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A Two-Step Rate-Control Model of Vinyl Acetate Synthesis

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The kinetics of vinyl acetate synthesis reaction was studied in an integral reactor over zinc acetate catalyst supported on active carbon. Nineteen Hougen–Watson models including those reported in the literature and a two-step rate-control model were subjected to discrimination using a differential response function. The latter model—adsorption of acetylene and of acetic acid as rate controlling—was found to satisfactorily describe not only the present data but data reported in the literature as well. While the kinetic parameters were found to agree closely with the reported values, the observed temperature dependence of adsorption parameters was explained as due to side reactions involving the catalyst itself. Multiple-response modeling is recommended to understand the system better.

INTRODUCTION

The kinetics of vinyl acetate synthesis starting from acetylene and acetic acid has been studied by many investigators (*1–12*). Most of these studies have been carried out in a differential reactor with less than 8% conversion and there has been considerable disagreement among them. Because of the generally low conversion employed in these studies, it is doubtful if these data can be used successfully for the design of an industrial reactor where conversion of acetic acid may be more than 80%. A comprehensive survey of literature on the subject has been presented by Valstar (*8*), who has also reported exhaustive experimental studies on the system. By a judicious analysis of data from a differential reactor, he concluded that a three-parameter model with adsorption of acetylene as the rate-controlling step is adequate. He also observed that the adsorption equilibrium constant for vinyl acetate could not be estimated using differential reactor data alone and hence calculated it from integral data. The main drawback of his model is the dependence of this parameter on the mole ratio of the reactants. He has not explained this rather unexpected observation but indicated that the true mechanism is probably more complicated than envisaged by him. El-Sawi (*10*) has analyzed data obtained in a nonisothermal integral reactor and concluded that the three-parameter model of Valstar may be reduced to one with a single temperature-dependent parameter without causing any significant error. It may be noted, however, that in a system where two different mechanisms hold in two different ranges of temperature, a nonisothermal analysis may be misleading, since as pointed out by Carberry (*13*), the temperature dependence of the adsorption parameters in the intermediate temperatures may not be as expected. Goyal *et al.* (*12*) have discriminated among 12 models using data obtained in a differential reactor. The initial rate concept and the nonnegativity of parameters have enabled them to reject 10 models including the Varstar model. It may be pointed out that any discrimination based entirely on the criterion of nonnegativity of parameters precludes a truly unbiased comparison among rival models, since the existence of several sets of optimum parameters satisfying a model cannot, in general, be ruled out. It is remarkable, however, that except for Goyal *et al.* (*12*) and Yamada (*3*), all other investigators on

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the subject have concluded that adsorption of acetylene alone is the rate-controlling step.

In modeling chemical reactions, it is a common practice to treat the rate equations as algebraic and compare the calculated and observed rates in some statistical sense for regression and model discrimination. In practice, however, the rates are never directly measured except in the case of a well-mixed reactor. Therefore, to facilitate the use of an algebraic model, a pretense of direct rate measurement in an integral reactor is made by (a) restricting the conversion to a low value or (b) numerically differentiating the concentration with respect to time to obtain point rates. Both methods cannot be considered accurate because of the obvious need to handle differences in small numbers. For these reasons, an integral reactor has been used in the current studies to observe the progress of reaction and the parameters have been estimated using differential rate models, minimizing the sum of squared deviations between computed and observed time factors as follows:

$$\text{Min } \Delta(\mathbf{k}) = \sum_{i=1}^{N} [(W/F_{A0})_{i,o} - (W/F_{A0})_{i,c}]^2, \quad (1)$$

where $\mathbf{k}$ is the vector of parameters, N is the total number of experiments and $(W/F_{A0})_{i,o}$ and $(W/F_{A0})_{i,c}$ are observed and calculated time factors in the ith experiment, respectively; W being the weight of catalyst and F_{A0} being the molar feed rate of acetic acid. Minimization of Equation (1) has been done using a modified version of the "Complex" method (*14*) imposing nonnegativity constraints on all the parameters. Nineteen models, including those recommended by El-Sawi (model 5), Valstar (model 8), Goyal *et al.* (model 18), and a two-step rate-control model (model 19) have been discriminated. Finally, the two-step rate-control model and the Valstar model have been compared using the data reported by Cornelissen *et al.* (*9*).

