Self-Poisoning and Rate Multiplicity in Hydrogenation of Benzene

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The hydrogenation of benzene to cyclohexane is considered to occur by two parallel reaction schemes involving both π- and σ-bonded surface species as well as an intermediate π/σ complex of adsorbed benzene. Considering the π/σ and π forms to be reactive and the σ form to be inhibitive in hydrogenation, an overall rate model is proposed and high pressure rate data obtained in a gradientless reactor is used to estimate the model parameters. Both π/σ and π forms are found to contribute to the overall rate appreciably. Simulation using the regressed parameters has shown that even though the overall rate does not display a maximum similar to the one observed in low pressure kinetic investigations, the fractional rate due to the π/σ species does show such a maximum. This is explained as due to self-poisoning by the unproductive occupation of the sites by σ-bonded surface intermediate which effects only the reaction involving the π/σ species. It is suggested that this latter reaction is probably dominant at low pressure.

INTRODUCTION

Although the facile character of the catalytic hydrogenation of benzene (*1*) has been known for quite some time, the rate models that have appeared in the literature subsequently (*2–4*) does not seem to reflect this in any quantitative manner. This is probably important, since it is believed that benzene exists on the catalyst surface in at least three different forms (*5*) and that one of them—a π-bonded complex—can be reactive in more than one way (*6*).

van Meerten and Coenen (*3*) and later Franco and Phillips (*4*) have reported that the hydrogenation of benzene to cyclohexane over nickel at atmospheric pressure is well described by a kinetic model involving six sequential steps for the atomwise addition of hydrogen to benzene. Although their model explains the observed rate maxima satisfactorily, some of its features need closer examination. First, an apparent irregularity in the adsorption equilibrium parameter has been resolved by supposing that "the heat of adsorption range of benzene converted in the reaction shifts to

higher values at higher temperatures." This has led to the inclusion of an empirical constant in their model. Second, the rates of hydrogenation of cyclohexene and benzene calculated by them are approximately of the same order of magnitude, which, as they conceded, is not in agreement with the literature (*7*). Finally, the model does not seem to reflect well the role of different reactive and unreactive surface intermediates that are now known to exist. This is important especially since one such intermediate—σ-bonded species—though reactive in exchange reactions (*8*) can inhibit hydrogenation by competitive adsorption.

Much of the reported literature on the hydrogenation of benzene (*9–18*), with the exception of the work of Aben *et al.* (*19*), is restricted to atmospheric pressure and low conversion, whereas pressure in the neighbourhood of 20 atmospheres and conversion close to 100% are common in the commercial hydrogenation of benzene. In the present work, high pressure data in the complete range of conversion is obtained in a laboratory recycle reactor (*20*) and analyzed taking into account for the first time the influence of different surface intermediates on the rate of hydrogenation.

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THE PROPOSED MODEL

Spectroscopic (1), radio tracer (21, 22), and field electron emission (23) analyses of benzene chemisorbed on some group VIII transition metals have led to the speculation that both π- and σ-bonded species exist on the metal surface in equilibrium with each other. In an attempt to determine the structure of a rhodium benzene complex, π-cyclopentadienyl-hexakis (trifluoromethyl) benzene rhodium, Churchill and Mason (24) have proposed a nonplanar conformation of the aromatic nucleus having an angle of separation of 47.9°. Evidence has been obtained by them to show that two of the six benzene carbon atoms form quite localised σ bonds to the rhodium ion and that the remaining four are involved in a π-bonded structure, indicating the rhodium benzene linkage to be of the $\sigma-\pi$ type. Although π-arene complexes of rhodium and nickel need not be exactly alike, evidence exists for the formation of a very unstable (not isolated) π-hexamethyl benzene nickel ion (25). Besides, the presence of a broad band between 2760 and 3060 cm^{-1}—a range corresponding to the CH stretching vibration at a saturated carbon atom—in the infrared spectra of benzene chemisorbed on nickel (26) coupled with the absence of a similar band in the ir spectra of most known π benzene metal complexes (27) have led to the suggestion that benzene species bonded to the nickel surface loses its aromatic character (28, 29) without yet attaining that π complex structure and is probably somewhere in between (26). Such an intermediate form between the "horizontal" π-bonded species and the "vertical" σ-bonded species, has actually been postulated (30) to explain the mechanism of randomization between normal and fully deuterated benzene over platinum. This intermediate is envisaged to form when the plane of the rotating benzene molecule is about 45° to the catalyst surface (30), and is reported to be very reactive (31). Further, the chemisorption maximum

