HYDROPOLYMERIZATION OF ACETYLENE OVER PALLADIUM CATALYST

PART II: KINETIC INTERPRETATION

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Abstract

Initial rates of the three primary reactions of acetylene hydropolymerization over palladium catalyst, viz., conversions of acetylene to ethylene, butadiene and oil, have been determined by extrapolation from the once-through conversion data obtained at various space velocities. Based on these initial rate data, initial rate equations have been derived. Values of activation energies and frequency factors for the three primary reactions have been calculated from the respective equations for initial rate.

Introduction

Kinetics of palladium-catalysed reaction between acetylene and hydrogen has received very little study. Sheridan[1] from his studies on the acetylene-hydrogen reaction in static system observed the reaction over fresh palladium-pumice catalyst to resemble that over platinum, having first order rate with respect to hydrogen for both the ethylene and higher hydrocarbon ($> C_2$) forming reactions, except that the ethane formation over palladium was notably suppressed even in the presence of excess of hydrogen and that the yield of C_2-products was slightly less than that over platinum under comparable conditions.

Kinetics of acetylene hydrodimerization over palladium was studied by Gorin and Dereviyagina[2]. On the basis of the rate and yield data, butadiene-1, 3 was considered to be the primary product of the reaction with butylene as secondary. Also the reaction mechanism was presumed to involve either an addition of two units of $CH_2=CH.Pd$ followed by the elimination of atoms of 2Pd, or a union of PdH with a complex of Pd and an unsaturated hydrocarbon.

The present communication deals with the kinetic interpretation of the conversion data obtained on the hydropolymerization reaction of acetylene over a Pd-catalyst as presented in Part I of the study[3].

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EXPERIMENTAL

The conditions of experiments (in Part I) under atmospheric pressure in a flow system and using a small volume (1.5 cm^3) of catalyst in order to obviate difficulties of the highly exothermic reaction were as follows:

Catalyst: Pd—ZnO—Cr_2O_3—Kieselguhr (0.02 : 5.0 : 4.6 : 100).

Size: −28 +35 Tyler mesh.

Feed composition: $C_2H_2 : H_2 : N_2$ = (1) 5 : 3 : 2; (2) 4 : 4 : 2; (3) 3 : 5 : 2 (4) 2 : 6 : 2 (mole ratio).

Volumetric space velocity 820 to 13120 hr^{-1} (at N.T.P.).

Reaction temperature 220° to 320°C.

Ethylene, butadiene-1, 3 and butenes, all in gas phase in the product, were determined by analysis, whereas heavier hydrocarbons, collected as liquid by cooling product gases, had been termed collectively as 'oil' and determined through material balance with nitrogen as the tie component.

RESULTS

Initial Rates of Acetylene Conversion: It has been shown in the previous communication[3] that hydropolymerization of acetylene over palladium consists of three primary reactions, namely (*a*) hydrogenation of acetylene, to ethylene, (*b*) dimerization and hydrogenation of acetylene to butadiene-1, 3 and (*c*) hydrogenative polymerization of acetylene to oily hydrocarbons.

In order to evaluate the initial rates of the above three reactions, once-through conversion data, expressed as mole of acetylene per mole of feed converted into (i) ethylene and ethane, (ii) butadiene-1, 3 and butenes, and (iii) oil, are plotted in Figs. 1 to 3 against 'time factor' defined as gm. of catalyst x hr./moles of feed. The slopes of the curves are then determined by extrapolation to zero time factor. Data on the initial rate of conversion of acetylene to the three primary products, so determined, are presented in Table 1.

Reaction Mechanism: Initial rate equations corresponding to various postulated reaction mechanisms have been derived following the procedure outlined by Hougen and Watson[4] and separately tested with the initial rate equations given below, which are derived on the assumption that all the three reactions take place between adjacently adsorbed acetylene molecules and hydrogen atoms, and that the rate controlling step for both the ethylene and butadiene forming reaction is the adsorption of acetylene.

