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Gas-Phase Hydration of Ethylene on Boron Phosphate

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The gas-phase hydration of ethylene catalyzed by boron phosphate has been investigated at atmospheric pressure in the temperature range from 290 to 360°C. A rate equation has been established from conversion data at four temperatures from 290 to 320°C, which indicates that hydration proceeds by a surface reaction with preferential adsorption of water. The reaction rate and adsorption equilibrium constants have been calculated from the initial rate data by a nonlinear least-squares procedure.

NOMENCLATURE

A, B, M	subscripts referring to water, ethylene and ethanol
E_0	activation energy
k_r	reaction rate constant
k_A, k_B, k_M	adsorption rate constants
K_A, K_B, K_M	adsorption equilibrium constants
K_p	equilibrium constant
p_A, p_B, p_M	partial pressures
P	total pressure
r	surface reaction rate
r_0^+	initial rate
R	water/ethylene molar ratio in the feed
R_g	gas constant
T	absolute temperature
z	molar fraction of ethanol in the exit gas
τ	spatial time

INTRODUCTION

The kinetics and mechanism of the gas-phase catalyzed hydration of ethylene have been investigated by several authors. Mace and Bonilla (*1*), working with a tungstic oxide/silica gel catalyst, obtained results in agreement with a rate equation which indicated that hydration proceeds by a surface reaction between ethylene and water without preferential adsorption of reactants and without retardation by adsorption of the ethanol product. Dalin (*2*) interpreted the ethylene hydration over phosphoric acid supported on aluminium silicate or on silica gel by the Chirkov theory (*3*) of heterogeneous and homogeneous acid catalysis. Gel'bshtein *et al.* (*4*), working with a phosphoric acid/silica gel catalyst, by adopting the Taft mechanism (*5*) with the assumption that the limiting step is the conversion of the π-complex of H^+ and C_2H_4 into the carbonium ion $H_3C{-}C^+H_2$, derived a rate equation in the form

$$\text{rate} = k(p_B - p_M/p_AK_p) \qquad (1)$$

or alternatively, from the water pressure dependence of the phosphoric acid concentration,

$$\text{rate} = (k'/p_A^{0.5})(p_B - p_M/p_AK_p). \qquad (2)$$

Kinetic equations which fitted the experimental results have been given by Pis'man (*6*), over catalysts containing tungsten oxides, Boreskov *et al.* (*7*), over a reduced tungstic oxide/silica catalyst, Kuribayashi and Kugo (*8*), over a solid phosphoric acid catalyst, and Platanov (*9*), over H_3PO_4 on $Al_2(SiO_4)_3$ and on a cracking catalyst.

In the literature other authors have treated the kinetics and mechanism of the gas-phase catalyzed hydration of olefins.

Dale *et al.* (*10*), from the rates of hydration of 2-butene to 2-butanol over boric and phosphoric acids on alumina, attempted to establish the mechanism of reaction. The experimental data, though limited, appeared to conform best with a surface reaction mechanism involving the dissociation of the adsorbed reactants. Kuchkarev and Shuìkin (*11*) concluded that hydration of olefins in the presence of $ZnCl_2$, or ZnX_2 in general, usually proceeds through carbonium ion formation. According to Ogino (*12*), the kinetics of the hydration of propylene on metal–sulfate–silica gel catalysts can be expressed satisfactorily by a rate equation derived under the assumption that the rate controlling step is a surface reaction between water and propylene, both adsorbed.

The present paper pertains to the gas-phase hydration of ethylene on boron phosphate at atmospheric pressure. The catalytic system has been proposed since 1932 (*13*), and has been reinvestigated more recently (*14–16*). A connection between surface acidity and catalytic activity has been established on the basis of parallel decrease of acidity and activity with the temperature of catalyst pretreatment (*14*) and by different methods of catalyst preparation, through which boron phosphates of different acidity have been obtained (*15*, *16*).