of benzene over nickel reported by Tetenyi and Babernics (21) seems to suggest that benzene is chemisorbed in a sequential process probably with an endothermic second step. If it is assumed that the π/σ transition complex (30) is actually the precursor to the well defined π- and σ-bonded surface intermediates, the loss of aromatic character by the adsorbed species even if it does not resemble any known organometallic π complex may be explained. Since this process has to be necessarily a sequential one, it may also explain the chemisorption maximum cited earlier. On the strength of these remarks, the following scheme for benzene chemisorption is being proposed in this work
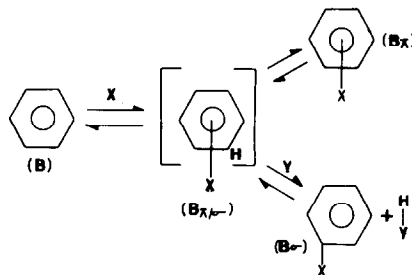

SCHEME 1. Chemisorption of benzene. (B_π and B_σ are the respective π- and σ-bonded complexes and $B_{\pi/\sigma}$ is the intermediate species and X and Y denote the benzene and hydrogen adsorption sites, respectively).

It has been suggested (6) that π/σ complex may react sequentially as per the Rooney mechanism (32) with a single atom of adsorbed hydrogen at a time and the π complex may react in the van der Waals layer with six adsorbed hydrogen atoms simultaneously as per the Rideal mechanism (33), whereas the σ-form is unreactive if not inhibitive in hydrogenation (5). Thus, the following two reaction schemes may be identified:
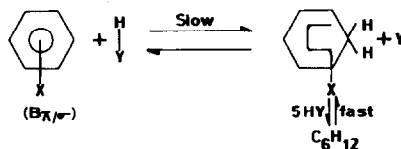
SCHEME 2. Hydrogenation of benzene via Rooney mechanism.
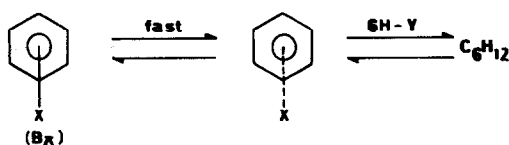
SCHEME 3. Hydrogenation of benzene via Rideal mechanism (the dotted line indicates that the species is lodged in the van der Waals layer).

Assuming that all species of adsorbed benzene occupy one type of sites and hydrogen occupies a different type of sites (34), application of Hougen–Watson methodology (35) yields the following rate equations for reactions by Schemes 2 and 3:

r_1 (by Scheme 2)

$$= \frac{k_1 K_{B_{\pi/\sigma}} p_B \sqrt{K_H p_H}}{(1 + \bar{K}_B p_B)(1 + \sqrt{K_H p_H})} \quad (1)$$

r_2 (by Scheme 3)

$$= k_2 p_B \left[\frac{\sqrt{K_H p_H}}{1 + \sqrt{K_H p_H}} \right]^6 \quad (2)$$

Where $\bar{K}_B$ in Eq. (1) is given by

$$\bar{K}_B = K_{B_{\pi/\sigma}}(1 + K_{B_\pi} + K_{B_\sigma}/\sqrt{K_H p_H}) \quad (3)$$

In Eqs. (1)–(3), k's are the rate constants and K's are adsorption equilibrium constants. Since the two reaction schemes are parallel to each other the overall rate, r, is given by their sum. Thus,

$$r = r_1 + r_2 \quad (4)$$

The form of Eqs. (1) and (2) indicate that r_2 may predominate whenever $\bar{K}_B p_B$ and $\sqrt{K_H p_H}$ are large compared to unity (very high pressure operation). Conversely at lower pressures, r_1 alone may be important.