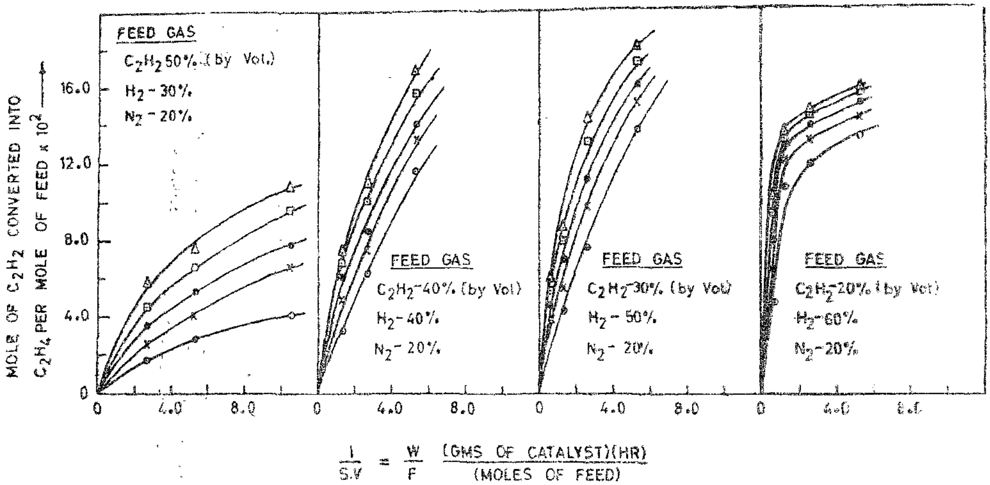

FIG. 1

FIG.1. PLOTS OF ETHYLENE YEILD VS. TIME FACTOR (W/F) AT REACTION TEMPERATURES OF 230° C (-○-), 240° C (-×-), 250° C (-●-) 260° C (-□-) AND 270° C (-△-)

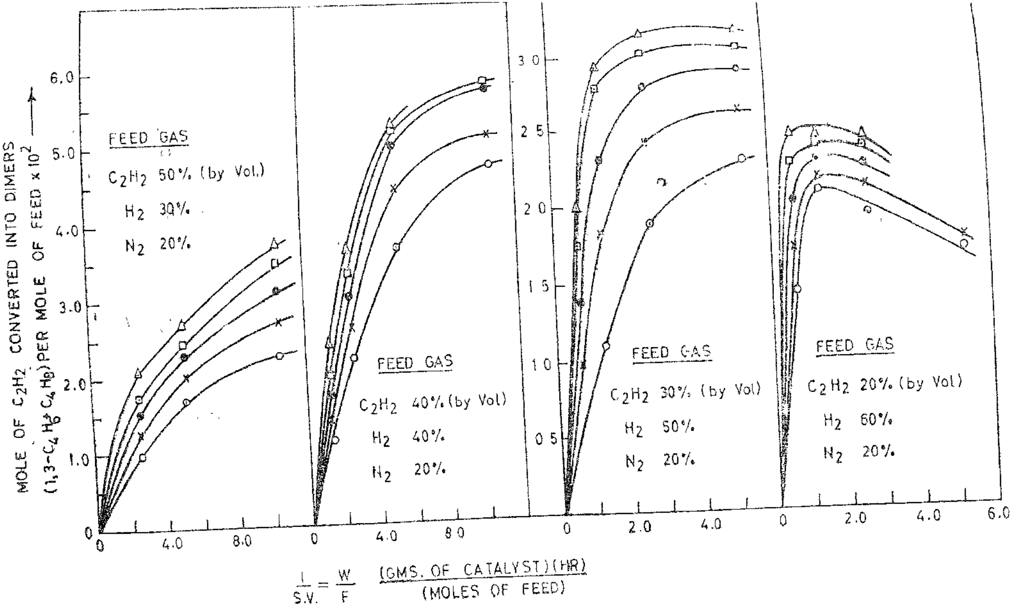

FIG. 2

FIG. 2. PLOTS OF DIMER YIELD VS. TIME FACTOR (W/F) AT REACTION TEMPERATURES OF 230°C (-○-), 240°C (-×-), 250°C (-●-), 260°C (-□-) AND 270°C (-△-).

