Catalytic Hydroboration in Gas Phase*

—A Kinetic Study of the Reaction of the Diborane with Ethylene and Propylene by Pd-Carbon Catalyst—

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Summary: A new catalytic hydroboration of olefins in the gas phase has been proposed. The kinetics of the reaction of diborane with ethylene or propylene in the presence of a Pd-carbon catalyst was investigated at 30°C to 50°C. The initial rate of the reaction, r_i , was expressed by $r_i = k p_B^{1/2} P_O$, where P_B and P_O denote the initial partial pressures of diborane and ethylene or propylene, respectively, and k the rate constant. The activation energy was 6 and 1.5 kcal/mol for ethylene and propylene, respectively. These activation energies were much smaller than those for noncatalytic hydroboration found in literature. The reaction mechanism was interpreted in terms of the rate-determining step which is the attack of the olefin on the dissociated diborane on the catalyst. The reaction mechanism was further confirmed by the adsorptions of diborane, ethylene and propylene.

1 Introduction

Numerous investigations on hydroboration reaction in the liquid phase were provided by H. C. Brown et al.¹⁾, but only very few such investigations in the gas phase are available. Hydroboration of ethylene from diborane to form triethylborane in the gas phase was first discovered by Hurd²⁾. Since the process was noncatalytic, yields of the products were very small, and they could only be detected by mass spectrometry. A kinetic study of noncatalytic diborane-ethylene reaction was also investigated by Whatley and Pease³⁾. They indicated that the reaction did not proceed at temperatures higher than 120°C and it should be maintained at above the stoichiometric ratio for triethylborane formation ($1B_2H_6 : 6C_2H_4$), because under the reaction conditions, there are possibilities of an explosion with a composition of lower ratios. Noncatalytic hydroboration of other olefins, allene and acetylenes in the gas phase were also investigated by Lindner and Onak⁴⁾ with sufficiently high molar ratios of B_2H_6 to olefins at 60°C to 65°C for 24 hours. No risks of an explosion were reported in the literature⁴⁾. The absolute rate of reaction of borane with ethylene in the gas phase was investigated by Fehlner⁵⁾, who found that diborane

did not directly react with ethylene in the presence of borane.

However, the studies on the hydroboration reaction on solid catalysts at rather lower temperatures have not yet been published. The authors presumed that hydroboration in the gas phase would proceed in the presence of a solid catalyst, and they attempted to study the reaction of diborane with ethylene on a Pd-carbon catalyst at room temperature. The reaction proceeded smoothly, and triethylborane was obtained in fairly good yields. In order to clarify the reaction mechanism of this new process, the authors investigated kinetically the hydroboration reaction on the Pd-carbon catalyst, using ethylene and propylene.

2 Experimental

The reaction of diborane with ethylene or propylene was carried out at 30°C to 50°C in closed circulation apparatus equipped with a small trap in which the products were collected. Diborane was produced by $NaBH_4$ reacting with $BF_3 \cdot Et_2O$ in a diglyme (diethylene glycol dimethyl ether) solution at room temperature under a N_2 atmosphere. The diborane was purified by freezing with liquid nitrogen and pumping off the impurities followed by distribution. The ethylene used was obtained from Takachio Shoji Co. and the propylene was supplied from Nippon Petroleum Co. They were purified by low-temperature distillation. The Pd-carbon

* Received May 29, 1975.

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1. B_2H_6 33.3 C_2H_4 313 2. B_2H_6 37.1 C_3H_6 310
3. B_2H_6 30.0 C_2H_4 164 4. B_2H_6 37.1 C_3H_6 211
unit : mmHg

Fig. 1 Typical Pressure-Time Plots of Catalytic Hydroboration at 50°C

catalyst was supplied from Kawaken Fine Chemical Co. The surface area of the catalyst containing 3% Pd was 1,030 m^2/g as determined by the BET method. The catalyst was calcined at 450°C under vacuum for 1 hour before use.

The known quantities of diborane and olefin, with high molar ratio of olefin to diborane were premixed at room temperature and then admitted into the reaction vessel which was held at constant temperature. The change of pressure with time followed, since the total amount of the reacting gases decreased as the reaction proceeded.