The rate model (Eqs. (1) to (4)) is characterized by two reaction rate constants, k_1 for the hydrogenation by Scheme 2 and k_2 for the hydrogenation by Scheme 3, adsorption equilibrium constants, K_H, for hydrogen and $K_{B_{\pi/\sigma}}$ for benzene, and two additional equilibrium constants, K_{B_π} and K_{B_σ} for the transformation of the "inclined" π/σ complex to the "horizontal" π form and to the "vertical" σ form, respectively. The temperature dependence of these constants is of the Arrhenius type as follows

$$k = k_\infty \exp(-E/RT) \quad (5)$$

$$K = \exp(\Delta S/R - \Delta H/RT) \quad (6)$$

where k is the reaction rate constant, K is the equilibrium constant for adsorption or other surface process, and k_∞, E, ΔS, and ΔH are respectively the frequency factor, activation energy, entropy, and enthalpy.

The parameters are estimated by nonlinear regression by minimizing the sum of squared deviations of the measured and calculated rates as below:

$$S = \sum_{i=1}^{N} (\hat{r}_i - r_i)^2$$

where $\hat{r}_i$ is the measured rate in the ith experiment and r_i is the rate computed using Eqs. (1)–(4) for the ith experimental conditions.

EXPERIMENTAL

In the present studies, Berty internal recycle reactor (20), wherein well mixed conditions can be easily attained, has been employed. Benzene containing less than 1 ppm thiophene and hydrogen of 99.99% purity have been used as reactants. Nitrogen, when used to alter the partial pressure of hydrogen, is also of 99.99% purity. The experimental set up is shown schematically in Fig. 1. The catalyst employed in this study is nickel alumina with 39% nickel. Rate data at four temperatures (120, 130, 150, 170°C) and a pressure of 20 atm have been obtained in the complete range of conversion choosing the points of observation at random. These data are presented in Table 1. Conversion of benzene has been estimated by gas–liquid chromatography.