THE PLUG FLOW INTEGRAL REACTOR

The vinyl acetate synthesis reaction which may be represented as

$$\underset{(A)}{CH_3COOH} + \underset{(B)}{C_2H_2} \rightarrow \underset{(R)}{C_2H_3OOCH_3C}$$

may be considered to take place in an isothermal integral reactor of length L packed with zinc acetate on activated carbon catalyst. If the reactor is considered free from axial dispersion, the differential mole balance yields the following equation for concentration of the product:

$$\frac{d(vC_R)}{dz} = \rho r(\mathbf{k}, p_A, p_B, p_R), \quad (2)$$

where C_R is the concentration of R; p_A, p_B, p_R are partial pressures of A, B, R, respectively, v is the feed velocity, ρ is the bulk density of the catalyst, and z is the length coordinate of the reactor. If F_A is the molar feed rate of acetic acid at any cross section of the reactor, the conversion, x, of acetic acid is defined as

$$x = (F_{A0} - F_A)/F_{A0} = 1 - F_A/F_{A0}. \quad (3)$$

If the initial total molar feed rate is F_{T0}, then the ratio of initial molar feed rate of acetic acid to the total molar feed is

$$\epsilon = F_{A0}/F_{T0} = F_{A0}/(F_{A0} + mF_{A0}) = 1/(1 + m), \quad (4)$$

where m is the initial molar feed ratio of acetylene to acetic acid. Using Eqs. (3) and (4), the feed velocity and the partial pressures of various species may be expressed as follows:

$$\begin{aligned} v &= v_0(1 - \epsilon x), \\ p_A &= p_{T0}\epsilon(1 - x)/(1 - \epsilon x), \\ p_B &= p_{T0}\epsilon(m - x)/(1 - \epsilon x), \\ p_R &= p_{T0}\epsilon x/(1 - \epsilon x), \end{aligned} \quad (5)$$

where v_0 is the initial feed velocity and p_{T0} is the total pressure at the inlet. If $\zeta(= z/L)$ is the dimensionless length of the reactor, Eq. (2) may be recast into the dimensionless form:

$$\frac{dx}{d\zeta} = (\rho L/C_t v_0 \epsilon) r(\mathbf{k}, x), \tag{6}$$

where $\rho L/C_T v_0 \epsilon$ is recognised to be W/F_{A0} referred to earlier. For the sake of computation, Eq. (6) may be written as:

$$(W/F_{A0})_{i,c} = \int_0^{x_i} \frac{dx}{r(\mathbf{k}, x)}. \tag{7}$$

Starting from an initial set of parameters $\mathbf{k}_0$, Eq. (7) may be recursively solved for all the N experiments and substituted in Eq. (1) to minimize (**k**). In the present work, the integration of Eq. (7) has been done numerically.

THE RIVAL MODELS

Single-Step Rate Control

The reaction under consideration has been shown to be significantly irreversible (*15*). Using the guidelines proposed by Hougen and Watson (*16*) 17 models were derived based on single-step rate control. These include the models proposed by Valstar (*8*) and El-Sawi (*10*). The model proposed by Goyal (*12*)—ionized adsorption of acetylene and acetic acid as rate controlling—has also been included in the discrimination studies.

Two-Step Rate Control

The thermogram of zinc acetate, the catalyst for this reaction, has been reported to be flat only up to 180°C (*12*), and above 200°C zinc acetate decomposes giving acetic anhydride and zinc oxide or acetone, carbon dioxide, and zinc oxide (*17*). A quantitative analysis of this decomposition has been made by Gerlach *et al.* (*18*), who observed that by prolonged heating of zinc acetate catalyst at 200°C and above in an atmosphere of nitrogen the acetate had completely disappeared and that by passing acetic acid vapor over it at about the same temperature subsequently the zinc oxide deposited was transformed completely to zinc acetate. The latter process is one of the methods employed for manufacturing zinc acetate from zinc oxide (*19*). These reactions observed by Gerlach *et al.* are given by the following equations:

$$Zn(OOCH_3C)_2 \rightarrow ZnO + O(OOCH_3C)_2,$$

$$2CH_3COOH + ZnO \rightarrow Zn(OOCH_3C)_2 + H_2O.$$

In the vinyl acetate synthesis at temperatures higher than 180–200°C it is reasonable to expect the above two reactions to take place in addition to the main synthesis reaction. Unless the rates of these two reactions are exactly equal, thereby leaving the catalyst concentration unchanged, the rate of the main synthesis reaction is bound to be affected. As explained later, this type of system is best analyzed using multiple-response modeling. An alternative, though less satisfactory, explanation may be found in the use of a multistep rate-control model.