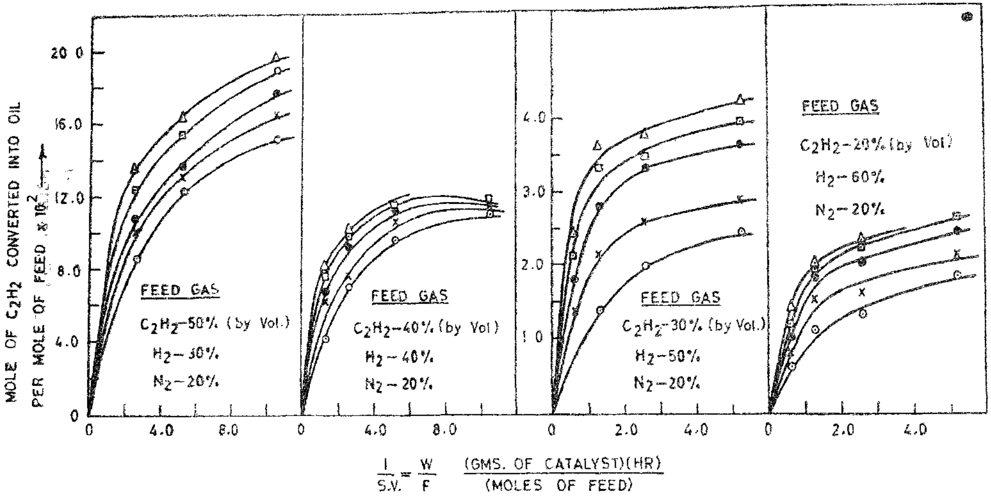

FIG. 3

FIG. 3. PLOTS OF OIL YEILD VS. TIME FACTOR (W/F) AT REACTION TEMPERATURES OF 230°C (-⊙-), 240°C (-×-), 250°C (-●-), 260°C (-⊡-) AND 270°C (-△-).

TABLE 1

Initial Rates of Conversion of Acetylene to Primary Products

Feed Composition $C_2H_2 : H_2 : N_2$ (Mole Ratio)	Reaction Temp. °C	$\frac{\text{Moles of } C_2H_2 \text{ converted to products}}{\text{gms. of catalyst} \times \text{hr.}} \times 10^2$ C_2H_2	$C_4H_6-1, 3$	
5 : 3 : 2	230	0.98	0.44	3.70
	240	1.33	0.55	4.70
	250	1.83	0.68	5.80
	260	2.25	0.85	6.75
	270	2.60	1.10	6.95
4 : 4 : 2	230	2.15	0.80	3.00
	240	3.02	1.05	3.80
	250	3.90	1.35	4.75
	260	4.45	1.65	5.25
	270	5.13	2.15	5.70
3 : 5 : 2	230	4.40	1.20	1.50
	240	5.80	1.60	2.40
	250	7.25	2.05	3.10
	260	8.00	2.65	3.65
	270	9.45	3.30	4.15
2 : 6 · 2	230	10.60	2.12	0.95
	240	12.50	2.80	1.60
	250	15.80	3.70	1.90
	260	17.50	4.65	2.45
	270	19.00	5.60	2.70

The initial rate equations are

$$r_{0\,(e)} = a_{H_{21}}/(a + b\cdot a_{A_1})^2 \qquad [1]$$

$$r_{C\,(b)} = a_{H_{21}}/(a' + b'\cdot a_{A_1})^2 \qquad [2]$$

$$r_{0\,(o)} = a_{A_1}/(a'' + b''\cdot\sqrt{a_{H_{21}}}) \qquad [3]$$

where $r_{0\,(e)}$, $r_{0\,(b)}$ and $r_{0\,(o)}$ are the initial rates of formation of ethylene, butadiene-1, 3 and oil, expressed in gm. moles of acetylene converted to respective products per gm. of catalyst per hour, and a, b, a', b', a'', b'' are constants in the respective equations.