EXPERIMENTAL

Apparatus. A schematic diagram of the experimental equipment is shown in Fig. 1. The flow rate of ethylene was measured with a bubble flow meter (A) and sent to a thermostated presaturator (B); it then passed through the saturator (C) which was kept at a slightly lower temperature. The reactor (D) consisted of a 2.5 cm i.d. Pyrex glass tube 24 cm long. The catalyst in the reactor was supported, through glass wool, by an aluminium perforated plate fixed at a Pyrex glass sheath containing a thermocouple by which the temperature of the catalyst bed could be measured in all points. The reactor was enclosed in an electrically heated bronze jacket (E), the temperature of which was maintained constant by a thermoregulator to within an accuracy of ±0.1°C. The gas mixture from the reactor was condensed in the traps (F) and (G) in series, which were kept at temperatures of 0 and −30°C, respectively.

Catalyst. The boron phosphate catalyst was prepared by mixing equimolar amounts of 85% H_3PO_4 and $H_3BO_3 < 230$ mesh and keeping the mixture at 100°C up to practically constant weight. The obtained solid was crushed and screened to give a distribution of particle diameters. Before being used, the catalyst was calcined in a muffle for 4 hr at 300°C. The catalyst, so pretreated, showed a surface area (BET), (measured by a Carlo Erba Sorptomatic apparatus), of 24 m^2/g and a total acidity ($pK_a = +4$ to -8.2), (measured by titrating a 23–28 mesh boron phosphate in anhydrous benzene in the presence of Hammett indicators), of 0.31 mmoles of *n*-butylamine per g of catalyst.

Analytical procedure. The solution was analyzed by a gas chromatograph (Carlo Erba Model C apparatus equipped with thermal conductivity detector), where ethanol and water could be determined. A 2 m column of 20% Carbowax 1500 on

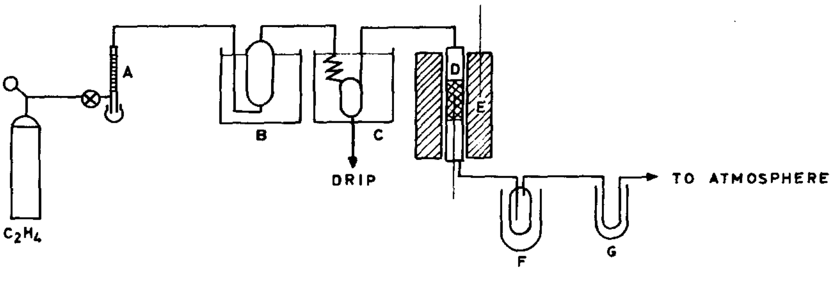

FIG. 1. Diagram of the experimental equipment.

Teflon was used. The column was kept at 120°C. The rate of helium gas flow, as carrier gas, was about 3 liters/hr. The ethylene was a pure grade product, with purity superior to 99%.

Preliminary Tests

Tests performed in the absence of catalyst gave no measurable conversion of ethylene to ethanol. Generally, the fresh catalyst showed a higher activity, which after the first 8 hr became approximately constant up to 30 hr (*17*). Because a reproducible behavior of the catalyst was found only after the first 8 hr, the conversion data, reported below, have been evaluated and averaged on five time-spaced measurements taken in the range 8 to 25 hr of the catalyst time-on-stream.

Ethyl ether was never found in the reaction product.

Runs have been carried out using particles of diminishing diameters to test if diffusional resistances within the catalyst could be important. The kinetic data, reported here, have been obtained on 23–28 mesh catalyst; the results obtained on 32–35 and 48–60 mesh catalyst insured that pore diffusion influence was negligible (*17*). Again, working with different amounts of catalyst and different flow rates, as shown in Table 1, external diffusion appeared not to be the rate limiting step.