Cornelissen *et al.* (*9*) have suggested that at temperatures higher than 210°C and lower partial pressures of acetic acid, adsorption of acetic acid alone may be rate controlling. If that is accepted, adsorption of acetylene as well as of acetic acid may be rate controlling at the intermediate temperatures. Further, if the rate of reaction between zinc oxide and acetic acid is limited by adsorption of acetic acid, it might appear reasonable to assume that while the vinyl acetate synthesis reaction at constant catalyst concentration is controlled by adsorption of acetylene alone, the rate of change of catalyst concentration is controlled by the adsorption of acetic acid, so that the overall reaction rate is limited by the adsorption of acetylene and of acetic acid. On this basis, the two-step rate-control model has been derived following the guidelines proposed by Hougen and Watson.

These 19 models have been classified according to the species adsorbed and the controlling mechanism and listed in Table 1.

EXPERIMENTAL DETAILS

The experimental setup is shown in Fig. 1. It consists of three main sections—feed

TABLE 1

The Reaction Rate Models

Model No.	Model identification	Species adsorbed	Rate control	Rate expression
1	A/A	A	Adsorption of acetic acid	kp_A
2	AB/A	A, B	Adsorption of acetic acid	$kp_A/(1 + K_Bp_B)$
3	AR/A	A, R	Adsorption of acetic acid	$kp_A/(1 + K_Rp_R)$
4	ABR/A	A, B, R	Adsorption of acetic acid	$kp_A/(1 + K_Ap_A + K_Rp_R)$
5	B/B (El-Sawi)	B	Adsorption of acetylene	kp_B
6	AB/B	A, B	Adsorption of acetylene	$kp_B/(1 + K_Ap_A)$
7	BR/B	B, R	Adsorption of acetylene	$kp_B/(1 + K_Rp_R)$
8	ABR/B (Valstar)	A, B, R	Adsorption of acetylene	$kp_B/(1 + K_Ap_A + K_Rp_R)$
9	AR/R	A, R	Desorption of vinyl acetate	$kp_Ap_B/(1 + K_Ap_A + K_{AB}p_Ap_B)$
10	BR/R	B, R	Desorption of vinyl acetate	$kp_Ap_B/(1 + K_Bp_B + K_{AB}p_Ap_B)$
11	ABR/R	A, B, R	Desorption of vinyl acetate	$kp_Ap_B/(1 + K_Ap_A + K_Bp_B + K_{AB}p_Ap_B)$
12	A/S	A	Surface reaction	$kp_Ap_B/(1 + K_Ap_A)$
13	B/S	B	Surface reaction	$kp_Ap_B/(1 + K_Bp_B)$
14	AB/S	A, B	Surface reaction	$kp_Ap_B/(1 + K_Ap_A + K_Bp_B)^2$
15	AR/S	A, R	Surface reaction	$kp_Ap_B/(1 + K_Ap_A + K_Rp_R)$
16	BR/S	B, R	Surface reaction	$kp_Ap_B/(1 + K_Bp_B + K_Rp_R)$
17	ABR/S	A, B, R	Surface reaction	$kp_Ap_B/(1 + K_Ap_A + K_Bp_B + K_Rp_R)^2$
18	AB/I (Goyal)	A, B	Ionized adsorption of acetylene and acetic acid	$K_Ap_A/(1 + K_AK_Bp_Ap_B)$
19	ABR/AB (present work)	A, B, R	Adsorption of acetylene and of acetic acid	$kp_B/(1 + K_Ap_A(1 - k_Bp_B/k_Ap_A) + K_Rp_R(1 + k'_B/k'_AKp_A + 1/Kp_A))$

preparation, reaction and product separation sections.