3 Results and Discussion

3.1 Initial Rate

Typical pressure-time plots are shown in **Fig. 1**. An induction period of few minutes was observed in every case. The induction period was attributed to the adsorption of the reactants as will be described later. After the induction period the reaction proceeded rapidly and then gradually. Rates at various reaction times are plotted in **Fig. 2**. The initial rates were estimated by extrapolation of these plots to $t=0$. The initial rates thus obtained agreed roughly with slopes at the initial stages as shown in **Fig. 1**. The effects of the initial partial pressures of diborane and olefin on the initial rates were examined at

Fig. 2 $\Delta P/\Delta t$ vs. t Plot (The numbers are the same as in Fig. 1)

1. B_2H_6 37.1 mmHg, Olefin C_3H_6 ,
Reaction temp. 50°C
2. B_2H_6 30.0 mmHg, Olefin C_2H_4 ,
Reaction temp. 50°C
3. B_2H_6 30.0 mmHg, Olefin C_2H_4 ,
Reaction temp. 40°C

Fig. 3 Dependence of Olefin Partial Pressure on the Initial Rate, r_i

40°C and 50°C (**Figs. 3** and **4**). From **Figs. 3** and **4** the reaction was first order with respect to the partial pressure of olefin and half order with respect to diborane. Therefore, the rate equation is represented by

$$r_1 = kP_B^{1/2}P_O \quad (1)$$

The initial pressure estimated by the above extrapolation was proportional to the total

Table 1 Initial Rates and Rate Constants

Diborane-Ethylene Reaction				Diborane-Propylene Reaction			
Temp. 50°C				Temp. 50°C			
Initial Press. (mmHg)		r_i (mmHg/min)	k (mmHg/min)	Initial Press. (mmHg)		r_i (mmHg/min)	k (mmHg·min)
B_2H_6	C_2H_4			B_2H_6	C_3H_6		
30	164	114	0.182	37.1	120	28.6	0.039
30	173	175	0.185	37.1	197	44.3	0.037
30	200	209	0.191	37.1	211	46.8	0.036
30	217	224	0.188	37.1	215	46.9	0.036
30	280	271	0.177	37.1	231	48.9	0.035
30	328	335	0.184	37.1	266	57.8	0.036
33.3	313	266	0.184	37.1	310	70.0	0.037
12.7	180	112	0.175	12.5	180	23.4	0.037
15.2	180	120	0.171	17.3	180	28.0	0.037
17.0	180	131	0.177	23.8	180	33.1	0.038
20.0	180	129	0.194	35.0	180	41.6	0.039
25.3	180	156	0.172				av. 0.037
			av. 0.182				
Temp. 40°C				Temp. 40°C			
30	180	160	0.162	48.5	216	45.2	0.030
30	204	171	0.153	48.5	200	47.5	0.034
30	248	186	0.137	48.5	173	42.1	0.035
30	264	209	0.145	48.5	110	24.6	0.032
30	284	237	0.151	39.0	180	42.7	0.038
30	330	290	0.160	29.5	180	31.3	0.032
23.5	180	136	0.156	23.2	180	28.6	0.033
17.9	180	125	0.164	22.9	180	26.7	0.031
15.6	180	105	0.147	16.9	180	25.9	0.035
			av. 0.147				av. 0.033
Temp. 30°C				Temp. 30°C			
30	188	113	0.110	37.1	133	24.3	0.030
30	199	122	0.112	37.1	184	32.3	0.029
26.1	181	106	0.115	37.1	212	38.7	0.030
19.1	183	85	0.104				av. 0.030
			av. 0.110

1. C_3H_6 180 mmHg 2. C_2H_4 180 mmHg
Reaction temperature 50°C

Fig. 4 Dependence of Diborane Partial Pressure on the Initial Rate, r_i

pressure of the reactants fed to the reactor. Thus, the rate constants at 30°C to 50°C were calculated by Eq. (1) and are shown in **Table 1**. The rate of hydroboration of ethylene was greater by a factor of about 3 to 4 than that of propylene. The activation energies of hydroboration of

ethylene and propylene were calculated to be 6 and 1.5 kcal/mol, respectively. The frequency factor in propylene hydroboration is expected to be smaller than that in ethylene hydroboration, because there may exist some steric hindrance with the former. The steric hindrance in the hydroboration reaction in the liquid phase is also shown by Brown¹. The activation energy of noncatalytic hydroboration of ethylene was obtained as 37.3 kcal/mol³* which is much larger than ours. The rate constant of the catalytic reaction at 40°C is roughly comparable with that of the noncatalytic reaction at 177°C. It will be noted that hydroboration in the gas phase is greatly promoted by the presence of the catalyst.

From the experimental results, the following reaction scheme can be considered. The dissociative adsorption of diborane on the catalyst will take place.