Results and Discussion

Results of the kinetic runs are summarized in Table 1, where the molar fraction of ethanol in the exit gas mixture is given at different spatial times (defined as ratio between the catalyst weight and the volumetric rate of stream entering the catalyst bed), reaction temperatures, and water/ethylene molar ratios in the feed. The runs (except those footnoted) have been carried out with 15.6 g of catalyst. Because of the very low values of conversion which were less than 10^{-3}, the differential material balance of the plug-flow catalytic reactor may be written as

$$dz = (R_g Tr/P)d\tau \qquad (3)$$

At first, the initial rate, $r_0^+ \equiv (dz/d\tau)_{\tau \to 0}$, was derived from the conversion data at four temperatures, from 290 to 320°C. As reported in Fig. 2 against R, the initial rate appears to have a maximum value which falls in the range 0.4 to 0.6 of the water/ethylene molar ratio.

First approach to derive a process mechanism was the comparison between the theoretical rate expressions following hypothesized mechanisms and the experimental behavior of r_0^+ *versus* R.

Mechanisms which assume that reaction between adsorbed molecules is very rapid and the overall reaction rate is limited by

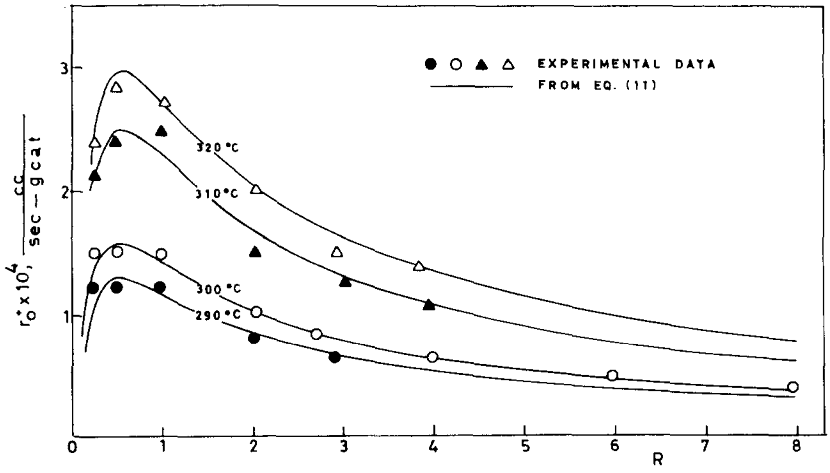

FIG. 2. Initial rate *versus* water/ethylene molar ratio in the feed. Comparison between the experimental data and the Langmuir–Hinshelwood model.

TABLE 1

Hydration of Ethylene at Atmospheric Pressure on 23–28 mesh Boron Phosphate

Reaction temperature (°C)	R	τ $\left(\frac{\text{sec g cat}}{\text{cc}}\right)$	$z \times 10^4$
290	0.25	1.09	1.12
	0.25	1.93	2.20
	0.49	1.09	0.97
	0.49	1.97	2.01
	0.98	1.09	1.16
	0.98	1.99	1.81
	2.03	1.06	0.80
	2.03	1.96	1.32
	2.88	1.10	0.68
	2.88	2.05	1.12
300	0.25	1.11	1.14
	0.25	2.02	2.22
	0.25	3.84	2.75
	0.33	1.10	1.21
	0.33	2.01	2.15
	0.33	3.85	3.13
	0.51	2.02	1.83
	0.51	3.82	3.06
	0.98	1.12	1.23
	0.98	2.02	1.91
	2.01	1.08	0.98
	2.01	1.98	1.34
	2.64	1.32	0.87
	2.64	2.02	1.25
	2.64	2.63	1.29
	2.64	8.01	2.08
	2.64	0.79[a]	0.55
	2.64	0.97[a]	0.78
	2.64	1.30[a]	0.82
	2.64	2.02[a]	1.28
	2.64	3.96[a]	1.61
	3.97	1.98	0.90
	3.97	2.07	0.95
	3.97	3.78	1.15
	5.96	1.07	0.44
	5.96	2.16	0.69
	5.96	3.96	1.02
	7.95	3.82	0.79
310	0.24	1.08	1.82
	0.24	1.10	1.90
	0.24	1.95	2.30
	0.24	1.96	2.45
	0.49	1.10	1.99
	0.49	1.96	3.03
	0.98	1.09	2.02
	0.98	2.00	3.15
	1.99	1.07	1.23
	1.99	2.01	2.21
	3.00	1.09	1.02
	3.00	1.95	1.70
	3.93	1.07	0.99
	3.93	2.03	1.56
320	0.24	1.09	1.88
	0.24	1.97	2.16
	0.49	1.08	2.22
	0.49	1.97	2.95
	1.02	1.07	2.09
	1.02	1.92	3.03
	2.06	1.07	1.48
	2.06	1.94	2.47
	2.92	1.09	1.49
	2.92	2.03	2.08
	3.80	1.12	1.36
	3.80	2.06	1.91
330	0.99	1.08	2.20
	0.99	1.99	2.58
350	0.99	1.09	1.81
	0.99	1.98	2.02
360	1.97	3.17	1.93