Since the initial reaction rates are derived from slopes of conversion curves extrapolated to zero time factor, thus implying very high feed rate, diffusional resistances may be assumed to be negligible. Consequently, the interfacial concentrations of acetylene (a_{A_i}) and hydrogen ($a_{H_{2i}}$) in Eqs. [1] to [3] have been substituted by the corresponding bulk-phase concentrations and, with the total pressure being one atmosphere, have been expressed in terms of mole fractions, namely, n_A and n_{H_2} respectively, so that the initial rate equations, finally selected (Figs. 4 to 6) for the three primary reactions, are as follows

$$R = (\sqrt{n_{H_2}})/r_{0\,(e)} = a + b \cdot n_A \qquad [4]$$

$$R' = (\sqrt{n_{H_2}})/r_{0\,(b)} = a' + b' \cdot n_A \qquad [5]$$

$$R'' = n_A/r_{0\,(a)} = a'' + b''\sqrt{n_{H_2}} \qquad [6]$$

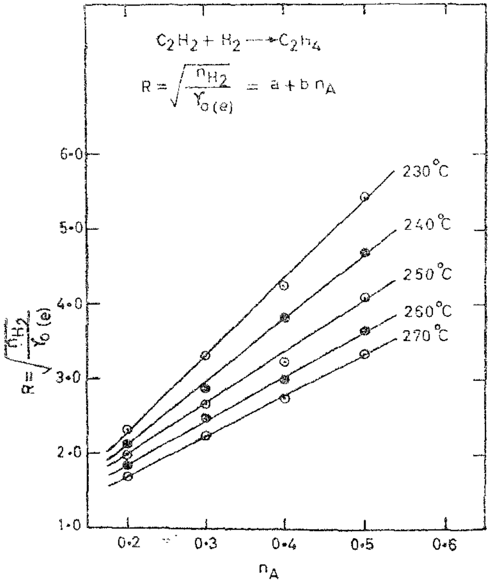

FIG. 4

Correlation of initial rate data on the conversion of acetylene to ethylene.

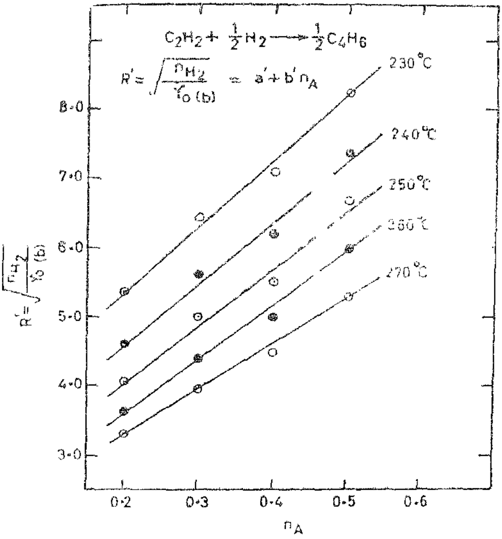

FIG. 5

Correlation of initial rate data on the conversion of acetylene to Butadiene.

Evaluation of Constants

The values of the constants a and b of Eq. [4] are determined by noting the intercept (on the R-axis) and slope of the straight line plot in Fig. 4. The constants a', b', a'' and b'' are also evaluated in the same way.

Since these constants are products and quotients of rate and equilibrium constant values, their temperature dependence can be expressed by an equation of the Arrhenius form, such as

$$a = m \times \exp. (n/T)$$

where m and n are constants and T is the temperature in °K.