RESULTS AND DISCUSSION

It is evident from Fig. 2 that the correspondence between the calculated and the observed rates is reasonable, the correlation coefficient and the standard deviation
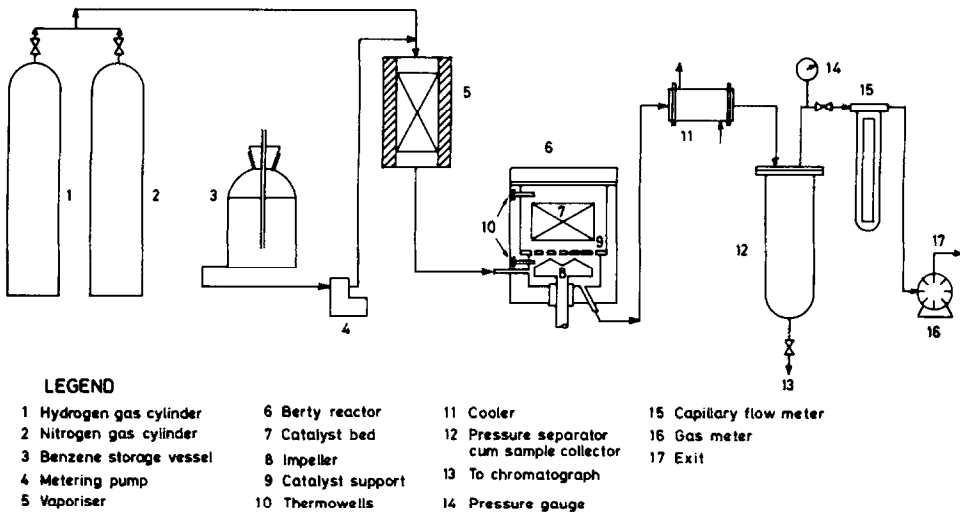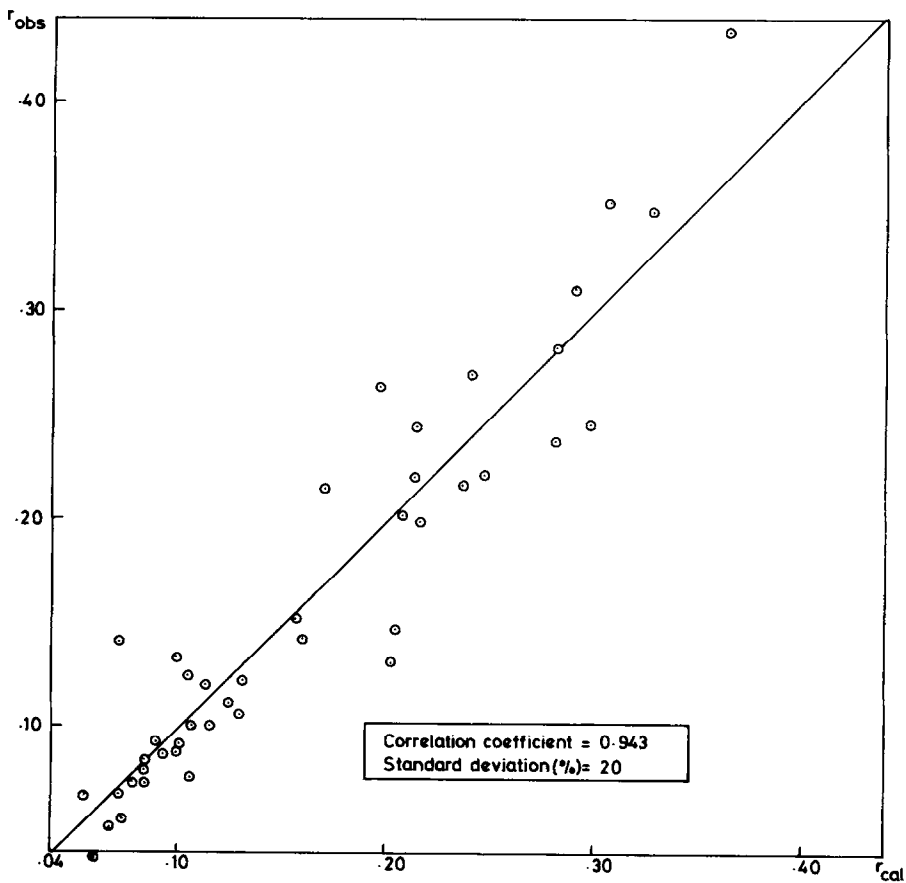
FIG. 1. Experimental assembly.

FIG. 2. Comparison of calculated and experimental rates.