Acetylene from a gas cylinder is passed through concentrated sulfuric acid to remove phosphine and arsine, which are poisons to the catalyst. Further passing of acetylene through active carbon, silica gel, and calcium chloride ensured the removal of moisture and other impurities. Glacial acetic acid usually contains 1–3% water. The removal of water is necessary since it promotes formation of byproducts. The dehydration is done by adding a stoichiometric quantity of acetic anhydride to glacial acetic acid and refluxing. Under hot conditions the water present in the acid reacts with anhydride to form acetic acid. It is analyzed for purity before use.

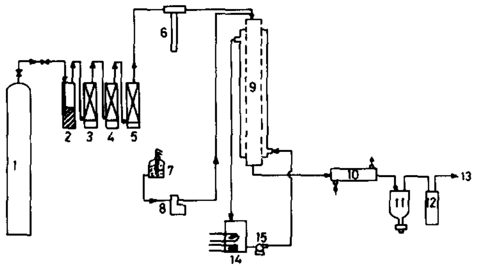

FIG. 1. Flow diagram for vinylacetate synthesis. (1) Acetylene cylinder; (2) sulfuric acid bubbler; (3) active carbon trap; (4) silica gel trap; (5) calcium chloride trap; (6) acetylene flowmeter; (7) acetic acid storage; (8) acid metering pump; (9) reactor; (10) condenser; (11) collection trap; (12) ice and salt trap; (13) outlet gases; (14) heating oil storage; (15) oil circulating pump.

The reactor is a 900-mm-long stainless-steel tube of 22 mm diameter. A helical coil attached to the reactor serves as a vaporizer. An additional heating zone is provided in the reactor by filling a portion of it with ceramic beads. The central portion of the reactor contains alternate layers of the catalyst and inert glass beads which serve as a diluent to the catalyst. The reactor section which is about 400 mm long is kept at the desired temperature by circulating oil in the outer jacket. The oil is heated or cooled as necessary. The axial temperature noted by an iron–constantan thermocouple remained practically constant over the entire length of the catalyst bed.

The products from the reactor are passed through a chilled water condenser, where most of the vinyl acetate and acetic acid are condensed. Conversion is determined by gas chromatographic analysis of the condensed product and also of the outgoing gases using a 2.4-m column of 25% carbowax 20 *M* with hydrogen as the carrier gas. A commercial catalyst, supplied by Messrs. Harshaw Chemical Co., was used in the present studies.

By preliminary experiments it was ensured that interphase and intraparticle gradients are negligibly small. Conversions in the range of 0–80% have been obtained in the time factor range of 0–505 g(cat) hr/g · mol at 170, 180, and 190°C and a molar ratio of 5 : 1. Table 2 summarizes the observations.

RESULTS AND DISCUSSION

The mean residual sum of squares (MRSS) is a measure of the accuracy of a model. An examination of the relative magnitudes of the MRSS values for various models, given in Table 3, shows that the two-step rate-control model—adsorption of actylene and of acetic acid as rate-determining steps, (ABR/AB)—appears to be the best of all models considered. At 170°C, the two-step rate-control model is as accurate as the models due to El-Sawi or Valstar. Goyal's model does not appear to be much favored in comparison with either of these models. At 180°C, the two step rate control model appears to be highly favored in comparison with the El-Sawi model while it is slightly more accurate than the Valstar or Goyal models. However, at 190°C—the maximum temperature studied—the two-step rate-control model is definitely better than the Valstar model and is far superior to the other two models. It is interesting to note that the El-Sawi model, which is almost as accurate as the two-step rate-control model at the lowest tempera-

TABLE 2

Summary of Experimental Observations[a]

Expt No.	Time factor for *i*th experiment $(W/F_{A0})_{i,0}$ g(cat) · hr/g. mol	Conversion in the *i*th experiment, x_i		
		170 °C	180 °C	190 °C
1	120	0.1052	0.1711	0.2845
2	150	0.1311	0.2091	0.31
3	160	0.1376	0.2229	0.36
4	200	0.185	0.27	0.4099
5	240	0.2	0.3321	0.4901
6	280	0.2312	0.3824	0.584
7	320	0.2613	0.4247	0.604
8	330	0.23	0.415	0.5999
9	340	0.2923	0.4755	0.6566
10	400	0.3233	0.5147	0.7044
11	440	0.353	0.5625	0.744
12	480	0.3824	0.5867	0.784
13	505	0.4001	0.575	0.8

[a] Molar ratio of acetylene to acetic acid = 5 : 1.