[a] Runs carried out with 7.79 g of catalyst.

the rate at which continued adsorption of one of two reactants takes place (adsorptive equilibrium for the other reactant and for the product is established) give

$$r_0^+ = R_g T \frac{k_A R}{R + K_B P + 1} \quad \text{(adsorption of A controlling)} \quad (4)$$

or

$$r_0^+ = R_g T \frac{k_B}{(K_A P + 1)R + 1} \quad \text{(adsorption of B controlling).} \quad (5)$$

Plainly, if adsorption of A is rate limiting, r_0^+ must increase with increasing R, approaching the limiting value $R_g T k_A$ as $R \rightarrow \infty$; on the other hand, if adsorption of B is rate limiting, r_0^+ must decrease continuously with R, approaching zero as $R \rightarrow \infty$. Obviously, the previous mechanisms are not consistent with the experimental results shown in Fig. 2; therefore, they may be rejected.

Likewise, the Eq. (2) by Gel'bshtein, derived from the Taft mechanism, cannot be applied to our results, because it requires r_0^+ decreasing with R.

If the Rideal model is assumed and the reaction between water adsorbed and gas-phase ethylene is hypothesized as the controlling step while equilibrium concentrations of water and ethanol are considered established on the surface, the initial rate becomes

$$r_0^+ = R_gTk_rK_AP \times \frac{R}{(K_AP + 1)R^2 + (K_AP + 2)R + 1} \qquad (6)$$

the maximum value of which occurs at $R_{\max} = \sqrt{1/(K_AP + 1)}$. By substituting $K_AP = 1/R^2_{\max} - 1$ into Eq. (6), we obtain

$$r_0^+ = R_gTk_r \times \frac{(1/R^2_{\max} - 1)R}{R^2/R^2_{\max} + (1/R^2_{\max} + 1)R + 1} \qquad (7)$$

i.e., the experimental initial rate, plotted *versus*

$$\frac{(1/R^2_{\max} - 1)R}{R^2/R^2_{\max} + (1/R^2_{\max} + 1)R + 1},$$

should give a straight line. On the contrary, the experimental data, with $R_{\max}$ values obtained by graphical interpolation, do not seem to fall on a straight line (*18*). If in the Rideal model the ethylene is supposed adsorbed on the catalyst and reacting with the gas-phase water, the maximum value of r_0^+ should occur at $R_{\max} = (K_BP + 1)^{1/2}$, which contrasts with the experimental values of less than unity.

The mechanism applied by Szonyi and Graydon (*19*) to the gas-phase hydration of acetylene has been tried, where a steady state is assumed between the rate of adsorption of water on the surface and the rate of removal of water by ethylene from the gas-phase. It gives

$$r_0^+ = R_gTk_rk_A \frac{R}{k_AR^2 + (k_r + k_A)R + k_r}, \qquad (8)$$

the maximum value of which occurs at $R_{\max} = \sqrt{k_r/k_A}$. Eq. (8), with the substitution $k_A = k_r/R^2_{\max}$, becomes

$$r_0^+ = R_gTk_r \times \frac{R/R^2_{\max}}{R^2/R^2_{\max} + (1/R^2_{\max} + 1)R + 1}. \qquad (9)$$

As in the Rideal model, this mechanism may be rejected. Likewise, substitution of ethylene by water gives an initial rate which is inconsistent with the experimental data.