TABLE 1

Summary of Experimental Observations

S. No. (i)	Temperature (°C)	Partial pressure of benzene (atm)	Partial pressure of hydrogen (atm)	Conversion[a] (%)	Rate ($\hat{r}_i$) $\left(\dfrac{\text{moles benzene converted} \times 10^2}{\text{g(cat)} \cdot \text{h}}\right)$
1	2	3	4	5	6
1	120	2.21	16.4	51.2	9.24
2	120	2.85	16.4	37.4	10.1
3	120	2.40	12.5	47.1	8.49
4	120	3.03	12.8	33.7	9.10
5	120	2.64	5.48	42.0	3.78
6	120	3.18	6.27	30.5	5.49
7	120	0.91	18.2	36.7	6.62
8	120	1.73	17.3	40.4	7.29
9	120	2.00	16.9	43.9	7.92
10	120	3.68	4.39	19.2	5.21
11	130	1.39	16.4	68.6	12.4
12	130	2.77	16.4	39.1	14.1
13	130	2.00	12.3	55.4	9.99
14	130	2.36	6.40	47.8	8.61
15	130	2.16	4.40	37.7	6.79
16	130	1.33	18.2	28.4	7.68
17	130	1.55	17.3	44.3	12.0
18	130	2.00	16.8	45.3	12.2
19	130	3.29	3.66	27.6	7.46
20	130	3.59	4.34	21.3	8.66
21	130	3.37	7.64	26.0	10.6
22	150	1.16	16.4	73.4	20.0
23	150	0.62	11.6	85.4	15.4
24	150	1.22	11.9	72.8	26.4
25	150	0.48	2.27	78.2	14.1
26	150	1.82	5.67	59.7	21.5
27	150	0.92	18.2	36.3	14.7
28	150	1.08	17.3	54.0	21.9
29	150	1.53	16.9	54.4	22.1
30	150	2.65	2.44	41.4	11.2
31	150	2.28	1.91	49.2	13.3
32	150	2.48	6.48	45.0	24.4
33	150	2.48	16.4	66.5	27.0
34	170	0.36	16.4	90.7	24.5
35	170	0.50	11.5	88.0	23.8
36	170	0.85	4.42	80.3	21.7
37	170	0.85	3.23	74.8	20.2
38	170	2.32	1.81	40.5	13.1
39	170	1.33	4.97	69.7	28.3
40	170	1.54	5.25	65.1	35.2
41	170	1.02	6.62	76.3	31.0
42	170	0.57	16.4	85.9	34.9
43	170	0.83	16.4	80.3	43.5

[a] Conversion (%) = $\dfrac{\text{moles benzene converted}}{\text{moles benzene fed}} \times 100$.

being 0.943 and 20%, respectively. Further, the calculated partial rates (r_1 and r_2) given in Table 2 are comparable indicating that hydrogenation has occurred by both schemes to an appreciable extent. The regressed parameters (Table 3) are, thus, representative of the model and it remains to be seen to what extent these are consistent with the reported literature on the system.

Rate and Adsorption Parameters

The activation energies of reactions (Schemes 2 and 3) are estimated to be 8.32 and 12.15 kcal/g · mol, respectively which are well within the reported range of 8–13 kcal/g · mol (*2–4, 9–18*). The estimated change in the enthalpy of adsorption of hydrogen (2.04 kcal/g · mol) compares well with the reported value (2.07 kcal/g · mol) by van Meerten and Coenen (*2*). Their contention that hydrogen reactive in benzene hydrogenation is loosely bound on the nickel surface (*34*), thus, appears to be tenable. A similar comparison for chemisorption of benzene is not possible since adsorption parameters for the individual adsorbed species are not reported. Besides, benzene chemisorption is not independent of hydrogen partial pressure, since one of the adsorbed species of benzene arises due to dissociative chemisorption which liberates hydrogen. However, knowing the value of the apparant equilibrium constant, $\bar{K}_B$ (Eq. (3)), the change in the enthalpy of adsorption of benzene lumping all species into one may be approximated. This value at 0°C and 0.01 atm hydrogen partial pressure is about 29 kcal/g · mol, which is reasonably close to the value (25 kcal/g · mol) at 0°C reported by Yu *et al.* (*28*). The higher value is only to be expected, for the ratio of the apparent benzene adsorption equilibrium constant to the true value $(1 + K_{B_\pi} + K_{B_\sigma}/\sqrt{K_H P_H})$ being always greater than unity overestimates the equilibrium constant at all temperatures, if the presence of different surface intermediates is ignored. This, incidentally, is only a restatement of the proposed shift in the heat of adsorption range