TABLE 3

Mean Residual Sum of Squares for Various Models

Model no.	Model identification	Mean residual sum of squares (MRSS)		
		170°C	180°C	190°C
1	A/A	521.92	291.54	267.15
2	AB/A	521.84	291.31	267.08
3	AR/A	522.08	293.38	267.31
4	ABR/A	521.84	292.46	267.15
5	B/B (El-Sawi)	318.08	442.46	793.85
6	AB/B	317.31	443.23	793.08
7	BR/B	317.31	244.54	73.85
8	ABR/B (Valstar)	317.23	244.54	73.85
9	AR/R	536.62	302.85	301.38
10	BR/R	536.77	303.46	302.69
11	ABR/R	535.85	305.69	298.69
12	A/S	536.62	302.46	302.15
13	B/S	537.46	303.46	302.61
14	AB/S	536.23	300.85	301.
15	AR/S	536.69	303.62	302.69
16	BR/S	536.69	317.54	303.15
17	ABR/S	536.69	305.69	302.
18	AB/I (Goyal)	529.85	291.54	267.23
19	ABR/AB (present work)	317.23	228.92	35.08

ture studied, is not valid compared to the latter at the highest temperature. The percentage variation about the mean explained by a model (R^2) is also a good measure of the accuracy of the model, though this must be applied with restraint to the nonlinear models. While the R^2 values for the three reported models and the present model are found to compare well at 170°C, a marked shift in favor of the latter model at higher temperatures has been observed. It may be concluded, thus, that the two-step rate-control model is as accurate or even better than all the models reported earlier at all the temperatures studied.

Figures 2A, B, and C compare the calculated and observed time factors for those four models at 170, 180, and 190°C, respectively. It is seen that, while at 170°C the corresponding calculated values of time factors for all models except the Goyal's model coincide, the divergence between them increases with temperature. It is also seen that at all temperatures the two-step rate-control model describes the data more satisfactorily than other models.

