in Ref (*3*) (Fig 6) In both of these plots we note that ln K_B at 453 K lies slightly to the left and the value at 463 K lies significantly to the left of the straight-line relationship This deviation prompted Badilla-Ohlbaum's postulate of a change in mechanism at about 453 K

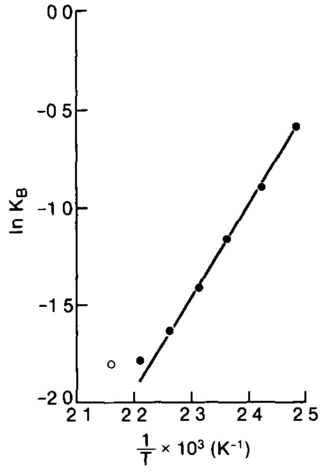

FIG 2 Effect of temperature on K_B values calculated via the Yoon/Vannice equation

TABLE 1

Kinetic and Thermodynamic Parameters

	E_a (kcal mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1}K)
Reaction			
Ref (*1*)[a]	62 8 to 108 8		
Ref (*2*)	59 9		
Benzene			
(Eq (1))[b]		−40 6	−105 1
(Eq (2))[b]		−29 2	−89 8
(Ref (*1*))		−71 1 to −104 6	−125 5 to −200 8
Hydrogen			
(Eq (2))[b]		−10 8	−103 4

[a] Average for seven catalysts 89 1

[b] Temperatures ≤ 453 K

With regard to thermodynamic feasibility, the values of $\Delta H_B{}^0$ and $\Delta S_B{}^0$ determined via both Eqs (1) and (2) satisfy the criteria for physical reasonableness That is, they are both negative, $|\Delta S_B{}^0|$ is less than $S_B{}^0$, and, in addition, $\Delta S_B{}^0$ falls within the guideline developed by Boudart *et al* (*4*) and Vannice *et al* (*5*) $10 \text{ e u} \leq -\Delta S_B{}^0 \leq 12\ 2 - 0\ 0014 \Delta H_B{}^0$ Table 2 places $\Delta S_B{}^0$ within the calculated limits

Thus, we see that the Yoon/Vannice rate expression based on data obtained at benzene partial pressures between 10 and 100 Torr (1 Torr = 133 3 Nm^{-2}) can also correlate the data obtained at benzene partial pressures of 0 05 to 3 6 Torr over an alumina-promoted synthetic ammonia catalyst The Yoon/Vannice expression is simpler in form than is Badilla-Ohlbaum's, and implies a more reasonable rate-determining

TABLE 2

$-\Delta S_B{}^0$ (J mol^{-1}K^{-1})

Mechanism	Lower limit	Actual value	Upper limit
Yoon/Vannice (*1*)	41 8	105 1	107 8
Badilla-Ohlbaum (*2*)	41 8	89 8	91 9

step in the mechanism—a two-body rather than a seven-body reaction Both mechanisms yield values of $\Delta H_B{}^0$ and $\Delta S_B{}^0$ which meet accepted criteria for physical reasonableness However, neither mechanism gives a fully satisfactory explanation of the kinetics at benzene partial pressures of 0 05 to 3 6 Torr over the fused iron catalyst, insofar as the dependence of ln K_B on temperature is concerned (Fig 2 and Fig 6 Ref (*3*)) The deviation from the linear relationship at or near that temperature at which the rate is a maximum does suggest a change in mechanism The significant advantage of the Yoon/Vannice rate expression over the Badilla-Ohlbaum expression is its ability to correlate the data over the entire temperature range in which cyclohexane was the only reaction product detected, that is, both above and below the rate maximum

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