*) The authors calculated the activation energy from the results of Whatley and Pease³ at temperatures between 130°C and 170°C.

where C denotes the catalyst and $\text{BH}_3(\text{a})$ the adsorbed state of the dissociated diborane. And the reaction is further followed by:

where $n=2$ or 3 .

Thus, diborane is adsorbed dissociatively on the catalyst, and the dissociated diborane reacts consecutively with the olefin to form II, III and then IV. The adsorbed species (IV) will be desorbed from the surface into the bulk by Eq. (6). By considering the Eqs. (2) to (6) the stoichiometric hydroboration reaction of olefin (Eq. 7) can be shown to be

If one assumes that the amounts of the adsorbed species (II) to (IV) can be neglected in comparison with (I), as the amount of trialkylborane is so small at the initial stage, the concentration of the dissociated diborane can be assumed as the Langmuir-type adsorption as follows

$$v = \frac{K_2^{1/2} P_B^{1/2}}{1 + K_1^{1/2} P_B^{1/2}} \quad (8)$$

Assuming further that step (3) is rate controlling, the initial rate of the reaction is given by Eq. (9), as the reverse reaction of step (3) can be neglected,

$$r_1 = kvP_0 = k \frac{K_2^{1/2} P_B P_0}{1 + K_1^{1/2} P_B^{1/2}} \quad (9)$$

here k ; the rate constant K_1 ; the equilibrium constant of step (2), $K_2 = K_1 v_m$, v_m ; the amount of diborane adsorption saturated. If $K_1^{1/2} P_B^{1/2}$ is negligible as compared with 1. Eq. (9) can be written as follows,

$$r_1 = kK_2^{1/2} P_B^{1/2} P_0 = k_r P_B^{1/2} P_0 \quad (10)$$

here, $k_r = kK_2^{1/2}$. Eq. (10) is similar to Eq. (1) derived from the experimental results. Under the assumption that the other step is rate-controlling, various initial rate equations are introduced, but all these equations are not adaptable the experimental results. For instance if Eq. (4) is rate-controlling, the rate equation is expressed approximately as follows,

$$r_1 = k_r P_B^{1/2} P_0^2 \quad (11)$$

this equation does not agree with Eq. (1). Another mechanism to be considered is the reaction between the dissociated diborane and adsorbed olefin on the catalyst. However, the rate equation was not consistent with the experimental results, because the adsorption of olefin did not follow the Langmuir-type equation. (see 3.3) When the adsorption of diborane or olefin is the rate-controlling step, the rate equation depends only on either diborane or olefin partial pressure, which did not agree also with the experimental results.

3.2 Adsorption of Diborane

Experiments on adsorption of diborane over the Pd-carbon catalyst were carried out at 42°C and 45.4°C with the static method equipped with a trap. After attaining the adsorption equilibrium, the remaining diborane was condensed in the trap cooled with liq. N_2 until the manometer reading was zero, then evacuated slightly. The stop-cock between the adsorption vessel with the trap and manometer was closed, and the liq. N_2 was removed to evaporate the condensed diborane from which the amount of physical adsorption of B_2H_6 was calculated. The amount of diborane chemisorption was therefore, presumed to be the difference between the amount of the initial adsorption and that of the evaporated. The equilibrium pressure of chemisorption was calculated from the initial equilibrium pressure (P_e) and the ratio of the amount of chemisorption to the total amount of adsorption. The above adsorption procedure was repeated at several diborane pressure levels, and the equilibrium amounts and pressures of chemisorption were estimated. Thus, the isotherm of chemisorption at two relatively narrow temperature ranges was obtained as shown in **Fig. 5**. One of the examples of such adsorption is shown in **Table 2**.

The adsorption isotherm was plotted according to the Langmuir equation (Eq. 12) for the dissociative adsorption of diborane; reciprocal of the amount adsorbed, v vs. that of the square root of diborane partial pressure, $P_B^{1/2}$

$$v = \frac{K_1^{1/2} v_m P_B^{1/2}}{1 + K_1^{1/2} P_B^{1/2}} \quad (12)$$

As shown in **Fig. 6**, the $1/v$ vs. $1/P_B^{1/2}$ plot showed good linearity, and the equilibrium constants, $K_1^{1/2}$, of adsorption at 42°C and 45.4°C were 0.616 and 0.542, respectively. By Eq. (13) derived from the Clausius-Clapeyron equation and

v : the amount of diborane adsorbed
 P_B : the partial pressure of diborane
 Fig. 5 Adsorption Isotherm of Diborane Chemisorption