The values of the parameters of the

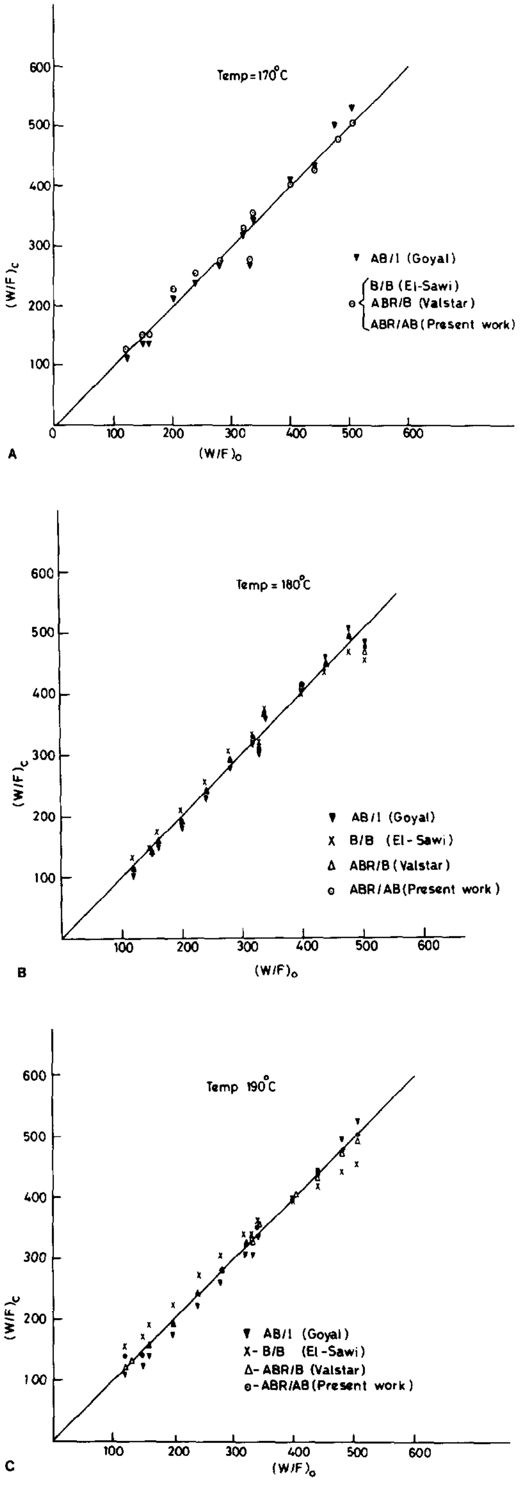

FIG. 2. Comparison of the present model with reported models, for calculated and observed time factors.

model are given in Table 4. The temperature dependence of the rate constant (Fig. 3) shows the expected behavior. The activation energy (22.6 kcal/g. mol) and the preexponential factor (1.478×10^8 g. mol/g(cat)/hr/atm) are only slightly different from those reported in the literature (*9*). However, the temperature dependence of the adsorption parameters is not anticipated. Carbery (*13*) has pointed out that when two or more steps are rate controlling, Arrhenius dependence of temperature is generally not expected to hold good for the regressed parameters which are combinations of two or more intrinsic parameters and hence are, at best, "apparent" values. This argument may not be taken as support for the model proposed and the applicability of a completely different mechanism such as a multiple response model, is not ruled out.

For example, if the activation energy for the zinc acetate decomposition reaction is higher than that of the recombination reaction of zinc oxide and acetic acid, the former reaction proceeds faster at higher temperatures and there may be a progressive depletion of zinc acetate from the surface of the catalyst resulting in a decrease in the concentration of active sites. Thus, the consequent fall in the adsorption rate is not only due to increased temperature but due to reduced active sites concentration and a new adsorption equilibrium may be reached. In the present analysis it is not possible to find out the extent to which the equilibrium shift is due to rise in temperature and due to reduced concentration of active sites. Therefore, the adsorption equilibrium constants regressed at higher temperatures may not be the true or intrinsic equilibrium constants but only "apparent" ones. For example, if isothermal adsorption of a single component is considered, the following relation is valid at equilibrium:

$$K_A = (C_T - C_l)/C_A C_l = (C_T/C_l - 1)/C_A, \quad (8)$$

TABLE 4

Values of the parameters for the Two-Step Rate-Control Model

Temp (°C)	Rate constant (g · mol/g(cat)/hr/atm)	Acetic acid adsorption equilibrium constant (atm)	Vinyl acetate adsorption equilibrium constant (atm)	Surface reaction equilibrium constant (atm)	Ratio of acetylene adsorption constant to acetic acid adsorption constant	Rate of acetylene desorption constant to acetic acid desorption constant
170	0.1011×10^{-2}	0.3782×10^{-1}	0.1495×10^{-2}	4.161	0.5864×10^{-1}	0.7346
180	0.1884×10^{-2}	0.4100×10^{-1}	0.9153	2.421	0.6708×10^{-1}	0.5319×10^{-1}
190	0.3005×10^{-2}	0.1827×10^{-1}	0.8942	2.410	0.4797×10^{-1}	0.6968×10^{-1}