Equations of this form, which have been derived from the best-fit straight-line plots on logarithm constant—reciprocal temperature co-ordinates (Fig. 7), are

$$a = 4.236 \times 10^5 \times \exp\,(-7.141 \times 10^3/T) \qquad [7]$$

$$b = 2.831 \times 10^{-4} \times \exp\,(5.297 \times 10^3/T) \qquad [8]$$

$$a' = 1.365 \times 10^{-3} \times \exp\,(3.914 \times 10^3/T) \qquad [9]$$

$$b' = 9.307 \times 10^{-2} \times \exp(2.337 \times 10^{3}/T) \tag{10}$$

$$a'' = 1.811 \times 10^{2} \times \exp(-1.842 \times 10^{3}/T) \tag{11}$$

$$b'' = 1.479 \times 10^{-13} \times \exp(1.635 \times 10^{4}/T) \tag{12}$$

Computing Product Distribution Pattern

The product distribution pattern in acetylene hydropolymerisation can be related to the initial rates of conversion of acetylene to the primary products in the following way :

$$\%\ C_2H_2 \text{ converted to } C_2H_4 = \frac{r_{0\,(e)} \times 100}{r_{0\,(e)} + r_{0\,(b)} + r_{0\,(o)}} \tag{13}$$

$$\%\ C_2H_2 \text{ converted to } C_4H_6\text{-1, 3} = \frac{r_{0\,(b)} \times 100}{r_{0\,(e)} + r_{0\,(b)} + r_{0\,(o)}} \tag{14}$$

$$\%\ C_2H_2 \text{ converted to oil} = \frac{r_{0\,(o)} \times 100}{r_{0\,(e)} + r_{0\,(b)} + r_{0\,(o)}} \tag{15}$$

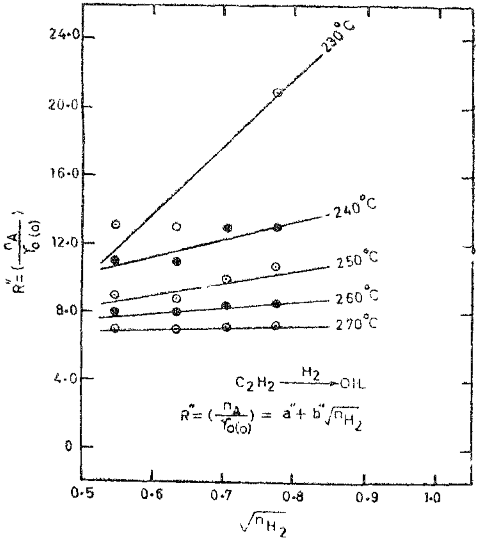

FIG. 6

Correlation of initial rate-data on the conversion of acetylene.

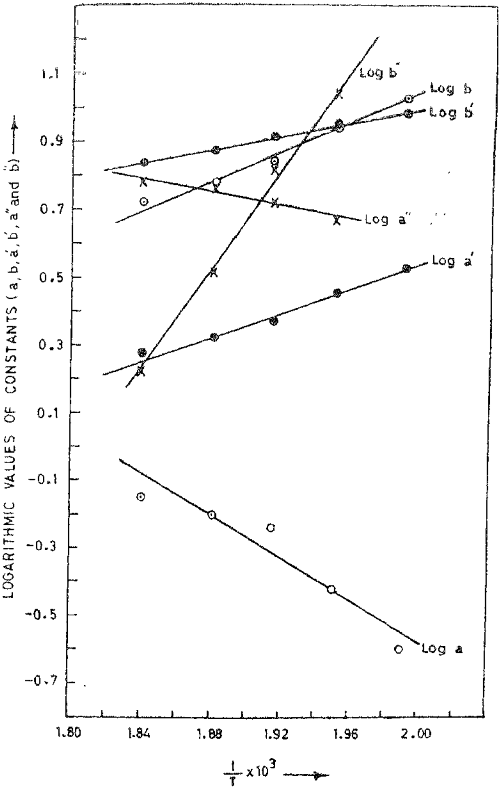

FIG. 7

Logarithm constant-reciprocal temperature plots.

The initial yield of butadiene-1, 3 as obtained from Eqs. [14] is equal to the overall yield of dimers, namely, butadiene-1, 3 and butenes, since butadiene-1, 3 is the primary product and butenes are produced secondarily from it.