TABLE 2

Calculated Total and Partial Rates

S. No. (i)	$\left(\dfrac{\text{moles benzene converted} \times 10^2}{\text{g(cat)} \cdot \text{h}}\right)$		
	Calculated Rate (r_i)	Calculated rate due to reaction 1 (r_{1i})	Calculated rate due to reaction 2 (r_{2i})
1	2	3	4
1	8.90	2.78	6.12
2	10.7	2.78	7.92
3	8.43	2.46	5.97
4	10.1	2.49	7.61
5	5.95	1.65	4.30
6	7.37	1.77	5.60
7	5.53	2.90	2.63
8	7.76	2.84	4.92
9	8.42	2.81	5.61
10	6.69	1.47	5.22
11	10.5	4.99	5.53
12	16.0	5.00	11.0
13	11.5	4.46	7.06
14	9.31	3.35	5.96
15	7.11	2.80	4.31
16	10.7	5.20	5.52
17	11.4	5.10	6.30
18	13.1	5.05	8.03
19	8.32	2.55	5.77
20	9.87	2.78	7.09
21	13.0	3.63	9.39
22	21.7	12.7	9.00
23	15.6	11.5	4.10
24	19.7	11.6	8.15
25	7.15	6.10	1.05
26	17.1	9.02	8.11
27	20.5	13.1	7.41
28	21.4	12.9	8.49
29	24.8	12.8	12.0
30	12.5	6.31	6.21
31	9.92	5.62	4.30
32	21.5	9.48	12.0
33	24.1	12.7	11.4
34	29.9	24.8	5.14
35	29.1	23.1	6.00
36	23.8	18.1	5.68
37	20.8	16.4	4.41
38	20.3	13.2	7.10
39	28.4	18.8	9.60
40	30.7	19.1	11.6
41	29.2	20.3	8.90
42	32.9	24.8	8.05
43	36.6	24.9	11.7

TABLE 3

The Estimated Model Parameters

Parameter	$k_{1\infty}$	E_1	$k_{2\infty}$	E_2	ΔS_H	ΔH_H	$\Delta S_{B_{\pi/\sigma}}$	$\Delta H_{B_{\pi/\sigma}}$	ΔS_{B_π}	ΔH_{B_π}	ΔS_{B_σ}	ΔH_{B_σ}
Value	5.17×10^3	8.32	3.27×10^5	12.2	−3.08	−2.04	−14.8	−11.3	6.02	4.28	−35.2	−16.3

Note. $k_{1\infty}$ and $k_{2\infty}$ have the units g · mol/h/g(cat)/atm; E_1, E_2, ΔH_H, $\Delta H_{B_{\pi/\sigma}}$, ΔH_{B_π}, ΔH_{B_σ} have the units kcal/g · mol; ΔS_H, $\Delta S_{B_{\pi/\sigma}}$, ΔS_{B_π}, ΔS_{B_σ} have the units eu/g · mol.
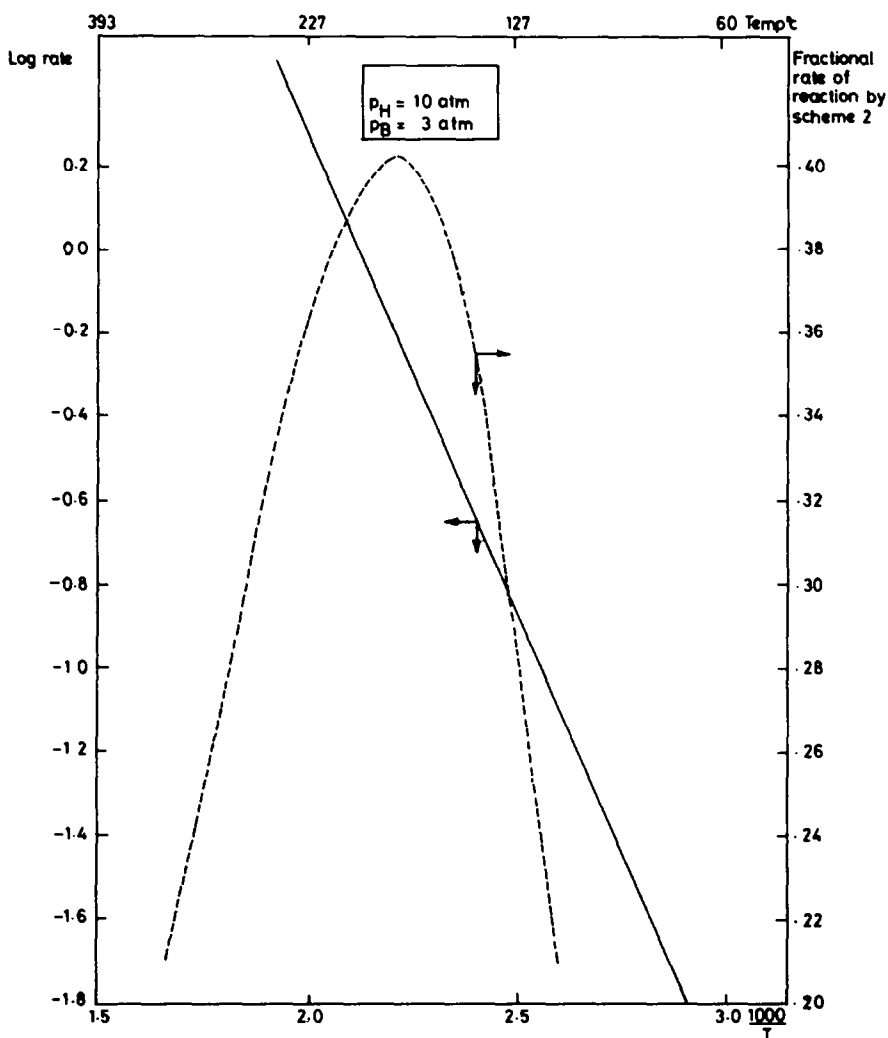