Let us now consider the Langmuir–Hinshelwood model, where equilibrium concentrations of water, ethylene, and ethanol are assumed to be established on the surface of the catalyst, with the reaction occurring between adsorbed reactants. Under these conditions, the rate equation becomes

$$r = \frac{k_rK_AK_B}{(K_Ap_A + K_Bp_B + K_Mp_M + 1)^2} \times (p_Ap_B - p_M/K_p) \qquad (10)$$

and the initial rate is given by

$$r_0^+ = R_gTPk_r \frac{K_AK_BR}{[(K_AP + 1)R + K_BP + 1]^2}. \qquad (11)$$

The function $r_0^+(R)$ in Eq. (11) shows a maximum value at

$$R_{\max} = (K_BP + 1)/(K_AP + 1)$$

and its behavior with increasing R is similar to the experimental. Further calculations have been carried out to determine the values of the reaction rate and adsorption equilibrium constants. Equation (11) is a nonlinear function, and the rearrangements tried to linearize it did not give physically consistent values of the constants. Therefore, we directly analyzed this function, through minimizing the sum of the squares of the error terms by an iterative gradient technique. To do so, a simple program, written in BASIC time-sharing language, which ran starting from not unreasonable values of the constants, was implemented on an HP 2116B computer; rapid convergence was obtained. The values of the constants, calculated by the above method, are reported in Table 2. When employed in

TABLE 2

REACTION RATE AND ADSORPTION EQUILIBRIUM CONSTANTS OF WATER AND ETHYLENE FROM THE LANGMUIR–HINSHELWOOD MODEL

Temperature (°C)	$k_r \times 10^7$ $\left(\frac{\text{mole}}{\text{sec g cat}}\right)$	K_A (atm^{-1})	K_B (atm^{-1})
290	0.38	2.38	0.79
300	0.94	1.55	0.31
310	2.61	1.09	0.18
320	5.00	0.90	0.11

Eq. (11), they gave initial rate curves (solid lines in Fig. 2) which agree fairly well with the experimental data.

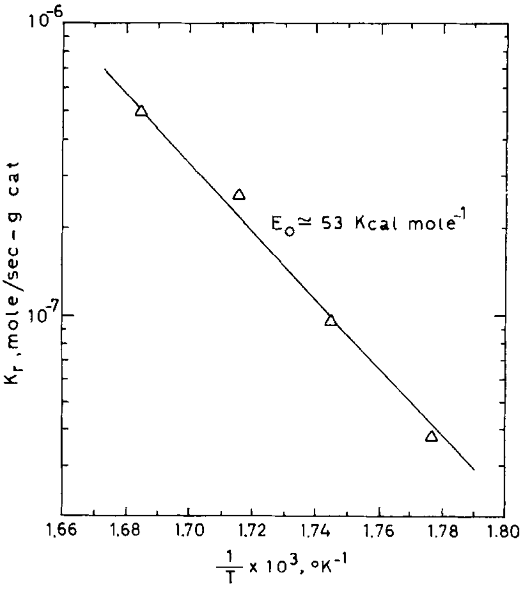

FIG. 3. Temperature dependence of the reaction rate constant from the Langmuir–Hinshelwood model.