Table 2 An Example of Diborane Adsorption
 Experiment at 45.4°C

Initial pressure of B_2H_6 *)	12.00 cmHg
Equilibrium pressure of B_2H_6 (P_e)*2)	4.34 cmHg
Pressure when B_2H_6 evaporated*3)	4.07 cmHg
Equilibrium pressure of chemisorption*4)	1.22 cmHg
Amount of the irreversible adsorption	0.225 mmol/g

catalyst used; 0.2 g, dead volume of the apparatus; 140 cm³

*1) In this case the dead volume is 59 cm³, because the trap (volume 80.98 cm³) is under vacuum.

*2) The pressure exhibits the sum of the equilibrium pressures of physical and chemical adsorptions. The dead volume including the adsorption vessel is 163.3 cm³.

*3) The dead volume is 140 cm³ including the trap in this case.

*4) This pressure was calculated as follows

$$P = \frac{(\text{total amount of adsorption}) - (\text{amount of physical adsorption})}{(\text{total amount of adsorption})} \times P_e$$

Eq. (12), the heat of adsorption was 15 kcal/mol.

$$K_1^{1/2} = K_0 \exp(Q/2RT) \quad (13)$$

The heats of adsorption for various amounts are shown in Fig. 7, and the initial heat of adsorption was obtained as 20 kcal/mol from the extrapolation to the zero amount of adsorption (see Fig. 7). The difference in the values from Eq. (13) and extrapolation is ascribable to the heat of adsorption which greatly depends on the equilibrium constant for adsorption of small amounts.

The dissociative adsorption of diborane on the catalyst was experimentally shown to be valid, and the amount of chemisorption was found to be

Fig. 6 Plot of $1/v$ vs. $1/P_B^{1/2}$ by Dissociative Adsorption Equation of Langmuir

Fig. 7 Heat of Adsorption for Various Amounts of Diborane and Olefin Adsorption

also small. The value of P_B is small and the term $K_1^{1/2}P_B^{1/2}$ can be neglected with respect to 1 in the denominator of Eq. (8). Fripiat and Tongelen⁶) and Mashchenko⁷) have already reported the results of dissociative adsorption of diborane on silica, silica-alumina and alumina catalysts. The dissociative adsorption of diborane may occur in the induction period shown in Fig. 1.

Catalyst used : 0.2 g at 40°C
Fig. 8 Adsorption Isotherm of Ethylene and Propylene

When either diborane or olefin above was admitted into the reaction vessel with the catalyst, the pressure change in the manometer was observed for few minutes and then the pressure attained a constant value. When, for instance the initial pressures of B_2H_6 , C_2H_4 at 50°C or C_3H_6 at 30°C were 60, 345.2 or 194.5 mmHg, their pressure drops were 4, 18 or 45 mmHg, respectively during the few minutes. The pressure change of olefin was larger than that of diborane. The large pressure drop in the induction period in **Fig. 1** can be ascribed mainly to the adsorption of the olefin.

3.3 Adsorption of Ethylene and Propylene

With the same apparatus used in section 3.2, adsorptions of ethylene and propylene at 38°C and 40°C were examined. The irreversible amounts of adsorption of ethylene and propylene could not be measured, because they were so small to be within the range of experimental errors. Their adsorption isotherms are shown in **Fig. 8**. The amount of propylene adsorbed was larger than that of ethylene. The plot of $\log v$

Fig. 9 Plot of Freundlich Equation

vs. $\log P$ from the Freundlich equation showed good linearity (**Fig. 9**), and the Langmuir equation was not applicable to the olefin adsorptions. The constants of the Freundlich equation, $v = kp^{1/n}$, at 38°C and 40°C are calculated as follows (here v is given by ml)

$k = 7.02$	$1/n = 0.551$	at 38°C for ethylene
$k = 5.26$	$1/n = 0.604$	at 40°C
$k = 32.9$	$1/n = 0.319$	at 38°C for propylene
$k = 29.4$	$1/n = 0.355$	at 40°C

The heats of adsorption of ethylene and propylene at their initial stages (see **Fig. 7**) calculated from the Clausius-Clapeyron equation were found to be 14.6 kcal/mol and 6 kcal/mol, respectively. The results of adsorption of the olefins suggest that physical adsorption will be taking place on the catalyst surface.

The mechanism considered in the Eq. (2) to (6) seems to be plausible from the results of the olefin adsorption studies.

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