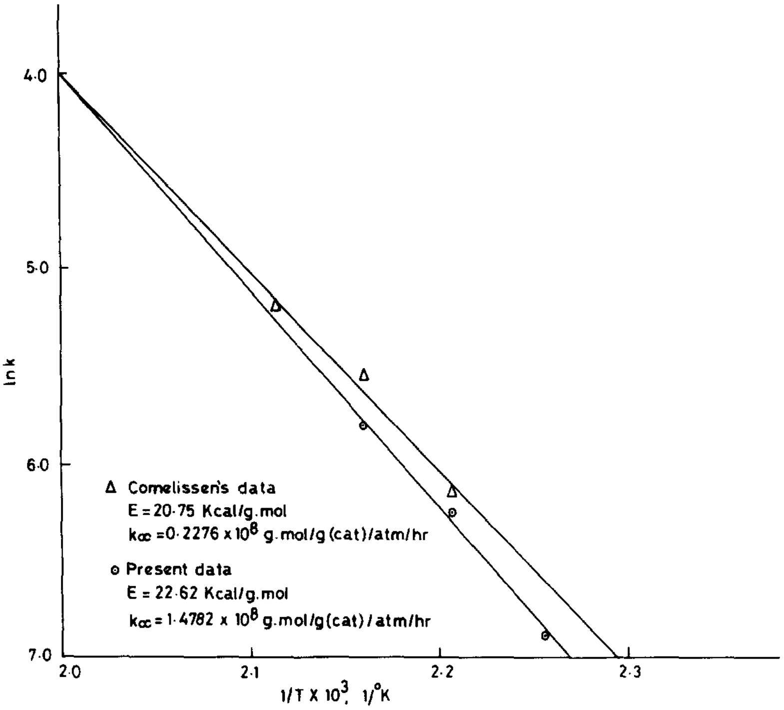

FIG. 3. Comparison of temperature dependence of rate constant in two step rate control model using reported data and present data.

where K_A is the equilibrium constant, C_T is the concentration of active sites, C_A is the bulk phase concentration of A and C_l is the concentration of vacant sites. If the bulk phase concentration, C_A, is constant, C_l, the vacant sites concentration is solely dependent on temperature, thus making K_A only temperature dependent. As in the present case, if C_T also becomes a function of temperature, there is no way to find out whether the ratio C_T/C_l increases, decreases, or remains constant except by independent adsorption experiments or by multiple-response modeling, wherein all the three reactions—decomposition of zinc acetate, reaction between zinc oxide, and acetic acid and vinyl acetate synthesis—are considered to take place simultaneously at higher temperatures. Multiple-response modeling of this series–parallel reaction network requires the knowledge of not only the conversion of acetic acid but that of

TABLE 5

Comparison of Two-Step Rate-Control Model with Valstar's Model using Data Reported by Cornellissen (9)

Model No.	Model identification	Mean residual sum of squares (MRSS)			Percentage variation about mean explained by the model (R)²		
		180 °C	190 °C	200 °C	180 °C	190 °C	200 °C
8	ABR/B (Valstar)	108.97	169.2	154.4	99.19	98.27	95.63
19	ABR/AB (present work)	98.28	148.85	119.33	99.27	96.47	96.12

zinc acetate at different temperatures, molar ratios, and initial zinc acetate concentrations on the catalyst.

The two-step rate-control model and the Valstar model are further compared using the integral reactor data at molar ratios of 4:1 and 1.5:1 reported by Cornelissen *et al.* (*9*). The results as summarized in Table 5 show a trend similar to the one observed by using the data from the present studies. An examination of the MRSS and R^2 values in Table 5 reveal that the higher the temperature the higher is the divergence between these models, the two-step rate-control model always being more accurate. The temperature dependence of the rate constant obtained using Cornelissen's data is shown in Fig. 3 alongside the corresponding plot obtained using the present data. They compare very well.

SUMMARY AND CONCLUSIONS

Vinyl acetate synthesis using zinc acetate catalyst has been studied in an integral reactor over a wide range of conversion. Using differential response equations, 19 reaction rate models including the models already reported in the literature have been examined. A two-step rate-control model—adsorption of acetylene and acetic acid as rate controlling—has been found to be statistically consistant at all temperatures studied. It has also been found that the same model satisfactorily describes the integral reactor data reported by Cornelissen (*9*). It appears that simple power law rate model (El-Sawi's model) involving only the partial pressure of acetylene, though satisfactory at low temperatures is not valid at higher temperatures. The temperature dependence of rate constant compares well with that reported in the literature. The observed temperature dependence of adsorption parameters, though not common, may be due to the extraordinary function of the catalyst as one of the reactants in a side reaction. Since the concentration of active sites is likely to change because of the predominance of the side reactions involving the catalyst itself at higher temperatures, the observed equilibrium constants for adsorption may not be true ones. Multiple-response modeling may give a better insight into the system.

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