The initial rates of conversion for a given C_2H_2-H_2-N_2 feed composition have been calculated from Eqs. [4], [5] and [6] after evaluating the constants at given temperatures from Eqs. [7] to [12]. Calculated values on product distribution derived from these by using Eqs. [13], [14] and [15] are recorded in Table 2, for comparison with the experimental values taken from Part I.[3] Agreement with the calculated values is, in general, found to be much better at lower (*e.g.* 30%) rather than at higher (*e g.* 60%) overall conversion of acetylene. This is, however, expected as reactions at lower conversions are closer to initial conditions for which alone the rate equations have been derived.

TABLE 2

Product Distribution Pattern: Calculated *Vs.* Experimental

Feed Compositon (Molar Ratio) $C_2H_2 : H_2 : N_2$	Temp. °C	Calculated values			Moles of C_2H_2 converted to products 100 moles of C_2H_2 reacting Values from experimental plots					
		C_2H_4	Dimers	Oil	C_2H_4 (a)	C_2H_4 (b)	Dimers (a)	Dimers (b)	Oil (a)	Oil (b)
5 : 3 : 2	250	21.6	8.4	70.0	22.5	28.5	9.0	9.5	68.5	60.0
	275	26.5	10.5	63.0	27.0	30.0	10.0	10.0	63.0	60.0
4 : 4 : 2	250	38.6	13.3	48.1	40.5	43.0	12.5	14.5	47.5	42.5
	275	41.1	16.0	42.9	41.5	44.0	14.0	14.0	44.5	41.0
3 : 5 : 2	250	57.5	16.9	25.6	57.0	65.0	17.0	17.0	26.0	18.0
	275	55.4	20.8	23.8	56.0	61.0	20.0	17.0	24.0	22.0
2 : 6 : 2	250	47.0	16.7	9.3	72.0	72.5	18.0	16.5	10.0	11.0
	275	66.3	23.7	10.0	67.0	70.0	23.0	20.0	10.0	10.0

Note: (1) Columns (a) and (b) correspond to once-through total acetylene conversions of 30% and 60% respectively.

(2) Dimers consist of butadiene–1, 3 and butenes.

Effect of Feed Dilution

Product distribution pattern deduced from Eqs. [13] to [15] for different C_2H_2-H_2 feed concentrations, after calculating the corresponding initial rates from Eqs. [4] to [6] and [7] to [12], indicates that it is greatly influenced by absolute concentrations besides the relative ones of C_2H_2 and H_2. Thus, decreasing C_2H_2 and H_2 concentrations, while keeping $C_2H_2 : H_2$ ratio constant, would produce more of ethylene and less of oil and vice-versa. Table 3 presents the computed product distribution patterns for $C_2H_2 : H_2$ feed ratio of 1 : 1 vis-a-vis experimental results quoted from Part I of the study[3].

TABLE 3

Effect of Feed Dilution with Inert Gas on Product Distribution

Feed Composition (Mole Ratio) $C_2H_2 : H_2 : N_2$	Temp. °C	Moles of C_2H_2 converted to products / 100 moles of C_2H_2 reacting: Calculated values C_2H_4	Calculated values Dimers	Calculated values Oil	Values from exptl. plot C_2H_4	Values from exptl. plot Dimers	Values from exptl. plot Oil	A%
2 : 2 : 6	250	59.0	13.4	27.6	58.5	13.5	28.0	26.2
	275	54.3	19.4	26.3	53.8	19.6	26.6	31.6
3 : 3 : 4	250	47.5	13.9	38.6	49.4	13.8	36.8	26.3
	275	47.4	17.7	34.9	49.1	17.7	33.2	35.0
4 : 4 : 2	250	38.6	13.3	48.1	41.9	12.0	46.1	35.8
	275	41.1	16.0	42.9	43.0	12.8	44.2	45.3
5 : 5 : 0	250	32.0	12.4	55.6	...	...	...	...
	275	35.8	14.2	50.0	...	...	...	...

Note. (1) Experimental-plot values correspond to A% once-through total conversion of acetylene for the flow rate 2624 cm^3 of C_2H_2 at N.T.P./cm^3 of catalyst × hour.