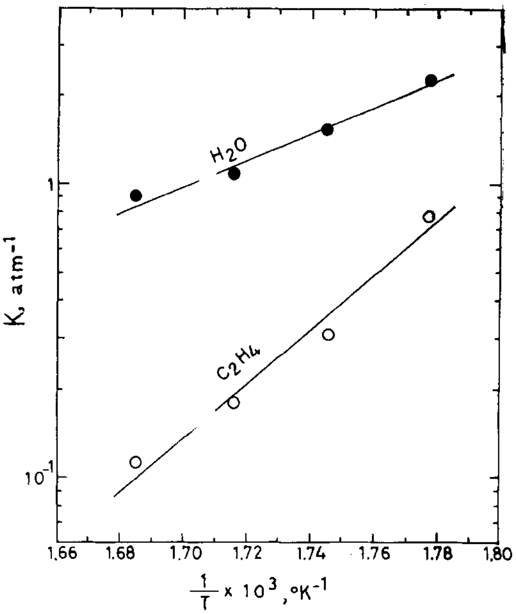

FIG. 4. Temperature dependence of the adsorption equilibrium constants of water and ethylene from the Langmuir–Hinshelwood model.

The reaction rate constant, reported in Fig. 3 against the temperature, conforms to the Arrhenius type equation, with an apparent activation energy of $\simeq 53$ kcal mole^{-1}. Linear plots of ln K_A and ln K_B are given in Fig. 4 with adsorption heats of $\simeq 21$ and $\simeq 41$ kcal mole^{-1} for water and ethylene, respectively. In addition, from this mechanism, the water appears to be preferentially adsorbed on the catalyst. By substituting the rate expression of Eq. (10) into the differential balance equation, it becomes

$$dz = \frac{R_gT}{P} \frac{k_rK_AK_B}{(K_Ap_A + K_Bp_B + K_Mp_M + 1)^2} \times (p_Ap_B - p_M/K_p)d\tau. \quad (12)$$

Along the integral reactor, because of the very low values of conversion, there are very small variations in the composition of reactants, i.e.,

$$p_A \simeq \frac{R}{R+1} P$$

and

$$p_B \simeq \frac{1}{R+1} P,$$

and K_Mp_M may be neglected. By these assumptions, integration of Eq. (12) gives

$$z = \frac{K_pPR}{(R+1)^2}\left[1 - \exp\left(-\frac{R_gTk_rK_AK_B(R+1)^2}{K_p[(K_AP+1)R + K_BP + 1]^2}\tau\right)\right]. \quad (13)$$

Employing the equilibrium constant values given by Gilliland (*20*), the molar fractions

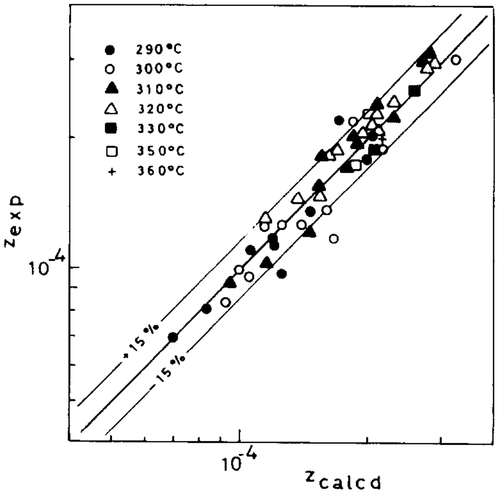

FIG. 5. Comparison between the experimental molar fraction of ethanol in the exit gas and that calculated by Eq. (13) from the Langmuir-Hinshelwood model.

of ethanol in the exit gas mixture from the integral reactor have been calculated by Eq. (13) and compared with the experimental values (Fig. 5). The constants from the Langmuir–Hinshelwood model having been calculated at four temperatures from 290 to 320°C, values of the constants at 330, 350, and 360°C have been obtained by extrapolation from the linear plots of Figs. 3 and 4. It appears that the molar fractions of ethanol predicted by the Langmuir–Hinshelwood model, where the constants have been calculated from the initial rates, are in good agreement with the experimental data.