FIG. 3. Temperature dependence of overall and fractional rates.

introduced by van Meerten and Coenen (2) and their arbitrary constant, α, finds physical realisation, though in a different form.

The Self-Poisoning Effect

In the present model this apparent adsorption equilibrium constant $\bar{K}_B$ (Eq. (3)) indicates a kind of self-poisoning which affects the rate due to Scheme 2. The fact that this leads to a maximum in rate is easily verified by differentiating twice the quantity, $1 + K_{B_\pi} + K_{B_\sigma}/\sqrt{K_H P_H}$, with respect to temperature for the set of parameters given in Table 3.

The relative magnitudes of the two rates determine whether this maximum can be observed experimentally. In the present high pressure studies, the reaction rate due to Scheme 3 is quite appreciable (Table 2) and the overall rate is not much influenced by the self-poisoning. However, the fractional rate by Scheme 2, r_1/r, must reflect this effect since a high pressure operation cannot conceal this fundamental self-poisoning phenomenon. This is shown in Fig. 3 where the calculated overall rate (solid line) and the fractional rate by Scheme 2 (broken line) are plotted against temperature. Whereas the overall rate monotonically increases in this range of temperature, the fractional rate shows a well-defined maximum at about 181°C which can be attributed to the self-poisoning effect in Scheme 2. The overall rate in low pressure kinetic investigations have been reported to show a maximum between 135 to 200°C (36, 37), indicating that Scheme 2 probably predominates at low pressure.

Though the model presented here explains most of the observed features of the system in question, it must be emphasized that more fundamental investigation regarding the identity of all the surface species involved is necessary to establish its correctness beyond reasonable doubt.

CONCLUSIONS

Using data obtained in a well mixed recycle reactor at elevated pressures, it is pro-

posed that the hydrogenation of benzene to cyclohexane may occur by two parallel reaction schemes involving three surface intermediates. It appears that the rate maximum that has been reported in low pressure investigations of this system can also be observed at high pressure but for the fractional rate due to one of the schemes. Self poisoning due to unproductive occupation of active sites by σ-bonded surface intermediate in this particular reaction scheme is thought to be responsible for this behavior. The temperature at which this maximum has appeared is within the range reported for the similar maximum in low pressure studies for the same system.

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