(2) Dimers consist of butadiene—1, 3 and butenes.

Activation Energies for the Primary Reactions

It is apparent from Eq. [4] for the conversion of acetylene to ethylene that the rate is of first order with respect to hydrogen.

$$r_{0(e)} = \frac{n_{H_2}}{(a+b \cdot n_A)^2} \qquad [16]$$

Given a definite concentration of the reactant acetylene, *i.e.*, $n_A = \text{constant}$, Eq. [16] reduces to

$$r_{0\,(e)} = k_{0\,(e)} \cdot n_H$$

where $k_{0\,(e)} = 1/(a+b\cdot n_A)^2$ [17]

Here, $k_{0\,(e)}$ may be considered as the initial reaction rate constant valid for a definite value of n_A.

Similarly the initial reaction rate constant for acetylene hydrodimerization to butadiene-1, 3 when n_A is constant is given by

$$k_{0\,(b)} = 1/(a'+b'\cdot n_A)^2 \qquad [18]$$

Equation (6) for the conversion of acetylene to oil can be written as

$$r_{0\,(o)} = n_A/(a''+b''\cdot\sqrt{n_{H_2}}) = k_{0\,(o)}\cdot n_A \qquad [19]$$

where $k_{0\,(o)}$ is the initial reaction rate constant for hydropolymerization of acetylene to oil involving a constant concentration of hydrogen in feed.

The values of $k_{0\,(e)}$ and $k_{0\,(b)}$ have been calculated from Eqs. [17] and [18] assuming different concentrations of acetylene and each at different levels of temperature in the range 230° – 270°C, employing the value of *a*, *b*, *a′* and *b′* computed from Eqs. [7] to [12]. Likewise, $k_{0\,(o)}$ has also been evaluated by combining Eqs. [11], [12] and [19] for different values of n_{H_2}. From the slopes and intercepts of the log constant – reciprocal temperature plots (Fig. 8), activation energies and frequency factors, for each of the primary reactions have been calculated. These are recorded in Tables 4 and 5. The values of activation energy, thus computed, are seen to be comparable to those derived by Sheridan[1] from reactions in static system on palladium-pumice catalyst, namely, 12 to 15 Kcal. per gm. mole (at 0° to 120°C) for both the hydrogenation and hydropolymerization reaction of acetylene. The value of activation energy at 0.2 mole fraction concentration of acetylene for the hydrogenation to ethylene (Table 4) is, however, seen to be unusually low.

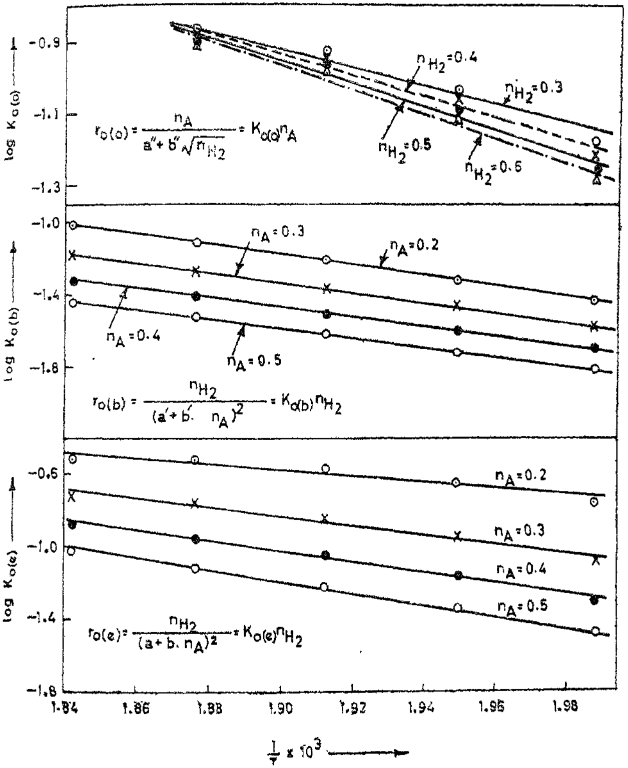

FIG. 8

Arrhenius plots for initial rate constants.