In addition to these reaction models, the mechanism which assumes rapid surface reaction, equilibrium concentrations of reactants established on the surface, and desorption of alcohol as rate limiting step, gives an initial rate

$$r_0{}^+ = R_gTP\frac{k_MK_pR}{(K_AP+1)R^2+(K_AP+K_BP+K_pK_MP^2+2)R+K_BP+1} \qquad (14)$$

with the maximum value occurring at

$$R_{\max} = \sqrt{(K_BP+1)/(K_AP+1)}.$$

Therefore, this model, which gives a function $r_0{}^+(R)$ not in contrast with the experimental behavior, must be tested as well. The values of the constants in Eq. (14), calculated by the previous iterative least-squares method assuming the Gilliland equation for $K_p(T)$ and $K_pK_MP^2R$ negligible ($K_pP < 2.2 \times 10^{-3}$), are reported in Table 3. From these constants, good agreement between the theoretical and experimental values for the initial rates and the molar fractions of ethanol in the exit mixture have been obtained (*18*). While k_M does exhibit a consistent temperature dependence with an activation energy of $\simeq$36 kcal mole^{-1}, water and ethylene show an endothermic adsorption with heats of $\simeq$8 and $\simeq$12 kcal mole^{-1}, respectively, the water being preferentially adsorbed on the catalyst.

TABLE 3

ADSORPTION RATE CONSTANT OF ETHANOL AND ADSORPTION EQUILIBRIUM CONSTANTS OF WATER AND ETHYLENE FROM THE PRODUCT DESORPTION RATE CONTROLLING MODEL

Temperature (°C)	$k_M \times 10^4$ $\left(\frac{\text{mole}}{\text{sec g cat}}\right)$	K_A (atm^{-1})	K_B (atm^{-1})
290	0.32	9.30	2.30
300	0.43	8.60	2.36
310	0.97	11.30	3.31
320	1.42	13.10	4.18

Since the endothermic adsorption, even if possible, may be considered quite rare (*21*), in order to investigate the physical consistency of this model, some runs have been carried out on the adsorption behavior of water and ethylene on a chromatographic column of boron phosphate. The retention time of water decreased with an increase in temperature (*18*), implying exothermic adsorption. Therefore, the product desorption rate controlling model, which gives endothermic adsorption of reactants, may be rejected. In addition, water presented a retention time higher than that for ethylene (*18*), i.e., a further support to the previous Langmuir–Hinshelwood model which gives $K_A > K_B$.

CONCLUDING REMARKS

The gas-phase hydration of ethylene on boron phosphate shows a kinetic behavior which may be interpreted on the Langmuir–Hinshelwood model. The same model has been applied by Mace and Bonilla (*1*) to the ethylene hydration on WO_3–SiO_2-gel catalyst. On the latter, water and ethylene were not adsorbed preferentially; but on BPO_4 water has an adsorption equilibrium constant higher than that for ethylene. In addition, the adsorption heat of water and ethylene on WO_3–SiO_2-gel catalyst and of ethylene on BPO_4 are alike ($\simeq$41 kcal mole^{-1}), less than the adsorption heat of water on BPO_4 ($\simeq$21 kcal mole^{-1}). The apparent activation energy on BPO_4 is rather higher ($\simeq$53 kcal mole^{-1}) than on WO_3–SiO_2-gel catalyst ($\simeq$30 kcal mole^{-1}).

Phosphoric acid based catalysts represent an important and extensively investigated class of catalysts for gas-phase ethylene hydration. While Gel'bshtein *et al.* (*4*), using a phosphoric acid/silica gel catalyst, applied a kinetic model based on homogeneous catalysis (which may be considered equivalent to the hypothesis that the active component is liquid aqueous phosphoric acid absorbed in the pores of the support), Kuribayashi and Kugo (*8*), using a solid phosphoric acid catalyst, interpreted the experimental data on the Langmuir–Hinshelwood model. The catalytic surface of BPO_4, because of its interactions with hydrolyzing water, may be considered to some extent similar to that of supported H_3PO_4. From this point of view, our results agree with the Kuribayashi and Kugo paper.

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