TABLE 4

Values of Activation Energies and Frequency Factors for Conversions of Acetylene to Ethylene and Butadiene

E_e=Activation energy (Kcal./gm. mole) for the hydrogenation of acetylene to ethylene ; A_e is the corresponding frequency factor.

E_b=Activation energy (Kcal./gm. mole) for the hydrodimerization of acetylene to butadiene —1, 3 ; A_b is the corresponding frequency factor.

The unit of frequency factor is gm. mole of acetylene converted per gm of catalyst per hour.

	Mole fraction of acetylene in feed			
	0.2	0.3	0.4	0.5
E_e	8.320	12.72	13.73	15.63
A_e	7.516×10^2	2.754×10^4	4.786×10^4	1.954×10^5
E_b	13.930	13.08	12.72	12.26
A_b	3.972×10^4	1.218×10^4	6.39×10^3	3.112×10^3

TABLE 5

Values of Activation Energies and Frequency Factors for Conversion of Acetylene to Oil

E_0=Activation energy, Kcal./gm. mole of acetylene converted to oil.

A_0=Frequency factor, gm. mole of acetylene converted to oil per gm. of catalyst per hour.

	Mole fraction of hydrogen in feed			
	0.3	0.4	0.5	0.6
E_0	11.44	13.22	14.61	15.25
A_0	6.683×10^3	3.556×10^4	1.288×10^5	2.323×10^5

CONCLUSION

The initial rate data on the hydropolymerization reaction of acetylene in a flow system over a Pd-ZnO-Cr_2O_3-Kieselguhr catalyst and in the temperature range of 230° to 270°C have been found to be in best accord with the initial rate equations derived on the assumptions that (a) the primary reactions comprising the conversions of acetylene to ethylene, butadiene and oily hydrocarbons, take place between adjacently adsorbed acetylene molecules and hydrogen atoms and (b) the rate controlling step for both the ethylene and butadiene forming reactions is the adsorption of hydrogen while that for the oil forming reaction is the absorption of acetylene.

However, in view of the simplifying assumptions[4] underlying the derivation of the rate equations, it has to be emphasized that the rate equations fixed for the hydropolymerization reaction of acetylene should at best be looked upon as satisfactory interpretations of the kinetic data rather than as confirming the postulated surface reaction mechanism on which their derivations were based

Thus, for atomically adsorbed hydrogen the surface concentration is proportional to the square root of activity of hydrogen in the fluid phase, whereas if molecular adsorption of hydrogen is assumed the surface concentration would be linearly proportional to the activity, so that, for the first case, the increase in surface coverage by hydrogen with increase in fluid-phase concentration of the same would be less marked than for the latter case. So, though the observed close accord of the kinetic data with a derived set of rate equations seemingly confirms the postulated mechanism of surface reaction between molecularly adsorbed acetylene and atomically adsorbed hydrogen, viewed from a different angle, the agreement may be considered as indicative of a physical situation where the catalyst surface is dominated by adsorbed acetylene, and as a result, hydrogen in the gas phase finds it difficult to reach the adsorption site.

NOMENCLATURE

a, b, a', b', a'', b'' = Constants in initial rate equations.

$a_{Ai}, a_{H_{2i}}$ = Interfacial activities of acetylene and hydrogen, respectively.

$k_{0\,(e)}, k_{0\,(b)}, k_{0\,(o)}$ = Initial reaction rate constants for acetylene conversions to ethylene, butadiene and oil, respectively.

m, n = Constants in Arrhenius equation.

$r_0(e), r_0(b), r_0(0)$ = Initial rates of conversion of acetylene to ethylene, butadiene and oil.

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SUPPLEMENT TO GLOSSARY OF INDIAN MEDICINAL PLANTS

By

B. N CHOPRA, I. C CHOPRA AND B. S VARMA

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